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Photo-catalytic activity test for titanium dioxide with artist’s pigments and dyes of the 20th century

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Zhaoxiang Chen
4182359

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Department of Materials Science and Engineering
Faculty of Mechanical, Maritime and Materials Engineering
Delft University of Technology

Abstract

Titanium dioxide was developed in 19th century and widely used as an artist's pigment since 20th century. Due to the photocatalsis of titanium dioxide, it can decompose the organics so that the organic dye and binders of painting could be destroyed, resulted in fading, chalking and loss of gloss. In order to figure out the potential dangers of titanium dioxide to the painting, a quick testing method by liquid state UV-VIS spectrometer is used to measure the photocatalytic activity of titania. However, it is proved not suitable for the testing of whole artist's pigment since many limitations of experimental process make the testing results inaccurate. In this case, solid state spectrometer is applied instead of liquid state spectrometer. A new photocatalytic activity test is developed, including the new sample preparation and measuring method. Based on the new developed testing method by solid state spectrometer, the influence of titanium dioxide on the degradation of selected artis's pigment or dye can be measured. And the problem of limitations of original testing method is solved well.

Key words: titanium dioxide, photocatalytic activity test, solid state UV-VIS spectrometer

Contents

1. Introduction

Titanium dioxide is widely used as a pigment all over the world since 1920s. At the same time, it can be used as photo-catalyst to degrade organics due to the creation of free radicals under UV light. In oil paintings, many artist's dyes and binders are both organic so that they can be degraded when mixing with titanium dioxide pigment, resulting in fading, chalking and loss of gloss. On the other hand, titanium dioxide pigment is currently used for restoration of paintings by restoration institutions. Therefore, it is significant to investigate the influence of photocatalysis of titanium dioxide, which is helpful for the restoration institution to aware the potential harm of titanium dioxide on paintings. In meantime, analysis of photo-degradation is so essential for protecting the paintings, which are regarded as cultural heritage of human beings that it is useful to find out protection method for reducing the effect of the environment and minimizing the photo-degradation rate.

Then, a quick testing method is required to study the photo-degradation of artist pigment and dye with titanium dioxide. It is well-documented that a testing method by liquid state spectrometer is feasible for the photo-catalytic activity study of titania with acid blue 9.[1] Following the same testing method, the selected pigments and dyes with titanium dioxides will be tested in this project so that the feasibility of the liquid state testing method can be inspected.

The project will start with repeating experiment with acid blue 9 used in previous project to check the repeatability of the method. Then, the photo-catalytic activity of titanium dioxides are measured with same experimental procedure, mixing with selected artist's pigments and dyes. Additionally, if the liquid state testing method is proved unfeasible, a testing method through solid state spectrometer will replace the original one. And the purpose of this project will be altered to develop a new feasible testing method by solid state spectrometer for photo-catalytic activity test.

In chapter 2, the report will describe the background information about the project, including the introduction of titanium dioxide, selected artist's pigments and dyes, selection criteria and equipment investigation. Experimental procedure for sample preparation will be shown in chapter 3, and the experimental results and discussion will elaborate in chapter 4. The report will end with the conclusion of this project and recommendation for further research.

2. Literature review

Titanium dioxide pigment was developed in 1920s. It is widely used in the world due to its brightness and whiteness[2]. But at the same time, titanium dioxide is used as a photo-catalyst under the UV light or visible light. Therefore, the organic colors or binders will degrade when they are used with titanium dioxide pigment, which may lead to color changing, chalking or fading of the paint[3]. The nonreversible damage of the paintings, especially of the masterpieces, is definitely a huge loss for our cultural heritage. Therefore, to protect the cultural heritage, we will mainly focus on the titanium dioxide effect on artist's pigments or dyes and try to figure out a suitable method that is able to test the photo-catalytic effect of titania on artists' pigments or dyes in short time period.

2.1 Introduction of titanium dioxide pigment

Titanium dioxide is one of the most essential parts of this project. As a white pigment, titanium dioxide pigment is widely used in the world due to its high brightness, whiteness, and opacity. It is usually mixed with other pigments or dyes and binders during the painting for adjusting the gloss, resulted in two effects on the paints. One effect is that titanium dioxide can protect binders from chemical oxidation by absorbing UV-light; the other one is that, based on the photoreaction of titanium dioxide, the organic dyes or binders mixed with titanium dioxide pigment can be degraded so that chalking, fading and loss of gloss will occur[4].

There are three types of crystal structures of titanium dioxide: rutile, anatase and brookite. Brookite is a relatively rare form compared with other forms and is not used for the production of pigments.[5] Hence, the crystal structure of titanium dioxide pigment is simply divided into two groups, rutile and anatase, as shown in figure 2-1.

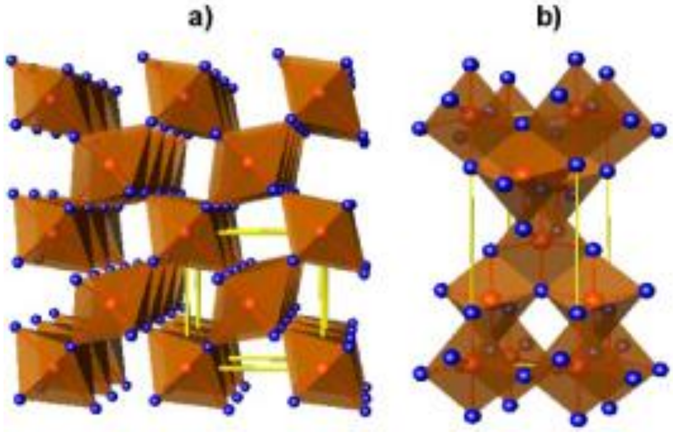

Figure 2- 1 crystal structure of rutile (a) and anatase (b)[6]

Both the rutile and the anatase have a tetragonal crystal structure, and possess photo-catalytic activity, but their characteristics are not exactly the same.[7] The energy gap of the rutile and anatase are nearly 3.0 eV and 3.2 eV. [1] Based on Planck's Equation,

$$E = h \times v = \frac{hc}{\lambda},$$

the absorbable wavelengths of light of rutile and anatase can be calculated, which are around 410 nm and 385 nm.

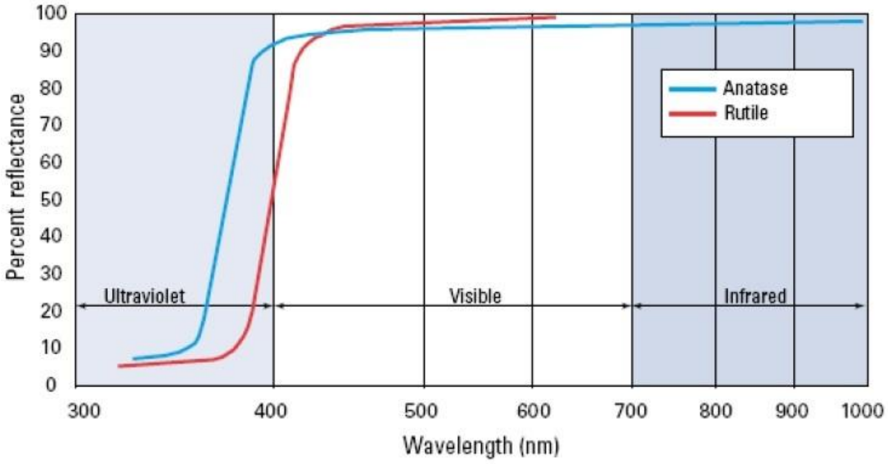

Figure 2- 2 the reflectance spectrum of titanium dixoide with different crystal structures

It can be seen from figure 2-2 that the absorption wavelength range of titanium dioxide is basically lower than 400nm, and the wavelength range of UV light is between 100 nm and 400 nm. Therefore, when titanium dioxide pigments are exposed to UV-light, electrons will be excited from valence band to conduction band and create electron-hole pairs. And the electron-hole pairs can generate free radicals (e.g. hydroxyl radical, super oxide) according to the chemical reactions with water and oxygen.[8] These free radicals play an important role in degradation of organics. They possess strong oxidize potential and are able to oxidize the organics and decompose them into by-products, such as water and carbon dioxide, which is shown in the figure 2-3.[9]

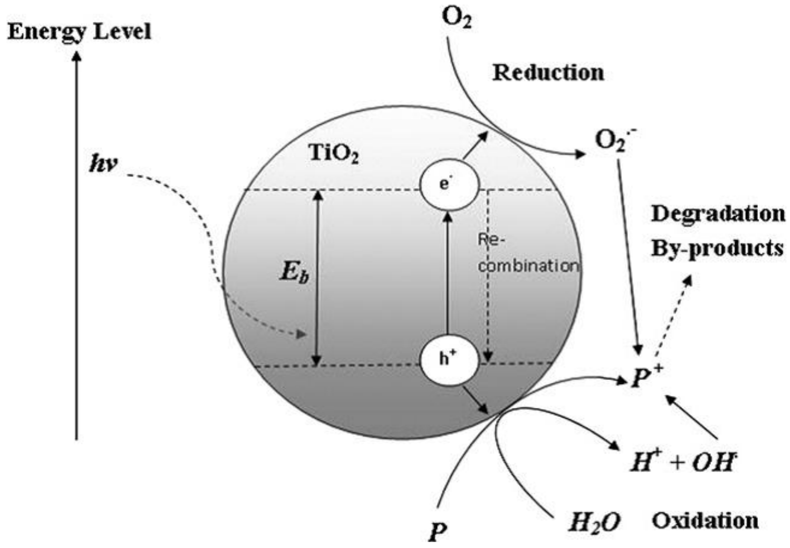

Figure 2-3 the mechanism of photo-catalysis of titanium dioxide[9]

Anatase is normally considered to possess higher photo-catalytic activity than rutile, since it has the higher Fermi level which results in relatively higher level of hydroxyl radicals on the surface.[10] In the meantime, the photo-catalytic activity of titanium dioxide pigment also relates to others factors, such as particle size and surface area. In general, with decreasing particle size, the degradation rate will increase since the particle size impacts the surface area. The surface area will increase as the particle size decrease, so that the number of active surface sites increase as well as the surface charge carrier transfer rate.[11] With larger surface area, more hydroxyl ions will adsorb on the surface and generate more hydroxyl radicals, resulted in higher photocatalytic efficiency.[12] Anatase usually possesses smaller particle size and larger surface area than rutile, leading to relatively higher photo-catalytic activity.

	Hombikat UV-100	Kremer 46200	Coated Hombikat uv-100
Crystal structure	Anatase	Rutile	Anatase
Particle size (nm)	10	170	Unknown
Surface area (m^2/g)	250	Unknown	Unknown
Coating	None	SiO_2 and Al_2O_3	Al_2O_3
Application	Catalyst	Artist pigment	

Table 2- 1 selected titanium dioxide samples and characteristics

There are three kinds of titanium dioxide studied in the project, Hombikat uv-100, Kremer 46200 and coating Hombikat uv-100. As is shown in table 2-1, Hombikat uv-100 and Kremer 46200 are used for different applications: Hombikat uv-100 is a catalyst, while Kremer 46200 is an artist pigment. Moreover, their characteristics are quite different with each other: Hombikat uv-100 (catalyst) has smaller particle size and anatase structure without coating, but Kremer 46200 (artists pigment) has rutile structure and larger particle size with coating of SiO_2 and Al_2O_3. Kremer 46200 is the stable artists pigment that is used for restoring the masterpieces of musea currently. Thus, it is meaningful to study the photo-degradation of artist pigments or dyes with Kremer 46200, which is helpful for us to figure out its photo-resistance and stability. Compared with Kremer 46200, Hombikat uv-100 possesses much higher photo-catalytic activity. This is also one of the most important reasons for selecting it as studied sample. In order to develop a quick photo-catalytic activity test, it is necessary to select a relatively active titanium dioxide so that the degradation result can be observed in a short time, which is helpful for the adjustment of experimental procedure. Additionally, there are many experimental results of Hombikat uv-100 obtained in the previous project. Using Hombikat uv-100 for new experiment is convenient for comparison of results.. Besides these selected titanium dioxides, the third sample of titanium dioxide is obtained by coating the Hombikat uv-100 with aluminum oxide using atomic layer deposition, which was performed by David Valdesueiro, Aris Goulas and J. Ruud van Ommen in Chemical Engineering Department of TU Delft.[13] This titanium dioxide is added for figuring out if the coating method can improve the photo-resistance of titanium dioxide. If it does, it will be a meaningful improvement for the painting restoration.

2.2 The reference dye and confirmatory experiments

Acid blue 9 is the dye chosen as the reference dye that was also studied in previous projects. The chemical formula of acid blue 9 is $C_{37}H_{34}N_2Na_2O_9S_3$, and the molecular structure is shown in figure 2-4. It is a safe and harmless dye, which is also used as a food colorant.[14] Acid blue 9 was selected as the testing dye in previous project due to the stability of acid blue 9 solution. It will not adsorbed on the surface of coated titanium dioxide so that there is less influence about the concentration of solution, resulted in deriving the relatively accurate results.[1]

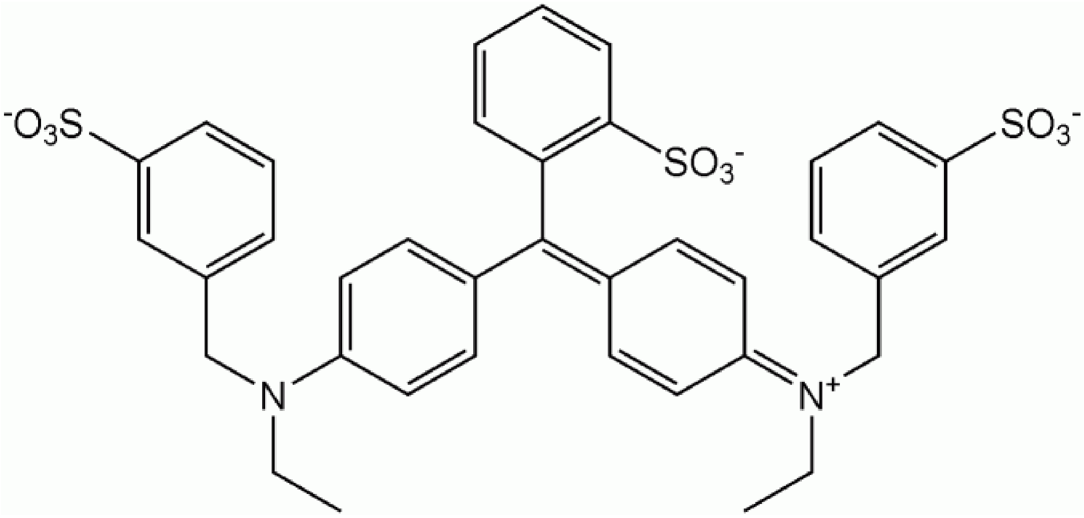

Figure 2- 4 molecular structure of acid blue 9

This project is mainly built up on the basis of the previous project.[1] Before starting the new experiment, it is necessary to repeat the documented experiment of previous project. Confirmatory experiment is useful for verification of the feasibility of the quick testing method as well as familiarization of experimental procedure and usage of testing equipments. Following the same experimental procedure, retesting degradation rate of acid blue 9 mixed with titanium dioxide pigment and comparison results are the first step of my project, which is quite essential and necessary. It is helpful for understanding the whole design of project in details via repeating the experiment, and in the meantime, it can prove the repeatability of previous project.

2.3 Selection criteria of artists' pigments and dyes

The main purpose of this project is studying the effect of titanium dioxide pigment on real artist's pigment and dye. Besides the reference dye, acid blue 9, there are several kinds of artists' pigments or dyes from 20th century to be tested in the project. The selection criteria for artists' pigments and dyes are described as follows:

1. The selected pigment or dye should be used as artist's pigment.

The artist's pigment is the primary target of this project. As one of the most important human cultural heritages, the oil paintings are necessarily protected from the photo-degradation so that we mainly focus on the study of the real pigments or dyes of painting. The pigment materials of other applications, such as catalyst, are the secondary choice in this project.

2. The selected pigment or dye should be kept using after 1920s

Titanium dioxide is widely used as artist's pigment since 1920s.[15] The selected pigment or dye is required to be popular or still used after 1920s at least, which means that the selected pigment or dye was possibly mixed with titanium dioxide pigment by artists in the real paintings. In this case, the research results will be much meaningful for the protection and restoration of contemporary paintings.

3. The pigment or dye should be fugitive or become fugitive when mixing with titania indicated in the literature.

Fugitive pigment is the pigment that is not lightfast or permanent. In other words, the fugitive pigment will fade in a relatively short time when exposed to light[16]. In general, there are two systems widely used for rating the lightfastness of pigments， American Standard Test Measure (ASTM) and Blue Wool Standard. American Standard Test Measure gives rating from Ⅰ to Ⅴ, and Blue Wool Standard is divided into eight levels. Ratings from Ⅳ to Ⅴ of American Standard Test Measure and one to three of Blue Wool Standard reveals that the pigments in these levels are fugitive[17]. Moreover, some pigment or dye is permanent but turns fugitive when mixing with titanium dioxide that is also taken into account for the selection. Choosing the fugitive pigments or dyes is due to the consideration of feasibility of experiment as well. It is more likely to observe the result in short period by using fugitive pigment or dye instead of permanent pigment or dye.

2.4 Selected artist's pigment and dye

Based on the criteria mentioned above, four pigments or dyes have been selected among hundreds of artists' pigments. The detailed information is shown as follows.

2.4.1 Alizarin crimson

Alizarin crimson, also named alizarin lake and alizarin red, has been regarded with great favor in arts since it was synthesized in 1868. The main component of alizarin crimson is alizarinor 1,2-dihydroxyanthraquinone, which is an organic compound with formula $C_{14}H_8O_4$ and the molecular structure is shown in figure 2-5[18,19].

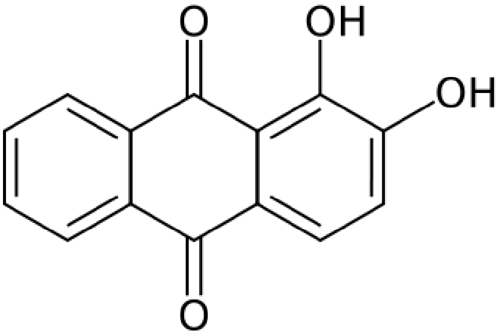

Figure 2- 5 molecular structure of alizarin

Currently, the synthetic alizarin is more prevalent using than the natural alizarin because the synthetic alizarin is much more homogeneous, and does not contains isomeric impurities.[20] It is widely used in industry, such as metal decorating inks and certain food wrapper inks usage. And the pigment is also applied to artist's pigment. It is interesting to notice that there are different descriptions about the lightfastness of alizarin crimson in different references. Some references believe that alizarin crimson is relatively fugitive so that it will eventually fade out due to the exposure to light.[21,22] However, some other references believed that alizarin crimson exhibits good fastness to light and will not fade on long exposure to daylight[18,20]. These contrary statements make alizarin crimson pigment become an attractive candidate of the selection. When mixing with titanium dioxide, alizarin is regarded as a fugitive pigment degraded under the exposure of UV-light.[23] And alizarin crimson tends to be converted into yellow from which it fades to a colorless condition[23,24,25]. Therefore, to figure out the permanence of alizarin crimson and prove reliability of these statements, alizarin crimson is chose as a subject to be investigated.

2.4.2 Prussian blue

Prussian blue is a kind of deep greenish-blue, which was manufactured from 1704. It was incidentally discovered by Heinrich Diesbach, and became a popular blue dye in Europe. Due to the fantastic tone and colorfastness, Prussian blue is currently kept using in painting. Prussian blue is an iron(Ⅲ) hexacyanoferrate(Ⅱ)whose formula is $Fe_7(CN)_{18}$[26], and the molecular structure is illustrated in figure 2-6.[27]

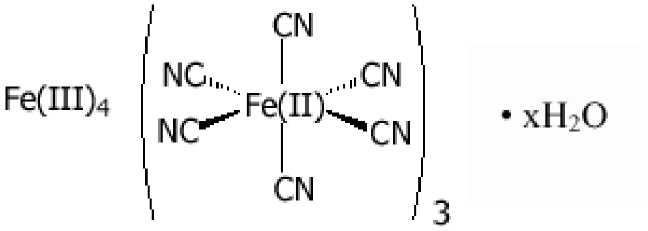

Figure 2- 6 the molecular structure of Prussian blue

Prussian blue is an inorganic pigment. It can be used as a stand-alone pigment and also made into green with Naples yellow.[26] When Prussian blue was developed, it became extremely popular at that time, and substituted other blue pigments immediately.[28]. Figure 2-7 shows the famous painting “Entombment of Christ”, painted by Pieter van der Werff. It is the oldest masterpiece where Prussian blue was used.[29] Prussian blue can be found in the sky and Mary’s veil.[30] Moreover, the French painters Antoine Watteau, Jean-Baptiste Pater and Nicolas Lancret used Prussian blue in their paintings as well[27].

