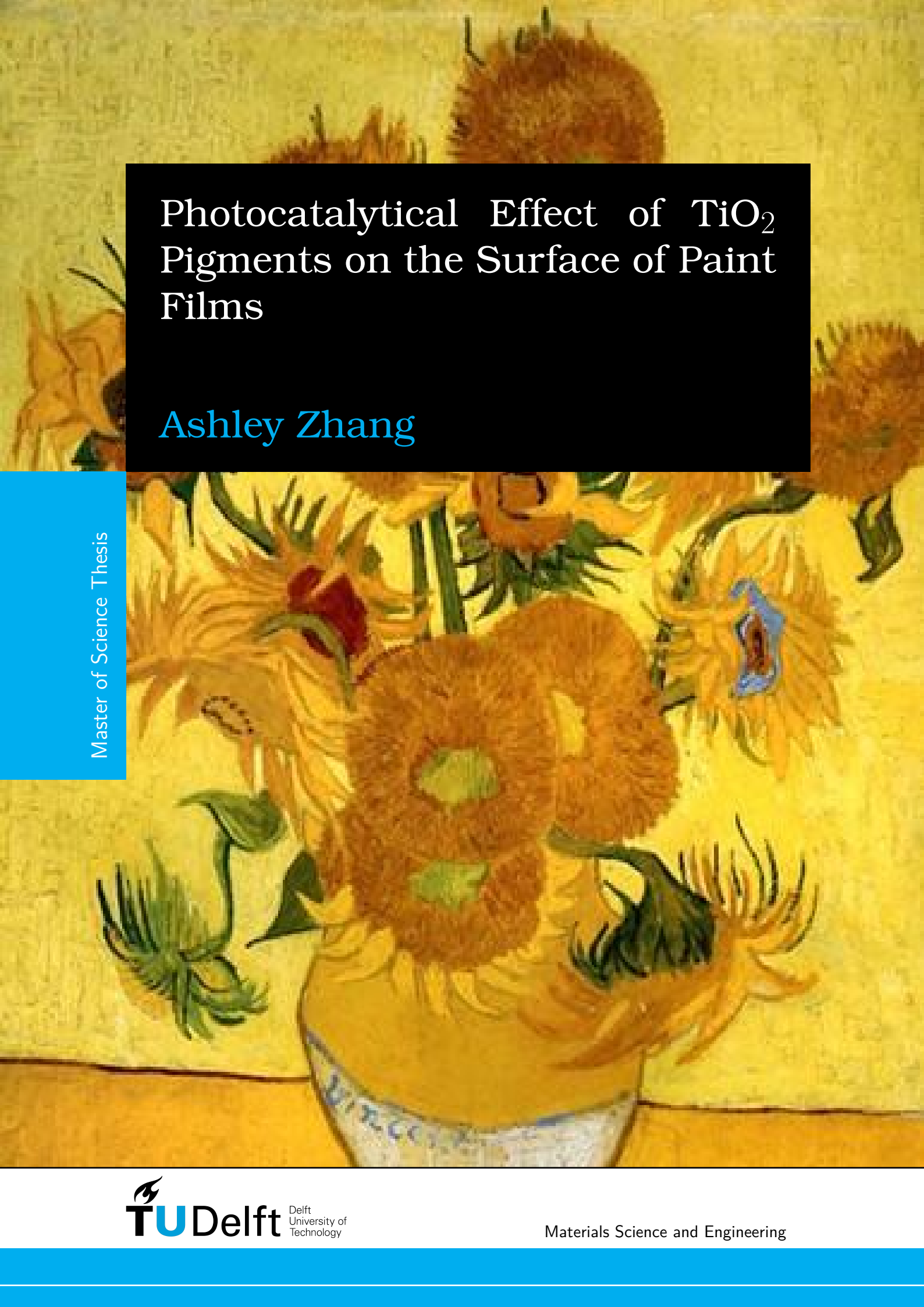


The background of the cover is a reproduction of a painting featuring several sunflowers in a vase. The sunflowers have large, textured heads in shades of brown and orange, with bright yellow petals. Green leaves and stems are visible at the base of the flowers. The painting style is visible with brushstrokes.

Photocatalytical Effect of TiO_2 Pigments on the Surface of Paint Films

Ashley Zhang

Master of Science Thesis

Photocatalytical Effect of TiO_2 Pigments on the Surface of Paint Films

MASTER OF SCIENCE THESIS

For the degree of Master of Science in Materials Science and
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Ashley Zhang

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Faculty of Mechanical, Maritime and Materials Engineering (3mE) · Delft University of
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DELFT UNIVERSITY OF TECHNOLOGY
DEPARTMENT OF
MATERIALS SCIENCE AND ENGINEERING (MSE)

The undersigned hereby certify that they have read and recommend to the Faculty of
Mechanical, Maritime and Materials Engineering (3mE) for acceptance a thesis
entitled

PHOTOCATALYTICAL EFFECT OF TiO_2 PIGMENTS ON THE SURFACE OF PAINT
FILMS

by

ASHLEY ZHANG

in partial fulfillment of the requirements for the degree of
MASTER OF SCIENCE MATERIALS SCIENCE AND ENGINEERING

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Supervisor(s):

Prof. Joris Dik

Dr. Klaas Jan van den Berg

Reader(s):

Prof. Joris Dik

dr.ir. F.S.T. Reader-two

ir. Th. Reader-three

Abstract

TiO₂ has been widely applied as white artistic pigment since 19th century. And the photocatalytic effect of TiO₂ makes it aggressive and causes degradation on painting surface. The damage of binder by TiO₂, also known as chalking, has been suggested as the main cause of the painting surface degradation and studied a lot. However, the danger to pigments used with TiO₂ together, especially the organic ones, is rarely noticed. In this study, artistic TiO₂ and industrial TiO₂ were studied: a Titanium white pigment from Kremer, industrial catalyst from Hombikat and Hombikat coated with Al₂O₃ in an atomic layer deposition process. The titanium dioxides were mixed with five colorant pigments and linseed oil into paints. After drying, the paint films were illuminated under artificial light to reveal the surface change caused by TiO₂.

After artificial light aging, the color, gloss and roughness of all films have changed. As expected, Hombikat TiO₂ is proved to induce most changes. The Hombikat TiO₂ degrades the binder and the colorant pigments in combination with light. The coating of Hombikat with Al₂O₃ shows little effectiveness in preventing the degradation. The Kremer TiO₂ mainly degrades the binder to cause surface change. The degradation of the binder contributes to the roughness increase mostly. The color of Green earth is not affected by any of the three titanium dioxides. Vermilion's blackening phenomenon is largely boosted by TiO₂. Prussian blue degrades faster than others. And the organic Indigo and Hansa yellow most likely to have broken molecular bondings caused by TiO₂.

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Ashley Zhang

Chapter 1

Introduction

Titanium dioxide has been used as white pigment since 1920s, both in industry and art work. As artistic pigment, TiO_2 is popular because of its high performance and low cost. However, the photo-catalytic effect of TiO_2 may induce surface deterioration of the paintings. When under illumination, the TiO_2 absorbs ultraviolet light and generates radicals, and these radicals would damage the surrounding organic materials, binders or organic pigments. So far, the degradation of the binder caused by TiO_2 has been studied a lot, but the degradable pigments' behaviors with TiO_2 have seldom been realized. Considering the massive use of TiO_2 pigments, it has a great chance that the paintings using both TiO_2 and the degradable pigments are in danger. The surface of these paintings may be damaged by the photo-catalytic effect of TiO_2 . This study firstly aims to find out the effect of TiO_2 on the surface of paint films containing degradable pigments, such as color, gloss and roughness. Secondly, it aims to reveal different behaviors of three kinds of TiO_2 and five colorant pigments. The chosen three TiO_2 have diverse properties and application, and four of the five colorant pigments have shown degradation potential in the past studies, and one permanent colorant pigment was chosen as reference.

In this study, paint films of TiO_2 and colorant pigments were made and the surface characterization of the paint films were measured, including color, gloss and roughness. Then optical light microscopy, X-ray diffraction, scanning electron microscopy(SEM) and energy dispersive X-Ray spectrometer(EDX) were used to exam the crystal structure change and elemental change.

In chapter 2, literature review gives several related aspects of the study, including introduction about TiO_2 pigment and its harm in art work, the binder used in paintings, the surface characterizations influencing the appearance and the museum precaution to reduce the damage by lighting. Chapter 3 describes the methods of investigation. The results and further thoughts from the experiments are presented in chapter 4. Finally, the conclusion and outlook of this study are given.

Chapter 2

Literature Review

This chapter firstly gives a brief introduction of TiO_2 pigment, from its general information(section 2-1) to its potential problems(section 2-2) in the art field, and establishes the criteria for the selection of five colorant pigments(section 2-3) which may have chance to be mixed with TiO_2 and suffer from degrading. Then the binder in paint(section 2-4) is introduced shortly. In section 2-5, the factors influencing painting appearance are discussed. At the end, the museum' light environment is given.

2-1 Brief introduction of titanium dioxide pigment[1]

Titanium was first detected in 1791 and the pigmentary potential of its oxide was not discovered until the early 20th century. Then titanium dioxide white has been widely used since 1920s, replacing the most important white pigment in history-lead white[9]. It is welcomed by the artists because of its brilliant white color, high hiding power, nontoxic nature (superior to lead white) and reasonable cost.[10]

Titanium dioxide has three crystal forms as in figure 2-1, tetragonal rutile, tetragonal prisms of anatase and orthorhombic brookite. Among these, only rutile and anatase are commercially utilized. Rutile is considered stable than the anatase. TiO_2 reflects all wavelength of visible light and absorbs ultraviolet light, so it is white to human eyes. Figure 2-2 shows the reflectance of two titanium dioxide crystal structures.

There are two types of TiO_2 pigments, the powders which normally contain more than 80% of titanium dioxide and titanium dioxide based composites which only contain 30-50%. And the composite pigments were manufactured and marketed only for a short period mainly in the United States, so it will not be discussed.

Here, only the synthetic TiO_2 will be discussed. The mineral TiO_2 can be neglected because it is not commonly used as pigments.[10] By now, there are two widely used processes to produce powder titanium dioxide pigments as in figure 2-3, the sulfate process and the more modern chloride process.

The reactions[11] involved in the sulfate process are:

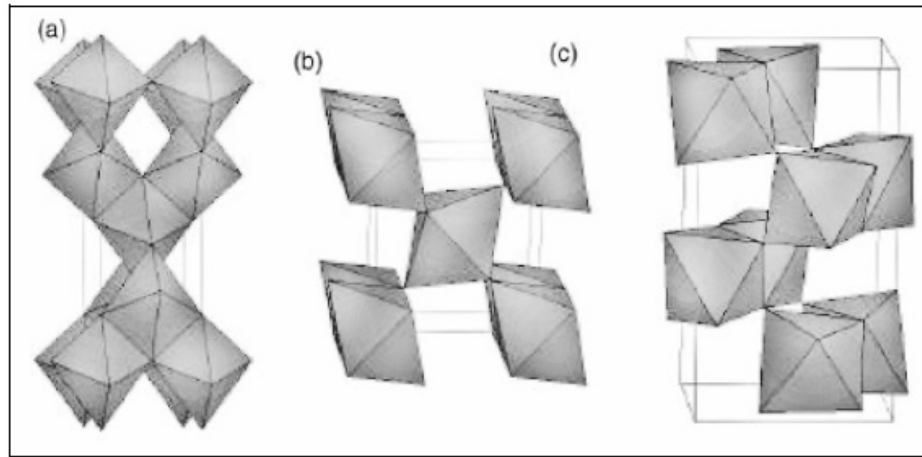


Figure 2-1: Crystal structures[5]: anatase (a), rutile (b), brookite (c).

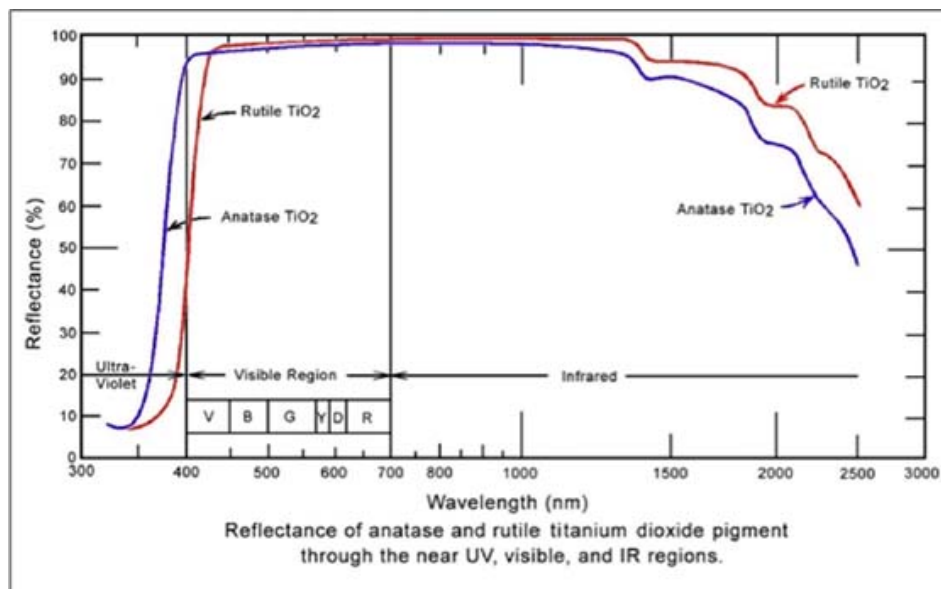


Figure 2-2: Reflectance of anatase and rutile[6].

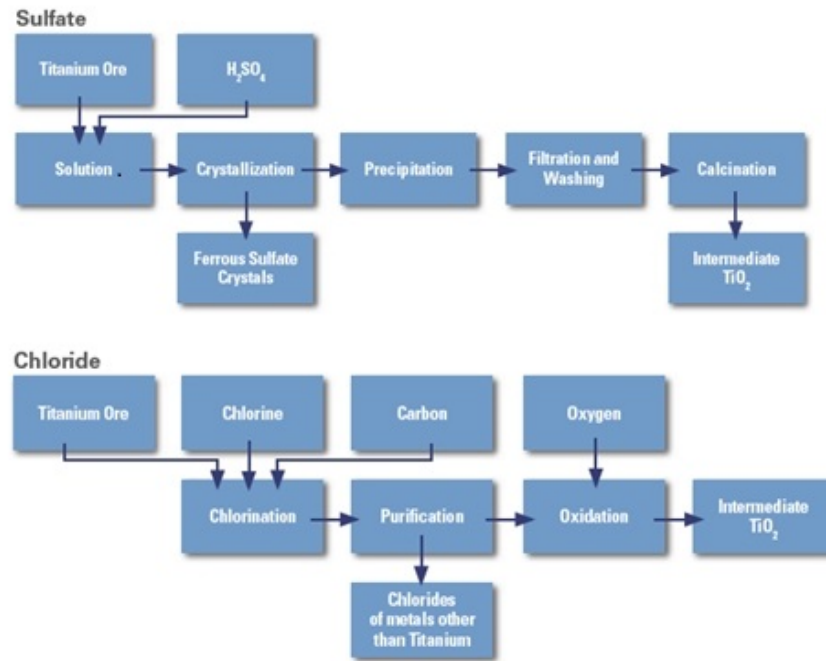
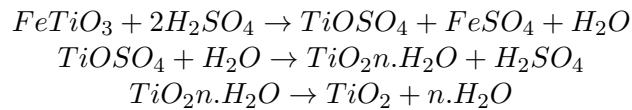
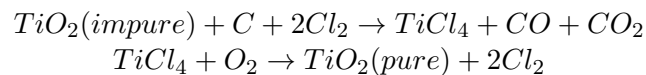


Figure 2-3: TiO₂ manufacturing process.



