

## PB15 AS 20<sup>TH</sup> AND 21<sup>ST</sup> ARTISTS' PIGMENTS: CONSERVATION CONCERNS

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### Abstract

Copper phthalocyanine (CuPc) provides the most important blue and green pigments from the 21<sup>st</sup> century artists' paints. This paper focuses on the blue pigments of CuPc, which are referenced in the *Colour Index* as PB15. The employment of PB15 as artists' pigments since the very beginning until now is summarized through archives of artists' color makers and current color charts. Moreover, for the first time, a review of the cases of PB15 identification encountered in the field of cultural heritage is presented. For each case reported in this study, the analytical methods that allowed identifying the blue pigment are specified. The significance and the relevance of various destructive and non-destructive methods, for this topic in particular are also discussed. Finally, the implications of PB15 in common conservation practices are outlined.

### 1 Introduction

Currently, the most important synthetic organic pigments in terms of world-wide production are azo and polycyclic pigments. The class of polycyclic pigments includes various chemical families such as phthalocyanine, perinone, perylene, diazozine, DPP (diketopyrrolo-pyrrole), indanthrene and quinacridone. Pigments from the chemical families cited above are frequently used as artists' pigments<sup>1</sup>. Phthalocyanine (Pc), notably copper phthalocyanine (CuPc) are significant blue and green organic artists' pigments since the 1970s<sup>2</sup>. The phthalocyanine molecule consists of four isoindole units (C<sub>8</sub>H<sub>7</sub>N) connected by four nitrogen atoms.

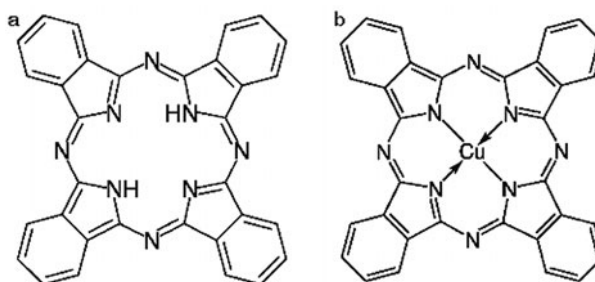


Figure 1: a) In the metal free phthalocyanine molecule, the central cavity contains two hydrogen atoms while in the b) copper phthalocyanine molecule; the central cavity contains a copper atom. N is nitrogen, H is hydrogen and Cu is copper.

The central cavity of phthalocyanine macrocycle allows the formation of metal complexes. As illustrated in Fig. 1, in the CuPc molecule the central cavity is occupied by a cation Cu<sup>++</sup>. Then, CuPc pigments are copper complexes of phthalocyanine. The process to make the coloring matters yet to be called phthalocyanines was first patented in 1928, by the Scottish Dyes<sup>3</sup>. Prof. Patrick Linstead and his co-workers elucidated the structure of this new class of compounds in 1933-34<sup>3-9</sup>. Linstead first used "phthalocyanine" in 1933. The term was forged starting from the radical - phthal due to the nature of the precursors used for their synthesis (derivative products of the phthalic acid), and from - cyan, due to the blue color of the first investigated phthalocyanine compounds (from Greek, *kuenos*, which means blue). Starting in 1934, the English company *Imperial Chemical Industries* (ICI) pro-

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duced the first CuPc blue pigment, with the molecular formula  $C_{32}H_{16}N_8Cu^{10}$ . In 1935, Robertson first recognized the polymorphism of the corresponding compound<sup>11</sup>. Currently, the  $\alpha$ -,  $\beta$ - and  $\varepsilon$ -CuPc polymorphs are industrially produced. The history, synthesis, properties and applications of metallized and unmetallized phthalocyanine compounds are reviewed in detail in Moser and Thomas<sup>10,12</sup>, Thomas<sup>13</sup>, Leznoff and Lever<sup>14</sup> and McKeown<sup>15, 16</sup>. In addition, information focusing specifically on phthalocyanine pigments may be found in general works devoted to synthetic organic pigments, notably in Herbst and Hunger<sup>1</sup>, Christie<sup>17</sup> and Lewis<sup>18</sup>.