Figure 2- 7 Entombment of Chris, painted by Pieter van der Werff [30]

Prussian blue is basically considered as a permanent pigment except when used in thin layers or mixed with white pigments.[18,31]. Experimental results indicated that Prussian blue mixed with lead white can change color under the exposure of light.[31] Additionally, Prussian blue could fade by the reduction in anoxic condition, and the fading will re-oxidize when Prussian blue re-exposed to the air.[32]

2.4.3 Indigo blue

Indigo blue, also named indigotin, is a deep, transparent blue whose formula is $C_{16}H_{10}N_2O_2$. The molecular structure is shown in figure 2-8.[33]

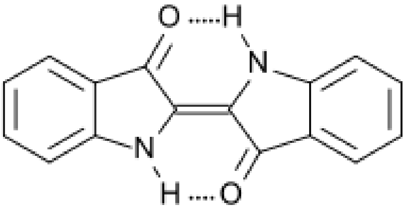

Figure 2- 8 molecular structure of indigo blue

Indigo blue is an organic pigment originally obtained from the plant in India, and used as an artist pigment since Ancient Egyptian times. It can be also found in the East Asian paintings that painted long time ago.[34] At the end of the nineteenth century, the synthetic indigo blue was developed. It can be made from coal tar. [18] The synthetic indigo blue possesses good tinting strength, and it is usually used as textile dyestuff for blue jeans. In the meantime, indigo blue is suitable to mix within oil media. The lightfastness of indigo blue is moderate so that it may rapidly fade under the exposure of light.[35] So far, the literature of indigo blue is manly related to its usage in textile industry, and the research about pigment degradation is still inadequate. Therefore, indigo blue pigment is selected for studying the photo-degradation in this project.

2.4.4 Vermillion

Vermillion is an opaque, bright red pigment which is obtained from cinnabar. The chemical component of vermillion is mercury sulfide (HgS) so that it is toxic as powder pigment or dispersed suspension.[18] Vermillion is a historical pigment and widely used as artist pigment all over the world. It was one of the most significant red pigments with large scale production. However, considering the toxicity of vermillion, the production of vermillion is limited in 20th century. [36] Vermillion is not considered as a permanent pigment. It was known that vermillion will be darkened under the exposure of light. The darkening of vermillion was found in painting of egg tempera.[37] Some reference shows that the impurities in alkali polysulfide lead to the transition of red to black.[38] In the meantime, there is another hypothesis on the mechanism of photo-degradation of vermillion that parts of HgS may convert into Hg(0) and S(0) when exposed to light. Hg(0) can be deposited on the surface of the remaining HgS, resulting in the darkening of vermillion.[39] It is worth noting that vermillion does not react with other permanent pigments, and it was generally used with lead white to get a fresh tint without formation of black lead sulfide. Thus, it is interesting to study the influence of titanium dioxide on the degradation of vermillion.

2.5 Equipments

2.5.1 UV-light box

UV-light box is composed of UV-lamps, magnetic stirring plate and cooling system, which is shown in figure 2-9. The UV-light box is equipped ten 18W UV-lamps providing 470±20 $\mu W/cm^2$, hanging up in the UV-light box. Eight of them is using during the photo-catalytic activity test. The magnetic stirring plate is placed within UV-light box, which is using for stirring the sample suspension. The rotation speed is set up at 600 rpm, using the same speed as the previous project.[1] The cooling system is the grey box shown in the figure. Since the temperature of sample suspension will increase under the exposure of UV-light, the cooling system is using for controlling the temperature within the UV-light box, and keeping it as constant. It is necessary to warm up the cooling machine for about an hour, and the working temperature of cooling system is 12^{o}C. There is a temperature detector on the top of UV-light box, which can reveal the temperature within the UV-light box. With the help of cooling system, the temperature of UV-light box is around 27^{o}C during the photo-catalytic activity test, which also depends on the temperature of environment.

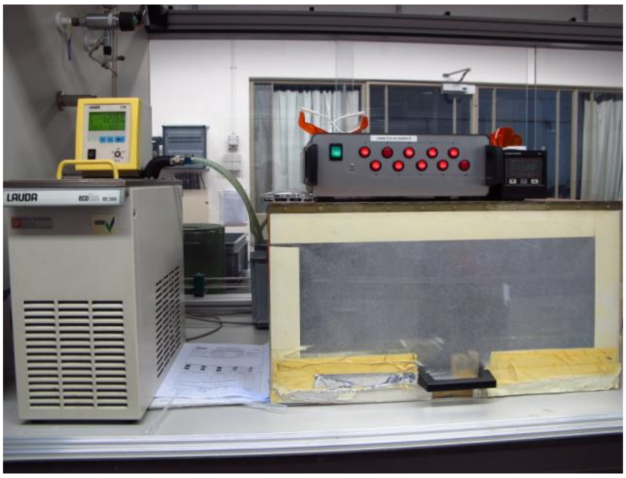

Figure 2- 9 UV-light box

2.5.2 Ultraviolet-visible spectrometer[40]

Ultraviolet–visible spectroscopy is one of the most important quantitative, analytical instruments in the laboratory currently due to its simplicity, speed, accuracy and cost-effectiveness. The word ‘ultraviolet–visible’ means that the incident light in the instrument is in the visible and adjacent-UV ranges. The principle of spectroscopy is shooting a beam of light strike on the object, and the light can be reflected, absorbed, transmitted, scattered or excite fluorescence. The color of chemicals is related to the absorbance, reflectance and transmission of light, which can be obtained through the detectors. However, it is difficult to measure the whole aspects of light. For instance, the absorbance of light for solid state sample cannot be measured. In general, the measurement depends on the sample.

There are two kinds of ultraviolet-visible spectrometer used in the project, UNICAM UV-500 and LAMBDA 900. UNICAM UV-500 is applied for testing the liquid state samples, while LAMBDA 900 is used for measuring the solid state samples.

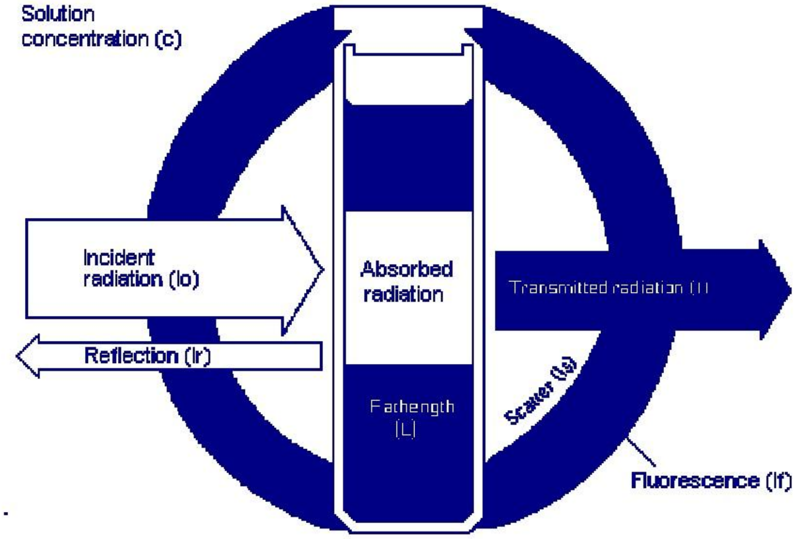

Figure 2- 10 interaction between light and sample

UNICAM UV-500 is a spectrometer that using for testing the absorption and transmission of liquid sample. The conditions of sample testing are to keep the reflection, scatter and fluorescence as minimum. It can measure the absorption of radiation as a function of wavelength. As is shown in figure 2-10, assumed that the intensity of incident light is I_0, the transmitted radiation is I and the cell length is L. Based on the Beer-Lambert Law applied for monochromatic light, the concentration in the solution is proportional to the absorbance (A):[40]

$$A = constant \times concentration \times cell\ length$$

$$A = \log_{10}\left(\frac{I_0}{I}\right) = K \times C \times L$$

where K is the constant and C is the concentration of solution. Thus, the intensity of absorption is directly proportional to the estimate of the concentration of sample.

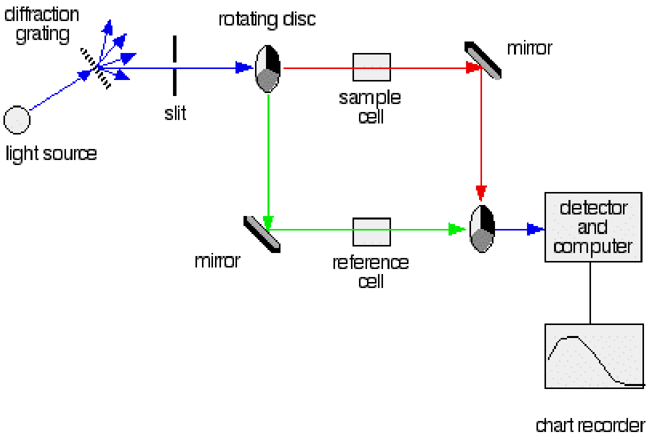

Figure 2- 11 the sketch of dual beam spectrometer[41]

UNICAM UV-500 is a dual beam spectrometer that the light source is separated into two paths by a rotating disc shown in the figure 2-11. The rotating disc consists of three sections: black section, transparent section and mirrored section. If the incident light hits the transparent section, it will pass through the testing sample. If the incident light hits the mirrored section, it will reflect to another mirror and pass through reference sample, which is the solvent of sample solution. If the incident light hits the black section, the light will be blocked. [41] Transmitted light can be received by detectors and transferred into current. In the case of dual beam spectrometer, the absorbance value of testing sample can be obtained by:

$$A = \log_{10}\left(\frac{I_0}{I}\right)$$

, where the intensity of light transmitted from reference sample is referred as I_0, while that of testing sample is referred as I.

The sample preparation for UNICAM UV-500 is very simple. The testing solution and reference solution are put into the cuvettes by pipet, but it is noteworthy that when placing the cuvettes into the spectrometer, it is not allowed to touch the smooth surface of cuvettes. Otherwise, the finger print will leave on the surface and it will lead to the inaccurate measurement.

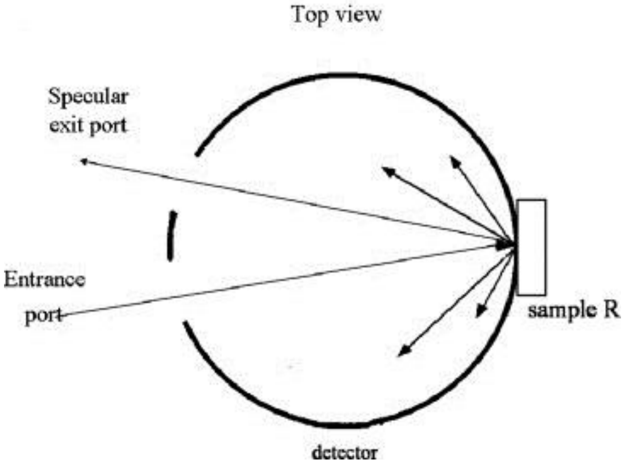

Figure 2- 12 the integrating sphere of LAMBDA 900[42]

LAMBDA 900 is used as a reflectance spectrometer, which can measure the reflection of solid state samples. For the solid state samples, the transmission, scatter and fluorescence of light can be neglected. So it assumes that the light can be only absorbed and reflected. Since the absorbed light is difficult to measure, the reflectance of light is derived by the detectors within the integrating sphere, which is shown in figure 2-12. Before each testing, it is necessary to do the ‘autozero’ testing by using the reference sample, which is made of barium sulfate whose reflectance is 100% in the range of 300nm to 800nm. The testing reflectance percentage of sample is the relatively quantity of the reference sample. The intensity of reflectance decreases as the concentration of sample increases.

For LAMBDA 900, the sample preparation is relatively complicated. It is basically divided into three steps:
(1) Putting the sample powder into the sample holder
(2) Putting the plastic cap on the sample holder and screwing it slowly to ensure that the powders distributed on the surface of glass homogeneously.
(3) Checking the testing sample layer to make sure the sample layer is ‘perfect’ and fastening the metal cap tightly for the stability of powders in the holder.

The amount of powders should be sufficient to cover the whole surface of watch-glass. For Hombikat uv-100, the amount using in photo-catalytic activity test is 50mg. Moreover, the powder sample has to be sufficiently dry. Otherwise, it will be difficult to distribute the powders homogeneously. Furthermore, the screwing of plastic cap should not be strenuous, or it will make the testing sample layer inhomogeneous.

Therefore, based on the testing equipments mentioned above, the relation between absorbance or reflectance and concentration can be found. Therefore, the changing of concentration and degradation of artist pigment and dye can be known through observing the changing of intensity of absorption and reflection.

3. Experimental procedures

The schedule of whole project contains three steps: confirmatory photo-catalytic activity test for acid blue 9, photo-catalytic activity test for selected artist's pigment with titanium dioxides by liquid state spectrometer and photo-catalytic activity test for selected artist's pigment with titanium dioxide by solid state spectrometer.

In photo-catalytic activity test, calibration line is firstly made for finding out the relation between the absorbance or reflectance and concentration. Then, the absorbance or reflectance of samples with different light duration is derived through the UV-Vis Spectrometer, and the concentration of the samples can be obtained by using the equation of calibration line. Based on the variation tendency of concentration, the photo-degradation rate can be observed.

The details of experimental procedure of each step are shown in this chapter.

3.1 Photo-catalytic activity test for acid blue 9 with titanium dioxide by liquid state spectrometer

The first step of this project is the repeat of experiment, using the same experimental procedure of previous project.[1] It is essential and necessary to repeat the experiment in order to confirm the repeatability and reliability of previous project results. In the confirmatory experiment, the referenced dye is acid blue 9, and the referenced titanium dioxide pigment is Hombikat UV-100.

Sample preparation basically consists of two steps. First step is the preparation of stock solution of acid blue 9, whose concentration is 0.3mM. The stock solution can be made by mixing certain amount of acid blue 9 with certain volume of water. The amount of pigment and volume of water are calculated based on the concentration.

The second step is making sample solutions with different concentrations by dilution of stock solution for calibration and photo-catalytic activity test. In the case of acid blue 9, the concentrations of five sample solutions for making calibration lines are 0.03, 0.0225, 0.015, 0.009 and 0.003mM, respectively. The equation of calibration line could be derived from testing absorbance of five sample solutions by combination the data of concentration and absorbance. And the starting concentration of the solution putting into the UV-light box is 0.03mM, which is one-tenth of that of stock solution. The detailed experimental procedure is exactly same as that of previous project, which is shown as follows:[1]

(1) 50mg of TiO_2 powders are measured and dispersed in 100ml 0.03mM acid blue 9 in 250ml beaker.

(2) Put beaker into an ultrasonic bath for 10 minutes.

(3) Add a magnetic stirrer into the dispersion, and cover the beaker with watch-glass, the beaker is put on a stirring plate (600 rpm) in a UV-light box (equipped with 8 18W UV-lamps

providing 470±20 $\mu W/cm^2$), the temperature is kept around 27^{o}C by using cooling system.

(4) In time intervals, a sample is taken from dispersion with pipet and then centrifuged twice in Savant Speedfuge HSC10AC at 5000 rpm for 5 minutes to remove the TiO_2.

(5) The samples with different light duration are measured with liquid state spectrometer to obtain the absorbance, and the concentrations of samples are calculated by using the equation of calibration line.

3.2 Photo-catalytic activity test for selected artist's pigments with titanium dioxides by liquid state spectrometer

The photo-degradation of selected artist's pigments with titanium dioxides are studied by using the same testing method of confirmatory test. For different artist's pigments, sample preparations are distinguished between each other due to the variation of solvent.

Each kind of artist pigment has different kind of solvent. Contrary to acid blue 9, artist's pigments hardly dissolve in the water. Most of them can just dissolve in organic solvent. Thus, the initial step is to figure out the solvent for each kind of artist pigment.

Alizarin crimson

There are two categories of alizarin crimson in this project. One is alizarin crimson dark, which is delivered from Rijksmuseum, the other one is 97% pure alizarin (1,2-dihydroxyanthraquinone), which is ordered from Sigma-Aldrich. The selected solvent for alizarin pigments is 1-hexanol, whose formula is $CH_3(CH_2)_5OH$. It is noteworthy that the absorbance of the alizarin solution with lower concentration is difficult to obtain by using liquid state spectrometer. Therefore, considering the influence of concentration on the measurement, the concentration of stock solution of alizarin pigments is adjusted to 0.09mM (alizarin crimson dark) and 0.15mM (97% pure alizarin), respectively. For making calibration line, the concentrations of alizarin crimson dark are set as 0.03, 0.0225, 0.015 and 0.009, while that of 97% pure alizarin are 0.15, 0.03, 0.0225, 0.015 and 0.009.

Prussian blue

There are three kinds of Prussian blue studied in the project. They are ordered from Rijksmuseum, Sigma Aldrich Company and Kremer Company, respectively. The Prussian blue pigment, which was delivered from the museum, is firstly used in this experiment. The selected solvent for Prussian blue is 10%wt oxalic acid. Oxalic acid is an organic compound with formula $H_2C_2O_4$.[43] The concentration of stock solution is 0.3mM, and five concentrations selected for making calibration line are 0.3, 0.21, 0.15, 0.09 and 0.03mM.

Indigo blue

The indigo blue pigment using in this project is delivered from Rijksmuseum, whose formula is $C_{18}H_{10}N_2O_2$. The candidates of solvent of indigo blue are relatively dangerous, and some solvents are even toxic. For instance, chloroform is one of solvent candidates of indigo blue, which is a common solvent in laboratory. But it is disqualified in selection since its health rating of NFPA is 2, which is moderate hazard for people. Compared with chloroform, dimethyl sulfide (DMSO) is less harmful that the health rating is only slight hazard. In that case, DMSO is selected as solvent of indigo blue. The concentration of stock solution is adjusted into 0.15mM so that the indigo blue can dissolve in the solvent homogeneously. To ensure that the solution is homogeneous, magnetic stirring is necessarily used to stir the solution for 1.5 hours.

Vermillion

The studied vermillion pigment is delivered from Aldrich Company with formula HgS. Since it is difficult to find out the suitable solvent for vermillion, vermillion can be only test in the form of suspension, so that liquid state spectrometer is not suitable for measuring the photo-catalytic activity of vermillion.

Then, after determined the solvent of each artist’s pigments, the sample solutions of each artist’s pigment for photo-catalytic activity test are prepared, following the same procedure mentioned in the section 3.1.

3.3 Photo-catalytic activity test for selected artist’s pigments with titanium dioxides by solid state spectrometer

During the experiments of photo-catalytic activity test for selected artist’s pigment by liquid state spectrometer, many unexpected limitations appear and hinder the experimental work. The details about the limitations will be discussed later. In order to avoid the limitations of the experiments, which are mostly related to the preparation of solutions, the solid state sample is considered to be used instead of liquid state. In this case, solid state spectrometer is suggested to use for photo-catalytic activity testing.

As is shown in section 3.2, liquid state sample preparations of different kinds of pigments are different due to the distinction of solvent of different pigments. However, for solid state sample preparation, selection of specific solvent for each pigment is not necessary since the solution of pigment is replaced by the suspension. In the case of suspension, water is the best choice for preparing suspension because it is suitable for the whole artist’s pigment, and has no influence on the photo-degradation of artist’s pigments. The experimental procedure for solid state spectrometer testing is basically divided into four portions, dispersion, exposure, separation and measurement. Each portion of experimental procedure is adjusted on the basis of previous experimental procedure for liquid state spectrometer.