The reactions[11] involved in the chloride process are:



The application range of titanium dioxide pigments is pretty wide, such as industry of paint, printing inks, plastics, paper and textile. Among those, the paint is the most important one. The industry paint has been developed since 1920s, and for the artists, the titanium dioxide was accepted as white pigment through 1930s.

The slow development of TiO₂ as artistic pigment is due to its high price, small experimental batches and limited access when it was first introduced. When these difficulties were conquered, it has been applied widely for its great performance. Figure 2-4 shows two paintings involved TiO₂ pigment. Here, the influence of TiO₂ on paints (combination of oil and pigments) will be discussed.

2-2 Potential problems

TiO₂ satisfies the expectation for a white pigment, but it is photochemically active[10, 12], as well. Photochemically active means the absorption of light can lead to chemical reactions. The band gap is 3eV for rutile TiO₂ and 3.2eV for anatase TiO₂. According to



Figure 2-4: A painting using TiO_2 pigment, (a) Spoonk, 1964, Marion Greenstone[7], (b) Story with a chicken, Martial Raysse[8].

the Planck's equation ($E = h\nu$) and the wavelength-frequency ($\nu = c/\lambda$) relationship, the wavelength needed to excite the electron from the valence band to the conduction band is approximately 380nm, which is in the ultraviolet light range. When irradiated, the TiO_2 absorbs ultraviolet radiation[13] and free electron-hole pairs will be generated. The holes and electrons are free to move to the crystal surface of titanium dioxide and react with the oxygen and water around to produce hydroperoxyl and hydroxyl radicals.[10] These radicals would then react with the organic binder[14] and cause degradation[15] of the painting film. This kind of degradation of the paint film is known as chalking[16].

Chalking chemically destroys and physically removes the binding medium, leaving loose pigment particles on the surface.[10] Therefore, a removable whitish layer on top of the paint films can be observed. It is believed the reactions are mainly oxidation.[16] Though the reductions happen occasionally, they are not efficient enough to be taking into consideration. The explanation refers to lower reducing and higher oxidizing power of electrons and holes. On the other hand, some researches[17] insist although titanium dioxide can merely change the chalking degradation rate, the presence of titanium dioxide is not the fundamental factor of polymer degradation. However, nowadays the chalking phenomenon is related to titanium dioxide most of the times.

Studies have shown that the degradation power of titanium dioxide is related to grade, type (anatase or rutile), coating status, manufacture process[14] of TiO_2 and the intensity of the UV lights[18]. For instance, the UV resistance can be improved by coating the TiO_2 . [19] Coating was applied to enhance the chalking resistance of titanium dioxide as early as 1910s.[20] And in the next few decades, more coatings were developed and made to the market.[10] The coating[17] of TiO_2 could be inorganic or organic. Zinc oxide, silica and/or alumina inorganic coating or the combination of these materials are widely used. The coatings can act as a physical barrier and prevent the formation of radicals on the pigment surface, thus lower the photo-catalytic ability of TiO_2 . Hence, thicker and more dense coating would lead to better durability of TiO_2 . For general use paints, 2-5% weight coating is enough, and for high performance requirement, 7-10% weight is commonly applied.[21] In modern pigment grade, the coating can be as much as 20% to 25% weight of the TiO_2 product.[10]

In the mean time, the conflicting results are reported, as well. TiO_2 can be used as stabilizer[22, 23], depending on concentration, processing treatment or presence of additives[24]. And Papliaka et al.[8] concluded that while mixture of anatase and rutile is accelerating aging process, the pure rutile is protecting other colorant. However, this protective effect will not be covered here.

The chalking degradation is between titanium dioxide and the organic binder. In a painting with TiO_2 pigment, besides the binder, other pigments can also suffer accelerated color degradation if they themselves are active or organic[14]. This is the main concern of this study.

2-3 Pigments selection

The degradation problem mentioned above may not just happen to the pigments used in the same time period with titanium dioxide white, but to pigments used even before TiO_2 was introduced, as conservators may use titanium dioxide white to restore the ancient masterpieces. Five pigments may be applied together with TiO_2 and have the potential to be degraded.

The five pigments are selected based on several criteria. Firstly, being used together with TiO_2 is required. The chance could be the overlap of the using time with titanium dioxide white pigments. Prussian blue has been found in the artists's palette together with TiO_2 [25] and it still exists in today's painting market. Indigo and Green earth have a longer history than TiO_2 and continue to be used today.[26] The current popular Hansa yellow is a relatively new pigment which was made a few years before titanium dioxide was introduced. In addition, the chance also could be pigment such as vermilion, one of the most important and widely used reds in art history.[27, 27–29]. It can be mixed with TiO_2 during conservation work. Secondly, pigments themselves should have color degradation potential; otherwise deterioration of color cannot be observed efficiently. Prussian blue, vermilion and indigo have been proved to be unstable in many studies. Hansa yellow is an organic pigment, which means it has the potential to be degraded by TiO_2 . Moreover, in order to acquire distinctive reactions of the active and permanent pigments, the claimed stable green earth pigment was chosen. Thirdly, the study of these five pigments mixing with TiO_2 has not been referred so far, so it is worth investigating. Among the five selected pigments, vermilion has been researched more thoroughly and several degradation mechanisms are proposed; others are not deeply understood.

Prussian blue is synthetic inorganic ferric ferrocyanide ($\text{Fe}_4[\text{Fe}(\text{CN})_6]_3 \cdot x\text{H}_2\text{O}$)[30]. Obviously, both the valence +2 and +3 Fe are included. It was first used by artists in around 1724 and has been a popular pigment for three centuries. Prussian blue can be identified by Fourier transform infrared spectroscopy (FTIR) and Raman spectroscopy.

According to the previous study, Prussian blue is very unstable, and will exhibit color change when exposed to the environment. The fading of Prussian blue differs under different conditions, such as moisture, vacuo(without air or moisture), saturated air.[31, 32] When exposed to light in both air and near-anoxic environment, Prussian blue has greater color change in near-anoxic than in air.[33, 34] After reexposed to air, some faded Prussian blue could recover.[35] Additionally, pure Prussian blue is proved stable, though its mixture with white pigments,



Figure 2-5: Painting containing green earth.

such as rutile titanium dioxide fades.[36–40] The mechanism of Prussian blue discoloration is believed to be the reduction of the iron(+3) elements.[41]

Green earth is made of native clay[30]. This inorganic pigment is a mixture of hydrosilicate of Fe, Mg, Al and K, and its formula is expressed as $K[(Al, Fe^{3+}), (Fe^{2+}, Mg)](AlSi_3, Si_4)O_{10}(OH)_2$. Green earth started being used since ancient times and continues in use today.[42] In the medieval paintings, it was applied as underpainting of flesh color (figure 2-5). Green earth can be identified by FTIR and Raman spectroscopy.

It is stable to light and air[43, 44], and is listed as permanent pigment by the German Society for Rational Painting Techniques[?]. The stability of green earth with different binders is proved.[35, 45] Here, it is mainly selected as a contrast pigment which will have no discoloration after UV aging. Even so, the green earth contains Fe element of different valences, and may also be oxidized or reduced by the radicals TiO_2 generated after absorbing UV light and then show the color change.

Vermilion is an inorganic red color pigment composed of mercuric sulfide (HgS), which is also known as cinnabar. It had been used since ancient times and was replaced by cadmium red at the end of 20th. During its long serving time, it was always the main red color on account of its good hiding power and permanence. Vermilion can be identified by Raman spectroscopy and Ultraviolet-Visible-Infrared (UV-VIS-IR) spectra. And owing to its crystal structure, it can be recognized by X-Ray diffraction (XRD).

Vermilion is considered one of the most effective photo-sensitizer for photo-oxidation.[46] It has a darkening problem after exposure to environment.[43, 47–50] At early time, the most popular hypothesis described the origin of blackening of vermilion as the conversion of vermilion (α - HgS) into black meta-cinnabar (α' - HgS).[51–54] However, recent studies[55, 56]

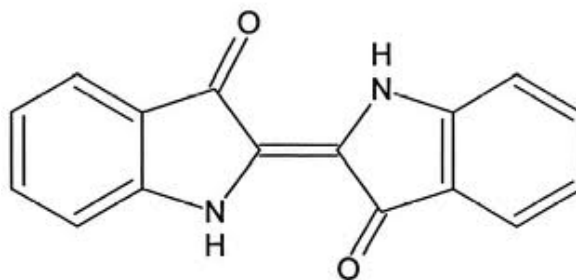


Figure 2-6: Indigo structure.

attacks this hypothesis and claims no evidence of meta-cinnabar examined at all. Cotte et al.[55] gave two mechanisms, one is involved with chlorine and the other is involved with sulfation. And respectively, grey chlorine-mercury compounds and sulfation of calcite are formed. Keune and Boon[56] proposed different hypothesis. They assumed during UV light illumination, some vermilion is converted into Hg(0) and S(0), and Hg(0) deposits on the surface making it black. In the mean time, Hg(0) and the remaining HgS react with chloride to form white mercuric chloride(HgCl₂). Moreover, the observation of light, alkali metal halides, high relative humidity and mineral impurities all accelerating blackening[57, 58] does not support the meta-cinnabar theory, either. Because the conversion of HgS to α' -HgS is simply structural change which should not be influenced by factors as impurities. However, there is also evidence about the permanence of vermilion, a green laser pointer with radiation at 532nm did not change the color of vermilion after one year's laser pointer radiation.[59]

Indigo is an organic blue pigment and its chemical formula is C₁₆H₁₀N₂O₂, which is also known as indigotin. Figure 2-6 shows the structure of indigo. It has been used since ancient time until now. The most popular and well-known application for indigo is being blue dye for jeans. Indigo can be identified by FTIR and Raman spectroscopy.

Until now, most researches of indigo focus on its application in textile. Its artistic pigment performance has been seldom studies. Indigo is claimed to be a very light fastness dye though its degradation as pigment has been mentioned frequently. When presenting in the upper layer, indigo can be unstable. Similarly with vermilion, there are a bunch of factors influencing the degradation, such as particle size, thickness of the paint layer and impurities. Light is also widely believed to be a pronounced element though the discoloration without light was observed, either. The fading process of indigo can be explained as indigotin being oxidized to smaller compounds. It can be decomposed mainly into 2-aminobenzoic acid, isatin, isatoic anhydride and 2-benzyl-3-indolinone.[60]

Hansa yellow is a newly developed organic pigment which only has a history of a few decades.[61] It contains elements as C, H, O, N and Cl. There are several varieties in this family offering a wide yellow-to-orange hue range. To distinguish them, letters and numbers are added to their names. Letter "G" indicates greenish yellow; "R" indicates reddish yellow and "X" indicates the series of yellow which is similar in shade but different in structure with older "G" yellows.

Hansa yellow has numerous varieties, and most of them have been claimed to be light fastness[8], but poor resistance to organic solvents[62]. Research about this series of colorant is not thoroughly until now. It means the behavior of Hansa yellow is mysterious and worth digging.

As a result, the selected 5 pigments firstly have already showed degradation in different degrees or have the deterioration potential; secondly they all have the chance to be used with TiO_2 in the art work. Therefore it is reasonable to suspect that when mixed with TiO_2 , they will exhibit accelerated discoloration.

2-4 Binder-linseed oil[2]

The function of the binders is to bind the pigment particles together. Linseed oil is one of the major binders. It is organic drying binder which means it can form solid films when exposed to air. Besides, walnut oil and poppy oil are popular binders as well.

After mixing the pigments with oil, the pigments particles will agglomerate together at first and leave oil surrounding them. So further grinding is needed to distribute the particles homogeneously in the oil. The needed amount of oil differs according to the absorption of pigments. Nevertheless, if too much oil is used, yellowing of paint film happens. Therefore, oil volume should be kept wisely.

Drying process[3] of the oil paint is not only physical but a complex series of chemical reactions with the atmosphere. The chemical reaction includes the oxidation of the oil and the reaction between the oil and the pigments. And these complicated chemical studies are considered in Berg's work.[63] Here, the study focuses on the concern of the pigments, not the binder.

2-5 Surface appearances of paintings[3, 4]

The appearance of paintings depends on the color and the gloss, which are actually the reaction consequences of the light and paint film surface. The light will be reflected, refracted, scattered or absorbed by the paint films, then getting into human eyes. The light absorption within the materials is associated with the color and the specular reflection is responsible for the gloss. Figure 2-7 shows the interaction between light and the object. Large portion of the light penetrates into the material and gets reflected by the pigment particles and then gets out as diffuse reflection. During penetration passage of the light, certain wavelength is absorbed by the pigment particles, so the diffused reflection shows color. In the same time, a small portion of light is reflected specularly and presents gloss. The specular reflection depends on the smoothness of the surface, the refractive index of the material and the incident angle.

One factor that influences the color and gloss is the roughness, which means the vertical deviation of a real surface from its ideal form. It is obviously that rough surface leads to decrease of the amount specular reflection and matter appearance. The rougher the surface is, the less glossy. The rougher surface causes the reflected light scattered in all directions, which contributes colorless reflected light to the diffuse reflection. Since the color is determined by its diffuse spectrum, the surface roughness would have effect on the color.[?] In the study, the color, gloss and roughness of the paint films before and after artificial UV aging will be measured to give insight of the surface changes.

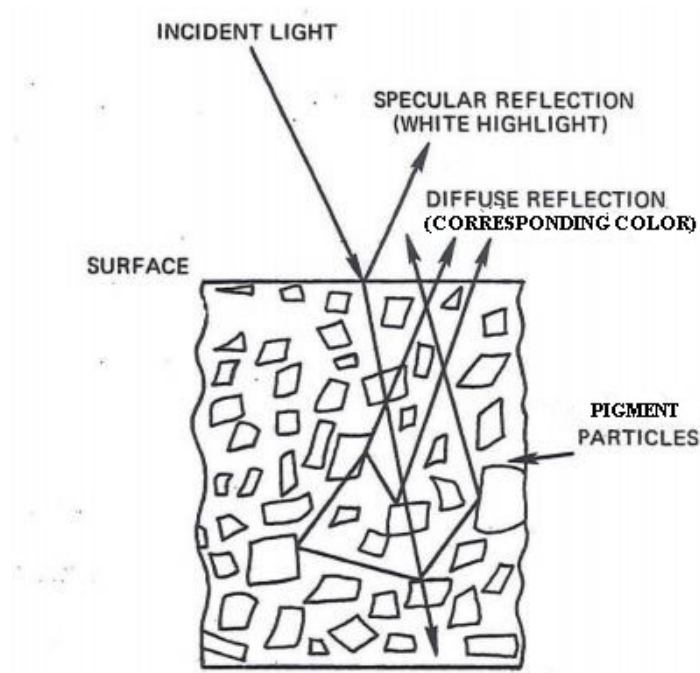


Figure 2-7: Microscopic cross section view of light interacting with object. Specular diffuse is responsible for gloss. Diffuse reflection results in the reflections by the pigment particles. And the selected wavelengths absorbing by the particles causes diffuse reflection presenting color.

2-6 Museum light environment

[64]

The museum collections have to be kept with great care, otherwise damages would be made to them. The light, heat, humidity and air pollution are all critical factors. Light contains UV and visible light, and UV is more dangerous because of its higher energy. Daylight, though has a small portion of UV light, still can destroy collections somehow. Under this circumstance, filters to block UV are equipped on the windows of museums using daylight during the day as light source. Besides daylight, tungsten, fluorescent lamps are the commonly used lightings for museums. Tungsten emits little UV light which makes it not a big threat. Same as the daylight, the fluorescent lamps also need filters to prevent UV light.

