

COLORIMETRIC ANALYSIS OF TWO WATERCOLOURS USED IN RETOUCHING

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Abstract

Prussia blue and phthalo blue have a particularly importance in retouching because they provided a considerable amount of green and they are also transparent, which will give strong clear greens when needed during the retouching practice. The objective of this experiment is to evaluate the colorimetric change of the two cited pigments, in watercolours, after being exposed to direct sunlight for one year, comparing the results with another two samples protected from solar radiation, and also analyse the spectral curves similarity between both. The pigments are of the brand Artist's Watercolour of Winsor & Newton. Colour variations were determined in the uniform colour space called CIELAB. The results show that phthalo is more stable than Prussian blue.

Keywords: Colorimetry; Prussia blue; Phthalo blue; Watercolours; Winsor & Newton; Retouching.

Introduction

The retouching practice depends on several factors such as the experience and knowledge of the conservator-restorer to choose and mix the pigments and the visual system and lighting conditions in which the work is displayed.

Research about the sensitivity of pigments to light and the different binders and solvents, are regularly updated. In the professional field of conservation-restoration, there are several materials that were tested to evaluate their behaviour, such as commercial watercolours, gouaches and inks used in retouching.

The main objective of this study is to assess the stability of Prussia and Phthalo blue watercolours of *Winsor&Newton* brand, after being exposed to direct sunlight for one year. A spectrophotometer was used to measure the colour differences. It is intended, according to the results, indicate which watercolours are more lightfast.

Below is a brief contextualization of colour vision and colour systems designed and recommended by the *Commission Internationale de l'Eclairage* (CIE) for colorimetric measurements, and also the importance of Prussia and phthalo blue pigments for retouching.

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Colour Vision

The retina includes several layers of neural cells, the photoreceptors named rods and cones. Rods and cones derive their respective names from their prototypical shape. Rods tend to be long and slim while peripheral cones are conical [1, 2]. However, the significant distinction between rods and cones is in their visual function. Rods serve vision at low luminance levels - *scotopic* vision -, while cones serve vision at higher luminance levels - *photopic* vision. There is only one type of rod receptor with a spectral peak at approximately 510 nm. But the cones can be subdivided into three species according to their differing responses to light wavelengths: long-wavelength (L), middle-wavelength (M), and short-wavelength (S). The L receptors have a peak response in the red, the M in the green and the S receptors in blue [2]. All these three types of cone cell that provide the most fundamental property of human colour vision, the trichromacy [3].

The response of the eye to light varies from individual to individual due to genetic issues. To measure the colour seen by the human perception, it was necessary to define a standard for human vision. So, in the 1920s W. David Wright [4] and John Guild [5] independently conducted a series of experiments on human sight which consisted in evaluate how much light from three primary lamps (red, green and blue) was needed to match the range of spectral colours. The results Wright and Guild could redefine data for determining colour-matching functions, which are the tristimulus values of the equal-energy spectrum as a function of wavelength. These functions are intended to correspond to the sensitivity of the human eye. All this discoveries laid the foundation for the specification of the primary colour space of the *Commission Internationale de l'Éclairage*, the CIE XYZ [6, 7].

In 1931 the CIE proposed a colorimetric system based on three theoretical, non-existent lights named X, Y, Z. The CIE XYZ 1931 Tristimulus system is an improved version of the RGB colour tristimulus system and uses non real or imaginary stimuli. This improvement allows all colours within its gamut to be expressed as positive numbers, unlike the RGB system, where some colours are outside its gamut and are expressed as negatives. The XYZ chromaticity co-ordinates are defined as x , y , and z . The results represent an average colour normal observer called standard observer. All spectral colours can be matched with positive amounts of these lights. The amounts are given by colour matching functions \bar{x} , \bar{y} , and \bar{z} [2].