Dispersion

For suspension, the homogeneity of sample is the primary factor taken into account. Following the same method as previous procedure, the suspension is put into the ultrasonic bath for 10 minutes. Additionally, it takes two hour for using magnetic stirring to stir the suspension in order to improve the homogeneity of suspension.

Exposure

After dispersion, the suspension is continued stirring by magnetic stirrer in UV-light box. Then, turn on the UV lamps and keep suspension under the exposure of UV light for certain time intervals.

Separation

Finishing previous steps, the next step is to turn sample suspension back into solid state, which will be test via solid state spectrometer. There are mainly two kinds of separating methods for separation of water. First method is taking suspension into two centrifuge tubes (50ml per tube), and centrifuging using IEC centra-4B centrifuge with 5000 rpm for 5 minutes for separation of water. Then, the water is removed from suspension by pipette. It is necessary to use water or acetone, which has higher evaporation rate than water, to wash the remained sample from the centrifuge tubes since the sample particles may stick on the wall of centrifuge tube. And, the washing suspension is put in dark and evaporated by itself overnight.

The second separation method is relatively original, and will take more time than the first method. The main procedure is putting the suspension in dark directly and making the suspension precipitate by itself for 2 hours. Two hours later, the heavier particles of sample will precipitate on the bottom of beaker, then the water on the top of suspension can be removed, and the sample precipitates are left to dry by itself overnight.

The second method is selected to be primary choice of separation method when studying the prussian blue pigment due to less influence on sample, even though it will take nearly two hours more than that of first method. However, when studying alizarin pigment, the precipitate speed of suspension of alizarin is so slow that it may take more than three days for precipitating. In that case, the centrifuging is selected as the separation method. Considering the effect of acetone, which is organic and may react with sorts of pigments, water is choose to use for washing the pigment on the wall of centrifuge tube. The amount of washing water is less than 5ml for each tube so that remained sample suspension will dry quickly by itself (around two days) at room temperature.

Measurement

When water of suspension evaporates, the remained mixed pigment sample will form a thin layer on the bottom of beaker. The pigment layer is scraped from the bottom of beaker and kept in an empty bottle. Before testing sample through solid state spectrometer, it is necessary to take certain amount of sample powder and put into the sample holder. Then, screw the cap and press the powders to ensure that they are uniformly distributed in the sample holder.

Before testing sample, it is essential to reset 100% reflection by using blank sample, which is made of $BaSO_4$. After that, the percentage of reflection of sample can be measured via solid state spectrometer.

In summary, the experimental procedure for solid state spectrometer is shown as follows:

(1) 50mg titanium dioxide pigment and specific amount of artists pigment are dispersed in 100 ml water to make suspension.

(2) The suspension is put in the ultrasonic bath for 10 minutes.

(3) Magnetic stirrer is put into suspension, and the suspension is covered with watch glass.

(4) The suspension is placed on magnetic stirring plate for stirring in dark for 2 hours, and the rotation speed is 600 rpm.

(5) The beaker is put on a stirring plate (600 rpm) in a UV-light box (equipped with 8 18W UV-lamps providing 470±20 μW/(cm)^2), the temperature is kept around 27^{o}C by using cooling system.

(6) The suspensions (100ml) are poured in two centrifuge tubes (50ml per tube), and centrifuged in IEC centra-4B centrifuge with 5000 rpm for 5 minutes

(7) The water centrifuged out of suspension is removed, and demi-water (less than 10ml in total) is using for washing the pigments on the wall of centrifuge tubes. Remained sample suspension will be kept in dark and evaporated by itself for days.

(8) Scraping the pigment layer from the bottom of beaker, and sample powders are stored in the bottle and prepared for analyzed with solid state spectrometer.

4. Results and discussion

4.1 Photo-catalytic activity test for acid blue 9 with titanium dioxide by liquid state spectrometer

4.1.1 Calibration

At the beginning of experiment, acid blue 9 solution is scanned from 300nm to 800nm by liquid state spectrometer. The most intense peak of absorbance, λ_{max}, is around 630nm so that the following tests are performed at 630nm. The scanning spectrum of absorbance of acid blue 9 is shown in figure 4-1.

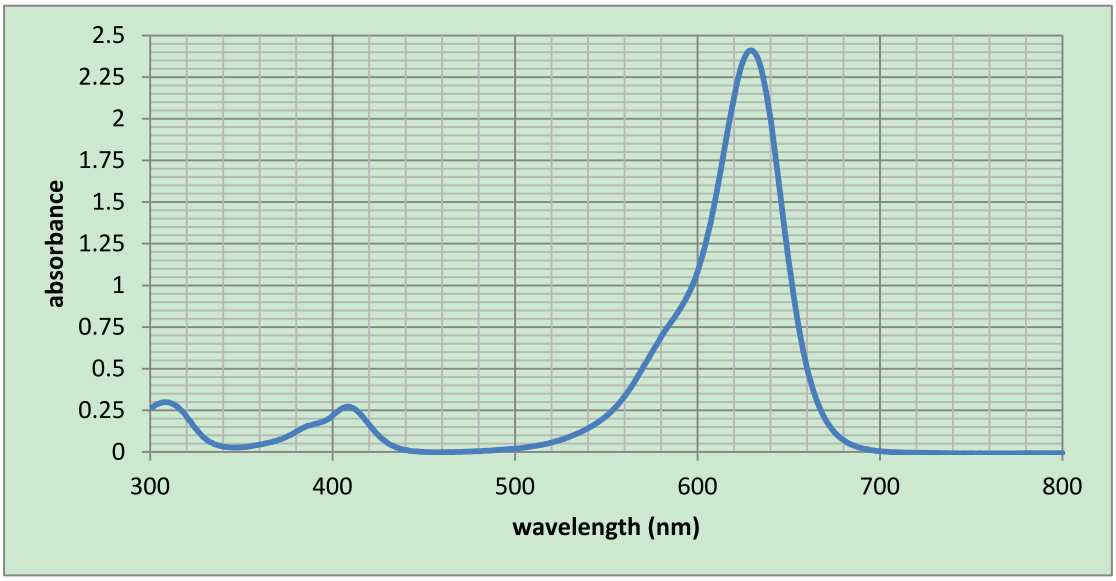

Figure 4-1 scanning spectrum of acid blue 9

Five sample solutions with specific concentrations, which are 0.003, 0.009, 0.015, 0.0225 and 0.03mM, are measured by liquid state spectrometer to obtain the absorbance data. Using the quant application of software, the linear equation of calibration line is generated based on the obtained data so that the relation between the concentration and absorbance can be derived.

When preparing the new stock solution or changing the testing cuvettes, the equation of calibration line is supposed to re-calculate. Since the cuvettes used for liquid state spectrometer testing are replaced in the process of project, there are two calibration lines of acid blue 9 solution, corresponding to different kinds of cuvettes. Besides these two calibration lines for old stock solution, there is another calibration line which is made for new stock solution with new cuvettes. All equations of calibration lines are used for calculate the concentration of corresponding samples. The calibration lines are shown in figure 4-2.

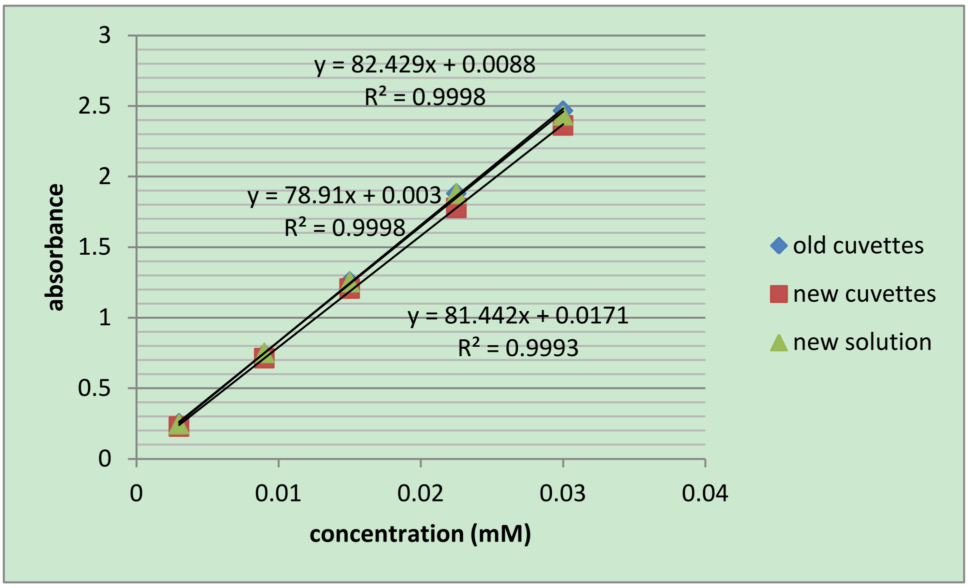

Figure 4- 2 calibration lines of acid blue 9

For old stock solution, the equation of calibration line for old cuvettes is,

$$y = 82.3534x + 0.0110, R^2 = 0.9998,$$

while that of new cuvettes is,

$$y = 78.9105x + 0.0030, R^2 = 0.9998,$$

For new stock solution, the equation is,

$$y = 81.4447x + 0.0171, R^2 = 0.9993.$$

4.1.2 Photo-catalytic activity test

In confirmatory experiment, acid blue 9 solution is mixed with two kinds of titanium dioxide pigment, Hombikat uv-100 and Kremer 46200. Basically, there are three prepared samples in each group for comparative testing. One sample is pure acid blue 9 solution regarded as reference sample. The other two samples are mixed with different kinds of titanium dioxide, respectively. In the first group, dispersing agent (calgon) are not introduced. The result of first group is named 'US' shown in the figure 4-3 and 4-4. For second group testing, ultrasonic bath and dispersing agent are introduced and the results named 'US+calgon', so that the results of two groups can be compared with each other to figure out the influence of dispersing agent on degradation rate.

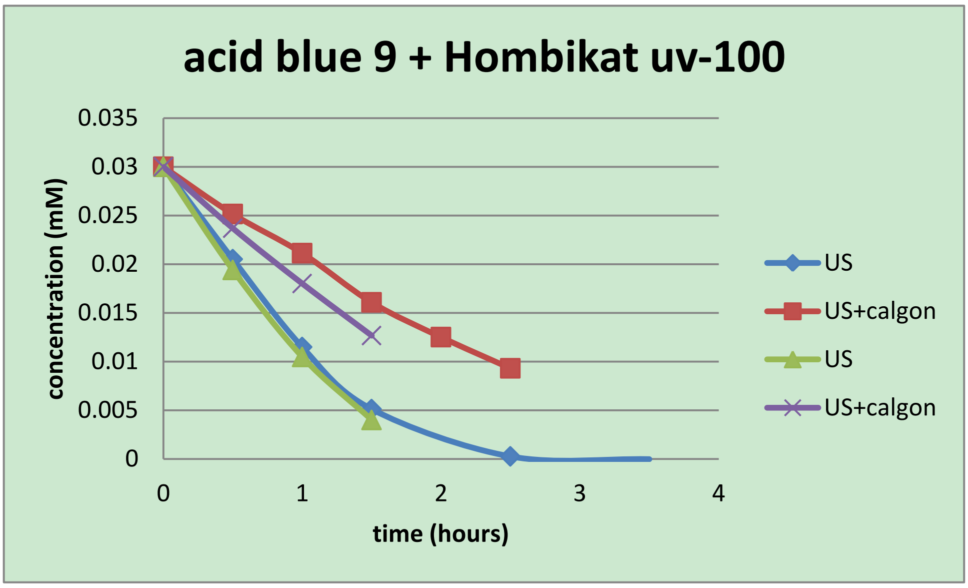

Figure 4- 3 degradation of Hombikat uv-100 of two comparative groups

For Hombikat uv-100, the photo-catalytic activity test has been done for twice, and the results are shown in figure 4-3. When acid blue 9 is mixed with Hombikat uv-100, the photo-degradation rate is fast. There is a relatively large difference of degradation rate between the 'US' dispersing method group and the group with dispersing method. The former degradation rate is nearly double times of that of later group. The dispersing agent is helpful to improve the homogeneity of sample solution.[1] But it also reduce the photo-degradation rate in meantime. Moreover, comparing the results of two experiments, the photo-degradation rate of the "US" groups are nearly the same, while the degradation rate of 'US+calgon' groups are different between each other. Therefore, it reveals that the influence of dispersing method on degradation rate is unstable that may also affect by other factors, such as temperature and humidity.

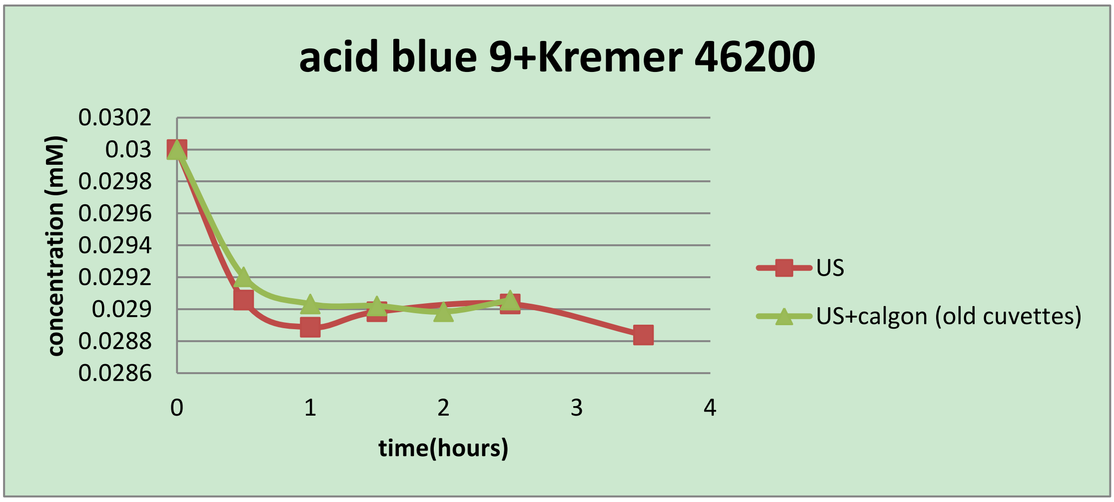

Figure 4- 4 degradation of acid blue 9 with Kremer 46200 in 4 hours

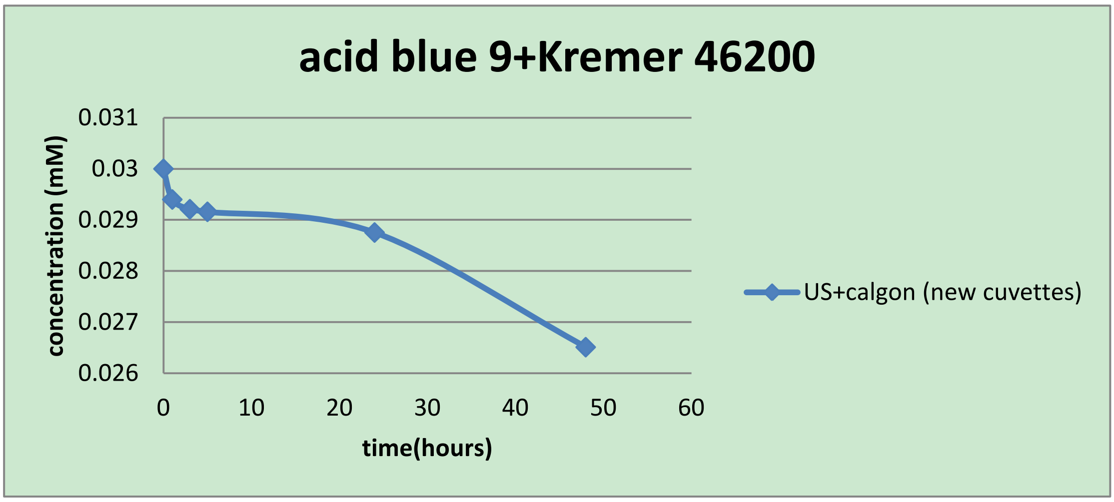

Figure 4- 5 degradation of acid blue 9 with Kremer 46200 in 48 hours

In the case of Kremer 46200, the degradation rate is much slower than that of Hombikat uv-100. As is shown in figure 4-4, the concentrations of samples gradually decrease at the beginning, and then remain as constant around 0.029mM after exposure of UV light for 2.5 hours. In order to figure out the further tendency of degradation, the photo-catalytic activity test lasts for 48 hours, and the result is shown in figure 4-5. The concentration continued to decrease after 24 hours. The concentration is reduced to nearly 0.0265mM at 48 hours.

Based on the results mentioned above, it can be concluded that the characteristics of titanium dioxide have a large influence on the degradation rate of mixed pigment. The concentration of samples mixed with Hombikat uv-100 decreases much faster than that of Kremer 46200 because of the large difference of characteristics between two kinds of titanium dioxide. There are three main differences between two titania: firstly, the particle size of Hombikat uv-100 is 10 nm, while that of Kremer 46200 is 170 nm.[1,44] Secondly, the surface area of Hombikat uv-100 is 250 m^2/g, which is nearly 18 times larger than that of Kremer.[1,44] Thirdly, the microstructure of Hombikat uv-100 and Kremer 46200 are anatase and rutile, respectively. [1] Since the degradation increases as the particle size decreases and surface area increases, and the rutile phase is more stable than the anatase phase, the photo-catalytic activity of Hombikat uv-100 is supposed to be higher than that of Kremer 46200, and the experiment results agree well.

Besides the two titanias mentioned above, there is another kind of titanium dioxide pigment tested with acid blue 9, that is coated Hombikat uv-100. There are three groups of testing results, which are shown in figure 4-6. Each group has two samples with different dispersing method, using ultrasonic bath only and ultrasonic bath with calgon. Based on the three groups results, the degradation rate of 'ultrasonic bath only' samples are similar to each other, but for the samples with added calgon, the degradation rate is relatively unstable. As is mentioned in previous section, the coated Hombikat uv-100 is obtained through controlled deposition of Al_2O_3 film so that the resistance of Hombikat uv-100 to UV-light should be improved.[15] However, comparing the degradation of coated Hombikat uv-100 shown in figure 4-6 with the results of Hombikat uv-100 shown in figure 4-3, there is no large distinction of degradation rate between two types of Hombikat uv-100. It is worth noting that, in the case of using ultrasonic bath only, acid blue 9 adsorbed on the coated Hombikat uv-100 during the centrifuging. The color changing of coated Hombikat uv-100 centrifuged from solution is observed that the white coated Hombikat uv-100 turns into blue. In that case, the concentration of test samples will be affected by the absorption. The measured value is supposed to be lower than the real value. That phenomenon explains the reason why the concentration of sample with coated Hombikat uv-100 at 30 minutes, which is around 0.015mM, is even lower than that of sample with uncoated Hombikat uv-100, which is nearly 0.02mM. Therefore, according to the experiment results, it cannot prove that the resistance of Hombikat uv-100 to UV light can improve by deposition of a thin Al_2O_3 layer.