Chapter 3

Experiments

This chapter will give description of the experimental methods used in the study. Section 3-1 shows details of the chosen materials. Then section 3-2 and 3-3 tell the preparation and treatment to the samples. The surface measurements, color, gloss and roughness of the paint films are described in section 3-4 and 3-5, respectively. The cross sections examination of the paint films are told in section 3-6, 3-7 and 3-8.

3-1 Raw materials

3-1-1 Titanium dioxide

The titanium dioxide used in this study are listed in table 3-1.

Table 3-1: Selected titanium dioxide

Titanium Dioxide	Structure	Coating	Particle size	Application
Kremer 46200	Rutile	Coated with SiO ₂ and Al ₂ O ₃	170nm	Art pigment
Hombikat UV-100	Anatase	Not Coated	10nm	Catalyst
Coated Hombikat UV-100	Anatase	Coated with Al ₂ O ₃		

Kremer TiO₂ has pretty big particle size and rutile structure. At the same time, the previous study by TU Delft student showed it has a perfect coating. Consequently, Kremer titanium dioxide should be stable and the previous study confirmed it. In earlier research, Hombikat UV-100 is proved to be highly photoreactive.[16] The crystal structure, coating status and particle size all support this point. The coating procedure of the coated Hombikat UV-100 was performed by David Valdesueiro, Aris Goulas and J. Ruud van Ommen in Chemical Engineering Department of TU Delft. The Al₂O₃ coating was deposited on the TiO₂ particles. And after deposition, the powder color turned from bright white to bluish, which is believed to a common phenomenon when coating titanium dioxide particles with Al₂O₃.

Here, Kremer and Hombikat titanium dioxides are supposed to degrade the paint films differently. The coated Hombikat can be compared to the original Hombikat TiO_2 to reveal the coating influence on the activity of titanium dioxide. In the following part of this paper, the "Hombikat TiO_2 " will be used referring to "Hombikat UV-100 TiO_2 ", and "Hombikat-C TiO_2 " will be referring to "coated Hombikat UV-100 TiO_2 ".

3-1-2 Colorant pigments

The colorant pigments information are given in table 3-2.

Table 3-2: Selected colorant pigments

Pigment	Chemical composition	Company
Prussian blue	Iron (+3) ferrocyanide	Sigma-Aldrich
Green earth	hydrosilicate of Fe, Mg, Al and K	RCE collection
Vermilion	Mercury(+2) sulfide	Aldrich
Indigo	$\text{C}_{16}\text{H}_{10}\text{N}_2\text{O}_2$	Sigma-Aldrich
Hansa yellow	C,H,O,N and Cl organic compound	Hoechst

The Prussian blue and Vermilion used here are all industrial pigments, not exactly art pigments. The Green earth, Indigo and Hansa yellow are all artistic pigments collected by the Rijksdienst voor Cultureel Erfgoed (RCE). Among these three, Indigo and Hansa yellow are manufactured by pigment companies, and the source of Green earth is not sure. The binder used is linseed oil provided by Van Beek art supplies. The batch number is 480204.

To provide more information and make the experiment data more accurate, three combinations of paint were made and aged. They are Vermilion+ BaSO_4 +linseed oil, Kremer TiO_2 +linseed oil and Hombikat TiO_2 +linseed oil.

3-2 Paint films preparing

The titanium dioxide pigments and the colorant pigments were mixed with linseed oil binder separately. The oil was added drop by drop into the powder pigment while stirring with a spatula. Then grinding by a mill (figure 3-1(a)) was conducted 2 times to disperse the pigment in the binder as homogeneously as possible. Each time involved 25 revolutions. Between the grindings, the mixture covering the mill plates was scraped together using spatula. After grinding, the mixture showed a pasty state which is called paint and suitable for painting. Since the size of the mill plate is limited, only about 0.5g pigment can be dealt with one time. To get enough paint for painting, 2 to 4 times paint-making were performed for each pigment. During this procedure, roughly calculation and weighing caused up to 10% weight error. Then the TiO_2 paint and the colorant paint were mixed and ground twice as before to guarantee a homogeneous color. Till now, the colored paints were ready and spread on the support of melinex using a drawdown bar (figure 3-1(b)) with a controlled thickness of 50 μm . Considering the largely diverse tinting power of the colorant pigments, the colorant- TiO_2 ratios are kept differently. Because of the difference between each batch of the paint and the calculation error, the colorant- TiO_2 ratios for one colorant pigment are slightly different.

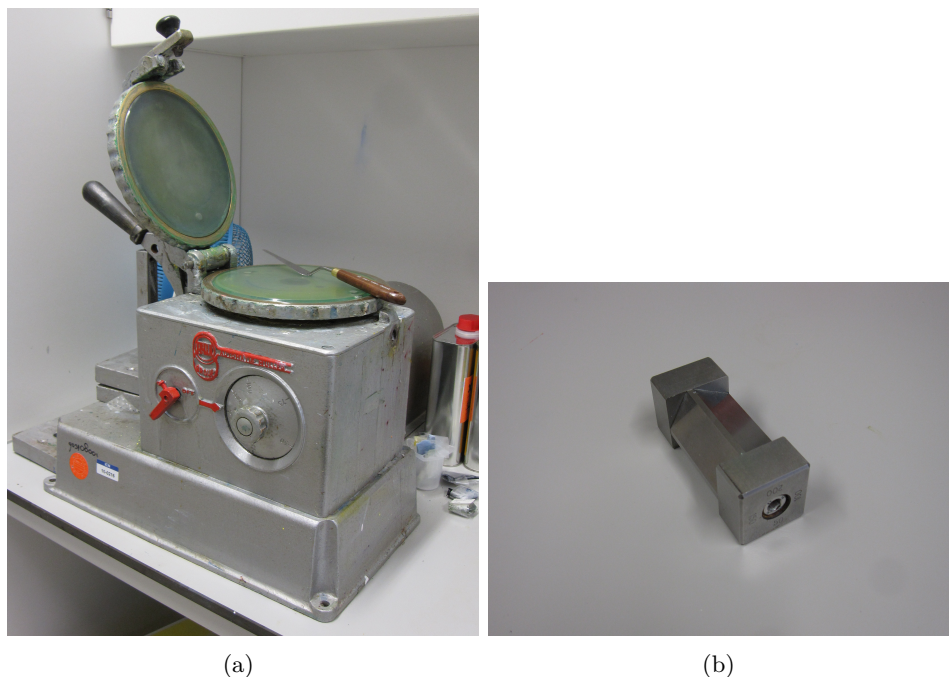


Figure 3-1: The equipments to make paint films, (a) the mill used to grind pigments, (b) the drawdown bar used to apply paint films.

Two pieces of paint films were made for each pigments combination. The painting films were placed under room temperature, humidity and natural light for about 3 weeks to dry.

Observation during the paint making: the Hombikat TiO_2 appeared yellowish color when mixed with oil. The Kremer TiO_2 did not change color. Green earth and Vermilion absorbed more oil and were hard to spread on the support. In the mean time, their tinting powers are weaker than the other three pigments, which means larger colorant pigment/ TiO_2 mass ratio is needed for these two to acquire a clear color.

3-3 Paint film samples aging

The drying process takes about three weeks on average under natural environment. And during the drying, no obvious optical changes have been observed. The paint films were illuminated under intensive artificial UV light after drying. The artificial UV aging was performed by Xenotest alpha, a universal weathering instrument for testing the light fastness and weatherability of materials under normal/high temperature and high energy conditions. Inside the Xenotest instrument, the samples were irradiated at 105000 lux by xenon lamp, which produces high UV irradiation. The temperature was kept at 50 degree centigrade, and the relative humidity was 40%. Half pieces of all the paint films were exposed for 5 days, and half pieces excluding the coated Hombikat TiO_2 -involved ones were exposed for 14 days. One hour in Xenotest equals to 0.25 museum years, so 5 days and 14 days represent 30 and 84 years of "natural aging".

The aged samples are in variable situations. Some areas are exposed to light directly. Some

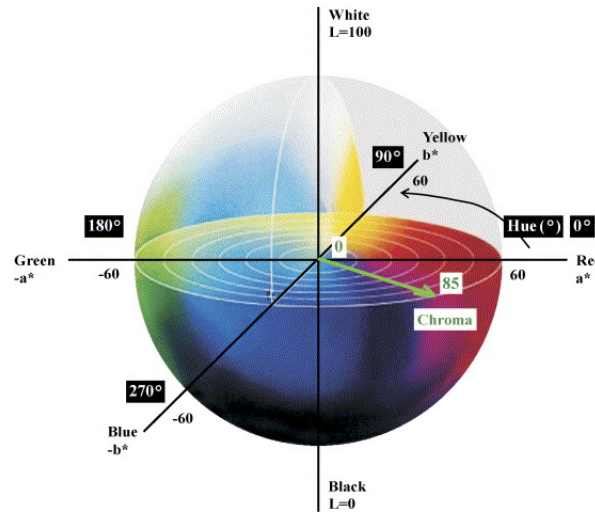


Figure 3-2: Color space. Color can be described by L^* (lightness, black=0 and white=100), hue (positive a^* =more red, negative a^* =more green, positive b^* =more yellow and negative b^* =more blue).

are exposed to light while covered with tape, and oxygen-free is assumed under this condition. In the mean time, small areas are covered from light.

3-4 Color and gloss measurement on the paint films

The color measurement was performed by a spectrophotometer (Konica Minolta CM-2600D) and Spectramagic software, using specular component included (SCI) method instead of specular component excluded (SCE) method. Even though the SCE measurements are more close to the visual appearance of samples, the SCI measurements are less affected by the surface gloss, in other word, the surface roughness (as mentioned in section 2-5).[65] The measured color value is interpreted by the CIE $L^*a^*b^*$ color space as figure 3-2. In this system, the L^* represents lightness, a^* and b^* represent hue positions. The color value can be calculated as $E^* = \sqrt{L^{*2} + a^{*2} + b^{*2}}$, and the color change can be evaluated as $\Delta E^* = \sqrt{\Delta a^{*2} + \Delta b^{*2} + \Delta L^{*2}}$. The expression of the color change shows the distance between the altered color and the original color, and the bigger the ΔE^* , the more color change.

The gloss is displayed in gloss unit (GU) in a scale from 0 to 100. The gloss of the samples was measured by Sheen Glossmaster (figure 3-3) with 3 angles (20° , 60° and 85°) at the same time. The measurement at 60° was chosen primarily. If the 60° value is less than 10GU, then the value at 85° will be taken, and if the 60° value is greater than 70GU, the 20° value will be taken as the gloss value. This operation can make the measurement as accurate as possible.[66] Additionally, the Glossmeter actually used was not the one supposed to be used, so the prepared sample area was smaller for the new Glossmeter, especially the 14 days aging samples. This may lead to relatively big inaccurate measurement of gloss.

The color was measured by placing the paint films on white and black surface. For each time, measurement was repeated 3 times at different positions. The 6 values of the color measurement did not fluctuate a lot, so the average of the 6 values was taken as the color



Figure 3-3: The glossmaster.

result. The gloss was measured 3 or 4 times depending on the surface area, and the final gloss value was also the average.

Both the color and gloss measurement are performed by collecting the light. The interaction between the light and the paint film happens at the surface and the inside layers. Therefore, the measured color and gloss values are contributed by two parts, the outmost surface and the inner layers. Obviously, the outmost layer makes the main contribution, however, the inner layers still count. $50\mu\text{m}$ original thickness paint films of Kremer TiO_2 and Hombikat TiO_2 were made and they were measured on black and white background. As shown in figure 3-4, the Hombikat TiO_2 shows different reflectance on black and white backgrounds. This means the color and gloss measured for the Hombikat TiO_2 -involved paint films are the superposition of both the top surface and the whole thickness. The Kremer TiO_2 at $50\mu\text{m}$ shows totally opacity. Hence, the light penetration depth in the Kremer-involved paint films can be roughly determined according to figure 3-5 [67]. In the figure, R_0 means the reflectance; R_∞ is the reflectance of a layer so thick that further increase of thickness will not change its reflectance remarkably; $C_{0.89}$ is the opacity of the layer; S is the scattering coefficient and X is the thickness. Assuming the TiO_2 layer is opaque at the thickness X , thus the opacity($C_{0.89}$) is 1 and R_∞ is 1, then the corresponding SX product can be located as approximate 50. The scattering coefficient is taken from McNeil's work[68] (figure 3-6) as about $24\mu\text{m}^{-1}$ (the average). Then the thickness X can be calculated as $2.1\mu\text{m}$. The light can reach inside the Kremer TiO_2 film as deep as $2\mu\text{m}$, therefore the color and gloss contribution is mainly based on the outmost $2\mu\text{m}$ surface for Kremer TiO_2 -involved films.

3-5 Surface roughness measurement

The surface roughness was obtained by Bruker 3D optical microscopy and Vision64 software. The surface roughness is expressed by S_q ($S_q = \sqrt{\iint (Z(x,y))^2 dx dy}$), which is the root mean square roughness over the complete 3D surface. Every sample was measured on 3 different positions and the average value was taken as the final roughness. The measurement parameters are indicated as in figure 3-7. Depending on the specific surface condition of the samples, white light or green light was chosen as shown in figure 3-7(a).

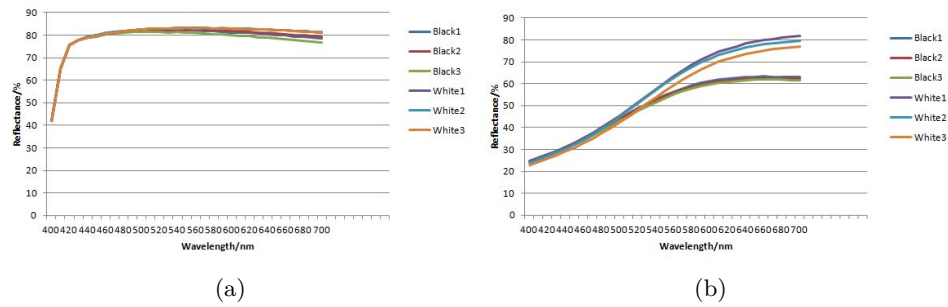


Figure 3-4: The reflectance of TiO_2 on black and white backgrounds, (a) the Kremer TiO_2 , (b) the Hombikat TiO_2 .

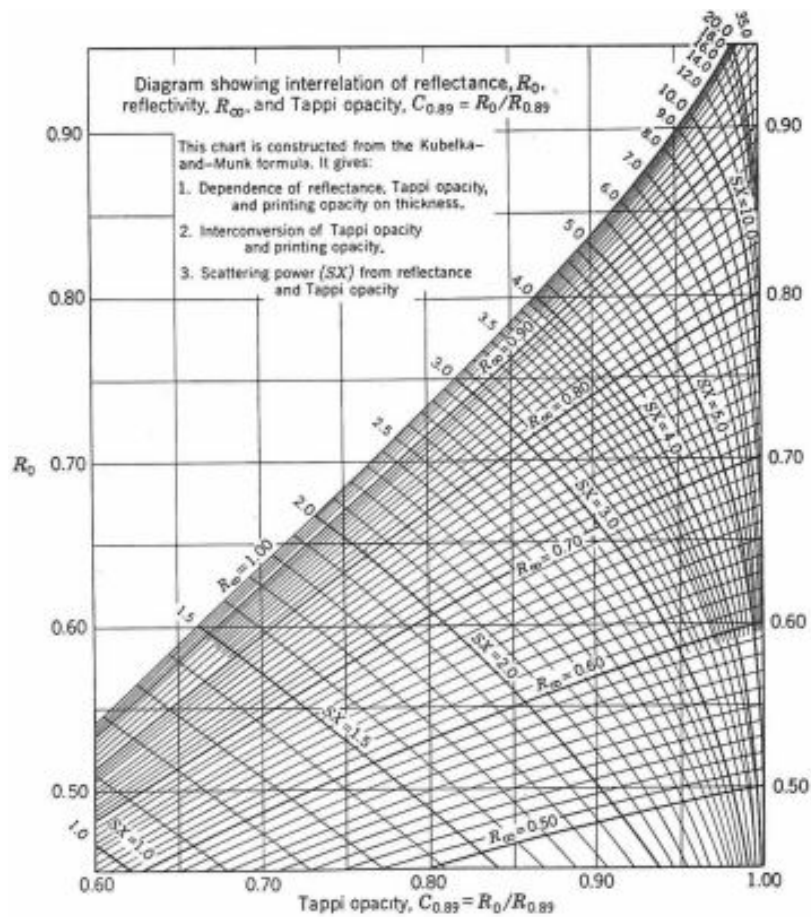


Figure 3-5: Reflectance-opacity chart.