Separate sets of three colour matching functions are specified for the 2° Standard Observer and 10° Supplementary Standard Observers [8]. Tristimulus values are determined based on the colour matching functions defined in 1931 by CIE. The colour matching functions are intended to correspond to the sensitivity of the human eye. But, as the colour sensitivity of the eye changes according to the angle of view or, in other words, to the object size, the CIE defined two standard observers, the first one in 1931 using a 2 field of view, hence the name 2 Standard Observer, and the second in 1964, using the CIE a 10 field of view, referred to as the 10 Supplementary Standard Observer [8-10].

After normalised the observer, CIE have to do the same with light because the spectral composition of different light sources can be very different. CIE published sets of standard illuminant data [10-13] and distinguished sources from illuminant. Colour scientists consider that sources are lamps that can be switched on physically, and illuminants are tables of typical spectral power for given source types. For example, standard illuminant D65 is a spectral power distribution of typical sunlight diffused by typical cloud coverage and has a correlated colour temperature of approximately 6500 K [10, 11].

Tristimulus values are percentages of the components in a three-colour additive mixture needed to match a colour. In the CIE system, they are designated as X, Y and Z, or as xyz values, the XYZ chromaticity coordinates which are used to form the chromaticity diagram. But this tristimulus values have limited use as colour specifications because they correlate inadequately with visual attributes. While Y relates to value (lightness), X and Z do not

correlate to hue and chroma [2, 10]. The most typical applications of this scale are some glass/plastic filter and coloured glass manufactures [14].

To overcome the limitations of the chromaticity diagram XYZ, the CIE recommended two alternatives, the CIE uniform colour spaces known as CIELAB and CIELUV. These spaces extend tristimulus colorimetry to three-dimensional spaces with dimensions that approximately correlate with the perceived hue, chroma, and value (lightness) of a stimulus. This is accomplished by a nonlinear transformation from CIE 1931 XYZ colour coordinates. The transformation stretches the XYZ colour space so that the resulting Euclidean distance between colour coordinates provides an approximation about how well lights may be discriminated [2, 15]. The CIE 1976 $L^*u^*v^*$ (CIELUV) system is now less widely used than the CIE 1976 $L^*a^*b^*$ (CIELAB) system and its derivatives [6, 15]. Another colour space is CIELCH ($L^*C^*h^\circ$). Both, CIELAB and CIELCH [16], are based on the trichromacy and the opponent-colours theory of colour vision. The trichromacy theory asserts that with three different coloured lights of variable intensities it is possible to mix them so as to match any other test light of any colour. The opponent colours theory says that two colours cannot be both green and red, or blue and yellow at the same time. As a result, single values can be used to describe the red/green and the yellow/blue attributes. However, while CIELAB uses Cartesian coordinates to calculate a colour in a colour space, CIELCH uses cylindrical coordinates. When a colour is expressed in CIELAB, L^* defines lightness, a^* denotes the red/green value and b^* the yellow/blue value; and when a colour is expressed in CIELCH the L^* defines lightness, C^* specifies chroma and h denotes hue angle, an angular measurement [3, 6].

The $L^*C^*h^\circ$ expression offers an advantage over CIELAB because is more easy to relate to physical samples, like the Munsell Color Scale [7].

To calculate the colour differences between the two colours evaluated in this paper, it will be use the CIELAB colour space. According with Brainard and Stockman [15] the CIE colour difference measure ΔE_{ab}^* of CIE 1976 $L^*a^*b^*$ provides only an approximate guide to the discriminability between two lights. The CIE has recommended a more involved method of computing small colour differences from the CIE $L^*a^*b^*$ coordinates that attempts to provide better prediction of small colour differences, referred as ΔE_{00} [6, 10, 17]. Both colour differences will be noted in this study.

Case study

Retouching is the process in which the conservator fills in the damaged area to approximate the appearance of the original art-object. Many considerations must be made about the materials used, including colour, gloss, application technique, transparency [18], solvents, among others [19]. The selection of lightfast pigments is essential to make a stable colour matching. Lightfastness describes the durability of a colour in daylight, which means therefore that is not only referring to the pigment, but always to the total system, i.e., pigment, binding medium, additives. A number of other factors like intensity of sunlight, temperature, moisture, oxygen or gas content of the air have also influence. The importance and combination of the various influencing factors vary depending on daytime and season as well as on geographic factors.