The *Colour Index Generic Name* of CuPc blue is *Pigment Blue 15* (PB15). In fact, PB15 includes six types of CuPc blue, namely, PB15:(0), the unstabilized  $\alpha$ -form, PB15:1, the non-crystallizing  $\alpha$ -form, PB15:2, the non-crystallizing and non-flocculating  $\alpha$ -form, PB15:3, the  $\beta$ -form, PB15:4, the non-flocculating  $\beta$ -form, and PB15:6, the  $\varepsilon$ -form. The unstabilized  $\alpha$ -CuPc blue is often referred to as PB15:0 instead of PB15. The last nomenclature is favored in the present work. Here PB15 is used to indicate the different CuPc polymorphs.

For all of them, the *Colour Index Constitution Number* is 74160, wherein "74" indicates the phthalocyanine class<sup>19</sup>. These pigments differ from each other's in stability, solubility and hue. For economical reason, PB15:5, which indicates CuPc blue in the  $\gamma$ -form, is not produced by manufacturers<sup>20</sup>. The main processes for making  $\alpha$ -  $\beta$ - and  $\varepsilon$ -CuPc blue pigments which are currently used in industry, are described in Herbst and Hunger<sup>1</sup>.

PB15 represents by far the most commercially important phthalocyanine blue pigments. The metal-free phthalocyanine ( $H_2Pc$ ) referenced in the *Colour Index* as PB16 and the cobalt phthalocyanine (CoPc), referenced as PB75 are much less common. Whereas PB16 is produced since 1939<sup>21</sup>, PB75 was introduced on the market just recently. The CuPc green pigments, PG7 and PG36, are both halogenated copper phthalocyanines derivatives; the green shade is achieved by substituting a certain number of hydrogen atoms by halogens in the CuPc molecule. The halogenated CuPc compounds, do not exhibit polymorphism. PG7 is a copper polychloro phthalocyanine containing 14-15 chlorine atoms, commercially available since 1936. PG36 is a copper polychlorobromo phthalocyanine containing 4-8 bromine atoms and 8-2 chlorine atoms, introduced on the market in 1959<sup>1</sup>. In this paper, only the PB15 types are discussed.

## 2 PB15 in modern and contemporary artists' paints

The first CuPc pigment, produced by ICI, was introduced on the market in 1935, under the name *Monastral Fast Blue*<sup>22</sup>. At this time the last blue pigments of importance introduced on the artists' palette were cobalt blue (first presented by Thénard in 1804) and synthetic Ultramarine blue (first synthesized by Guimet in 1826). The archives of artists' colors makers, such as product catalogues and color charts, are the earliest sources highlighting the use of CuPc blue in artists' colors. In England, the artistic material supplier Winsor & Newton first proposed an oil color based on

phthalo blue in 1937, under the name *Winsor Blue*<sup>23</sup>. In France, the Société Lefranc & Bourgeois followed in 1938 by introducing a phthalo blue-based paint, named *Hortensia Blue*<sup>20</sup>, in its oil colors range. A similar blue paint from Royal Talens, named *Rembrandt Blue*, was first mentioned in a product list dating from 1940<sup>23</sup>. *Hortensia Blue*, *Rembrandt Blue* and *Winsor Blue* remain available in current Winsor & Newton, Royal Talens and Lefranc colors ranges. These commercial appellations still indicate paints based on PB15. Despite the early introduction of CuPc in artists' colors, the mention of phthalocyanine on the paints tubes occurred much later. In *Standards of Artists' Oil Paints* published in 1960, it can be read<sup>24</sup>:

The standing committee on Commercial Standards CS98-42, Artists' Oil Paints, met on March 8 of this year for the first time in ten years. Mr Ralph Mayer is the current chairman of the committee, made up of representatives of Grumbacher, Bocour, Permanent Pigments, and other interested parties. At the meeting it was agreed that the chemical name "phthalocyanine" should be placed in parenthesis below any proprietary names that might be used, such as Grumbacher's Thalo, to indicate the true composition of the pigment.