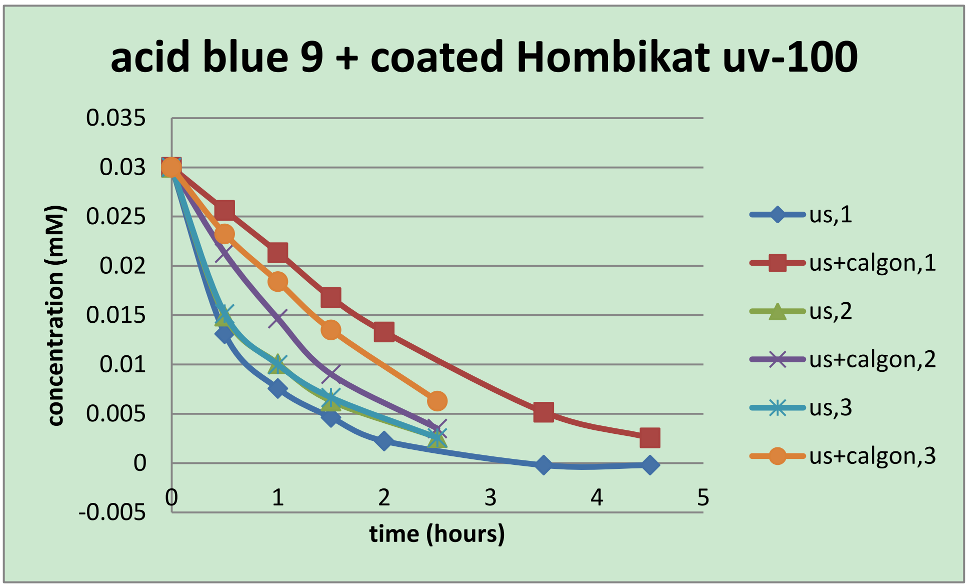

Figure 4- 6 degradation of acid blue 9 with coated Hombikat uv-100

4.1.3 The shift of wavelength corresponding to the most intense peak of absorbance

During the photo-catalytic activity test, there is an interesting phenomenon observed, that is the wavelength corresponding to the most intense peak of absorbance, λ_{max}, shifts with exposure time. To ensure the shift of peak, three groups of experiments are designed that acid blue 9 is mixed with three kinds of titanium dioxide, respectively. For each group, there are three sample solutions: pure acid blue 9 solution regarded as reference sample, mixture of acid blue 9 and titanium dioxide dispersed by ultrasonic bath only and the mixture dispersed by ultrasonic bath with dispersing agent calgon. The samples will be taken from each testing solution for certain time intervals, 0.5, 1, 1.5 and 2.5 hours, and scanned in the wavelength range from 300nm to 800nm by liquid state spectrometer. Then, the shift of the wavelength can be observed by comparing the spectrums.

Hombikat uv-100

Pure acid blue 9 solution is exposed under UV-light for 2.5 hours, and measured for four times with different light duration, which are shown in figure 4-7. As is shown in figure 4-7, four colored lines overlap completely, and the most intense peak of absorbance still remains at the same position. The corresponding intensity and wavelength of the peak are not altered, which means that there is no degradation of acid blue 9 solution occurred within 2.5 hours under the exposure of UV-light.

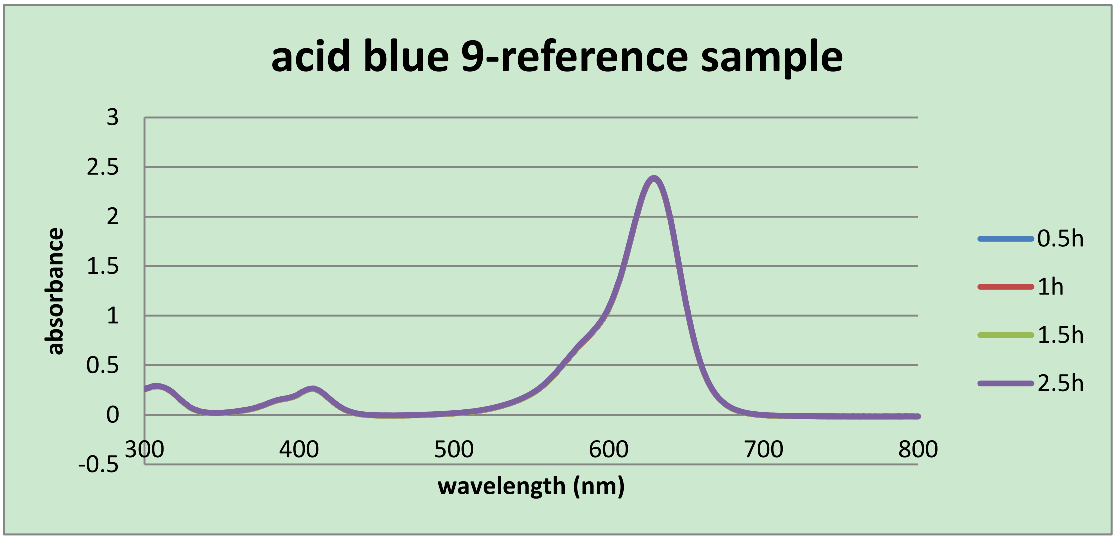

Figure 4- 7 degradation of pure acid blue 9 solution

When acid blue 9 is mixed with Hombikat uv-100, in both case of 'ultrasonic bath only' and 'ultrasonic bath with calgon', λ_{max} shifts to left and the intensity of peak decreases with exposure time increases. Comparing the spectra of these two situations shown in figure 4-8 and figure 4-9, it can be observed that in the case of 'ultrasonic bath only' the shift of wavelength is larger, which is changed from 630nm to 605nm. For the sample added with calgon, the shift of wavelength just turns from 630nm into 619nm.

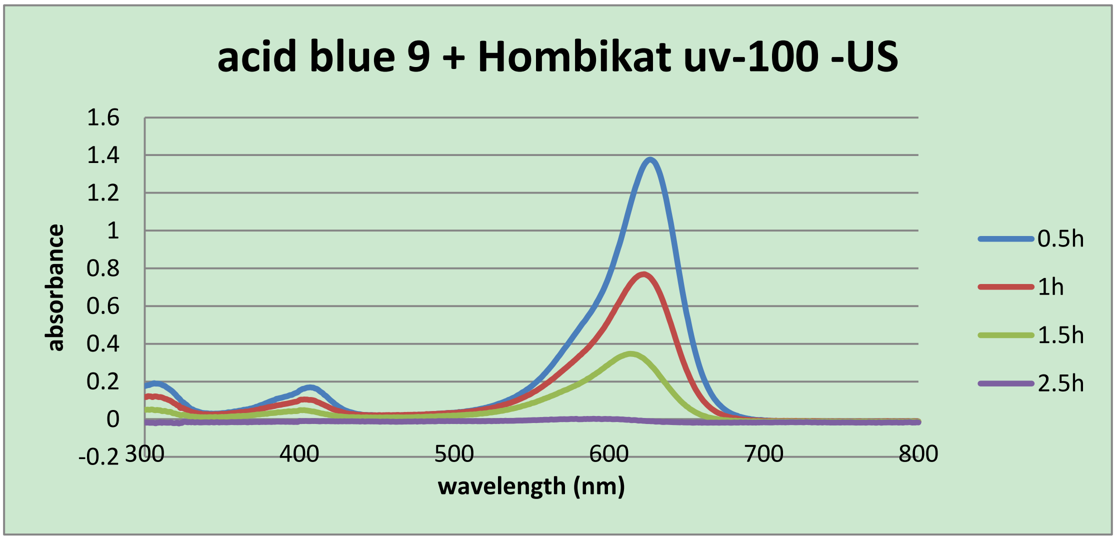

Figure 4- 8 the degradation of acid blue 9 with Hombikat uv-100

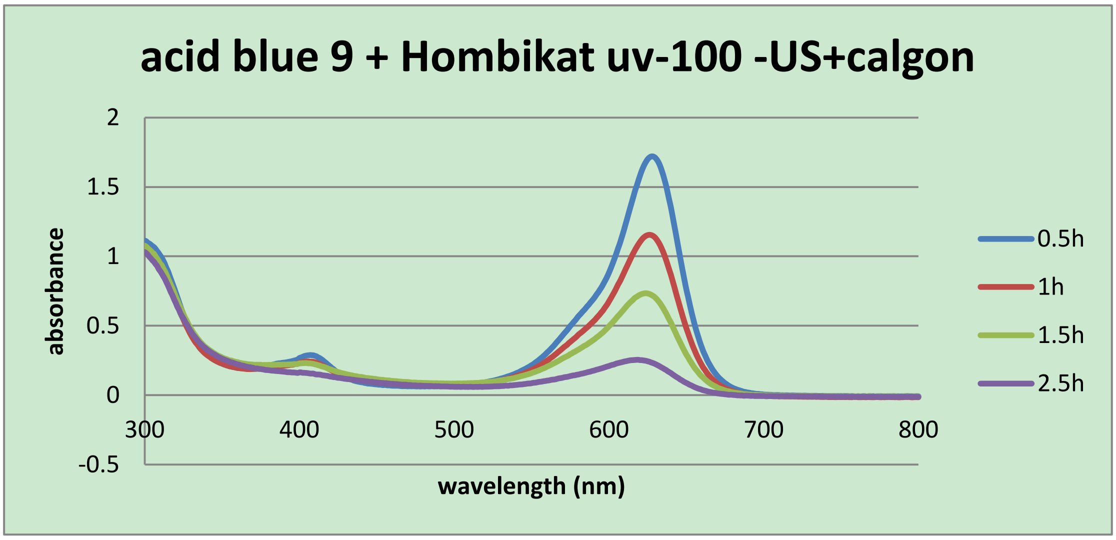

Figure 4- 9 the degradation of acid blue 9 with Hombikat uv-100 and calgon

Coated Hombikat uv-100

When using the coated Hombikat uv-100, the regularity of the shift of wavelength corresponding to the most intense peak is similar to that of the Hombikat uv-100, which are shown in figure 4-10 to figure 4-11. For reference sample, the position of the peak is stable that there is no change of intensity and corresponding wavelength. After adding the coated Hombikat uv-100, the shift of wavelength can be observed in both situations that mixed with and without calgon. When acid blue 9 mixing without calgon, λ_{max} shifts from 630nm to 619nm. In the case of acid blue 9 mixed with calgon, λ_{max} changes from 630nm to 621nm.

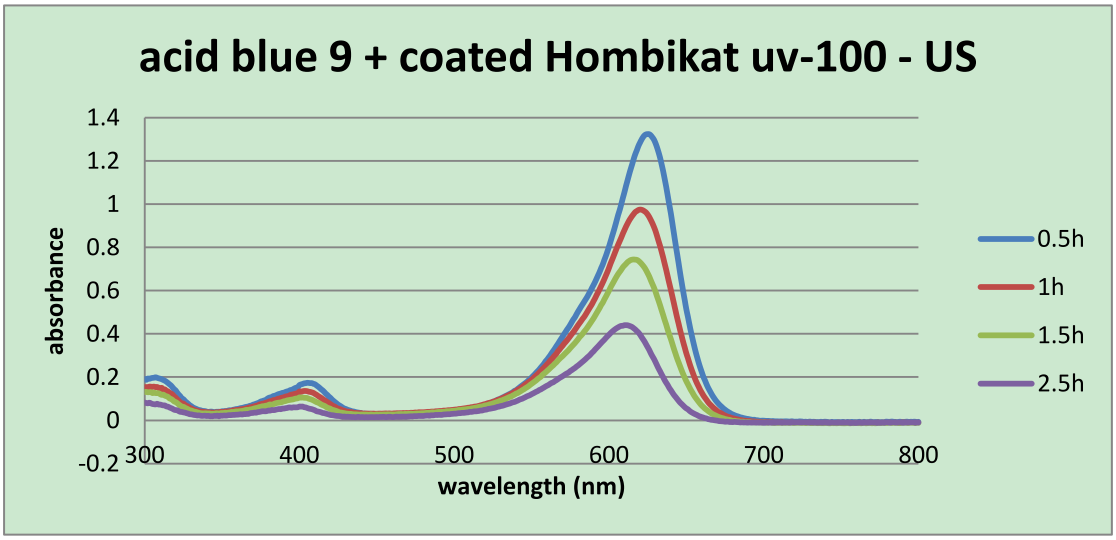

Figure 4- 10 the degradation of acid blue 9 with coated Hombikat uv-100

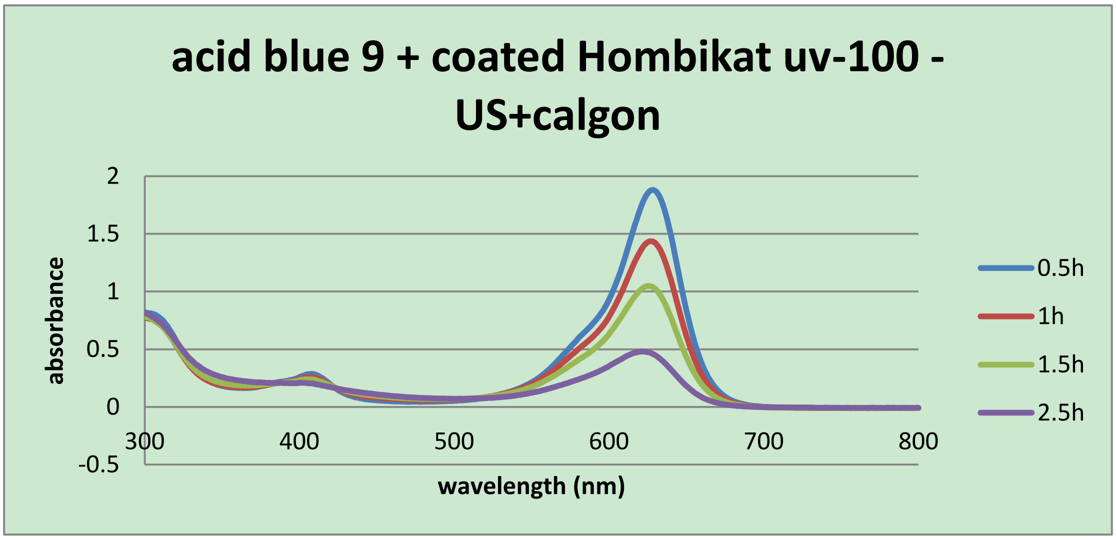

Figure 4- 11 the degradation of acid blue 9 with coated Hombikat uv-100 and calgon

Kremer 46200

As is mentioned before, Kremer 46200 is a very stable titanium dioxide due to its characteristics. Hence, the degradation rate is so slow that the concentration will be not changed so much. As is shown in figure 4-12, there is no shift of wavelength observed in the figures. For these samples, the spectrums of testing results in different time intervals coincident with each other. There is nearly no difference of intensity and corresponding wavelength for the peak between each testing results.

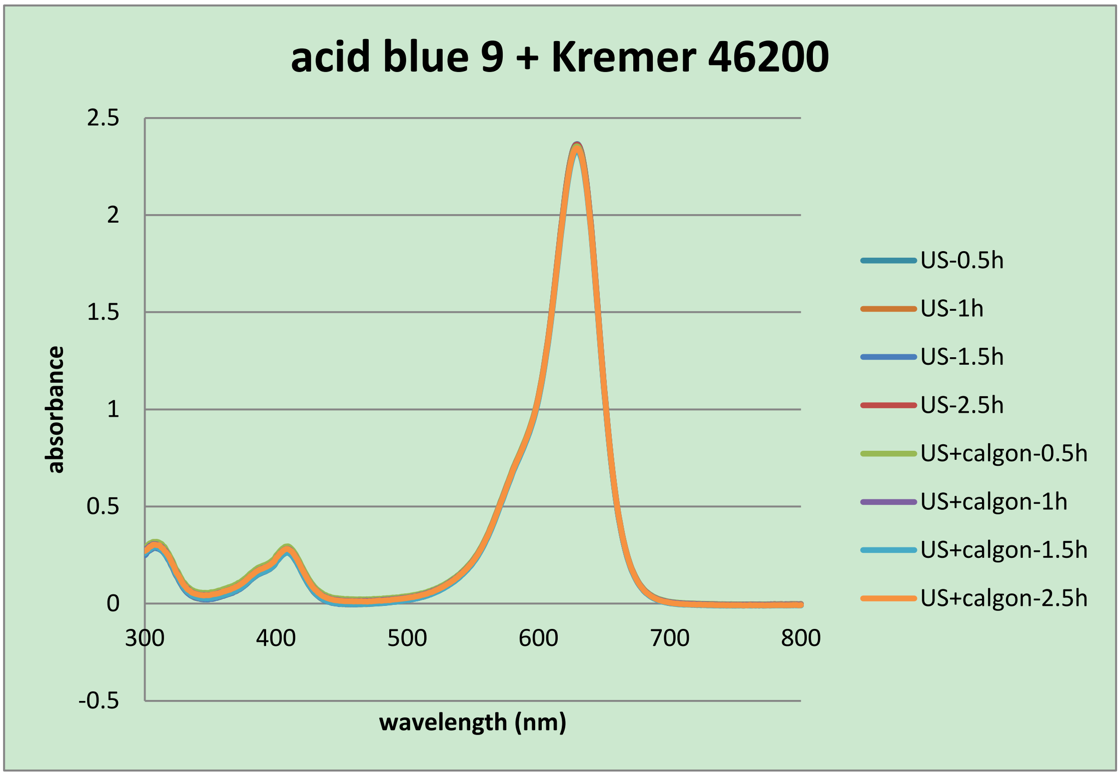

Figure 4- 12 the results of photo-catalytic activity test for the group of Kremer 46200

The wavelength corresponding to the most intense peak of absorbance shifts to shorter wavelength is termed the hypsochromic shift. Based on the results mentioned before, λ_{max} is reducing with the decreasing of concentration of acid blue 9 solution. Therefore, it is reasonable to assume that the shift of wavelength is related to the degradation. During the degradation, the organic molecules are ruptured by reaction with hydroxyl radical, which is a powerful oxidizing agent. The hydroxyl radical will attack the organics near the surface of titanium dioxide and decompose the organics into water, carbon dioxide and oxidized inorganic molecules. The general mechanism is shown as below:
Photons absorption of titanium dioxide:

$$\mathrm{TiO_2 + h\nu \rightarrow e^- + h_{BV}}^+ \tag{4.1}$$

Formation of hydroxyl radical:

$$\mathrm{H_2O + h_{BV}}^+ \rightarrow \mathrm{H^+ + \ {}^{\cdot}OH} \tag{4.2}$$

Oxidation of organic compounds by $\mathrm{{}^{\cdot}OH}$:

$$\mathrm{RH + \ {}^{\cdot}OH \rightarrow R^{\cdot} + H_2O} \tag{4.3}$$

Further oxidation of organics with oxygen:

$$\mathrm{R^{\cdot} + O_2 \rightarrow CO_2 + H_2O} \tag{4.4}$$

λ_{max} is determined by the molecular structure. Assumed that λ_{max} of intermediate degradation product of acid blue 9 is smaller than acid blue 9. During the degradation, the amount of intermediate product increase as the amount of acid blue 9 is reducing. Thus, the intensity of peak for intermediate product is higher than the peak of acid blue 9. Then, λ_{max} shifts to the left. On the other aspect, the shift of peak may also caused by changing polarity of solvent. However, the further mechanism has not figured out based on the existing results that could be finished by the further research.

4.2 Photo-catalytic activity test for selected artists pigment via liquid state spectrometer

After finishing the testing of acid blue 9, the selected artists pigments are to be measured in the same method. This section describes the photo-catalytic activity test of selected artist pigments. The testing results of each pigment will be shown in the following sub-sections.

4.2.1 Alizarin

As is mentioned in section 3.2, there are two categories of alizarin crimson in this project. They are alizarin crimson dark from Rijksmuseum and 97% pure alizarin (1,2-dihydroxyanthraquinone) ordered from Sigma-Aldrich. Both of two alizarins are dissolved into the solvent, 1-hexanol. The corresponding wavelengths of the most intense peak of absorbance for two alizarins (alizarin crimson dark and alizarin) are 503nm and 438nm, respectively. [45] And the calibration lines of two alizarins are shown in figure 4-13.