The search for stability and reversibility of the materials used in retouching is not new and has been the subject of interest from several national [20-22] and international theorists [23-25].

Research into the sustainability of retouching materials remains a priority in the 21th century. To achieve this aim, some industry professionals have developed investigations in order to determine the properties of stability, compatibility and reversibility of fillers [26-28], binding mediums [29-32], pigments [33-35], dyes [36, 37], paints [38-40] and varnishes [41, 42].

Some colorimetric studies applied directly to the technique of retouching are known in Portugal. One example is the interdisciplinary study of the once called *Instituto José de Figueiredo* in which he proposed the characterization of the sixteenth-century painter's palette Gregory Lopes by measuring colour parameters of six of his works. The equipment used was called a colorimeter MUSIS 2007 (Multi-Spectral Imaging System) [43], which makes the measurement between 355 nm and 1550 nm, and operates in HVC [44, 45] colour system. Another more recent study, from 2008, was made during the retouching practice of the Charola arch triumphal painting of the Convent of Christ, aimed to determine the colour matching, from previous loss compensation, after overlay one stain of green chromium [46].

Internationally many experiments using spectrophotometers had been made with intent of aid the conservators during the retouching process. One of the first references is Staniforth [47] which made in 1985 a review of metamerism and retouching focused on blue pigments, issue applied to other hues by Egan and Muir [48, 49]. Berns [50] proposes applying the single-constant simplification of the Kubelka-Munk turbid media theory [50-53] to the results obtained with the spectrophotometer to overcome the metamerism phenomenon, widely used in computer colorant formulation.

Marissa I. Haddock [54] with colorimetric measurements of the *Gamblin Conservation Colors*®, besides using Kubelka-Munk theory, tried to give support to the conservator by designing and creating a colour matching software program, with a friendly interface, specifically adapted to the needs and typical practices of art conservators.

In 2010 Andrew Hanson and Stig Evans [55] reported the use of a portable spectrophotometer for retouching. They used visual comparison of reflectance spectra in preliminary pigment identification. With a portable spectrophotometer, they obtained spectral measurements of blue sky areas in two paintings and of samples of two blue pigments, the Prussian blue and ultramarine blue. By examining the four spectra, the researchers were able to deduce which blue pigment is likely to be present in each painting and decide between pigments when selecting a palette for retouching.

Prussia and phthalo blue pigments

Prussian blue was one of the first synthetic inorganic pigments. Also known as iron blue, Berlin blue, Paris blue, Antwerp blue, and Chinese blue, Prussian blue is a complex chemical compound, ferric ferrocyanide ($\text{Fe}_4(\text{Fe}[\text{CN}]_6)_3$) [56, 57], whose chemical formula can contain other elements like sodium, ammonium, and/or potassium ions. PB27 was discovered by Heinrich Diesbach in 1704 and made available in artist's colours in the early 1730's [58]. The pigment was first mentioned in 1710, but its preparation was kept secret until 1724 [59]. Prussian blue is listed as CI Pigment Blue 27 (PB 27) in the Colour Index (1971). Antwerp blue and Milori blue are adulterated products to which a large amount of filler had been added [60].

Prussian blue (PB 27) was very popular from the 18th to the 20th century due to his high tinting strength and pure blue hue. However after 1970 it has often been replaced as an artists pigment by phthalocyanine blue (PB 15) [58, 61]. PB 27 is completely nontoxic and non-polluting and it has even been used as an oral antidote to heavy metal poisoning [62].

The ASTM (1999) rates the lightfastness of PB27 in watercolours as "excellent" (I). The lightfastness tests performed during this study have the same result after one year of direct exposure to sun light, but Prussian blue showed colour change across brands. The paints labelled as "Antwerp blue" suggest being less permanent.