Nowadays, instead of chemical names, most of the artists' colors suppliers use the *Colour Index Generic Name* to indicate the pigments present in their paints. In 2010, we have investigated thirty-five current ranges of artists' paints in order to evaluate the importance of PB15 among the 21<sup>st</sup> century artists' blue pig-

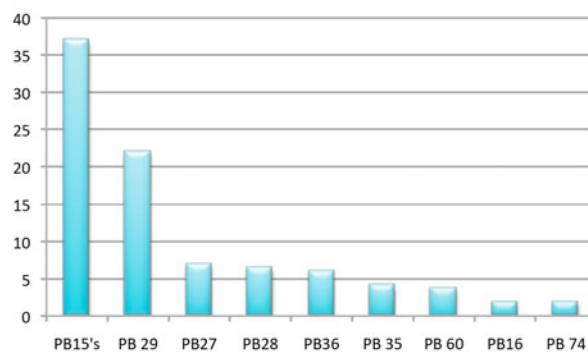


Figure 2: Proportions in percentages (%) of the different blue pigments (indicated by their *C.I. Generic Name*) used in contemporary artists' oil-based paints. PB15: Copper phthalocyanine (CuPc); PB29: Ultramarine blue; PB27: Prussian blue; PB28: Cobalt blue; PB36: Cobalt turquoise; PB35: Ceruleum blue; PB60: Indanthrone blue; PB16: Metal-free phthalocyanine; PB74: Cobalt zinc silicate blue. Figure taken from Defeyt<sup>2</sup>

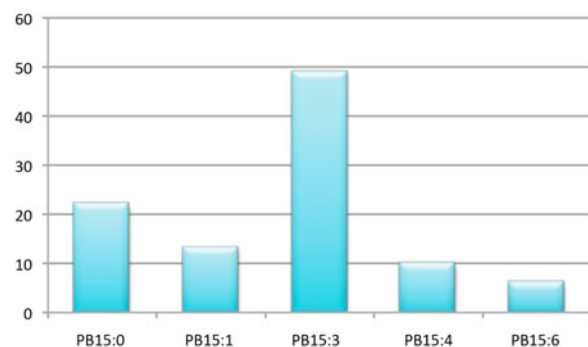


Figure 3: Proportions in percentages (%) of the five types of CuPc blue pigments, indicated by their *C.I. Generic Name*, used in current artists' oil-based paints. PB15:0 is the unstabilized  $\alpha$ -form, PB15:1 is the non-crystallizing  $\alpha$ -form, PB15:3 is the  $\beta$ -form, PB15:4 is the non-flocculating  $\beta$ -form and PB15:6 is the  $\varepsilon$ -form. Figure taken from Defeyt<sup>2</sup>.



Figure 4: Dried paint films obtained from various commercial phthalo blue-based paints on glass slides. Figure taken from Defeyt<sup>2</sup>.

ments<sup>2</sup>. This survey included several hundreds of blue paints from famous American and European brands, namely Archival oils, Art Spectrum, Blockx, Lefranc & Bourgeois, Graham, Maimeri, M. Harding, Old Holland, Pébéo, Lukas, Sennelier, Schmincke, Royal Talens and Winsor & Newton. The graphic presented in Fig. 1 shows the repartition of the different blue pigments encountered in the survey. The given percentages were calculated on the basis of the suppliers' declarations. Ultramarine, Prussian blue, cobalt blue and cerulean remain common, but PB15 clearly appears as the most widespread artists' blue pigment. Examples of dried paint films obtained from commercial phthalo blue-based paints are shown in Fig. 3. Almost half of the investigated blue paints contain a CuPc blue, alone or in combination with zinc white (PW4), titanium white (PW6), Ultramarine blue (PB29) or dioxazine purple (PV23). Actually, in the graphic presented in Fig. 1, PB15 includes PB15:0, PB15:1, PB15:3, PB15:4 and PB15:6. A second graphic showing the distribution of the five CuPc polymorphs is given in Fig. 2. PB15:3 appears as the most important PB15 type. Comparatively, the PB15:6 type is present in much lesser extent. Note that the PB15:2 type, the non-crystallizing and non-flocculating  $\alpha$ -form, is absent from the consulted colors ranges. PB75 (CoPc) is also absent from the survey while the presence of PB16 ( $H_2Pc$ ) appears rather marginal compared to the copper complex.