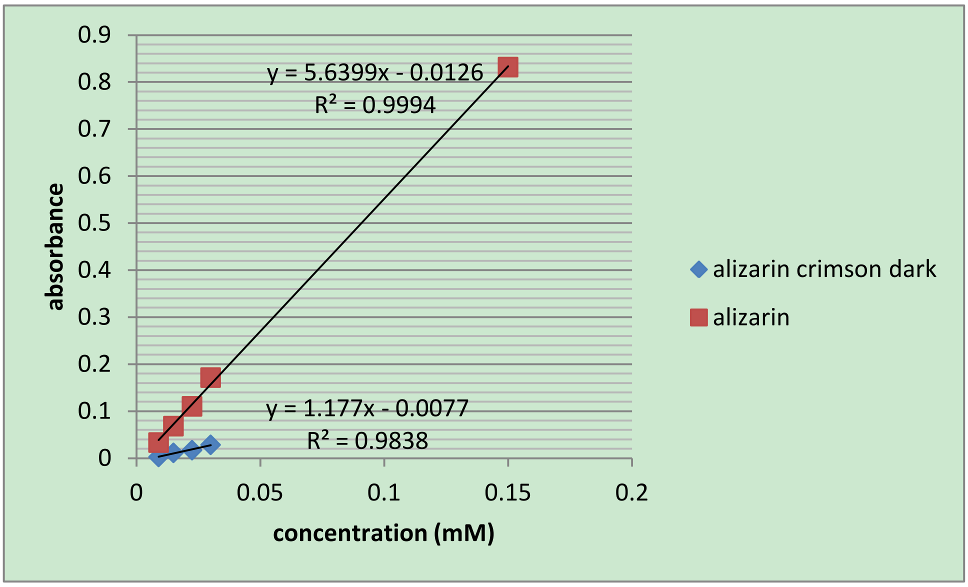

Figure 4- 13 calibration lines of two alizarins

The alizarin crimson dark of Rijksmuseum is considered as a mixture with alizarin instead of pure alizarin because some dark reddish particles will precipitate on the bottom of flask during preparing the stock solution for alizarin crimson dark. Additionally, the wavelength of the most intense peak of absorbance for alizarin crimson dark is quite different from the reference peak of alizarin, which is around 437nm.[46] In this case, it is difficult to control the amount of alizarin dissolved in suspension so that there exists an error in concentration of solution for alizarin crimson dark, which will affect the result of photo-catalytic activity test.

The alizarins are mixed with Hombikat uv-100 and Kremer 46200 for testing, respectively. When combined with Hombikat uv-100, the alizarin pigments are adsorbed on the surface of titanium dioxide so that pure Hombikat uv-100 particles cannot be centrifuged out individually. In that case, it will have a large influence on the accuracy of concentration of samples, which resulted in inaccurate testing results. But when mixing with Kremer 46200, there is no absorption problem. The photo-catalytic activity test of alizarins with Kremer 46200 lasts for 48 hours due to the stability of Kremer 46200, and the results are shown in figure 4-14. Due to the difference of solubility of two alizarins, the original concentrations of testing solutions are not the same. After exposure of UV light for 48 hours, the concentration of alizarin crimson dark decreases from 0.09mM to 0.053mM, while that of alizarin is reduced from 0.15mM to 0.13mM. Thus, the degradation rate of alizarin crimson dark is more rapidly than the alizarin.

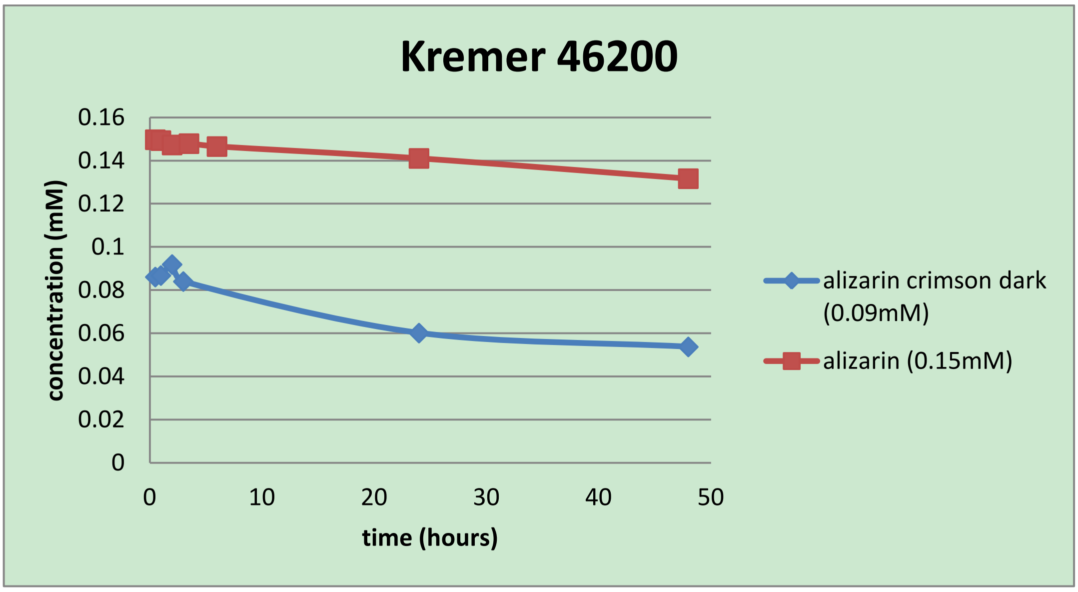

Figure 4- 14 the degradation of alizanrin crimson dark and alizarin

4.2.2 Prussian blue

The Prussian blue studied in this section is the Prussian blue delivered from Rijksmuseum. Based on the selection of solvents, oxalic acid is selected as the solvent for Prussian blue, and the concentration is 10 wt%. The wavelength corresponding to the most intense peak of absorbance is obtained by scanning the full wavelength range between 300nm and 800nm, which is 680nm. And the calibration line is shown in figure 4-15.[47]

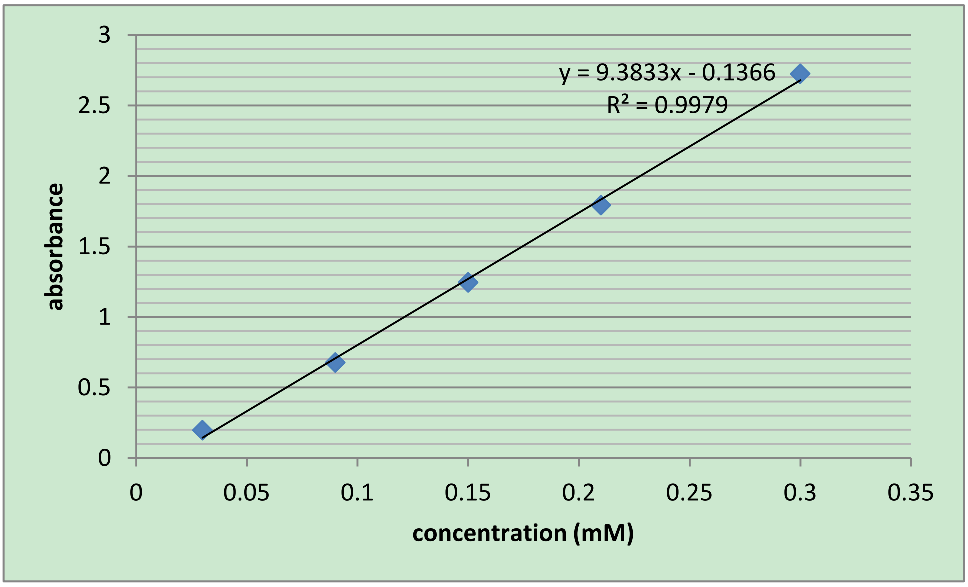

Figure 4. 15 calibration line of prussian blue in 10wt% oxalic acid

Prussian blue solution is combined with Hombikat uv-100 and coated Hombikat uv-100 for making the comparative experiments. However, the prussian blue can also adsorb on the surface of titanium dioxide so that the centrifuged solution cannot be used for measuring the absorbance since the concentration is inaccurate, affected by the adsorption.

4.2.3 Indigo blue

The indigo blue pigment is delivered from Rijksmuseum. In the case of indigo blue, the wavelength for the most intense peak of absorbance is 620nm. And the solvent for indigo blue is selected as dimethyl sulfoxide (DMSO). The calibration line of indigo blue is shown in the figure 4-16.

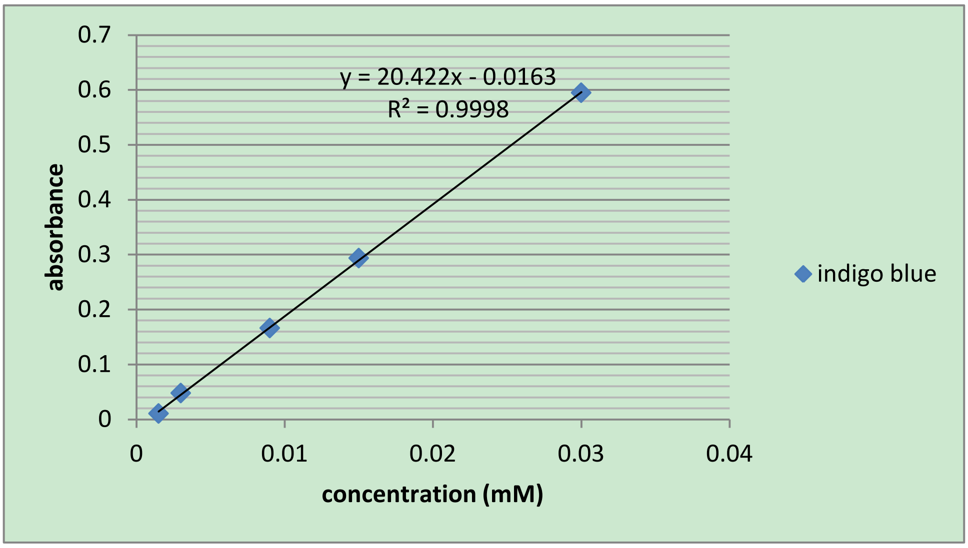

Figure 4- 16 the calibratrion line of indigo blue in DMSO

It is worth noting that the color of indigo blue solution in DMSO is altered when it place in dark for long time. The color will turn from blue to greenish blue, and finally become yellow. The mechanism of the phenomenon has not figure out in this project yet, which could be finished by further research. Since the indigo blue solution is unstable, the photo-catalytic activity test of indigo blue is suspended.

4.2.4 Vermillion

The vermillion pigment is ordered from Aldrich Company. Due to the insolubility of vermillion, there is no suitable solvent that be able to dissolve the vermillion without changing its chemical structure. In this case, the calibration line cannot be obtained through liquid state spectrometer measurement. It is difficult to do the photo-catalytic activity test in liquid state for vermillion.

4.2.5 Conclusion

According to the photo-catalytic activity test of selected artists pigment, it reveals that liquid state testing method is not suitable for measuring the photo-catalytic activity of artists' pigments, which cannot dissolve in the water, due to the limitations met during the experiments. The main limitations for liquid state testing are lists as follows:

Firstly, when mixing the pigments with titanium dioxide, the pigment may adsorb on the surface of titanium, especially for those possess relatively large surface area. It will lead to obtain an inaccurate absorbance corresponding to the inaccurate concentration.

Secondly, it is quite difficult to find out a suitable solvent for the artists' pigments. Most of them hardly dissolve in water. Sometimes, the pigment is even a mixture instead of pure compound, such as alizarin crimson dark delivered from Rijksmuseum. The concentration of stock solution will be inaccurate if the selected solvent cannot dissolve the pigment completely.

Furthermore, if the solvent is an organic compound, it will be also decomposed by titanium dioxide. For instance, oxalic acid and DMSO can be degraded by titanium dioxide photo-catalysts,[48,49] so that there may exist a competition of degradation between organic artist pigment and its organic solvent.

Therefore, photo-catalytic activity test in liquid state is not suitable for studying artist pigments. It is necessary to develop a new measurement, which can be widely used for testing the pigments. Solid state spectrometer is the main candidate of the testing method, and the detailed sample preparation method need to be designed.

4.3 Photo-catalytic activity test for selected artist's pigment with titanium dioxide via solid state spectrometer

This section shows the photo-catalytic activity test through solid state spectrometer. The developing process of sample preparation method for solid state spectrometer will be described, and the calibration line and results of photo-catalytic activity test will be discussed.

4.3.1 Development of sample preparation procedure

Before considering the design of sample preparation, it is essential to ensure the accuracy of measurement, reduce the error of testing result caused by the measurement. There are two main factors which may have a large influence on the accuracy of result, the stability of reference sample and the thickness of sample layer.

(1) stability of reference sample

As is mentioned in section 2.5.2, it is necessarily to do 'autozero' test before measurement everyday by measuring the reference sample, which is made of barium sulfate, so that the standards is unified. The reference sample is required to be a homogeneous surface, and the reflection percentage of each position of surface should be almost the same. However, sometimes, it found that there is a relatively large difference of the reflection percentage between different positions of reference sample due to the changing of humidity of reference sample. When the reference sample is wet, sample layer will absorb more light that resulted in a wrong reflection percentage obtained by solid state spectrometer. In that case, the reference sample has to be re-prepared. Otherwise, the testing results will not be comparative with the previous. So, besides 'autozero' test, it is important to check if the reflection percentage of different position of reference sample is similar.

(2) the thickness of sample layer

The absorption of light increased with the thickness of sample layer. Thus, it is necessary to check whether the effect of thickness on reflection percentage is large or not. Then, pure Hombikat uv-100 is used for checking the effect. The testing samples, 50mg and 100mg Hombikat uv-100, are measured for three times separately. As is shown in figure 4-17, the difference of reflection percentage for two samples is relatively small. The maximum difference value is around 3 %, which is acceptable. Therefore, the effect of thickness of sample layer can be neglected in this project.

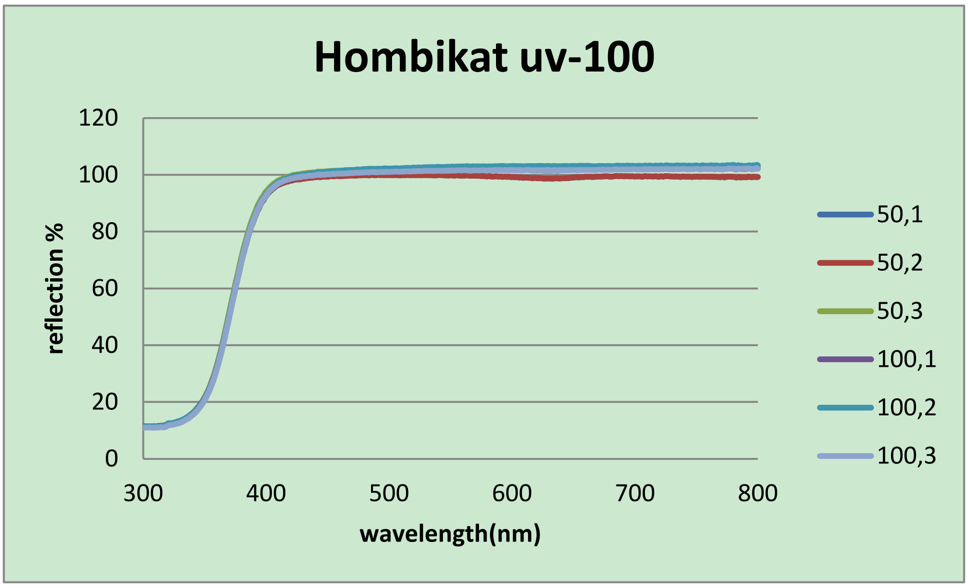

Figure 4- 17 results of pure Hombikat uv-100 with different mass

The new preparation method is adjusted on the basis of original method. In order to develop the new sample preparation procedure, there are some factors need to be taken into account:

Firstly, both titanium dioxide pigment and artist's pigment are required to mix within the water to form suspension. The sample preparation method necessarily ensures that the prepared sample suspension is homogeneous.

Secondly, after getting a homogeneous sample suspension, sample preparation method is required to remove the water from suspension and obtain solid state sample finally.

Thirdly, sample preparation method should not increase the temperature of sample so much, otherwise, higher temperature will influence on the degradation of pigments.

Last but not least, during the sample preparation, it is required to minimize the time of light exposure on sample, which will affect the accuracy of result in some degree.

Basically, the sample preparation method is divided into three steps: dispersing, exposure and separation.

Dispersing

Dispersing method is improved on the basis of the method for liquid state testing. It consists of two steps: Ultrasonic bath is the first step of dispersion which is using for breaking the agglomerates of titanium dioxide pigment. The time of ultrasonic bath is still 10 minutes, which is same as the original method of liquid state. After that, magnetic stirring is added as second step of dispersion. The suspension is put on the stirring plate (600 rpm) in dark for two hours to improve the homogeneity of suspension.

Exposure

The exposure step has already been discussed in the section 3.3.

Separation

There are many candidates of separation method. In general, the purpose of separation is to remove the water from suspension for obtaining a solid state sample, which can be used for measuring by solid state spectrometer. Therefore, the separation method consists of two portions: removing the water and drying the remaining sample.

(1) water removing method

Filtering is one of the most prevalent separation methods to separate the solid from the liquid. However, in this project, the particle size of titanium dioxide is quite small, for instance, the particle size of Hombikat uv-100 is merely 10 nm. Hence, considering the limitation of particle size, filtering is not suitable for this project. Centrifuging is another candidate for separation of water. The mechanism of centrifuging is accelerating the precipitation rate. When obtained the centrifuged sample, the water of sample will be removed by using pipette. It is used for separation of titanium dioxide from acid blue 9 solutions in previous experiments. Similarly, it can separate insoluble pigments from suspension. The last candidate of separation method is a relatively foundational way that is precipitating. Putting the suspension in dark directly after stirring and making the suspension precipitate by itself. It is a traditional and time-consuming method.

(2) drying method for remaining sample

There are few candidates of drying method due to the limitation of temperature and exposure. To avoid influence of results for the degradation rate, drying method should not increase the temperature of suspension and the time of exposure. Thus, evaporation of water from suspension by itself is considered as the suitable way for drying. The rest drying methods either increase the temperature of sample suspension or extend the time of exposure.

It can be conclude that there are mainly two kinds of experiment scheme candidates, which are using two different kinds of water removing method, respectively. The final scheme of experimental procedure will be selected by comparing the testing results of different sample preparation methods. There are two important aspects taken into account. One is the homogeneity of prepared sample. The other one is the repeatability of experiment. The scheme of precipitation is selected as the initial experimental procedure whose results are regarded as reference result. Prussian blue soluble and Hombikat uv-100 are selected to be test at first.

Both homogeneity of sample and repeatability of experiment are quite essential for developing an experimental procedure. In this case, two identical samples are prepared with the same preparation procedure: prussian blue (soluble) suspension, whose concentration is 0.3mM, mixed Hombikat uv-100 are prepared by using initial experimental procedure for twice. Each sample is measured twice with solid state spectrometer, and the results are shown in the figure 4-18.

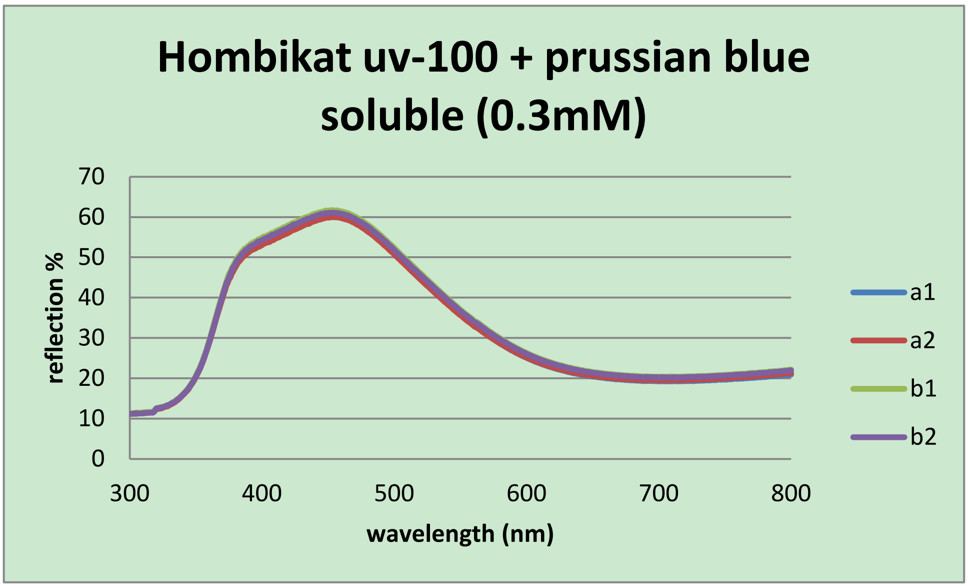

Figure 4- 18 the results of comparative experiments for repeatability and homogeneity with initial experimental procedure

As is shown in figure 4-18, four results of two samples are almost at the same position, which means that the repeatability of initial experimental procedure error is small, and the homogeneity of sample is reliable. The measurement is improved during the experiment process that the sample will be test for three times in specific positions instead of two times for random positions of the sample surface. Then, the average of three results will be calculated and used for making the calibration line and degradation rate. Five samples with different concentrations (0.03, 0.09, 0.15, 0.225 and 0.3mM) are prepared and measured. The results are shown from figure A-1 to figure A-5 in Appendix A. Based on these results, the homogeneity of sample has been proved again. Combined the results of five samples with different concentrations, the tendency of reflection percentage is shown in figure 4-19.