Prussian blue has been described as being both permanent and impermanent [58]. Field [63] (1845) indicated that Prussian blue was not noted for its permanence. Maximilian Toch [64] (1925) reported that PB 27 is not part of the permanent palette and should be avoided, especially in mixtures. Prussian blue is considered permanent based on experiments using full-strength colour paint outs. However, Levison [65] (1976) pointed out that this pigment is inappropriate for artists because PB 27 is permanent when pure, but it is not permanent when

mixed with white pigments. According with Berrie [58], earlier preparations of Prussian blue may have been less permanent than modern preparations due to a higher proportion of adsorbed impurities caused by less efficient washing of the final product or using less pure starting product. In 2004 Jo Kirby and David Saunders [66] study the fading of colour change of Prussian blue and they conclude that the *principal factor in the permanence of Prussian blues of different manufactures and dates appears to be the amount of extender present in the supplied pigment*. They also arrived to the conclusion that *different methods of preparation only affect permanence in as much as they lead to the incidental introduction of extender, either deliberately or due to inadequate purification of the product*.

Prussian blue (PB 27) is a deep, very transparent, vibrant green-blue, which appears almost black in masstone. It is greener than phthalocyanine blue, green shade. PB 27 is cooler and greyer when mixed with titanium white. The pigment can be added to bone black (PBk9) to produce deep, inky, and cold blacks [67]. Due to its high tinting strength must be handled with great care or it will quickly dominate other colours in a mixture or the bottom layer, when applied according to a distinctive retouching technique as *pointillism* or *selezione cromatica*. Its staining power is also important as it tends to stain any support and possibly subsequent paint layers. Prussian blue is avoided because it tends to take on a “bronze” [68] metallic sheen, particularly after heavy application [18]. With angular variation, it changes in colour from red to green to blue. According with Johnston–Feller, *the visual appearance of organic materials can occasionally be metal-like, particularly following exposure. Such materials may exhibit distinct colour in the specular reflection, just as metals do*. The phenomenon is generally termed “bronzing” [68].

As said, phthalocyanine blue (PB 15) is the alternative to Prussian blue (PB 27). Phthalos are more transparent, have higher chroma, and when mixed together, create clean mixtures.

Phthalocyanine blue belongs to the second most important class of colorant chemically similar to the natural organic structure porphyrin [57], which is the basis of hemoglobin and chlorophyll. Phthalocyanine blue was commercially introduced in 1935 under the name monastral blue; the green shades were introduced in 1938 [61].

Polymorphism has been widely recognized in these compounds with the discovery of various crystalforms of copper and other metal phthalocyanines. However, few of these have found substantial use as pigments. The principal pigmentary forms are: Phthalocyanines, Copper phthalocyanine, Polychloro copper phthalocyanine, Polychloro polybromo copper phthalocyanine [57]. Although many metal derivatives of phthalocyanine have been made, all of them blue to green in colour, the copper derivative is by far the most important. It is extremely stable and gives clean, bright cyan colours. Other metal phthalocyanines are less stable and/or are greener and duller [69]. Copper phthalocyanines are used both as pigments and as dyes. In this paper we will discuss the pigment blue copper phthalocyanine (PB 15).

In the visible region, phthalocyanines are limited to blue, cyan and green colours. However, their absorption may be extended into the near infrared and by suitable chemical engineering it is possible to reach the 700-1000 nm region [69].

Blue copper phthalocyanine (PB 15) is highly valued for its strength and transparency. When applied heavily it can take on a slight metallic sheen, although not to the same extent as Prussian blue (PB 27). The tinctorial strength of this colour can influence other colours in a mix. It is much lighter in masstone when leanly bound than is Prussian blue. Tints with white are cleaner than those with PB 27 [67]. The pigment is extremely fine and light in its powdered form. The ASTM (1999) rates the lightfastness of PB15 in watercolours as "excellent" (I).

Both this watercolours can be used in retouching, especially in paintings of 18th century forward, where the Prussian blue hue can be the dominant blue characterized by one reflectance that remains low towards the red region of the visible spectrum.

The aim of this study is to analyse the spectral curves similarity and the colour change of this two pigments in the brand *Artist's Watercolour* of Winsor & Newton.