### 3 PB15 in artwork analysis: a review of literature

Although the *Pigment Compendium*<sup>25</sup> signals only few identifications of CuPc pigments reported in paintings, many cases of artworks containing PB15 are described in conservation literature. As shown in Table 1 (section Works of art), the presence of PB15 has been highlighted, at least in twenty-three works of art, dating

from 1936 to 1992 and made by nineteen worldwide famous artists of the 20<sup>th</sup> century, namely, Schmithals<sup>26</sup>, Winter<sup>27</sup>, Penck<sup>26</sup>, Magritte<sup>28</sup>, Delvaux<sup>29</sup>, De Keyser<sup>30</sup>, Picasso<sup>31</sup>, Le Corbusier<sup>32</sup>, Chambers<sup>33</sup>, Riopelle<sup>34</sup>, De Saint Phalle<sup>35</sup>, Lichtenstein<sup>36</sup>, Dubuffet, Klein Rancillac<sup>37</sup>, Pollock<sup>38, 39</sup>, Judd<sup>40</sup>, Newman<sup>23, 41</sup> and Mondrian<sup>42</sup>.

With the exceptions of the outdoor painted sculpture *Three brushstrokes* by Lichtenstein, the untitled indoor painted sculpture by Judd and the *Untitled* mural by Le Corbusier, all the artworks listed in Table 1 are easel paintings. The case of *La lampe philosophique* painted by Magritte in 1936 points out the fact that the Belgian surrealist introduced the new blue in his palette only one year after its introduction on the market. Magritte was, therefore, one of the earliest painters using PB15. Francis<sup>43</sup>, Kandinsky<sup>44</sup> and Nolan<sup>45</sup>, also employed PB15 since such pigments have been identified in painting materials from their studio. Information on the concerned materials may be found in Table 1 (section Artists' materials).

Identifying phthalo blue affords chronological information valuable for dating and authenticating artworks. Indeed, when it is detected within original paint layers, the possibility of an artwork made before 1935 may be excluded. To date, at least seven fake paintings, supposedly made between 1896 and 1932, attributed to Popova<sup>46</sup>, Léger, Ernst, Pechstein<sup>47</sup>, Utrillo<sup>48</sup>, Ensor<sup>23</sup> and Kandinsky<sup>49</sup>, were unmasked thanks to the CuPc blue detection. It has also unveiled fake painted papyri presumably dating from 13<sup>th</sup> -1<sup>st</sup> BC<sup>50</sup>. Details on the unmasked forgeries are given in Table 1 (section Forgeries). The  $\alpha$ -form, which is the original form, was first commercially available in 1935<sup>10</sup>, while the  $\beta$ - and  $\epsilon$ -forms were first patented respectively in 1949<sup>51</sup> and 1962<sup>52</sup>. Although, the discrimination of CuPc polymorphs could provide supplementary technical and chronological information on the artworks, most often