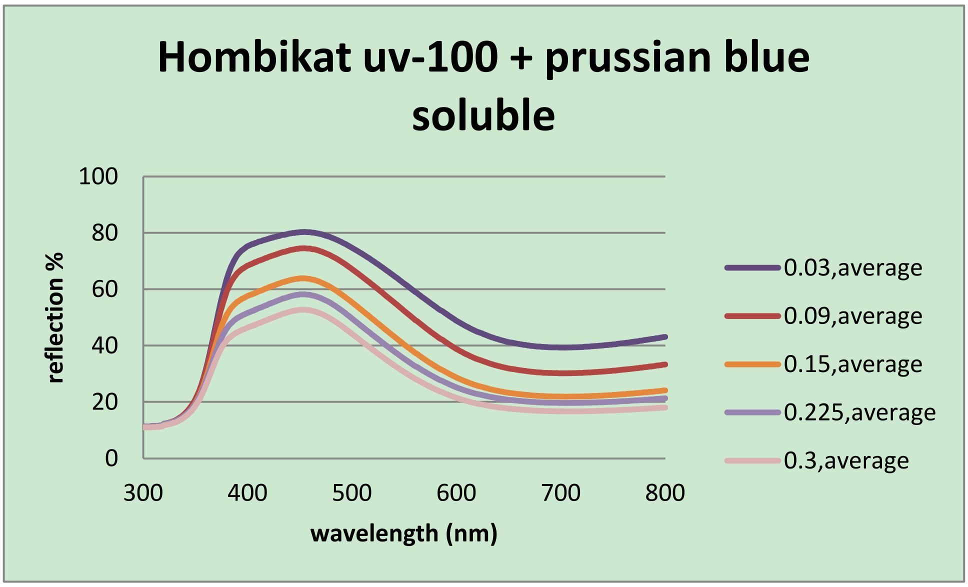

Figure 4- 19 the result of Prussian blue soluble mixed with Hombikat uv-100 with five different concentrations

As is shown in figure 4-19, the spectrum is basically separated into two parts in terms of wavelength: in the range of 300nm to 375nm, the reflection percentages of five samples are almost the same, which is affected by titanium dioxide. When the wavelength is larger than 375nm, the reflection percentage is increasing with the decreasing of concentration.

The wavelength corresponding to the most intense peak of absorbance is important to find out for making calibration line. In the case of reflectance, the wavelength corresponding to the lowest ebb is more essential. According to comparison of results, the lowest ebb of reflection percentage of samples does not correspond to the same wavelength. The range of wavelength is approximately between 699nm and 706nm. Since the difference of reflection percentage is quite small, it does not play an important role in making the calibration line. Thus, the wavelength corresponding to the lowest ebb of reflection percentage for Prussian blue is set up as 702nm, and the calibration line is shown in the figure 4-20. The power function is selected as the mathematical model to describe the calibration curve. The obtained calibration curves were described by different mathematical models, such as exponential function, logarithmic function, etc. Comparing their R-squared value, which is the coefficient of determination that indicated how well data points fit the curve, the power function's coefficient of determination is generally larger than others that come closer to 1. Therefore, the solid state calibration curve for is expressed by power function.

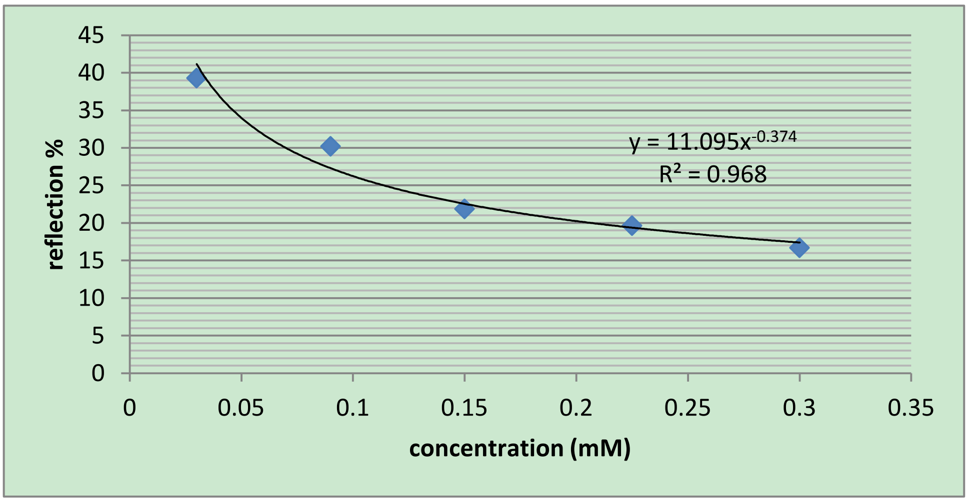

Figure 4- 20 calibration curve of prussian blue soluble with Hombikat uv-100

The equation of calibration line for liquid state sample is linear. So it was assumed that the calibration line for solid state is also linear. However, as is shown in figure 4-20, it is obvious that the calibration curve is not a linear line but a curve. If the concentration of Prussian blue is zero, the sample is equal to the pure titanium dioxide, of which reflection percentage is 100% at 702nm. Based on a linear calibration line, the reflection percentage cannot reach 100% when the concentration is zero. Thus, it is reasonable to believe that the calibration is a curve rather than a line. So far, the relation between reflection percentage and concentration is obtained within specific range of concentration. Measurement of more samples with different concentrations is necessarily for deriving the accurate equation for lower concentration.

After ensuring the feasibility of precipitating method, the scheme of centrifuging is to be test. To compare the results of different sample preparation method, the same pigments are used for preparing the sample. And the results of two different methods are compared with each other, which is shown in figure 4-21. Based on the figure 4-21, it found that the results of two schemes are almost the same, so that both of the schemes are feasible for sample preparation.

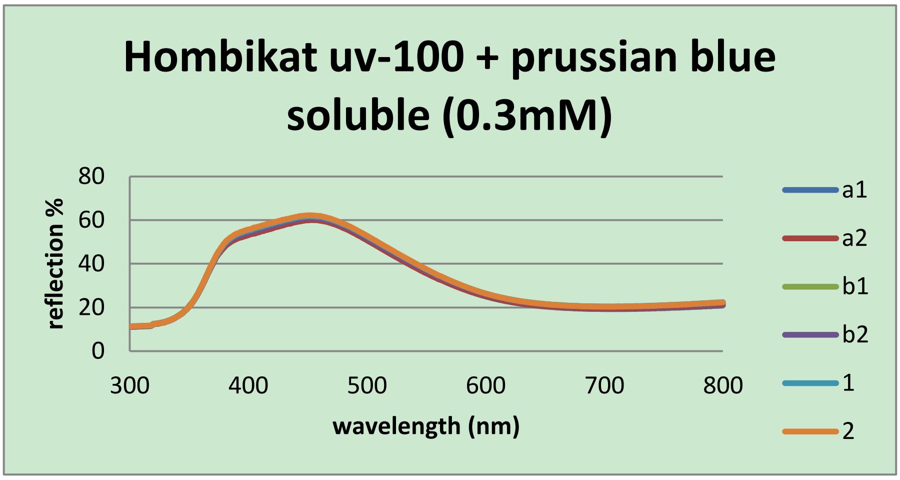

Figure 4- 21 comparison of results of precipitation and centrifuging method

During the further research, it is noteworthy that precipitating method is not suitable for every kinds of artist pigment. For instance, when preparing the alizarin samples, the precipitation rate of alizarin is too slow that it even cannot finish within 24hours. Therefore, the precipitation method is not good at the application of sample preparation for every kind of artists' pigments. In this case, the final scheme of experimental procedure is the scheme of centrifuging. The detailed procedure is shown as below:

(1) 50mg titanium dioxide pigment and specific amount of artists pigment are dispersed in 100 ml water to make suspension.

(2) The suspension is put in the ultrasonic bath for 10 minutes.

(3) Magnetic stirrer is put into suspension, and the suspension is covered with watch glass.

(4) The suspension is placed on magnetic stirring plate for stirring in dark for 2 hours, and the rotation speed is 600 rpm.

(5) The beaker is put on a stirring plate (600 rpm) in a UV-light box (equipped with 8 18W UV-lamps providing 470±20 $\mu W/(cm)^2$), the temperature is kept around 27°C by using cooling system.

(6) The suspensions (100ml) are poured in two centrifuge tubes (50ml per tube), and centrifuged in IEC centra-4B centrifuge with 5000 rpm for 5 minutes

(7) Removing the water from suspension by pipette, and washing the centrifuged particles from the wall of centrifuge tubes by demi-water (less than 10ml in total). The washing suspension is kept in the beaker in dark and evaporated by itself for days.

(8) Scraping the pigment layer from the bottom of beaker, and sample powders are stored in the bottle and prepared for analyzed with solid state spectrometer.

4.3.2 Results of the developed photo-catalytic activity test

After developing the experimental procedure of photo-catalytic activity test, several kinds of artists' pigments are tested by using solid state spectrometer. This section will describe the results of calibration and photo-catalytic activity test for each studied artist pigment.

4.3.2.1 Prussian blue soluble

With developed experimental procedure, prussian blue soluble is mixed with Hombikat uv-100 by using ultrasonic bath equipment, and separated by centrifuging equipment. The testing results of five samples with different concentrations are combined and shown in figure 4- 22, and the calibration curve is illustrated in figure 4-23.

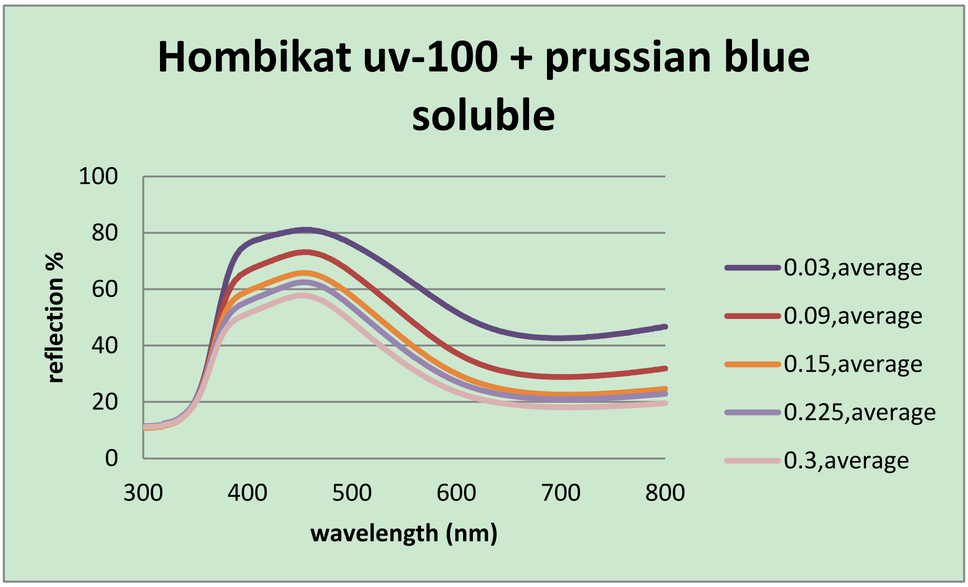

Figure 4- 22 the result of Prussian blue soluble mixed with Hombikat uv-100 with developed experimental procedure

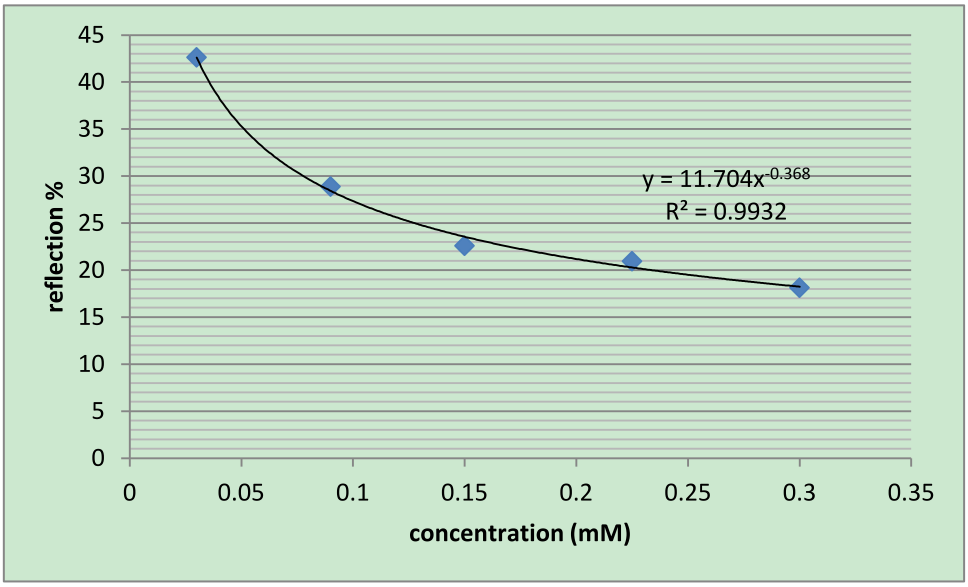

Figure 4- 23 calibration curve of prussian blue soluble with Hombikat uv-100 with developed experimental procedure

Comparing the figure 4-23 with figure 4-20, it found that there is almost no difference of the reflection percentage corresponding to the samples with same concentration. Only when the concentration is 0.03 mM, the distinction of reflection percentage is relatively larger than others, which is about 3%. According to comparison and analysis, it is believed that the difference of results is caused by the weighing. The least significant digit of scale is 0.1mg that always fluctuates in the range of ±0.1mg due to the effect of temperature, humidity and vibration of environment. When weighing the artist's pigment of the lowest concentration 0.03mM, the amount of Prussian blue soluble is quite small, which is approximately to 0.9mg, that there could exists a relatively large error during weighing the artist pigment in small amount.

To improve the accuracy of weighing and reduce the error, the amount of pigments and the volume of water are considered to be doubled. Then, the amount of Prussian blue soluble will increase to 1.8mg, and the influence of error will be much smaller than before. Therefore, a comparative experiment is designed to figure out whether the increasing of amount of pigments with same ratio will influence the reflection percentage or not. The concentration of sample is set as 0.3mM, and the detailed settings are shown in table 4.1.

	Prussian blue soluble	Hombikat uv-100	Water
1 times	9.2mg	50mg	100ml
1.5 times	13.8mg	75mg	150ml
2 times	18.4mg	100mg	200ml

Table 4- 1 the settings of comparative experiment

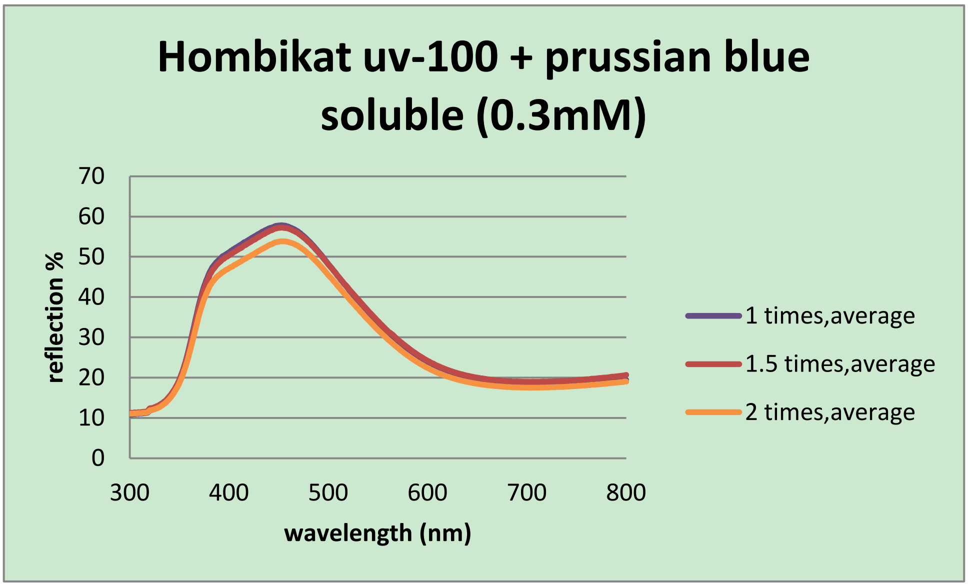

Figure 4- 24 the results of comparative experiment

Figure 4-24 reveals the results of comparative experiment. It found that the reflection percentages of three samples with the same ratio are nearly the same corresponding to the wavelength at 702nm. It means that the increasing of amount of pigments with same ratio has less influence on the testing result, and it can reduce the effect of error during the weighing at the same time. Therefore, in order to get the accurate calibration curve, another five samples are prepared with double amount of pigments with same concentrations as before. The testing results of five samples and calibration curve are shown in figure 4-25 and figure 4-26.

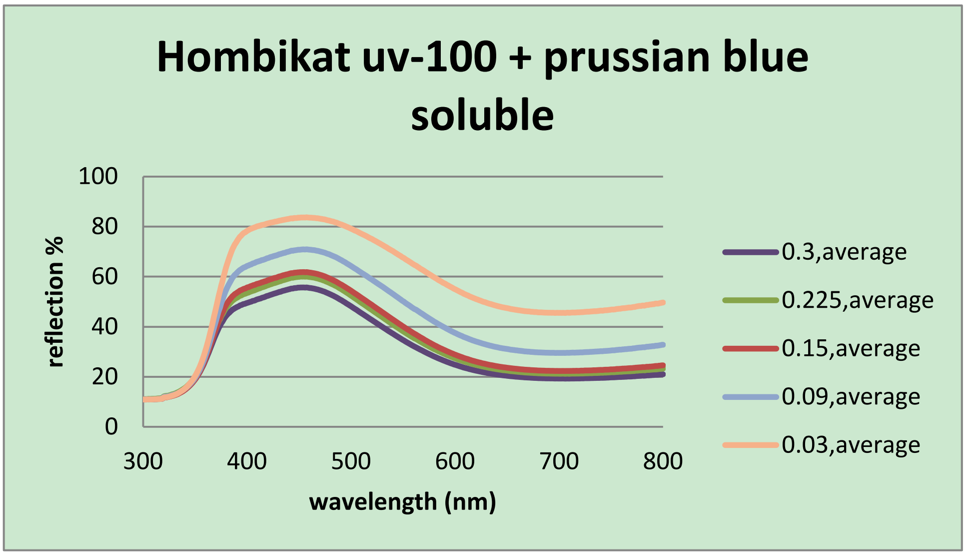

Figure 4- 25 the results of of Prussian blue soluble mixed with Hombikat uv-100 with developed experimental procedure in double amounts

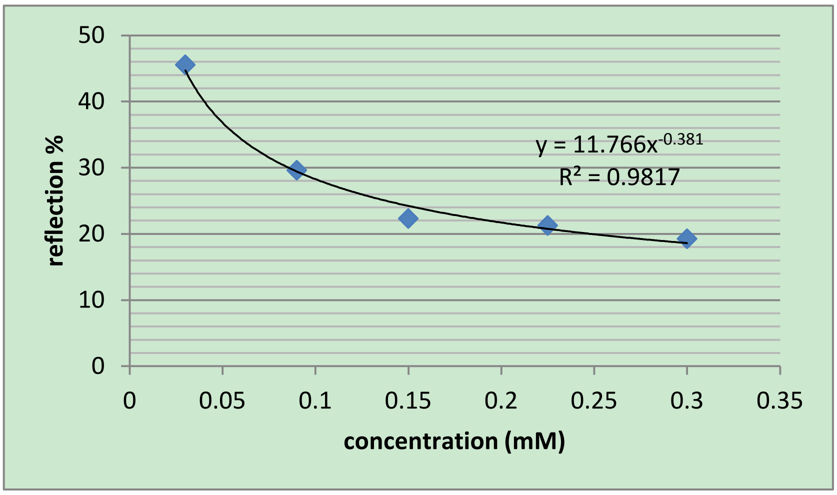

Figure 4- 26 calibration curve of prussian blue soluble with Hombikat uv-100 with developed experimental procedure in double amount

Combined three calibration lines of Prussian blue soluble, the relatively accurate calibration curve is obtained, which is shown in figure 4-27. The mathematical equation for non-linear solid-state calibration curve is determined to express as a power function, which describe the variation tendency with concentration of reflection percentage well. The equation can be only used in the range of concentration from 0.03Mm to 0.3mM. For the other part of concentration, the mathematical equation could be different. In this case, to obtain a more accurate equation for non-linear solid-state calibration curve, more samples with different concentrations are supposed to be measured, especially in range of concentration between 0 and 0.03mM.