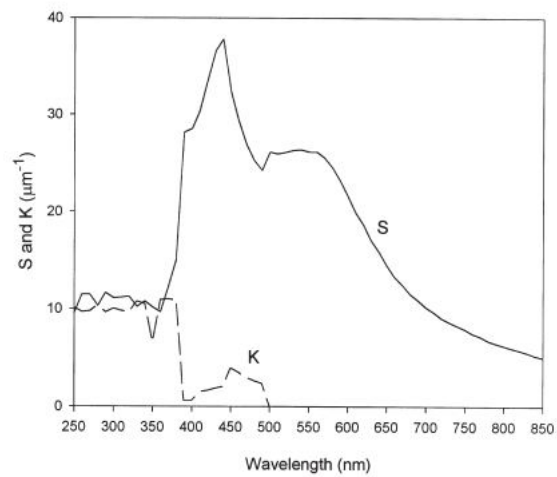


Figure 3-6: Scattering coefficient S (solid line) and absorption coefficient K (broken line).

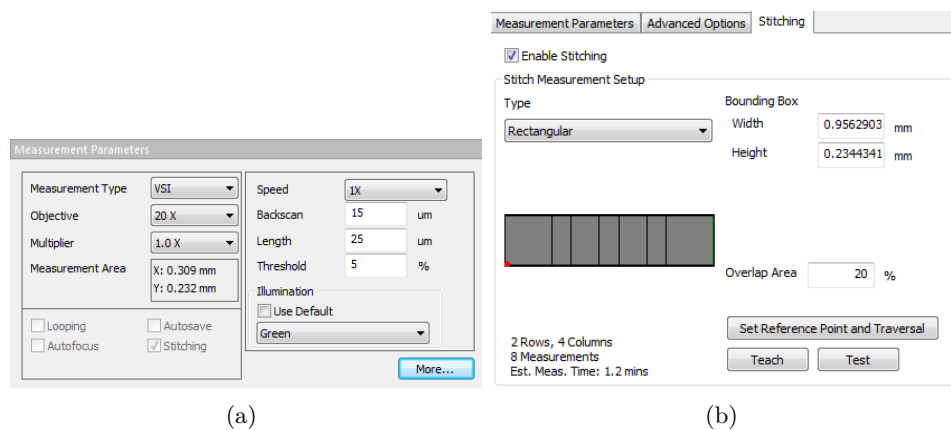


Figure 3-7: The roughness measurement setup, (a) measurement parameters, (b) the measured size.

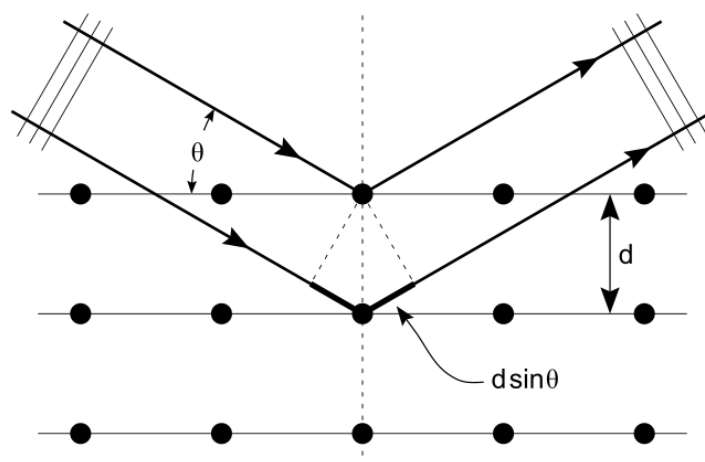


Figure 3-8: Schematic of diffraction geometry, the dots represent atoms or crystal units; d is the spacing between crystal planes and θ is the incident angle.

3-6 Optical light microscopy

Cross sections of paint films went through dramatic alterations (mainly the samples after 2 weeks of artificial aging) were observed under microscopy. Since color change is expected for the paint films, by the optical microscopy, the affected thickness of the film and the difference between the affected top surface and the unaffected inner layer can be distinguished.

3-7 XRD

To get insight of the possible crystal changes of the paint film surface, X-ray diffraction was employed on several samples. Some of the pigments, such as Vermilion and Prussian blue, have crystal structure and can be detected by the XRD. Even for the pigments with no crystal structure, it is possible to find different patterns after the UV light treatment.

Crystals have well arranged atoms and spacings as shown in figure 3-8. The incoming X-Ray, which has the same wavelength order with the crystal spacing d , gets scattered by the atoms in all directions and a diffraction pattern is produced. If the relation of angle θ , wavelength λ and spacing d satisfies Bragg's law $2d\sin\theta = n\lambda$ (n is integer number), the diffraction intensity will increase due to the constructive interference. Then the pattern of this crystal shows a peak at the certain angle. Since crystals have unique spacing d , they have peaks at their specific angles. Therefore the crystal structure can be identified by XRD.

3-8 SEM and EDX

The scanning electron microscopy was used to observe the cross sections further more. With Energy-dispersive X-ray spectroscopy(EDX), elements distribution and intensity can be figured out to determine the possible reactions happened during the aging.

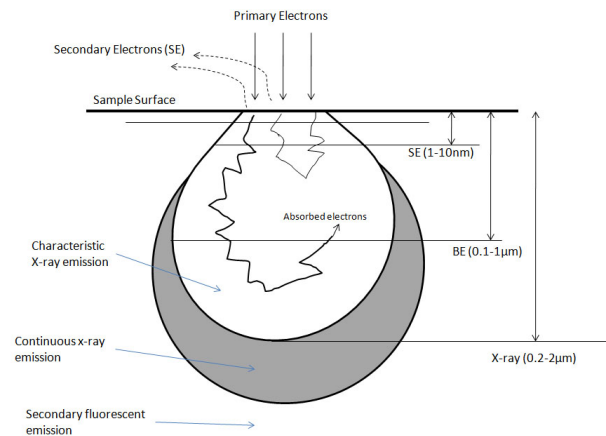


Figure 3-9: Schematic of SEM generated signals

The sample is scanned with an electron beam(primary electrons), and these electrons from the beam could interact with the sample atoms and generate different kinds of signals. The signals, including secondary electrons, back scattering electrons and characteristic X-ray, will be detected and give information about the topography and composition of the sample. The secondary electrons contain information about the surface of the sample and can produce high resolution image; the back scattering electrons differ with the target element' atomic number and can give the elements distribution; the characteristic X-rays can be detected to reveal the composition of the sample. The larger atomic number of the element, the brighter it will be in the analysis.

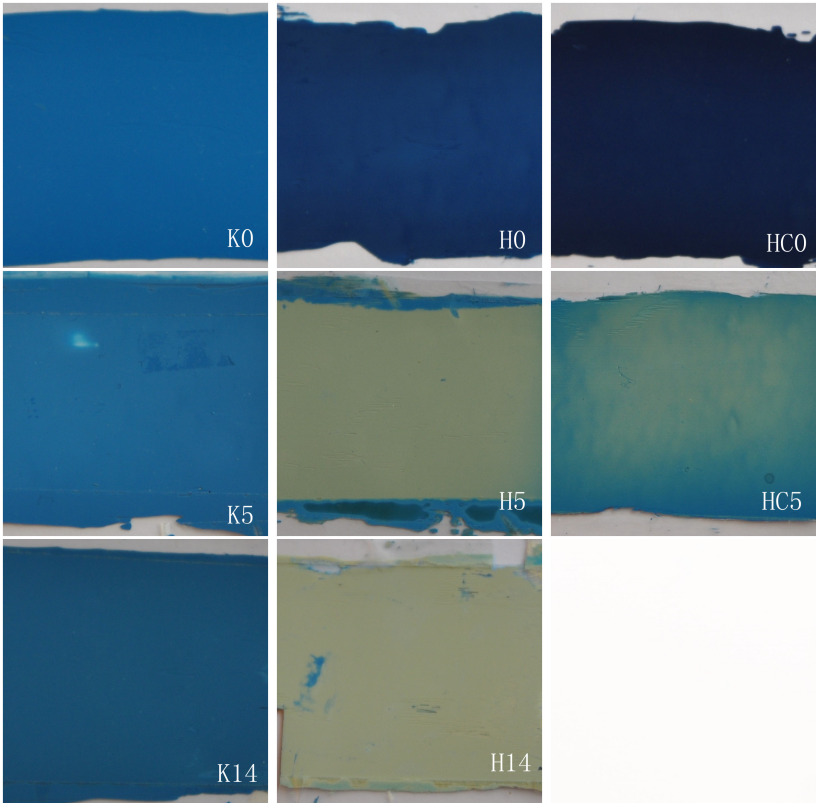
Results and Discussion

4-1 Results

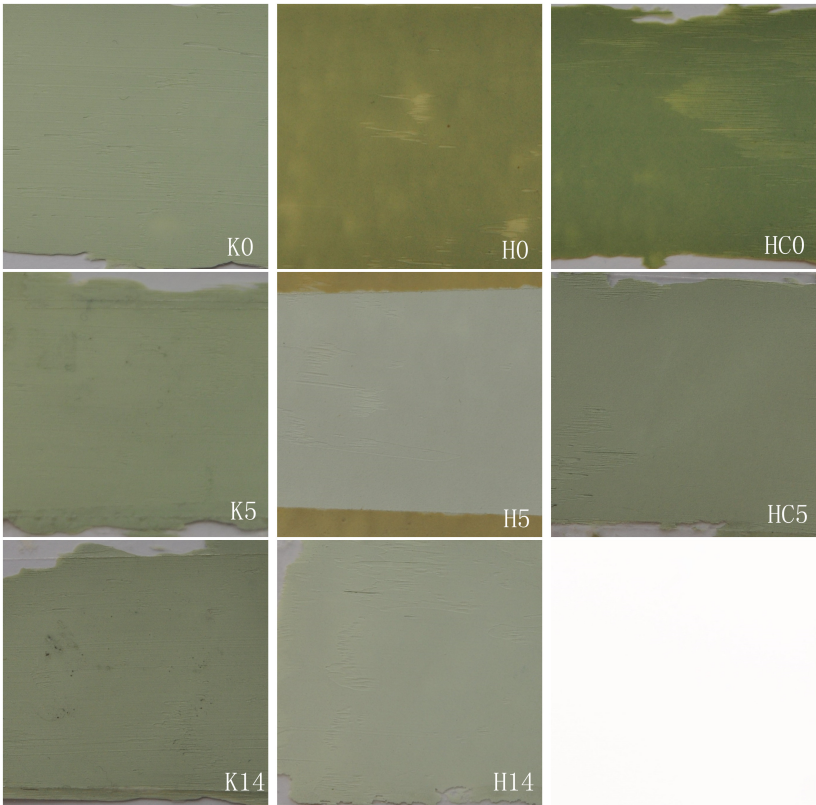
4-1-1 Color change - Visual and Quantitative observation

The unaged and aged samples are firstly observed by naked eyes. The appearance of all the samples in 3 stages can be shown from the photos in figure 4-0. And the quantitative color change is presented in figure 4-1. Because of exposure difference of the photos caused by technical inadequacy of the operator, the quantitative measurement should be relied when conflicts appear between these two observations. Obviously, the color has experienced transformations for most colorants and the behavior of the colorant pigments with different kinds of TiO_2 differs.

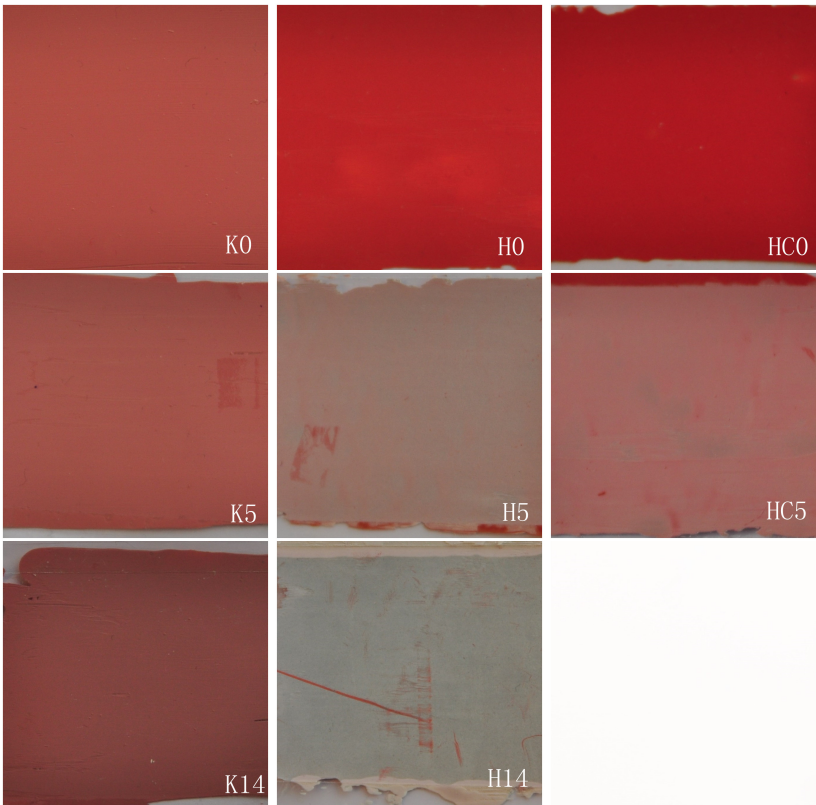
Generally, the colorant pigments has smaller color change with Kremer than with Hombikat TiO_2 . With Kremer TiO_2 , Green earth shows merely color change even after 14 days of aging. Hansa yellow and Indigo show small color change, mainly lightness change (the L^* coordinate change). The vermilion one after 14 days aging shows relatively obvious blackening. All these four pigments exhibit continued color during 14 days aging. Prussian blue has relatively large color change in the first 5 days of aging, and almost stops changing during the next 7 days. With Hombikat TiO_2 , Green earth still has the smallest quantitative color change, but from the visual observation, its color changes obviously. Indigo degrades from dark blue to light blue and the surface does not discolor uniformly after 5 days aging. Prussian blue degrades and almost turns to green color just after 5 days aging. Vermilion loses the red color and gains black appearance during aging. For these four pigments, the difference between 5 days and 14 days aging is not remarkably. However, Hansa yellow has the least color change after 5 days aging, but the most after 14 days. It loses the original yellow color and turns to white. With the coated Hombikat TiO_2 , Prussian blue, Vermilion, Hansa yellow and Indigo show less discoloration visually and quantitatively compared to their counterpart with original Hombikat TiO_2 . Green earth, nevertheless, shows slightly big color change than the one with uncoated Hombikat TiO_2 . Meanwhile, a layer of white power is spotted on these films with Hombikat TiO_2 .