Experimental

Spectrophotometer data

The portable spectrophotometer used in this study was the CM 2600 D manufactured by Konica Minolta [70]. The measuring head used had the size 8mm since the samples have 2 cm x 3 cm. The minimum intervals between measurements were 3 seconds for SCI (specular component included) and SCE (specular component excluded). The results were transmitted down a USB cable to computer for storage and manipulation on software called *Spectramagic NX*, also from Konica Minolta.

After the calibration performed, five readings were taken of each sample. With the computer application mentioned the data was obtained and the mean, the standard deviation, the coordinates $L^*a^*b^*$ and spectral curve were calculated.

Samples

The objective of this experiment is to evaluate the colorimetric change of two watercolours after being exposed to direct sunlight for one year, comparing the results with another two samples protected from solar radiation. The samples were painted directly from the tube to the *Fabriano Art* watercolour paper, of fine grain. The cards of 12.5 cm x 18 cm, were placed near a window facing west.

Colour difference evaluation: results and Interpretation

The *American Society for Testing Material* (ASTM) is the organization responsible for classifying and establishing permanence guidelines for the art materials. ASTM bases Lightfastness categories on the measured amount of colour change (typically fading) that occurs as a result of standard levels of accelerated or long-term ultraviolet light exposure. The ratings for the pigments were established in 1984 [71]. The lightfastness is divided into four categories: ASTM I - Excellent, ASTM II - Very good; ASTM III - Insufficient; ASTM IV - Very poor; ASTM V - Poor (not recommended for art supplies).

For evaluation of the colour lightfastness ASTM recommends ASTM D5383 [72] for a visual determination of the colour change or ASTM D4303 [73] if instruments for measuring colour (colorimeter or spectrophotometer) and other devices for accelerated aging test are available.

The use of the ASTM D5383 test has limitations since it can only estimate the change of colour in a short time, a few months or years in normal indoor exposure. The colour differences of the two watercolours of different brands were made following the ASTM D5383 and ASTM D4303 because the principal aim was to determine which colour is less permanent in short term.

To determine the colour stability tested, the results were divided into five categories, depending on the ASTM D4303 classification: ASTM I = $\Delta E^* ab \leq 4$; ASTM II = $4 \leq \Delta E^* ab \leq 8$; ASTM III = $\Delta E^* ab \geq 8 \leq 16$; ASTM IV = $\Delta E^* ab \geq 16 \leq 24$; ASTM V = $\Delta E^* ab \geq 24$.

Results

As seen, depending on the degree of change, known as the Delta E (ΔE), to each colour is then assigned a particular lightfastness rating set by ASTM standards. According to CIE, colour difference measured with ΔE_{ab}^* of CIE 1976 $L^*a^*b^*$ provides only an approximate guide to evaluate the discrimination between two colours. So, in this study the measurement were done with ΔE_{ab}^* of CIE 1976 and also with the recent method of computing small colour differences from the CIE $L^*a^*b^*$ coordinates referred as ΔE_{00} (CIE 2000).

Making comparison between the delta values of 1976 and 2000, we arrived to the conclusion that Prussian blue (PB 27) seems to be more stable with the new formula for calculating small colour differences.

In **table 1** are the L*a*b* results, with the indication of the standard deviation of the five measurements done with Prussian (PB 27) target and sample, and the delta values. PB 27 have a colour variation of less than $\Delta E^*_{ab} \leq 4$ with ΔE_{00} , which is equivalent to excellent permanence; in ΔE^*_{ab} the colour difference is $\Delta E^*_{ab} = 6,52$, equivalent to very good, ASTM II (Fig. 1).