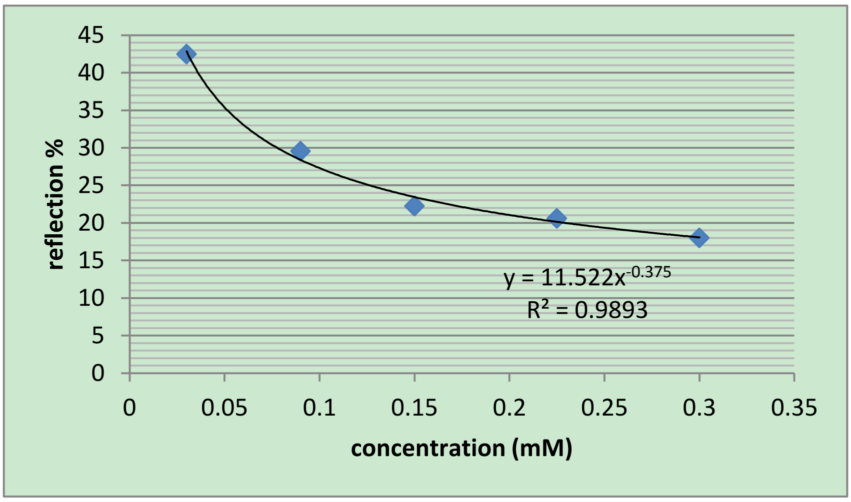

Figure 4- 27 final calibration curve of Prussian blue soluble with Hombikat uv-100

After obtaining the calibration curve, the photo-catalytic activity of Prussian blue soluble mixed with Hombikat uv-100 is measured in the time range of 24 hours. Four samples are prepared for the measurement in terms of different exposure time, 1, 3, 6 and 24 hours, and the original concentration is 0.3mM. Figure 4-28 shows the results of photo-activity test for Prussian blue soluble mixed with Hombikat uv-100, and there is no large changing of reflection percentage.

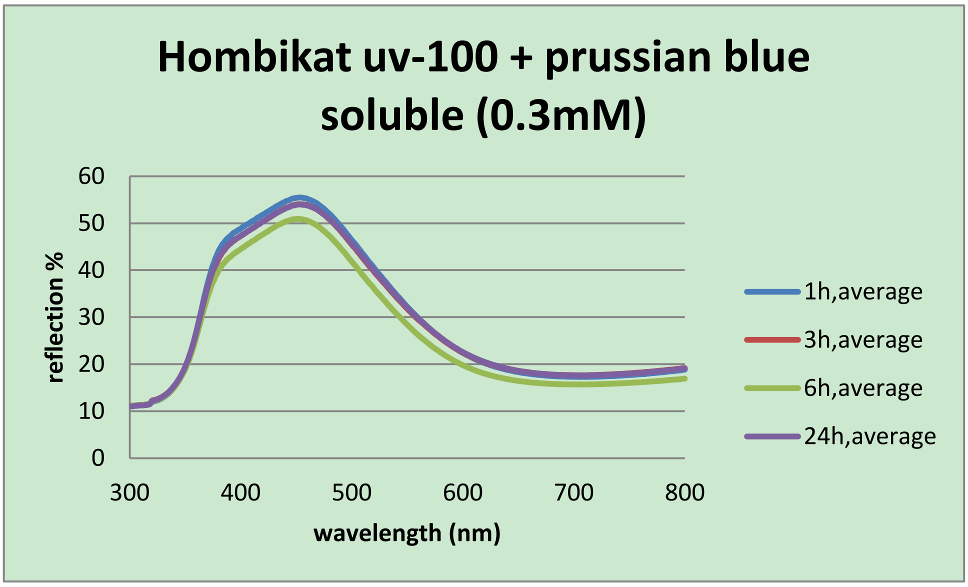

Figure 4- 28 prussian blue soluble degradation by Hombikat uv-100 within 24hours

Prussian blue soluble is regarded as a permanent pigment except when mixed with white pigments. It tends to fade under the exposure of UV light due to the photo-reduction to Prussian white, and the reaction is shown as follows:[50]

$$Fe^{III}\left[Fe^{II}(CN)_6\right]^{-}(aq) + e^{-} + h\nu \rightarrow Fe^{II}\left[Fe^{II}(CN)_6\right]^{2-}(s)$$

However, the fading will reverse when the Prussian blue access to the air since the oxygen in the solution is able to re-oxidize the Prussian white back to Prussian blue,

$$4Fe^{II}\left[Fe^{II}(CN)_6\right]^{2-}(s) + O_2(aq) + 4H^{+} \rightarrow 4Fe^{III}\left[Fe^{II}(CN)_6\right]^{-}(s) + H_2O$$

Therefore, the results of photo-catalytic activity test are just in keeping with the mechanisms of degradation for Prussian blue mixed with titanium dioxide that the reflection percentage basically keeps as a constant after exposure for 24 hours. For the result of sample for 6 hours, the reflection percentage decreases instead of increase that is not corresponding to the degradation mechanism, so that this result is considered as an error and to be neglected.

4.3.2.2 Prussian blue

The other kind of Prussian blue, which is delivered from Sigma Aldrich Company, is also mixed with Hombikat uv-100 and studied with the developed experimental procedure for compassion. According to the trial experiment, during the centrifuging, the solution centrifuged from the suspension with high concentration remained blue. It means that the Prussian blue didn’t adsorb on the surface of titanium dioxide completely. Hence, the concentration of samples for making calibration curve is reduced to 0.15, 0.12, 0.09, 0.06 and 0.03mM, and the original concentration for photo-catalytic activity test decreases to 0.15mM. Figure 4-29 and 4-30 show the testing results of samples with different concentrations and calibration curve at the wavelength of 702nm. The reflection tendency of spectrum from 300nm to 800nm is similar to that of Prussian blue soluble. And the calibration curve is also nonlinear.

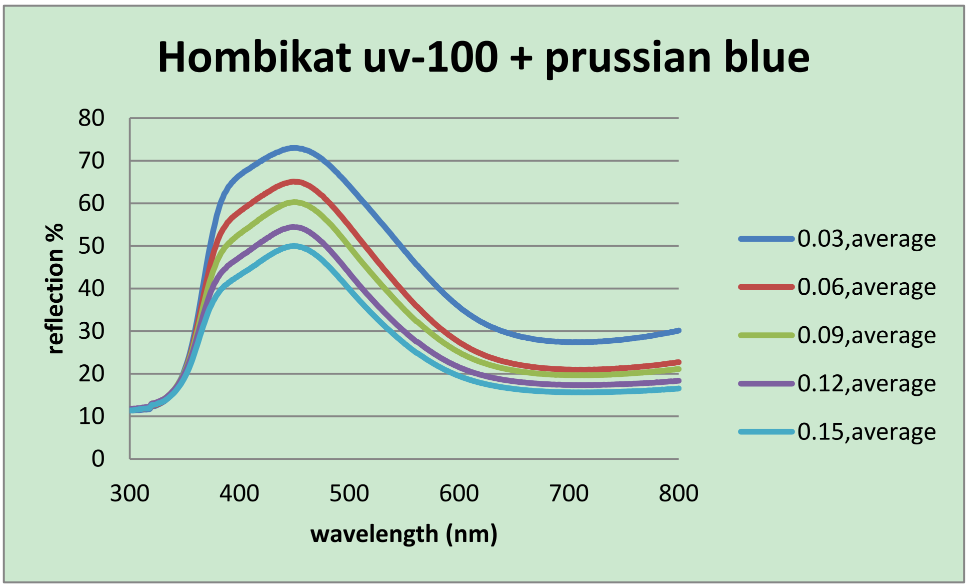

Figure 4- 29 the testing results of Prussian blue mixed with Hombikat uv-100

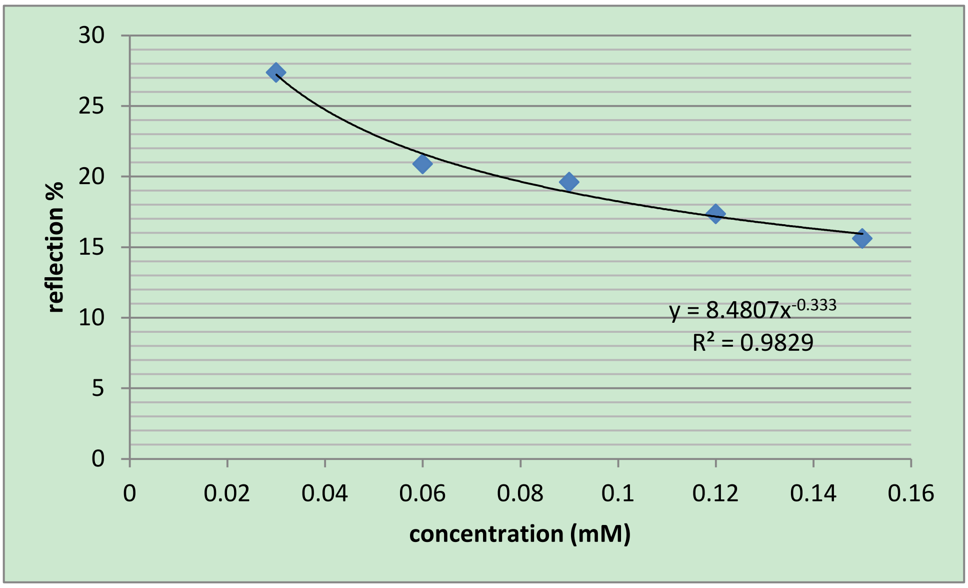

Figure 4- 30 calibration curve of prussian blue mixed with Hombikat uv-100

The results of photo-catalytic activity test for Prussian blue shows that the concentration of sample is not altered after the exposure of UV-light for 24 hours, which is shown in figure 4-31. It can be seen from the figure that the degradation rate of Prussian blue with Hombikat uv-100 is extremely slow, even though the Hombikat uv-100 is a relatively active photo-catalyst under the UV-light due to its characteristics. Therefore, the permanence and the reversibility of degradation of Prussian blue can be proved again.

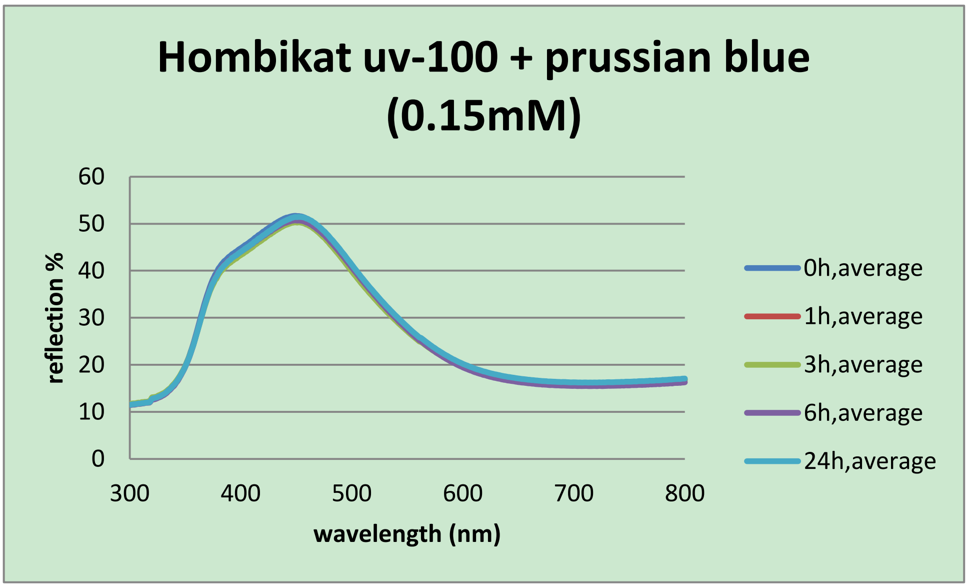

Figure 4- 31 the Prussian blue degradation by Hombikat uv-100 within 24 hours

4.3.2.3 Alizarin

The alizarin delivered from Sigma Aldrich is measured with developed testing procedure. It is a good opportunity to inspect the feasibility of developed experimental procedure. During preparing the suspension of alizarin, it found that the color of alizarin suspension will change. The pure solid alizarin is earthy yellow, and remained earthy yellow when added into demi-water. Whereas, after mixing with titanium dioxide (Hombikat uv-100), the suspension turns into red in short period. Based on the material safety data sheet of alizarin-Sigma, the alizarin turns from yellow to red when pH value in the range of 5.5 to 6.8, and become violet when the pH value is higher than 10.1, which means that the acidity and basicity have a large influence on the color of alzairn. Demi-water and Hombikat uv-100 suspension with demi-water are measured by pH meater, and the pH values of two suspensions are 5.84 and 6.95, respectively. The results explain the phenomenon of the changing of color properly.

In order to make the calibration curve for alizarin, five samples with different concentrations are prepared. The spectra of all samples are shown from figure A-6 to figure A-10 in Appendix A, and combined into figure 4-32. As is shown in the figures, the samples are homogeneous and testing results are generally identical. The wavelength corresponding to the lowest ebb is 490nm. The calibration curve is obtained by combination of results of five samples, which is shown in figure 4-33. In general, the reflection percentage is increasing when the concentration of sample is decreasing.

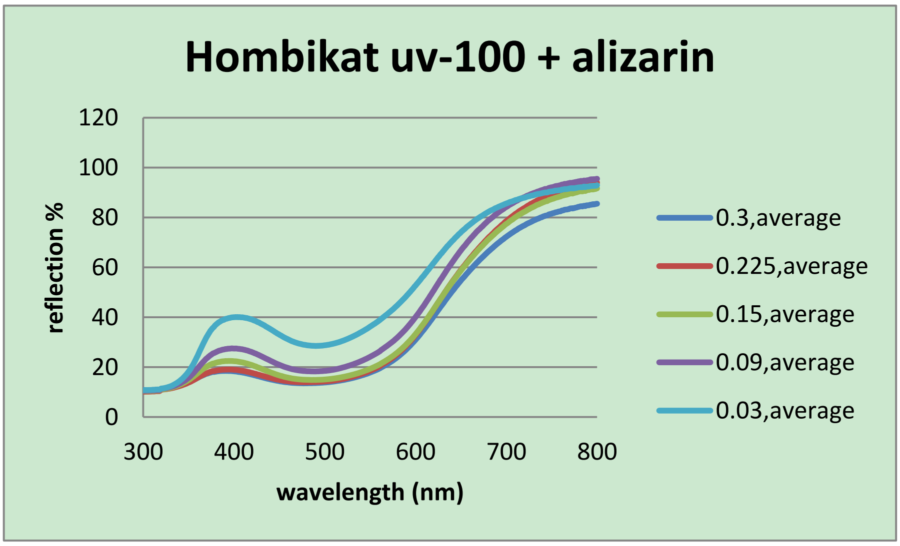

Figure 4-32 the testing results of alizarin mixed with Hombikat uv-100

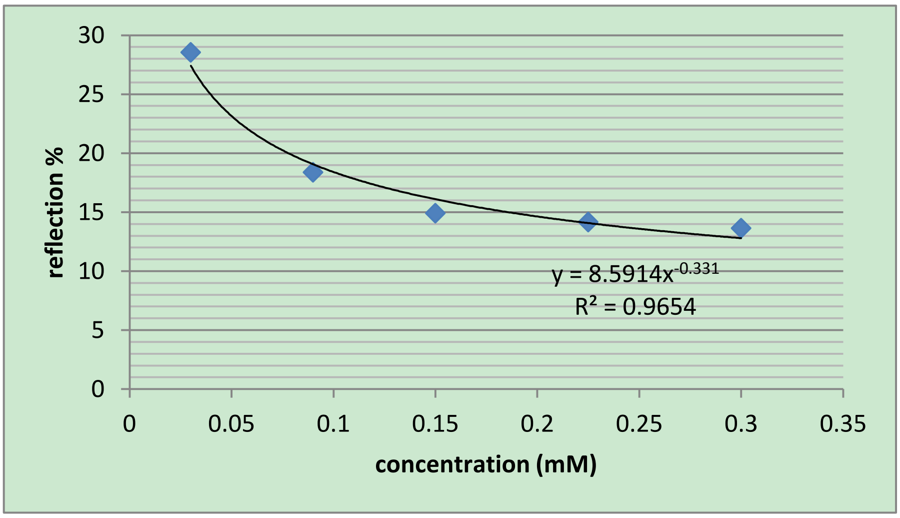

Figure 4- 33 calibration curve of alizarin mixed with Hombikat uv-100

Figure 4-34 shows the testing results of degradation of alizarin with Hombikat uv-100 within 24 hours. It found that the reflection percentage in terms of the wavelength at 490nm is increasing as the extension of exposure time. As is mentioned before, the organics can be oxidized and degraded by the free radicals with strong oxidize potential, and finally decomposed into water, dioxide. The result of sample with 24 hours exposure is a good evidence for that since the spectrum is basically equal to that of the titanium dioxide. It means that the alizarin has almost been degraded after the exposure of UV-light for 24 hours.

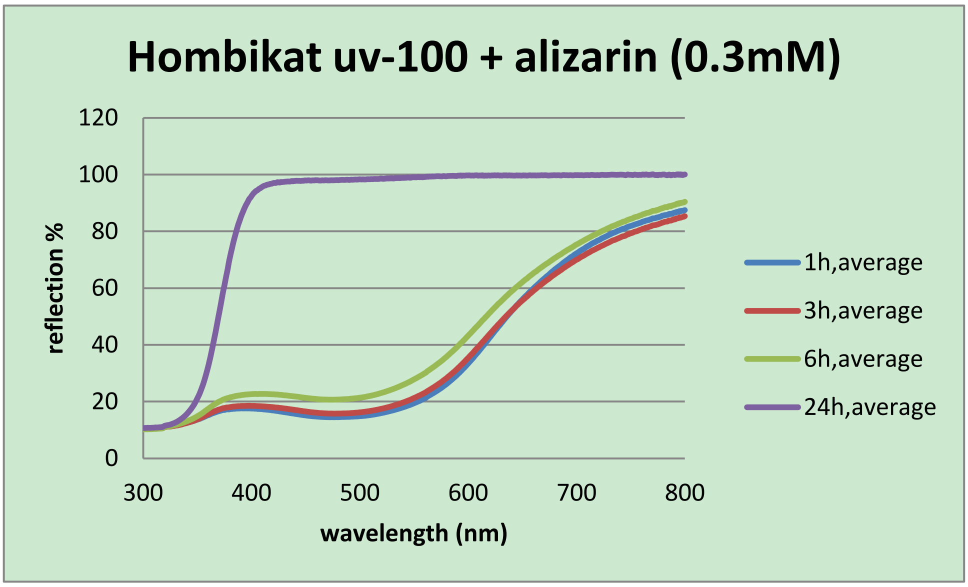

Figure 4- 34 the degradation of alizarin by Hombikat uv-100 with 24 hours

5. Conclusion and Recommendation

The aim of this project was to test the degradation of artist pigment with titanium dioxide quantitatively by using the ultraviolet-visible absorbance spectrometer, UNICAM UV-500, in liquid state. However, since the unexpected limitations of photo-catalytic activity test in liquid state, the original testing method is considered as the method for water-soluble pigment rather than the whole artists' pigments. The limitations are basically related with three main aspects. Firstly, parts of artist's pigment are mixture so that it cannot dissolve in one kinds of solvent completely. Thus, the concentration of prepared solution will be inaccurate, resulted in a wrong measurement of photo-catalytic activity. Secondly, artist's pigment probably adsorbs on the surface of titanium dioxide during the centrifuging, so that the concentration of remained solution is lower. Thirdly, the solvent of artist pigment may also be decomposed by titanium dioxide so that there exist a competition of photo-degradation between the solute and solvent, which can also lead to the inaccurate result of degradation rate.