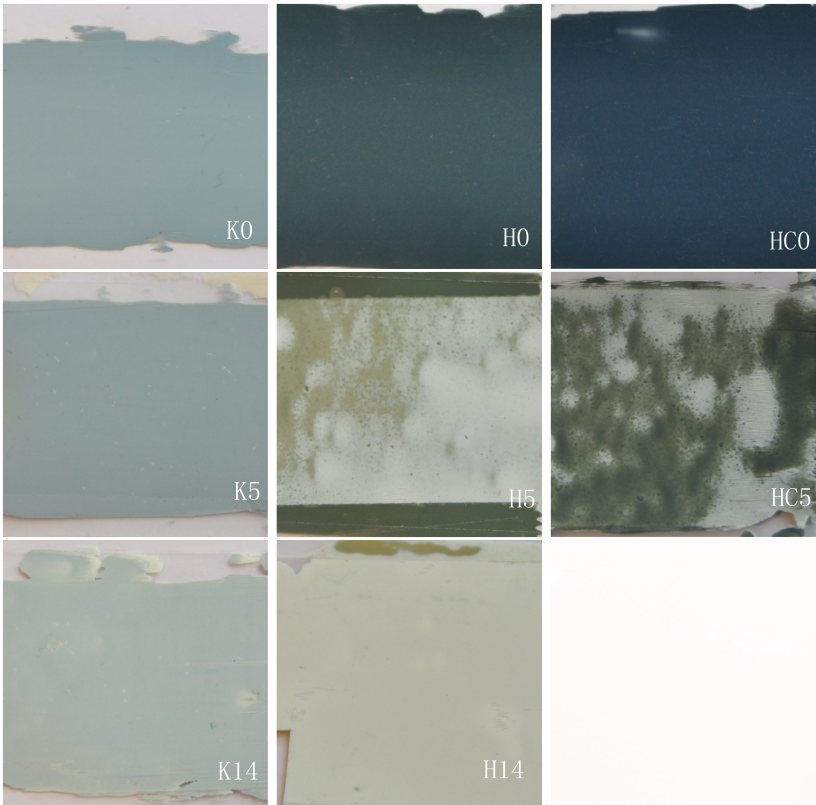
(a)



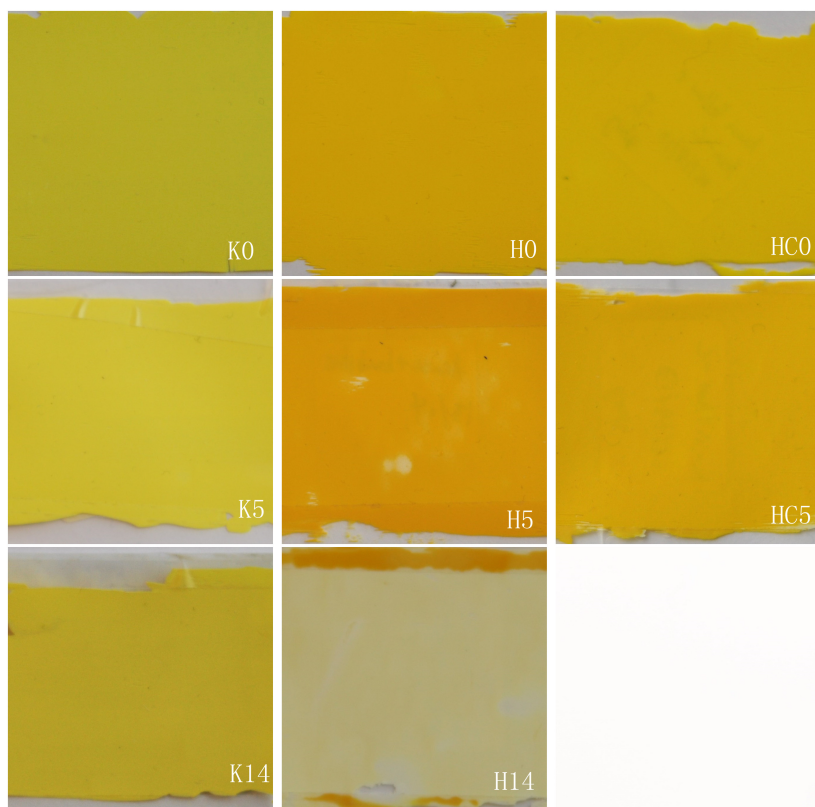
(b)



(c)



(d)



(e)

Figure 4-0: The photos of paint films, (a) Green earth, (b) Prussian blue, (c) Vermilion, (d) Indigo, (e) Hansa yellow.

For every colorant pigments, K0: with Kremer TiO_2 and 0 day aging; K5: with Kremer TiO_2 and 5 days aging; K14: with Kremer TiO_2 and 14 days aging;

H0: with Hombikat TiO_2 and 0 day aging; H5: with Hombikat TiO_2 and 5 days aging; H14: with Hombikat TiO_2 and 14 days aging;

HC0: with coated Hombikat TiO_2 and 0 day aging; HC5: with coated Hombikat TiO_2 and 5 days; HC14: with coated Hombikat TiO_2 and 14 days aging.)

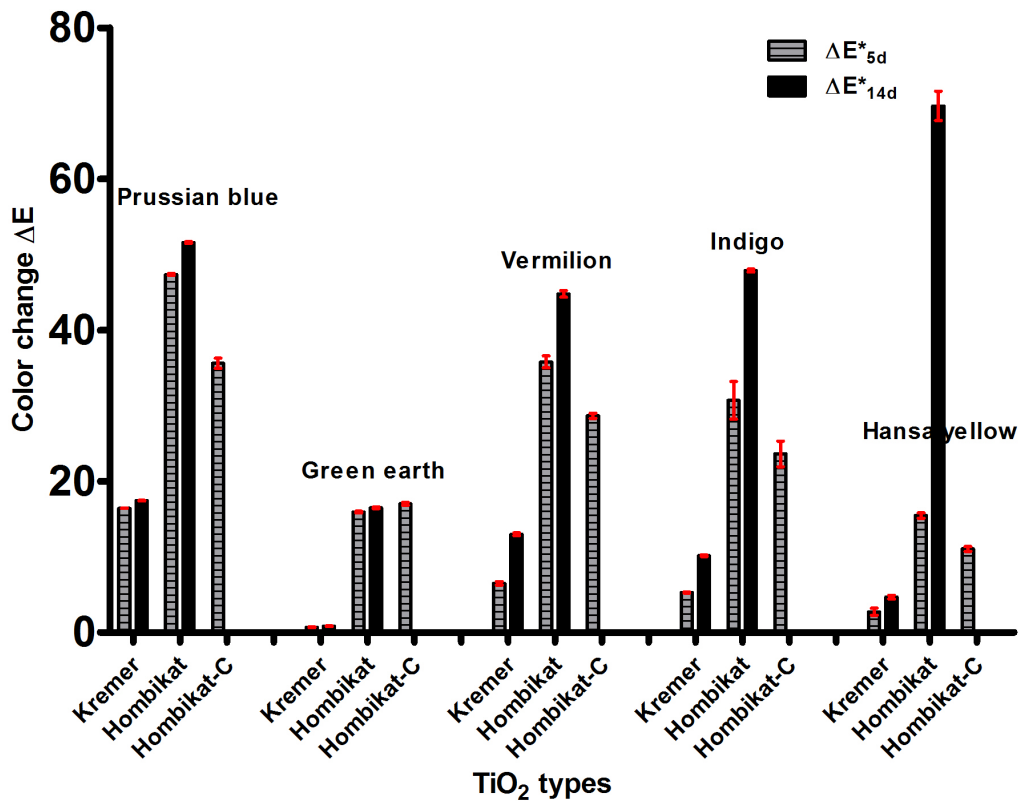


Figure 4-1: The quantitative color change of all the paint films. The error bars indicate standard deviations.

The close gray and black pair have the same ingredient but different aging time. Three pairs with the same colorant pigment are mixed with 3 types of TiO₂.

ΔE^*_{5d} is the color change between 0 day and 5 days aging,

ΔE^*_{14d} is the color change between 0 day and 14 days aging.

Contrast samples which are not illuminated by intensive light do not go through color change. For the aged samples, the surface facing the UV light degrades, while the back of the paint films does not change. During the artificial aging experiments, small parts of films are blocked by the holder from the artificial light, and they do not change color as in figure 4-2. In the same time, the edges of several films were covered with transparent tape. After the equivalent illumination, some of these parts exhibited diverse color change compared to the surface not covered with tape (figure 4-1(b) H5, 4-1(d) H5, 4-1(e) H14, 4-1(c) H14). The covered Hansa yellow and Indigo show brownish, both with Hombikat TiO₂. The covered part of vermilion with Hombikat TiO₂ shows white instead of blackening white.

TiO₂ paint films

To eliminate the influence of binder and TiO₂ color change, paint films with only binder and TiO₂ (Kremer and Hombikat) were prepared and aged for 80 hours. The three coordinates and color change are shown in table 4-1. From the table it is clearly that the color of Kremer

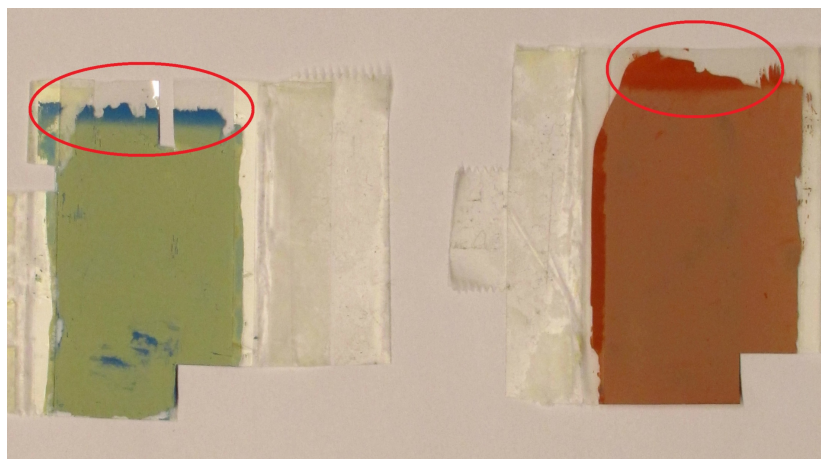


Figure 4-2: The unchanged parts (in the red circles are the areas protected by the holder from the light, here only two examples are given).

TiO₂ with binder does change much, and the main contribution for its color change is the b* coordinate. The color of Hombikat TiO₂ with binder changes a lot and the main contribution is also the b* coordinate. In both cases, the b* becomes more negative.

Table 4-1: The quantitative color change and three coordinates change

Titanium Dioxide	ΔE^*	ΔL^*	Δa^*	Δb^*
Kremer	1.9206	0.3397	0.4727	-1.8039
Hombikat	25.6567	10.5509	-2.3236	-23.1402

Vermilion with BaSO₄ paint films

Inspired by personal conversation, the paint films of vermillion with inert white BaSO₄[69] were made and then aged for one week (168 hours) to reveal the changes caused by the colorant pigment itself. The photos of the vermillion-BaSO₄ films are shown in figure 4-3. The original one on the left shows a bright and more red color while the aged one on the right showed less red and a bit blackening. The quantitative color change ΔE^* is 6.6086.

4-1-2 Gloss change

The color change is easy to perceive with the photos, but the gloss of them cannot be seen properly from the photos. The quantitative gloss is shown in figure 4-4.

The gloss of all the paint films decrease with aging time increasing. As mentioned in section 3-4, the facts that the area of the aged samples smaller than the area needed for the gloss measurement could lead to higher measured values. Taking this into consideration, generally, the gloss values of the aged samples should be lower. Along with the error bars, the decrease tendencies of the same colorant pigment with all three TiO₂ can be assumed to be similar. For the paint films with Hombikat-related TiO₂, after UV light treatment, the previous bright-colored, shiny and smooth surface was replaced by a vague, dim and removable layer as

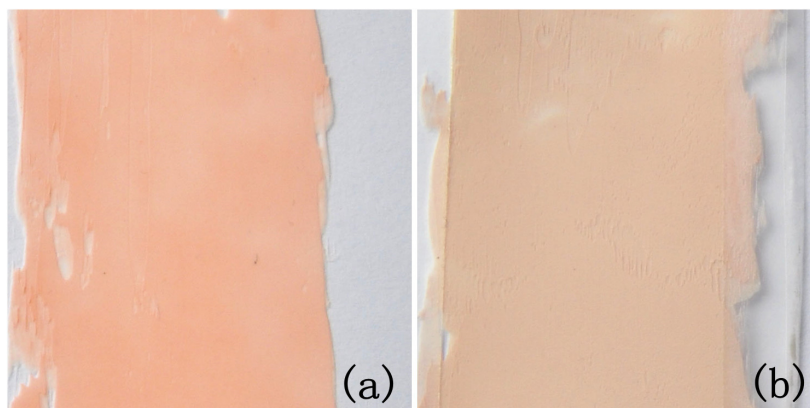


Figure 4-3: Photos of Vermilion and BaSO₄ paint films, (a) before aging; (b) after 1 week aging.

mentioned before. The paint films with Kremer TiO₂ do not form removable top layer after UV light aging.

Most paint films with Kremer TiO₂ have higher starting gloss values than these with Hombikat-involved films. This observation agrees with the brighter white color of Kremer TiO₂ paint during the preparing of the paints. In the mean time, when mixed with oil, the Hombikat TiO₂ shows darker and yellowish white.

Green earth has the mildest almost linear gloss change through the 14 days. The gloss change for Vermilion is linear and not sharp. Indigo and Hansa yellow have relatively bigger gloss change, and if taking the measurement error mentioned above into account, they both go through faster gloss loss in the second period of aging. Prussian blue has sharper gloss decrease in the first 5 days of aging, and the gloss change slows down in the following aging days.

4-1-3 Roughness change

Theoretically, the surface roughness can alter the diffuse reflection and then influence the gloss of the paint films. Here figure 4-5 is the roughness of the paint films before and after treatments.

Except from Green earth, the Kremer TiO₂-involved paint films have lower roughness than Hombikat TiO₂ ones. When making the paints, more oil was added for the Kremer TiO₂ because of its higher oil absorption. This could lead to smoother surface of the Kremer TiO₂ films. Green earth paint films have the roughest surface which can be attributed to the bigger particle size of this clay pigment. The amount of Green earth mixing with Kremer TiO₂ is about 10% weight more than with Hombikat TiO₂, and may causing rougher surface.

The same colorant pigment behaves similar with all three TiO₂. The roughness of Green earth and Vermilion films increase almost linearly and Green earth is getting rough slower than Vermilion. Indigo and Prussian blue have slower roughness increase at the first 5 days and faster increase in the second period aging. Hnasa yellow has obvious roughness grow with Kremer TiO₂, while has slight roughness grow with Hombikat TiO₂. If taking the error bar into consideration, roughness increases linearly with the increasing of the aging time for most of the surfaces. This is consistent with the more or less linear gloss decrease.