Table 1. Prussian Blue (PB 27) colorimetric results

PRUSSIAN BLUE Data name	Dominant Wavelength	L*	a*	b*	ΔL^*	Δa^*	Δb^*	ΔE^*_{ab}	ΔE_{00}
Target (without aging)	473,87	42,08	-8,39	-31,09	---	---	---	---	---
Standard deviation (σ)	---	0,042	0,053	0,079	---	---	---	---	---
Sample (natural aging)	475,66	44,4	-12	-26,18	2,32	-3,61	4,9	6,52	3,75
Standard deviation (σ)	---	0,055	0,013	0,066	---	---	---	---	---

The graphs used in this article are called spectral curves. The easiest way to understand them is simply as showing the amount of light that is reflected from the surface for each wavelength in the visible spectrum. The more that is reflected, the higher the curve will be at that point. To make the readability a little easier, above each graph is included a line showing the approximate range for each band of colour, running from Violet through Blue, Green, Yellow, Orange, and Red. The colour differences evaluation, delta-reflectance, are also noted through a coloured curve which goes up and down depending on the colour variation. The next graph (Fig. 1) is a representation of the spectral reflectance of Prussian blue (PB 27), before (white curve) and after (blue curve) aging. There is a little deviation between the two curves. This means that this watercolour of *Winsor & Newton*, in one year of natural light exposure, did not fade much.

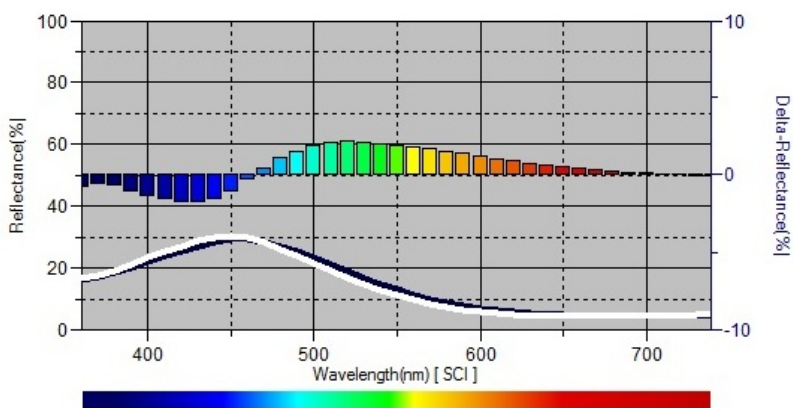


Fig. 1. Spectral reflectance of Prussian blue (PB 27) watercolour, before (white curve) and after (blue curve) aging. Delta-reflectance (%) with ΔE_{ab}^* of CIE 1976.

Table 2 gives the colorimetric results for phthalocyanine blue (PB 15) watercolour. This pigment reveals to be very stable in both colour difference systems: $\Delta E^*_{ab} = 1,3$ (**Graph 2**) and $\Delta E_{00} = 1,07$.

Table 2 . Pthalo Blue (PB 27) colorimetric results

PTHALO BLUE Data name	Dominant Wavelength	L*	a*	b*	ΔL^*	Δa^*	Δb^*	ΔE^*_{ab}	ΔE_{00}
Target	469,66	33,53	3,77	-39,75	---	---	---	---	---
Standard deviation (σ)	---	0,074	0,086	0,039	---	---	---	---	---
Sample (natural aging)	469,09	33,29	4,8	-39	-0,24	1,03	0,76	1,3	1,07
Standard deviation (σ)	---	0,026	0,045	0,027	---	---	---	---	---

The next graph (Fig. 2) is a representation of the spectral reflectance of phtalocyanine blue (PB 15), before (white curve) and after (blue curve) aging. Observing the graph is possible to conclude that the colour difference was very small, even more when compared with Prussian blue (PB 27).

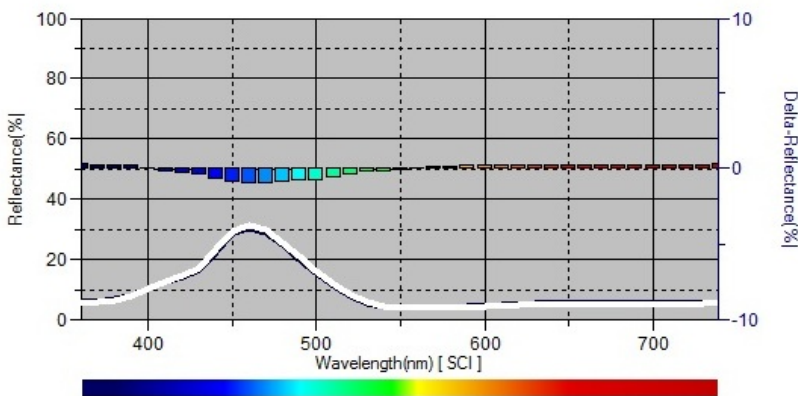


Fig. 2. Spectral reflectance of phtalocyanine blue (PB 15-) watercolour, before (white curve) and after (blue curve) aging. Delta-reflectance (%) with ΔE_{ab}^* of CIE 1976.