Works of art					
Artist	Title	Year	Type of PB15	Technique(s)	Reference
H. Schmithals	<i>Gletscherbach</i>	1953-1957	PB15:0	RS	26
F. Winter	<i>Federblüten</i>	1958	PB15:1	RS	27
A. R. Penck	<i>Young Generation</i>	1975	PB15:4	RS	26
R. Magritte	<i>La Lampe philosophique</i>	1936	Unspecified	RS	28
P. Delvaux	<i>Faubourg</i>	1956	Unspecified	RS	29
R. De Keyser	<i>Hal (3)</i>	1985	Unspecified	RS	30
P. Picasso*	<i>Still life with jug</i>	Undated	Unspecified	RS	31
	<i>Guitar</i>	Undated	Unspecified	RS	31
Le Corbusier	<i>Untitled</i>	1952	Unspecified	RS	32
J. Chambers	<i>Summer Visitor</i>	1964	Unspecified	RS, FTIR	33
J-P Riopelle	<i>L'hommage à Rosa</i>	1992	Unspecified	FTIR, XRD	34
	<i>Hommage à Duchamp</i>	1990	Unspecified	FTIR, XRD	34
N. De Saint Phalle	<i>Shooting Picture</i>	1961	Unspecified	PyGCMS, FTIR	35
R. Lichtenstein	<i>Three Brushstrokes</i>	1984	PB15:3	PyGCMS, FTIR	36
J. Dubuffet	<i>Mire G131 Kowloon</i>	1983	PB15:3	PyGCMS, FTIR, XRD	37
Y. Klein	<i>Monochrome vert</i>	1957	Unspecified	PyGCMS, FTIR, XRD	37
B. Rancillac	<i>La suite américaine</i>	1970	Unspecified	PyGCMS, FTIR, XRD	37
J. Pollock	<i>Untitled</i>	1946-49	Unspecified	LDI-TOF-MS	38
	<i>Mural</i>	1943	Unspecified	RIS	39
D. Judd	<i>Untitled</i>	1965	Unspecified	MALDI-TOF-MS	40
B. Newman	<i>Who's afraid of Red, Yellow and Blue III</i>	1967	Unspecified	Micro chemical test	23
	<i>Dyonysius</i>	1949	Unspecified	XRF, Vis. Reflectance	41
P. Mondrian	<i>Composition in Yellow, Blue and White</i>	1937	Unspecified	XRF, PCA	42
J. Hayls**	<i>A portrait of a Lady and a Boy with a Pan</i>	1655-59	Unspecified	EDX, PLM	56
Artists' material					
Artist's studio	Painting material	Year	Type of PB15	Technique(s)	Reference
S. Francis	Studio-made paint (GCI's ref. SF18)	<1994	PB15:1 or PB15:2	RS, FTIR	43
	Studio-made paint (GCI's ref. SF60)	<1994	PB15:3 or PB15:4	RS, FTIR	43
	Studio-made paint (GCI's ref. SF42)	<1994	Unspecified	RS	43
W. Kandinsky	Dry pigment (Heliogenblau)	ca. 1944	Unspecified	-	44
S. Nolan	Enamel paint, Ripolin®	1932-1953	Unspecified	PyGCMS, FTIR	45
Forgeries					
Attribution	Title	Supposed year	Type of PB15	Technique(s)	Reference
L. Popova	<i>Untitled</i>	1900-1935	Unspecified	RS	46
F. Léger	<i>Cubistic still life</i>	1913	Unspecified	XRF, RS	47
M. Ernst	<i>La Horde</i>	1927	Unspecified	XRF, RS	47
H. M. Pechstein	<i>Bridge over the Seine with barge</i>	1908	Unspecified	XRF, RS	47
	<i>Female act lying with cat</i>	1909	Unspecified	Micro chemical test, RS	47
M. Utrillo	<i>Untitled</i>	1923	Unspecified	RS	48
J. Ensor	<i>Carnaval</i>	189(6)	Unspecified	Micro chemical test	23
W. Kandinsky	<i>Untitled</i>	ca.1932	Unspecified	RS	49
Anonymous	<i>Painted papyri</i>	13th-1st B.C.	Unspecified	RS	50

Table 1 Cases of PB15 identification in works of art, painting materials from artists' studio and forgeries and employed analytical techniques. \* Uncertain attribution. \*\* PB15 has been identified in the overpaint layer.

the crystal form of the identified PB15 remains unspecified (see Table 1).

CuPc blue pigments contain approximately 10% of copper<sup>53</sup>. The X-ray spectroscopic techniques, such as PIXE (Particle Induced X-ray Emission), EDX-SEM

(Energy Dispersive X-ray spectroscopy-Scanning Electron Microscopy) and XRF (X-Ray Fluorescence) allow detecting copper in paint layers based on CuPc pigments but are often ineffective to detect the light elements (C, H and N) of the phthalocyanine molecule.

Obviously, PB15 cannot be identified on the basis of the copper detection only since many other pigments may contain this metal. In this context, elemental analysis has to be combined with complementary analytical techniques, for instance Raman spectroscopy<sup>47, 54</sup>.

Berns *et al.*<sup>41</sup> identified PB15 in a Newman's painting by combining XRF and visible reflectance, while Albertson *et al.*<sup>42</sup> identified the pigment in a Mondrian's painting by performing PCA (Principal Component Analysis) on XRF data. Due to the very small size of the pigment grains (200 nm to 0.5  $\mu\text{m}$ ) it is very difficult to identify CuPc by using optical microscopy<sup>25, 55</sup>. However, the blue pigment has been identified in an over paint from a 17<sup>th</sup> painting thanks to the combination of EDX and PLM (Polarized Light Microscopy)<sup>56</sup>. Apart from the X-ray spectroscopies, the detection of the copper contained in the CuPc molecule may be achieved through other techniques such as LIBS (Laser Induced Breakdown Spectroscopy). LIBS provides additional elemental information on the CuPc molecule since it allows the identification of the copper but also the carbon content through the characteristic emission of the CN species of the Pc ring<sup>57</sup>. In paint samples, however, the CN species could be also assigned to certain binding media such as those based on acrylic resins. For the characterization of PB15 in a commercial artists' paint sample, Kokkinaki *et al.*<sup>57</sup> completed the elemental analysis data from LIBS with isotopic and molecular mass analysis from LA-TOF-MS (Laser Ablation -Time Of flight- Mass Spectroscopy).