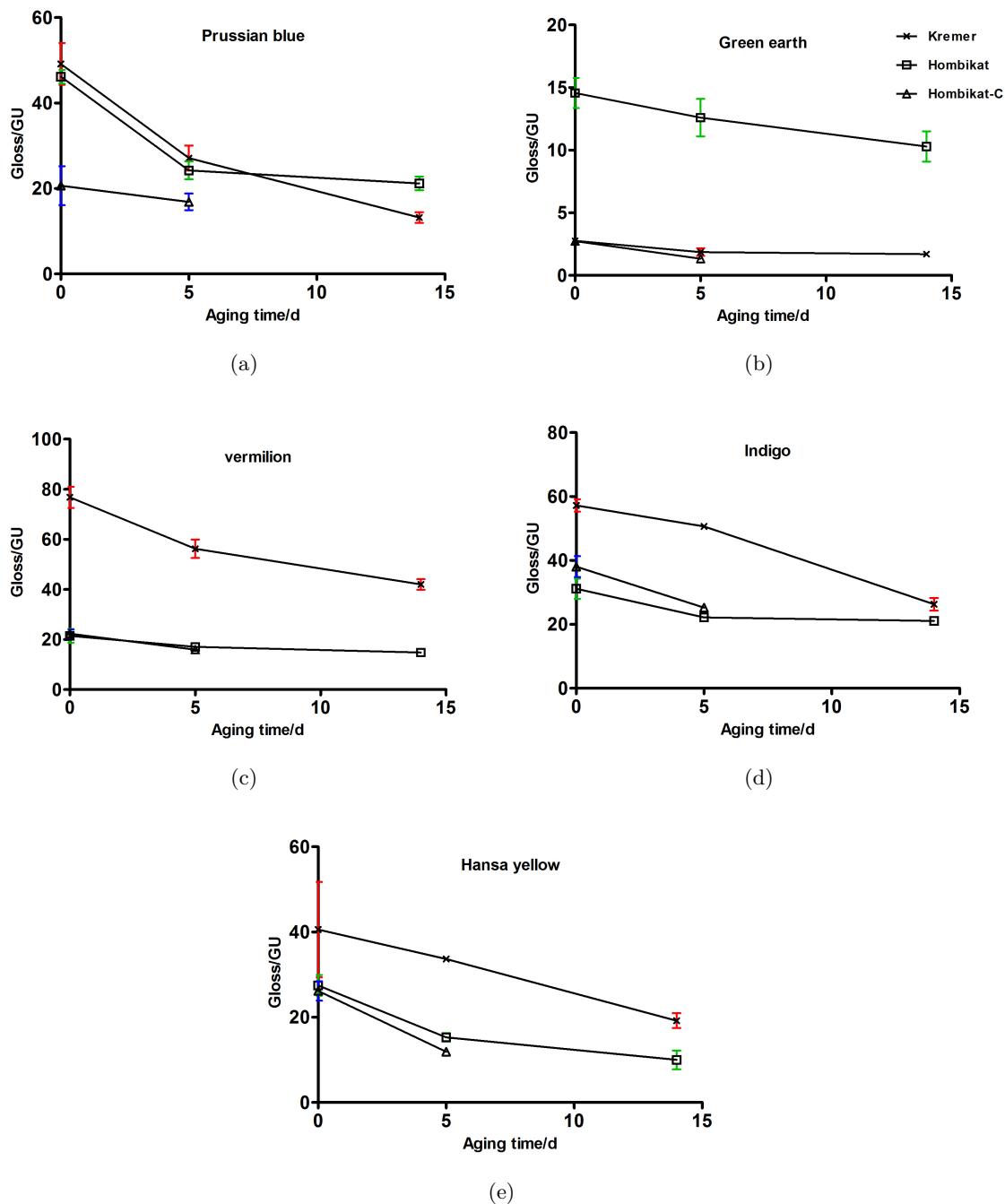


Figure 4-4: The gloss change of all the paint film with aging time. The error bars indicate standard deviations, and the missing error bars suggest too small deviations.

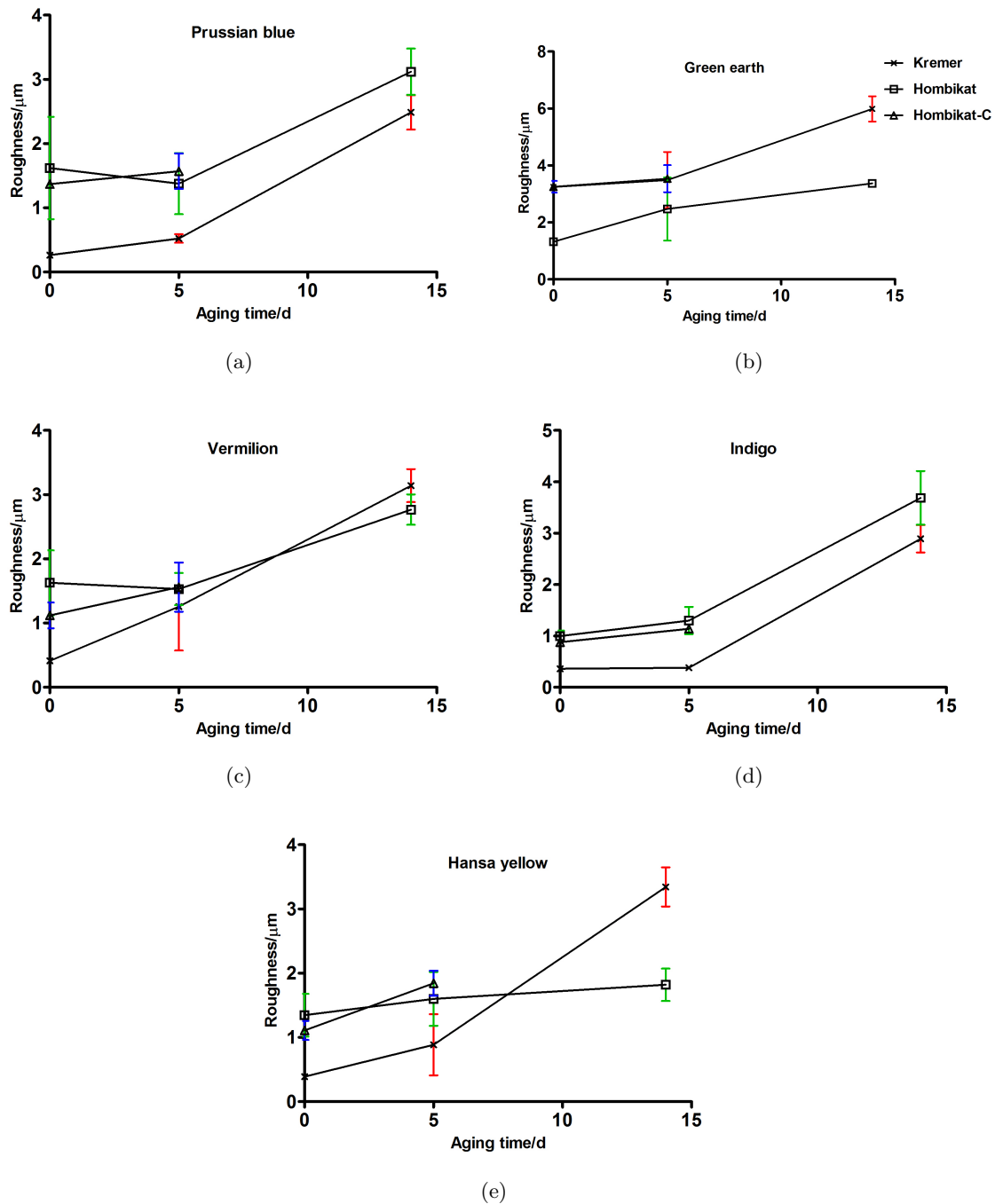


Figure 4-5: The roughness change of all the paint films with aging time. The error bars indicate standard deviations, and the missing error bars suggest too small deviations.

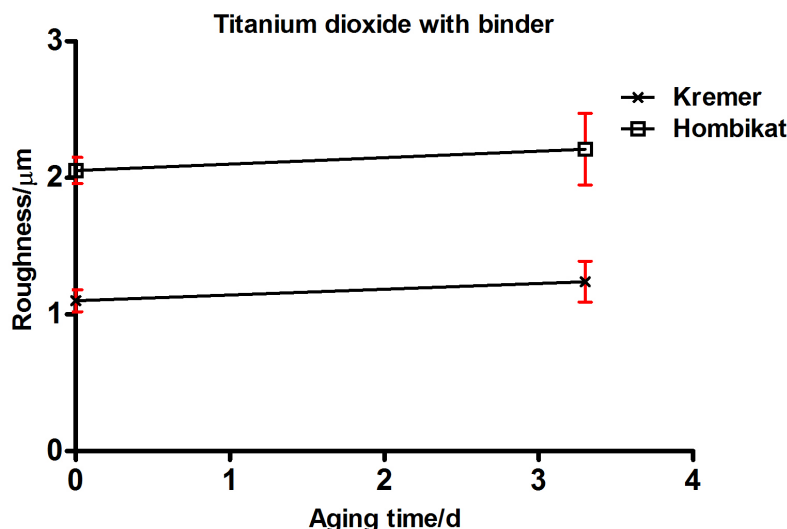


Figure 4-6: The roughness change for Kremer and Hombikat TiO₂ paint films. The error bars indicate standard deviations.

TiO₂ paint films

In figure 4-6, the roughness of Kremer and Hombikat TiO₂ paint films are shown. The roughness for both of them increase rather slow. However, since they were only aged for 80 hours, they may have bigger roughness change if the aging time could be longer.

Vermilion with BaSO₄ paint films

Figure 4-7 shows the roughness change of Vermilion and BaSO₄ paint films. It can be seen that the roughness change here has slightly flatter slope than the roughness change with TiO₂.

Roughness-Gloss correlation

The gloss and roughness change have confirmed the more rough, less glossy theory qualitatively. The general quantitative correlation between gloss and roughness cannot be verified here. Basically, the gloss is not only determined by the roughness of the surface, the refractive index of the material also plays a role. Since all the colorant pigments, even the Kremer and Hombikat TiO₂, have different refractive indexes, their gloss values will be influenced diversely. In this case, the roughness and gloss correlation can only be established with the same ingredients.

4-1-4 Optical light microscopy observations

The thickness of the film was 50 micrometers when first made, however, after drying, the thickness decreased a bit.

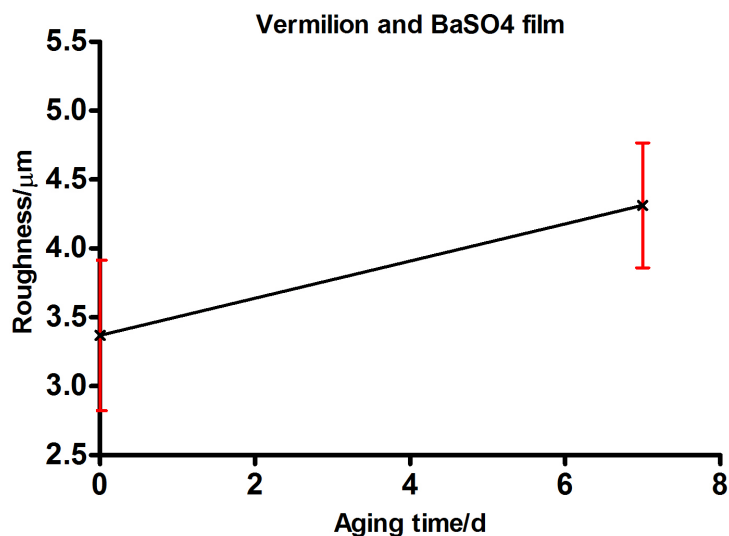


Figure 4-7: The roughness change for Vermilion with BaSO₄ paint films. The error bars indicate standard deviations.

Prussian blue

In figure 4-8, the cross sections of Prussian blue paint film with Hombikat TiO₂ (a) unaffected by UV light(4-8(a)) and (b) affected by UV light(4-8(b)) are shown. The upper outermost layer is the layer facing the UV light, and the layer at the bottom is the layer attached to the melinex. Both cross sections contain big white particles, which are considered to be the remaining incompletely ground TiO₂ particles. From the figures, it is clearly that the color of the affected top surface has changed. And the uniformly affected thickness is about 5 micrometers.

Green earth

Figure 4-9 shows the cross section of paint film with Green earth and Hombikat TiO₂. The big green particle inside is believed to be the green earth pigment particle. The top surface looks translucent, but it is caused by the physical reactions between the surface and the surrounding resin. At the bottom of the cross section, where no photo-catalytic effect at all, the surface layer also appears translucency. After excluded this point, the color of the top surface do not change obviously.

Vermilion

In figure 4-10, the cross sections of Vermilion paint film with Hombikat TiO₂ (a) unaffected by UV light(4-10(a)) and (b) affected by UV light(4-10(b)) are shown. The top layer turns black of which the thickness is approximate 5 microns. The Vermilion-involved paint film is the only one shows black affected top surface instead of whitish top layer.

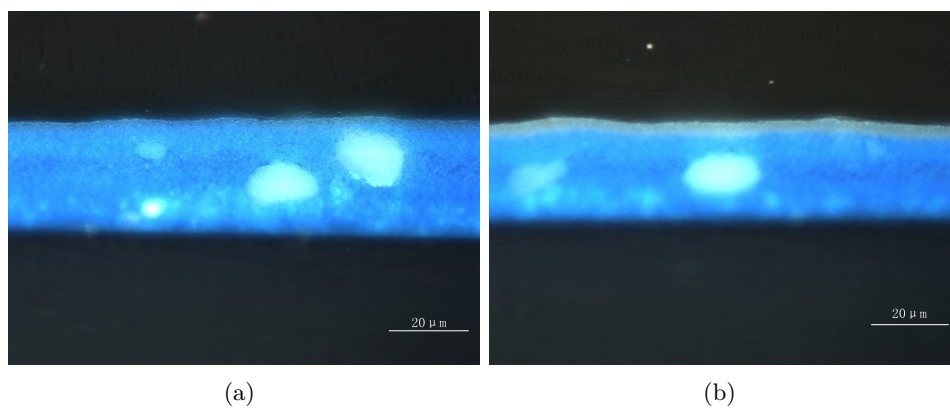


Figure 4-8: The cross sections of Prussian blue and Hombikat TiO_2 paint film, (a) without aging, (b) with 14 days aging.

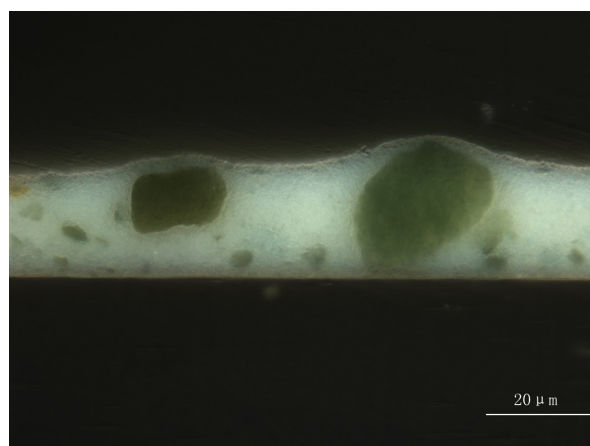


Figure 4-9: The cross section of Green earth and Hombikat TiO_2 paint film with 14 days aging.

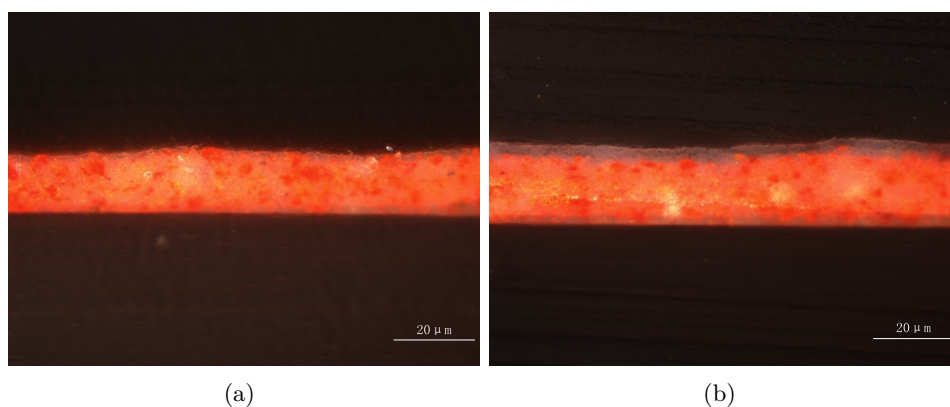


Figure 4-10: The cross sections of Vermilion and Hombikat TiO_2 paint film, (a) without aging, (b) with 14 days aging.