The spectral curve is like a “spectral fingerprint”. Through visual comparison of the reflectance spectra of the samples of the two blue pigments, the Prussian blue and the phtalo blue (Fig. 3 and 4), it is possible to say that there are a small difference between them. The reflectance spectra seem to be very similar, but phtalocyanine blue is far greener than Prussian and also a little more bluer.

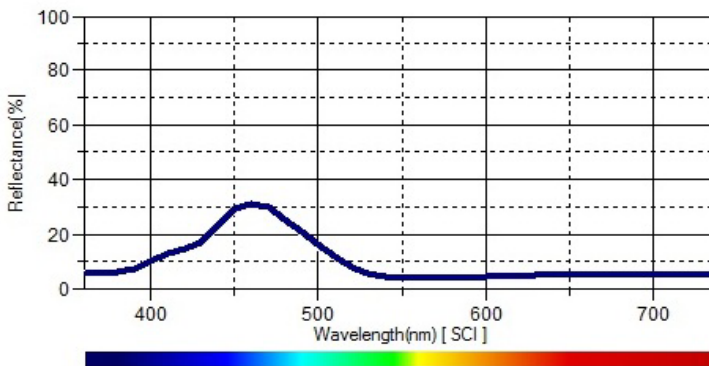


Fig. 3. Reflectance spectra of phtalocyanine blue (PB 15).

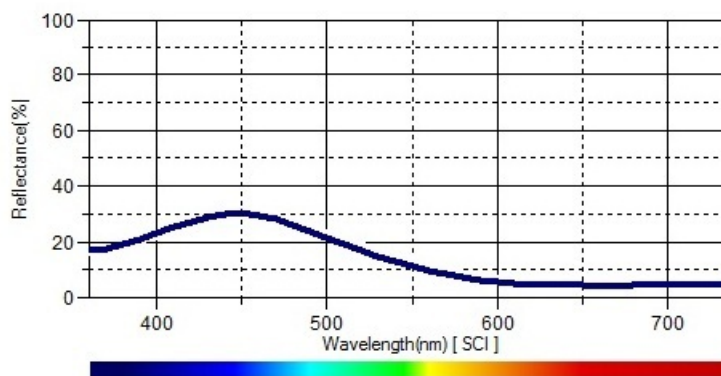


Fig. 4. Reflectance spectra of Prussian Blue (PB 27).

Conclusions

Before writing the principal conclusions of this paper, is important to recognize here that other materials of a given painting, in particular binders and pigments, can have colour alterations through time. However, this variant is not taken into account in this research.

The presented experimental study aimed to assess the colour change of two watercolours using a spectrophotometer.

Depending on the formula to calculate colour differences, CIE 1976 or CIE 2000, Prussian blue have $\Delta E^*_{ab} = 6,52$ and $\Delta E_{00} = 3,75$. However, besides the colour variation between the two formulas, the watercolour still remain in one good category, which is very good (ASTM II) to excellent (ASTM I), respectively.

Taking into account the results obtained with Prussian blue, and the variability in PB 27 across paint manufacturers, it is recommended that this pigment should be routinely put through a lightfastness test, and especially when marketed as “Antwerp blue”. It is our aim to perform in the future the same test using artificial aging.

Concerning to retouching, is suggested to avoid mixing Prussian blue with white pigments and use in this case the phtalocyanine blue which has a spectral reflectance similar to Prussian blue and is much more stable, having a colour difference of $\Delta E^*_{ab} = 1,3$ and $\Delta E_{00} = 1,07$.

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