Considering the limitations of the liquid state testing method, a new testing method by solid state spectrometer, LAMBDA 900, is introduced that the sample solution is replaced by the suspension. In this case, it is not necessary to find the solvent for artist pigment, but using water to prepare suspension. The sample preparation method has generally developed based on the trial experiments of Prussian blue soluble mixed with Hombikat uv-100. The prepared sample is homogeneous, and the feasibility and repeatability of experimental procedure is proved. Prussian blue and alizarin are also measured with the same testing method. And the results obtained through experiment are reasonable that can be explained by the mechanism of degradation of pigments with titanium dioxide, which indicates that the new testing method works well.

In the meantime, there still exist some works to do for the further research. Firstly, the equation of non-linear solid state calibration curve of new testing method is only available within the specific range of concentration so that measuring more points of the calibration curve is required to obtain a more accurate mathematical equation for calibration curve. It is noteworthy that the sample with lower concentration is difficult to prepare due to the inaccuracy of weighing caused by the limitation of scale. To ensure the accuracy of concentration of sample, the amount of artist pigment and titanium dioxide can be increase with same ratio, which has no influence on the reflectance results. It has already been proved in the section 4.3.2.1. Moreover, to figure out whether the new developed testing method has general applicability, it is suggested that more artist pigments with different kinds of titanium dioxide could be used for testing.

Acknowledgment

I would like to express appreciation to my mentors Prof. Dr. J. Dik and Prof. P. Kooyman for their guidance throughout my thesis project. I am grateful for their great patience in instruction. They taught me the basic professional attainments of science researcher and the importance of critical thinking in the science research. And I would also like to thank Ruben Abellon, Tanya Srivastava, Jence Mulder, Bob van Meijeren, Luuk van Kleef and Berend Tillema for their sincere help during my experiments. My thesis project could not go smoothly without their help. Last but not least, I want to thank my families and friends for encouragement and support in the period of thesis project so that I can challenge myself unceasingly.

Appendix A

Figures:

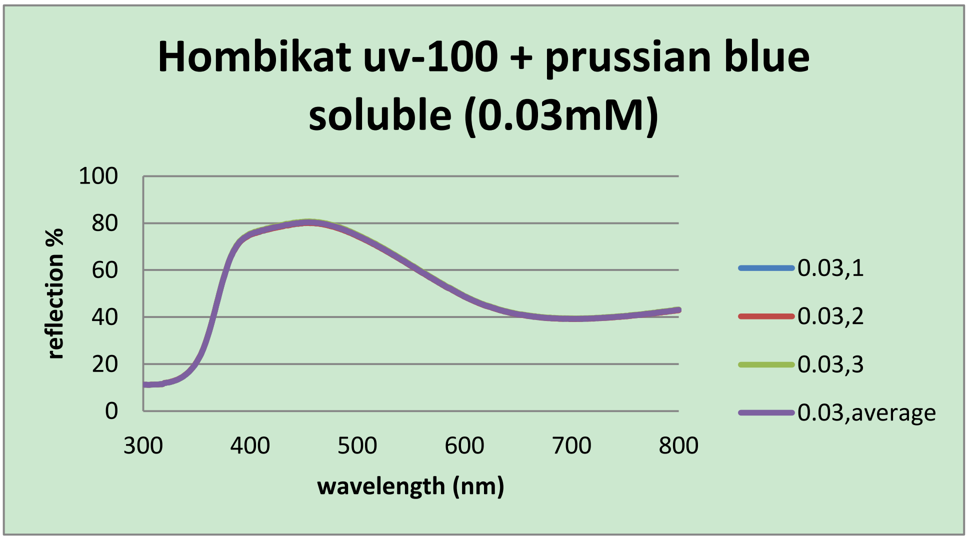

Figure A-1 the result of Prussian blue soluble mixed with Hombikat uv-100 in 0.03mM

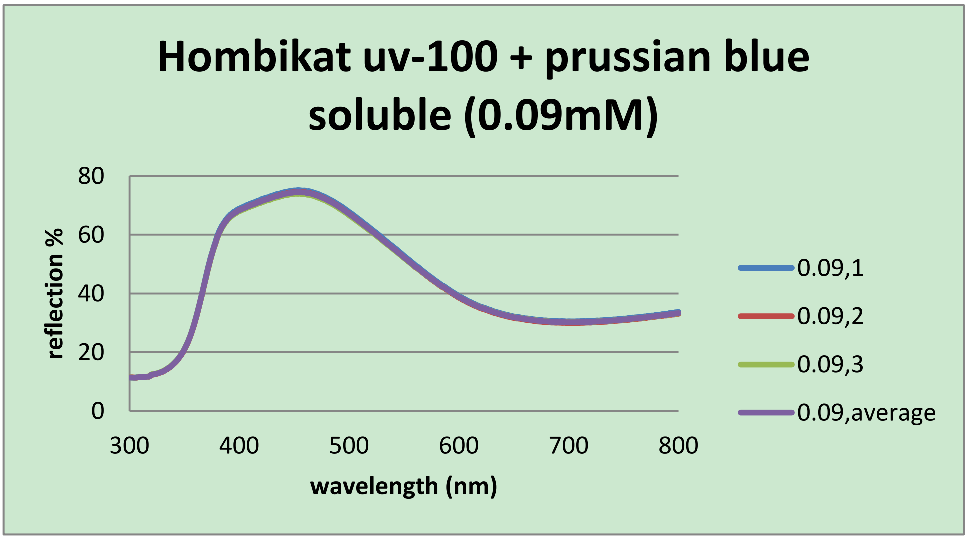

Figure A-2 the result of Prussian blue soluble mixed with Hombikat uv-100 in 0.09mM

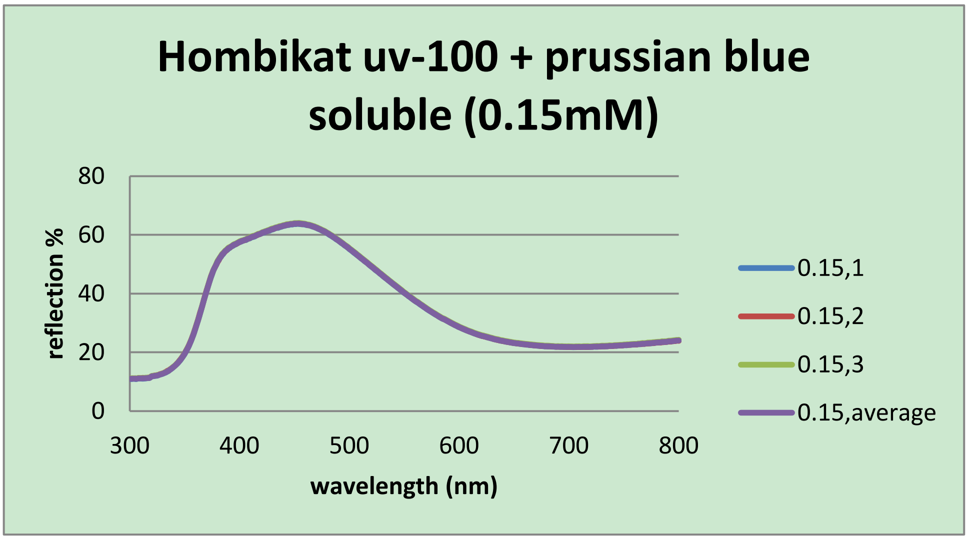

Figure A-3 the result of Prussian blue soluble mixed with Hombikat uv-100 in 0.15mM

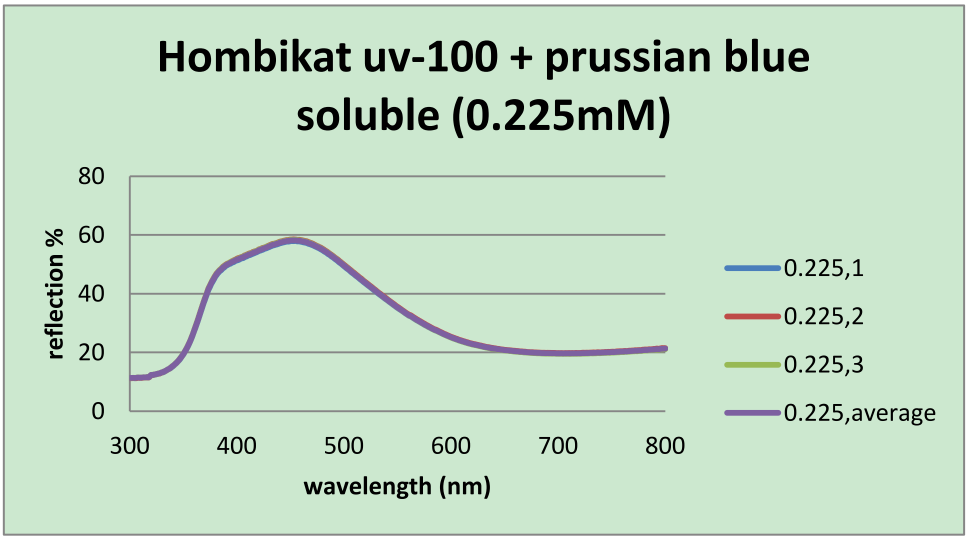

Figure A-4 the result of Prussian blue soluble mixed with Hombikat uv-100 in 0.225mM

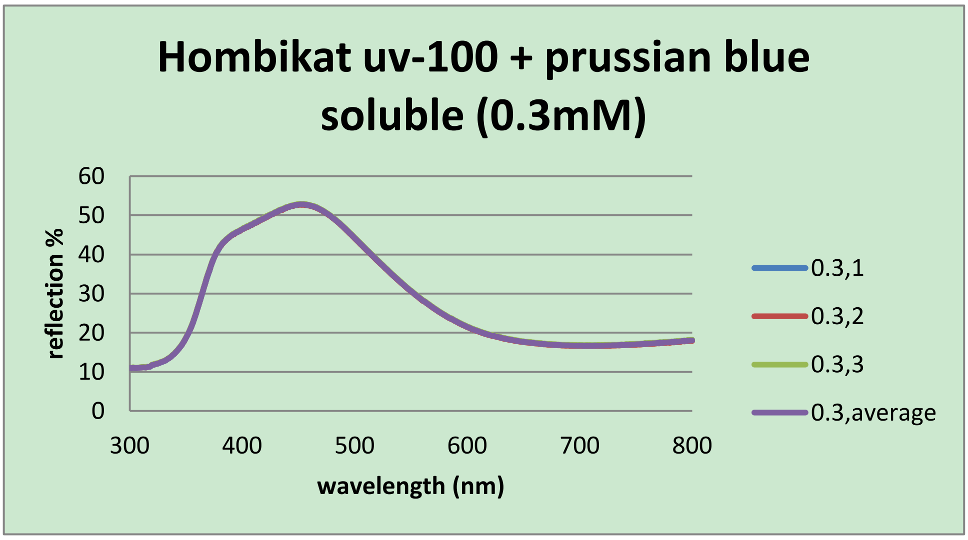

Figure A-5 the result of Prussian blue soluble mixed with Hombikat uv-100 in 0.3mM

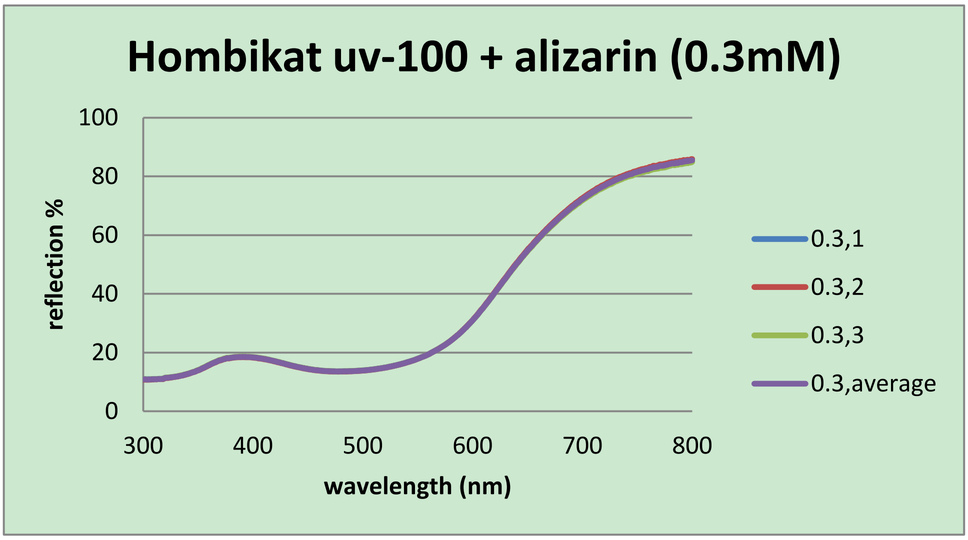

Figure A-6 the result of alizarin mixed with Hombikat uv-100 in 0.3mM

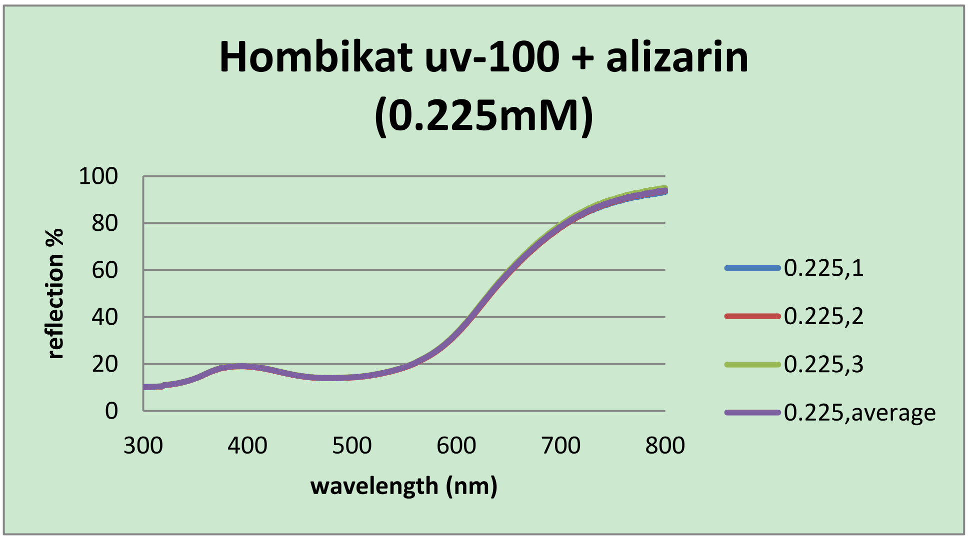

Figure A-7 the result of alizarin mixed with Hombikat uv-100 in 0.225mM

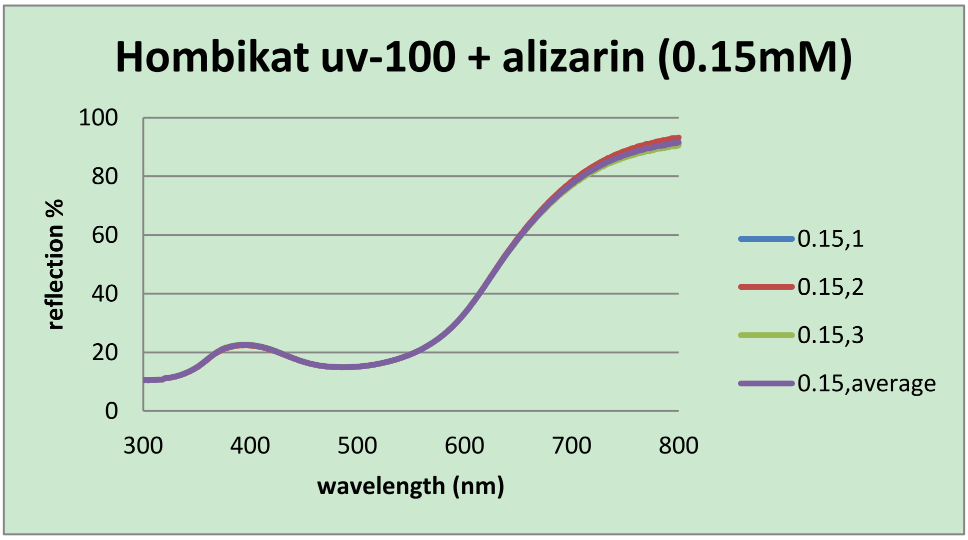

Figure A-8 the result of alizarin mixed with Hombikat uv-100 in 0.15mM

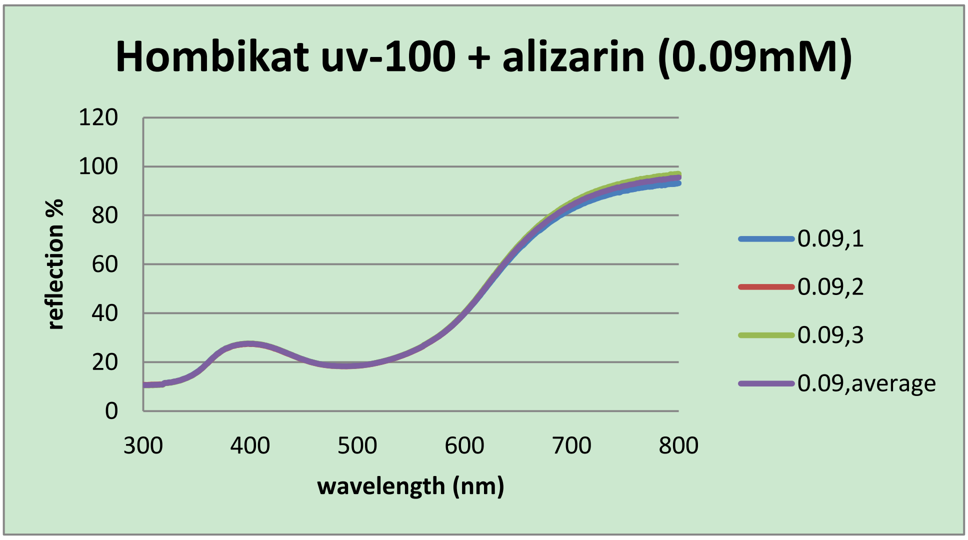

Figure A-9 the result of alizarin mixed with Hombikat uv-100 in 0.09mM

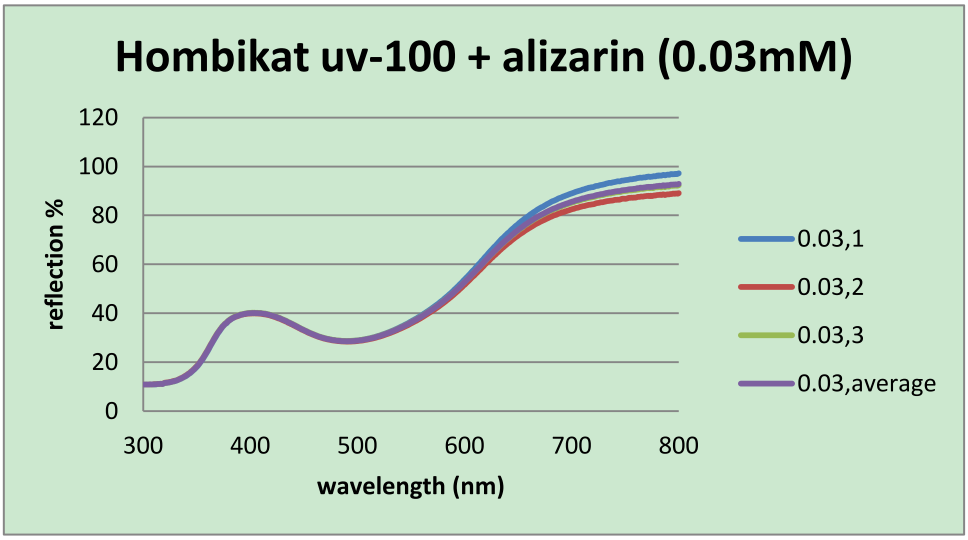

Figure A-10 the result of alizarin mixed with Hombikat uv-100 in 0.03mM

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