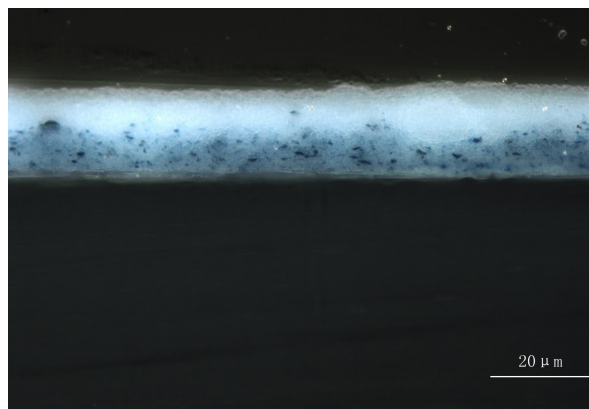


Figure 4-11: The cross sections of Indigo and Hombikat TiO_2 paint film with 14 days aging.

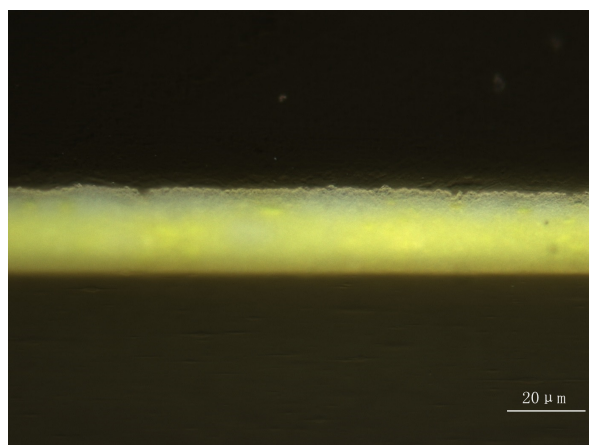


Figure 4-12: The cross section of Hansa yellow and Hombikat TiO_2 paint film with 14 days aging.

Indigo

Figure 4-11 shows the cross sections of paint film with indigo and Hombikat TiO_2 . As seen in the cross section, the affected thickness is remarkable and almost half of the cross section has change to white color.

Hansa yellow

Figure 4-12 shows the cross section of paint film with Hansa yellow and Hombikat TiO_2 . Although the color of this cross section surface has suffered great alteration from bright yellow to almost white (figure 4-0), the affected thickness is only about 8 to 10 micrometers.

These optical microscopy figures indicate a clear difference between the top surface and the inward part of the paint films. Except for the green earth paint film cross sections, all other top surfaces turn whitish or black (the vermilion case) at different thickness. The indigo with Hombikat TiO_2 paint film suffer the most from the Photo-catalytic effect, and half of the cross section has degrades.

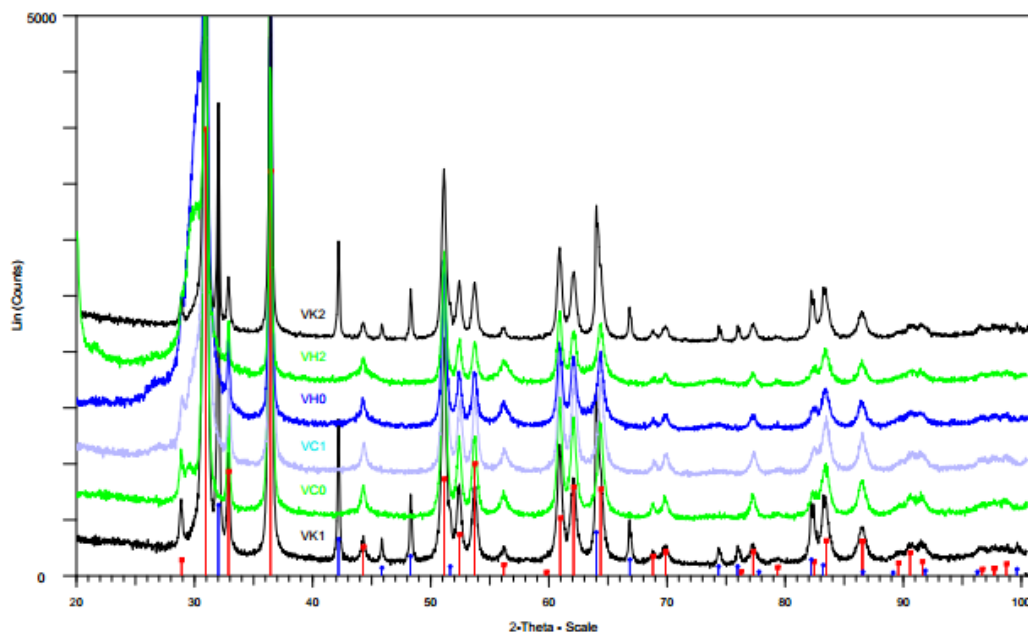


Figure 4-13: XRD patterns of the Vermilion paint films.

VK1: Vermilion + Kremer TiO_2 , 0d aging; VK2: Vermilion + Kremer TiO_2 , 14d aging;
 VH0: Vermilion + Hombikat TiO_2 , 0d aging; VH2: Vermilion + Hombikat TiO_2 , 14d aging;
 VC0: Vermilion + coated Hombikat TiO_2 , 0d aging;
 VC2: Vermilion + coated Hombikat TiO_2 , 14d aging.

The vertical lines, Red: cinnabar- HgS , Blue: rutile- TiO_2

4-1-5 XRD

XRD results of the vermilion-involved paint films (figure 4-13) show that only the peaks for the cinnabar can be found here. Meanwhile, the patterns of original and treated samples are similar, which indicates no obvious structure change has happened. However, this cannot be too sure, because after the paint films were made, they have not been stored in complete darkness. Considering the vermilion is pretty sensitive to light and easy to blacken, maybe the sample used as reference has already been transformed.

Identical with vermilion-involved paint films, others do not show much useful information (figure A-1 shown in the Appendix). This is mainly due to the non-crystal but amorphous structure of the pigments, especially for the organic pigments. In the same time, the surface modified by aging is as thin as a few micrometers, XRD may not be sensitive enough to detect the superficial material.

4-1-6 SEM-EDX

The SEM figures do not give much topography information. The structural transformations of the top layers cannot be seen from SEM figures. The EDX analysis gives elemental distribution situation.

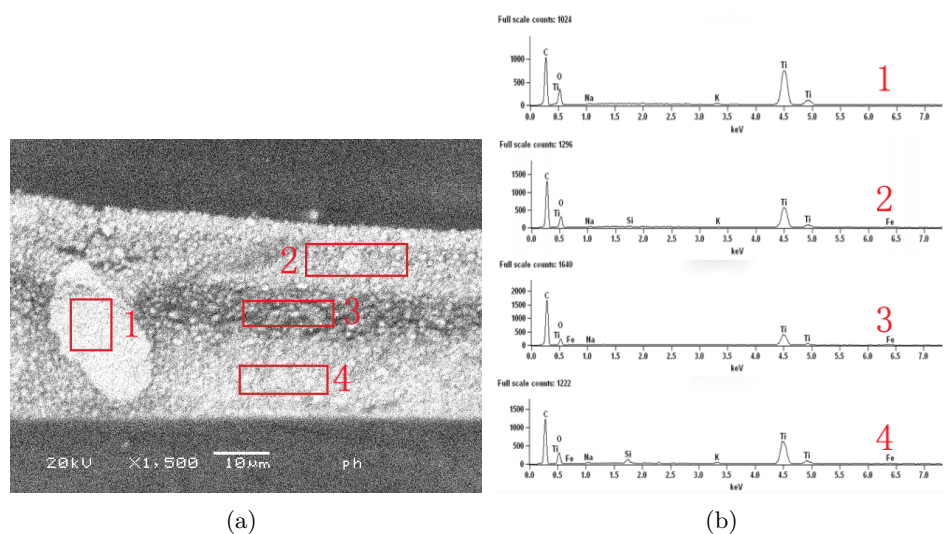


Figure 4-14: SEM and EDX figures, (a) SEM of Prussian blue and Hombikat TiO₂ cross section with 14 days aging, (b) EDX elemental analyses of the selected areas in (a).

Prussian blue

The Prussian blue figure 4-14(a) shows a strange sandwich configuration, the top and bottom layers are similar while the layer in the middle is distinct. This structure also can be seen in the optical microscopy (figure 4-8), though not as clearly as here. The white large particle (the selected area 1) is TiO₂, according to the elemental analysis on the particle (figure 4-14(b)). The analyses in 2, 3 and 4 area show these areas contain Prussian blue pigment elements and TiO₂, the only difference is that the blacker area 3 has less TiO₂ compared to areas 2 and 4. The TiO₂ shows brighter color in SEM picture. The formation of this configuration could be the repeating applying of the drawing bar during the paint film making.

Green earth

The EDX of Green earth is presented in the Appendix (figure A-2). It shows no significant change for green earth and Hombikat TiO₂ cross section. This is consistent with the observation of optical microscopy. Green earth is inert and not degraded by TiO₂ too much.

Vermilion

In figure 4-15(a), vermilion and Hombikat TiO₂ cross section is shown, and in figure 4-15(b), the elemental analyses of selected area in figure 4-15(a) are shown. The white particles (area 1) are vermilion particles and the darker areas (area 2 and 3) contain more TiO₂. No extra elements have been found in the cross section. The expected Cl did not show up, however, this assumption still cannot be rejected because the amount of Cl could be too small to be detected.

From the red area 4 in figure 4-15(a), a separation can be seen clearly. This could be the affected loose top surface peeling off or just caused by the operation.

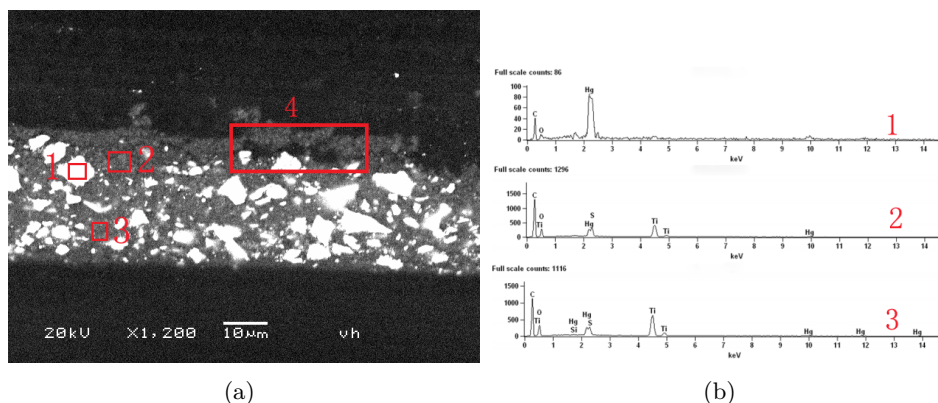


Figure 4-15: SEM and EDX figures, (a) SEM of Vermilion and Hombikat TiO_2 cross section with 14 days aging, (b) EDX elemental analyses of the selected areas in (a).

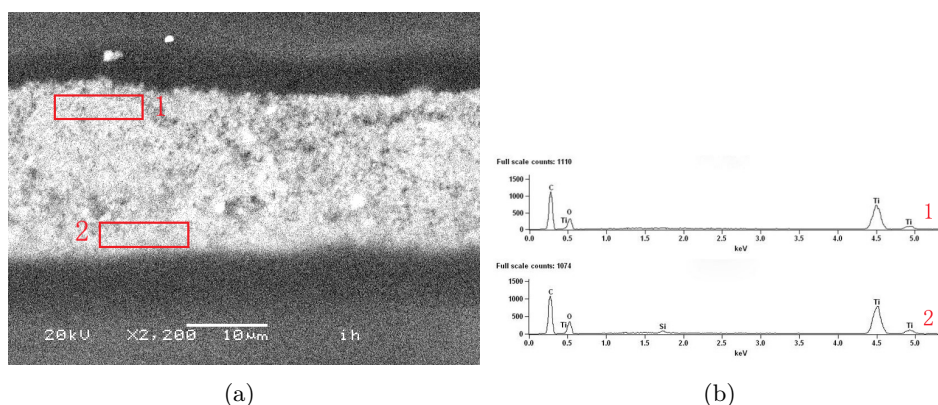


Figure 4-16: SEM and EDX figures, (a) SEM of Indigo and Hombikat TiO_2 cross section with 14 days aging, (b) EDX elemental analyses of the selected areas in (a).

Indigo and Hansa yellow

The elemental analysis of Indigo with Hombikat TiO_2 (figure 4-16) only managed to detect the original pigment composition Ti, C and O. In the same time, no obvious elements change are found through the cross section, indicating a proposal of intra-system degradation without outside contamination.

The analysis of Hansa yellow and Hombikat TiO_2 (figure 4-17) does not show much extra elements, either. But the intensities of Cl at the three positions are different. The darker particle (area 2) is the Hansa yellow pigment since it contains smaller atomic number elements. It is supposed to contain larger amount of Cl and it does. The near exposed surface position 1 has no Cl while the position 3 far away from the exposure has Cl left. The absence of Cl from the top surface indicates breakdown of the bonding and lose of the composition element.

From the EDX analyses, it can be seen clear that the outmost layer is pigments rich, which means the oil did not form thick layer on top of the films during the drying. And the affected thickness mentioned in section 4-1-4 has reached the pigment rich region. Therefore, the reactions happened in the film are indeed with the participation of both binder and colorant

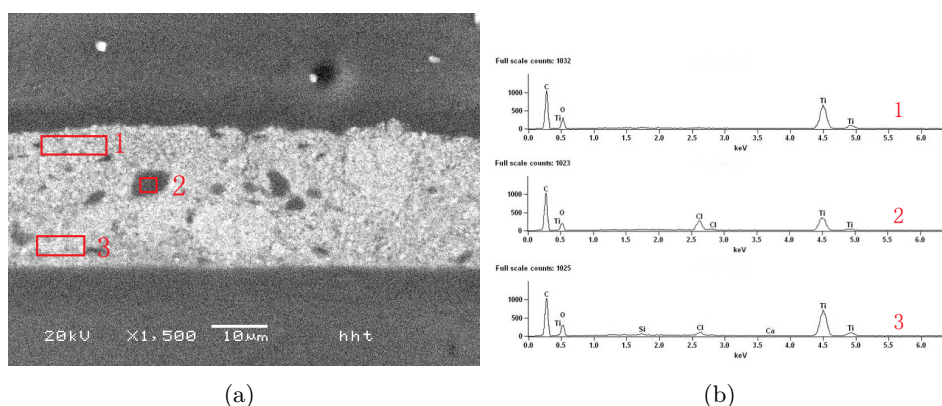


Figure 4-17: SEM and EDX figures, (a) SEM of Hansa yellow and Hombikat TiO_2 cross section with 14 days aging, (b) EDX elemental analyses of the selected areas in (a).

pigments.

An alien element Si appears in almost all of the cross sections. The only source of Si is the sand paper when preparing the cross sections. The interesting phenomenon is that Si is only found at the bottom of the cross sections but not the top surface except the Green earth cross section. The Green earth cross section has Si all through.

4-2 Discussion

4-2-1 Color and Gloss measurement correction

The accuracy of these measurement is considered firstly. In section 3-4, the possibility of multiple contribution of color and gloss measurement is discussed. The light penetration depth in Kremer TiO_2 paint film is roughly calculated as $2\mu\text{m}$, and the microscopy of the cross sections shows even for the more affected Hombikat films, the affected thickness is no much thicker than $2\mu\text{m}$. Therefore, the actual color change for Kremer-involved paint films should be slightly more than the measured one. The Hombikat TiO_2 -involved paint films has been proved not opaque enough, thus the measured color is the superposition of the outmost layer and the inner layers. Since the inner layers do not change color, the actual color change should be bigger than the measured one, for both 5 days and 14 days. The color measurement collects both specular and diffuse reflection lights, thus the penetration depth could play a role here. However, the gloss measurement only deals with specular reflection. Even the light can penetrate inside the paint films, the chance that the light can get out of the film right at the same angle with the specular reflected light is extremely small. Consequently, gloss is not influenced by the penetration depth of the light.

4-2-2 Photo-catalytic effect of TiO_2 on the surface

The surface of the paint films has altered in color, roughness and gloss. From the previous study of TU Delft student Birgit van Driel, the solo linseed oil change is small enough to

be neglected even after 28 days aging. Therefore the changes are believed to be induced by TiO_2 .

Color

The color change may have two contributions, the binder and the colorant pigments, since the TiO_2 itself will not change color. Section 4-1-1 (TiO_2 paints films) shows the color change of Kremer TiO_2 with oil paint film is pretty small, and this color change is mainly attribute to the binder change. After subtract the a, b, L changes of the binder, the color changes left should be the colorant pigments color change. However, the left color changes did not have big difference compared to the old ones. Still, the small influence cannot be neglected for Green earth and Hansa yellow films, which have little color change. And their pure color changes after eliminating are close to almost zero. That means the color change of these two mostly caused by the binder change. The Vermilion with BaSO_4 paint film shows that the Vermilion would suffer from color change under UV light without the existence of TiO_2 . The color change of Vermilion with Kremer TiO_2 film is about the same value of the color change of Vermilion itself, which indicates the Kremer TiO_2 does not induce color change, at least for the Vermilion pigment. In this situation, the Kremer TiO_2 could be regarded as having limited effect on the color change of the colorant pigments, but some effects on the binder. The Hombikat TiO_2 with binder goes through bigger color change, and visually, its color changed from yellow to white. L^* and b^* are the main contribution for its color change, and L^* becomes more positive while b^* becomes more negative. All the Hombikat TiO_2 involved films have L^* becoming more positive as main contribution, but not all of them (only the Green earth has the same changing tendency) have b^* change as main contribution. It indicates that the Hombikat TiO_2 with binder change does influence the color change of these films, but they are not the only factor which causes the color change, the colorant pigments themselves also have changed color.

Combining the discussion above and the description in 4-1-1, the color change discipline differs for the three TiO_2 . Kremer TiO_2 has a rutile structure and Hombikat TiO_2 has an active anatase structure, and the particle size of Hombikat is much smaller than the Kremer one. Kremer TiO_2 also has Al_2O_3 and SiO_2 coating to increase its chalking resistant and decrease its photo-catalytic effect. Basically, the rutile structure is widely considered more stable than the anatase structure and preferred by the artists. In the mean time, smaller particle size means more surface areas at where reactions can happen, leading to quick or thorough reaction. Thus it is not surprising to find a more stable performance of Kremer-involved paint films. Even though coating is used to enhance the property of TiO_2 , the coated Hombikat TiO_2 in this study does not effectively increase the stability of the original one. Two hypotheses are proposed for the reason. One is that the coating is not perfect enough to stop the photo-catalytic effect of TiO_2 . The other is that the coating material Al_2O_3 can lead the generated electrons and hole to the particle surface as well.

Besides, the Hombikat TiO_2 , both uncoated and coated, causes formation of a whitish removal layer, indicating happening of chalking. The Kremer TiO_2 does not help forming obvious removal layer, but since the binder has been altered by it, the layer may be just not evident enough. This layer could be a barrier to protect the inner layer from the UV light. With the protection, some colorant pigments with Hombikat TiO_2 do not suffer more color change in

the second period of aging. While with Kremer TiO_2 , which did not form protective layer, the color change in the second period is significant for most of the colorant pigments.

Roughness and Gloss

Same as the color, roughness change caused by TiO_2 may also have contribution from the binder with TiO_2 . Section 4-1-3 (TiO_2 paints films) shows limited roughness change for Kremer and Hombikat TiO_2 after 80 hours of aging, and section 4-1-3 (Vermilion with BaSO_4) shows relatively large roughness change for Vermilion with BaSO_4 after 7 days aging. In the BaSO_4 film, BaSO_4 will not change considering its inert chemical property, and Vermilion may not change much considering its small color change (4-1-1 Vermilion with BaSO_4), so the binder could be the reason of the roughness increase since it can be degraded by light directly. Since the binder degradation is about breaking the bonding of polymers, it is reasonable to make the assumption that the binder degradation needs more time, thus, the relatively small roughness change of TiO_2 +oil film could be due to too short aging time. In the same time, even the color of Green earth pigment (with all three TiO_2) does not change, the surface roughness changes, which is possibly the degradation result of the binder. With these assumptions, it could be said that the binder is the most important factor to influence the paint film roughness.

The continued roughness change demonstrates the degradation is happening all the time. The color change of Kremer TiO_2 -involved films and gloss change are consistent with it, while the color change of Hombikat TiO_2 -involved paint films is not supporting this directly. The reason could be the new formed powder layer. Further degradation was happening mainly in this layer instead of developing inside the film. In this case, the roughness can still get larger in this layer, but the color cannot change too much because this layer has already faded to whitish color. And this layer is the product of degraded binder as discussed before. Therefore, it is clearly the binder has influence on the roughness of the paint films.

4-2-3 Colorant pigments behavior

As above, four of the five colorant pigments go through color change caused by TiO_2 , and their degradation mechanisms will be discussed here. The Green earth pigment shows no color with Kremer TiO_2 as mentioned above. When mixed with Hombikat TiO_2 , it has similar color change value with the only Hombikat TiO_2 paint film, indicating no color change for Green earth pigment, either. Therefore, the color of Green earth pigment is not affected by either TiO_2 . Besides, the XRD and EDX, even though not sensitive, show no crystal and elemental alternation for it. All these probably indicate this pigment has not been change. Green earth is regarded as a permanent pigment and this study confirms that the color of Green earth will not be affect by TiO_2 in a relatively long time under UV illumination.

When mixed with inert BaSO_4 , Vermilion goes through color change by itself. The Kremer TiO_2 does not induce more color change and Hombikat TiO_2 seems to boost the color change of Vermilion. The Vermilion with Hombikat TiO_2 shows not only blackening, but chalking. The mechanism of its blackening has been discussed in the past. And the meta-cinnabar, Hg-Cl compound and $\text{Hg}(0)$ product are proposed and some of them have found evidence.

However, in this study, XRD and EDX have not found any evidence to support each mechanism hypothesis. The lack of sensitivity of these two techniques could be one of the reason. And the other reason could be the amount of accumulated alien elements is too small to be detected.

Prussian blue has relatively big color change even with Kremer TiO₂, but the XRD and EDX show no obvious crystal and elemental change. The color coordination a^* becomes negative (towards the green color). Considering its composition with Fe³⁺ and the green color of Fe²⁺, it is possible that the Fe³⁺ has been reduced during the aging. And the single element oxidation or reducing apparently needs less energy and takes less time. If it could be the reason, then it is reasonable to explain the faster color change for Prussian blue than others.

Indigo and Hansa yellow are both organic pigments, and have similar behavior, as showing bigger difference between the 5 days and 14 days aging. While other colorant pigments do not have this feature. The EDX of Hansa yellow exhibits missing Cl element at the altered top surface, suggesting the color loss could be caused by the molecular bonding breaking. Considering the same organic nature, Indigo could go through the same degradation mechanism. However, since Indigo only has C, H, O and N elements, which is also the composition of the organic binder, the EDX cannot provide solid evidence of its bonding breaking. The bonding breaking can also explain the difference between two periods of aging, because the molecular bonding needs more energy to be broken. In the study, more energy means more illumination, in other words, more aging time.

4-2-4 The factors influencing degradation

The photo-catalytic effect of TiO₂ is proved to have influence on the degradation. The same pigments with different kinds of TiO₂ show different color decay. It indicates that TiO₂ does play a role during the degradation of the paint films, and different TiO₂ have different degradation grade. The visual observation (section 4-1-1) and optical microscopy (section 4-1-4) all show that the photo-catalytic effect is superficial. The whole paint film is about 30 μm , while the affected thickness is only as much as 5-8 micrometers. This agrees with the fact that only the light-exposed side has degraded and the back light-shielded side is not affected. As seen in figure 4-2, degradation will not happen without light, even the environment is exactly the same. These observation suggests that one of the essential factors during the degradation is the UV light.

The amount of TiO₂ also affects the degradation extent. Because of the high tinting power of indigo pigment, the film samples made from Indigo contain larger amount of TiO₂. Consequently, with little colorant and much TiO₂, the degradation is most likely to happen and the affected thickness is thicker than other colorant pigment films.

Section 4-1-1 indicates color difference between tape covered film and exposed film. When there is no contact with air, reactions happen as well. There are two possibilities. On one hand, reactions take place without presence of extra elements from the outside. This can be true if reduction or oxidation happen between the pigments and the binder. On the other hand, the material in the tape takes part in the reaction. Thus, the oxygen and contaminations in air may not essential for the degradation.

4-2-5 Brief outlook

There are several points could be done further to make the story more convincing. Firstly, the aging time of the TiO_2 with oil could be increased to the same time as the colorant films to precisely observe the influence the effect of the binder color change. And in the same time, techniques to examine the organic binder degradation can be applied to reveal the exact binder change (also for the Kremer ones). Moreover, the TiO_2 film could be aged for more time to figure out the roughness change caused by the binder. If it is the case, then it can be the strong evidence that the binder is responsible for the roughness change. Secondly, the coating material of the Hombikat TiO_2 can be changed to SiO_4 in the future research. And characteristic should be done to reveal the coating status of the TiO_2 to provide more information. Thirdly, the color of Green earth does not change, but whether the pigment itself changes or not is not for sure and worth digging. Lastly, the blackening mechanism of Vermilion can be studied more carefully with subtle methods. Prussian blue has a typical (CN) group and FTIR can be used to find out if the group stays after aging. And in the mean time, Fe^{2+} and Fe^{3+} should be identified to make sure the color changing cause. As for the organic pigments, gas chromatography can be used.

Chapter 5

Conclusion

The photo-catalytic effect of TiO_2 does influence the appearance of the paint films. The color, gloss and roughness of the films are all altered, though the affected thickness of the film is thin. The photo-catalytic effect of TiO_2 is superficial within short time. The 3 kinds of titanium dioxide behaved diversely on the color of the films. Kremer TiO_2 is the most stable one, having affected the color of the films the least. And the effect is mainly to the binder instead of the colorant pigments. Besides, the Kremer TiO_2 avoids the paint film chalking mostly. The Hombikat TiO_2 influences not only the binder but the colorant pigments. In the mean time, the coating the TiO_2 can increase the stability, but not ideal in this study. The roughness of all the paint films increase with aging time, and binder degradation is believed to be the main reason for it. Gloss of the films decreases with the roughness going up.

The colorant pigments show different degradation states. Green earth does not suffer color change from all three TiO_2 . Vermilion has degradation tendency itself, and the existence of TiO_2 has boosted the degradation of it. Prussian blue degrades relatively quickly and could be attribute to the transformation from Fe^{3+} to Fe^{2+} . The organic Indigo and Hansa yellow degrade most possibly because of the breakdown of the molecular bondings inside the system, which can happen without the presence of oxygen and moisture.

Furthermore, several factors influence the degradation. UV light is the necessary accelerating factor of TiO_2 -induced degradation. The degradation could happen without the presence of oxygen, moisture and Cl_2 . This kind of degradation mainly causes a brownish appearance.

In the future work, the examination of these cross sections can be done further to distinguish exact elemental composition and structure of the top surface. For instance, Fourier transform infrared spectroscopy(FTIR) can be used to detect the existence of Prussian blue in the top surface. And more precisely methods can be used to exam the vermilion cross section.

Appendix A

Figures:

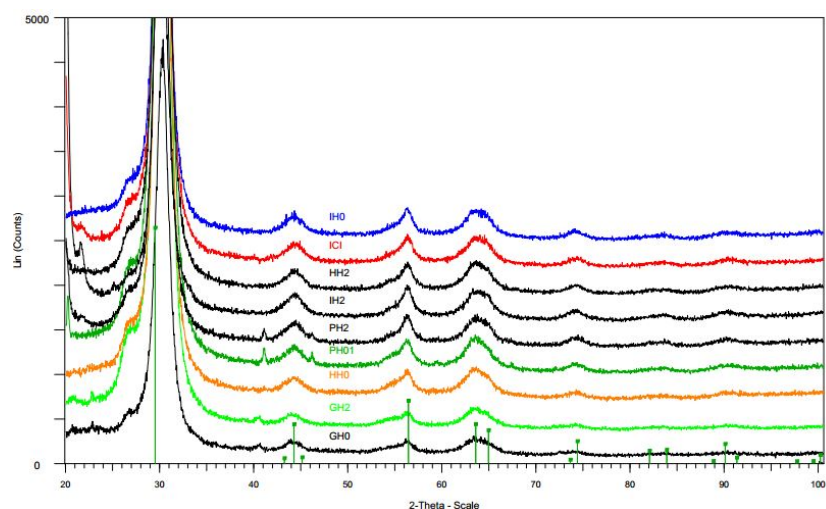


Figure A-1: XRD patterns of paint films.

PH01: Prussian blue + Hombikat TiO₂, 0d aging; PH2: Prussian blue + Hombikat TiO₂, 14d aging;

GH0: Green earth + Hombikat TiO₂, 0d aging; GH2: Green earth + Hombikat TiO₂, 14d aging;

HH0: Hansa yellow + Hombikat TiO₂, 0d aging; HH2: Hansa yellow + Hombikat TiO₂, 14d aging;

IH0: Indigo + Hombikat TiO₂, 0d aging; IH2: Indigo + Hombikat TiO₂, 0d aging;

IC1: Indigo + coated Hombikat TiO₂.

The vertical lines, **Green: anatase-TiO₂**

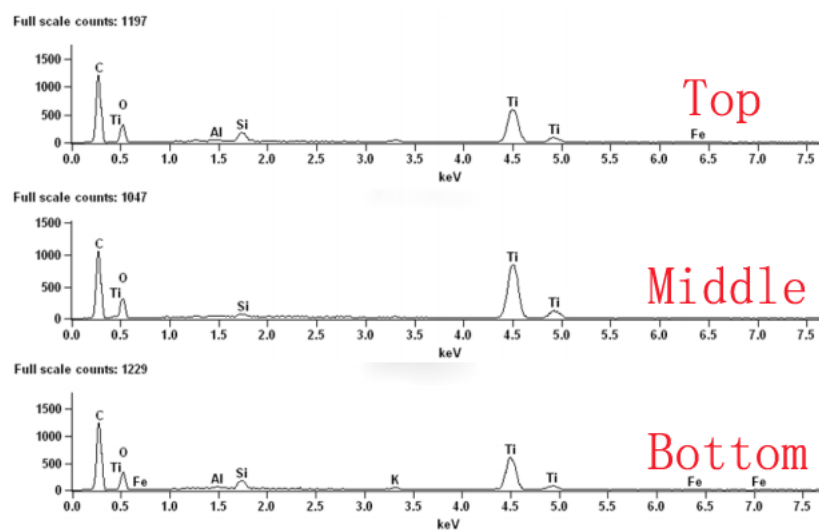


Figure A-2: EDX of top, middle and bottom layer of Green earth and Hombikat TiO_2 cross section with 14 days aging.

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