The Raman and FTIR (Fourier Transform Infra-Red) spectroscopies are both molecular analytical techniques. FTIR and Raman spectra recorded for PB15 specimen are available in the IRUG (Infrared and Raman Users Group) database.

Many studies have shown that Raman spectroscopy (RS) was very efficient to detect CuPc blues and greens in paints layers, even in the case of complex mixtures poor in phthalocyanine pigments. In fact, CuPc blue pigments exhibit a typical Raman pattern easily recognizable in spectra recorded on paint samples, irrespective to the PB15 concentration.<sup>27, 58, 59</sup> In Table 1, it may be observed that in many cases of artwork studies, performing Raman analysis only led to the PB15 identification. Note, however, that thermal degradation problems induced by an excessive laser power may arise<sup>60-62</sup>. Through their Raman study of dry pigment samples of PB15, Defeyt *et al.*<sup>59</sup> have pointed out that Raman band positions in the 1100-1200  $\text{cm}^{-1}$  and 100-150  $\text{cm}^{-1}$  regions and fourteen Raman band intensity ratios vary with the alpha, beta and epsilon CuPc polymorphs. The authors proposed to exploit these differences for discriminating the three crystal forms in paint layers. Unfortunately, in aged paint samples the spectral interpretation is not always straightforward concerning the CuPc polymorph distinction. To overcome the problem a procedure combining RS and LDA (Linear Discriminant Analysis) has been developed<sup>63</sup>. Until now, this procedure has been applied on more than twenty real paint samples<sup>2</sup>. Recently, Beaulieu-Houle *et al.*<sup>64</sup> reported that pressure-tuning Raman spectroscopy could be helpful for the alpha and beta CuPc distinction. The authors noticed different pressure-induced spectral changes in the 800-900  $\text{cm}^{-1}$  and 1100-1200  $\text{cm}^{-1}$  regions for the alpha and beta polymorphs.

FTIR is very useful for detecting organic pigments in paint samples. Nevertheless, to ensure the CuPc blue identification, the use of complementary analytical techniques is often required. The efficiency of the FTIR technique strongly depends on the PB15 concentration present in the analyzed paint layer. CuPcs are high tinting pigments used in low proportion by the artists' color makers<sup>1</sup> e.g. 10% is used in the Amsterdam, Rembrandt and Van Gogh oil-based paints from Royal Talens<sup>65</sup>. As a consequence in the FTIR spectra recorded for paint samples, the intensities of the IR bands induced by PB15 are generally quite weak. Note that the efficiency of FTIR in organic pigments detection may be largely improved by extracting them from paint samples by means of solvent and acid immersions<sup>60</sup>. The positions of the IR bands arising in the 715-735  $\text{cm}^{-1}$ , 765-785  $\text{cm}^{-1}$  and 865-885  $\text{cm}^{-1}$  regions, potentially provide indicators for the  $\alpha$ - $\beta$ - and  $\epsilon$ -CuPc polymorph distinction<sup>59</sup>.

Depending on the nature of other components in the paint system, the interpretation of the FTIR results may become very complicated due to the IR band overlapping. In oil-based paints, a strong IR absorption induced by the binder may overlap the strongest PB15 IR band reported at 715-735  $\text{cm}^{-1}$ . For acrylic paints, the strong IR band induced by the acrylic resins at ca 750  $\text{cm}^{-1}$  may hide the PB15 IR absorption arising at 750-760  $\text{cm}^{-1}$ . In presence of chalk, an overlapping of the filler and PB15 IR bands at 865-885  $\text{cm}^{-1}$  may be also expected<sup>66</sup>. It can be observed in Table 1 that when the RS technique has not been employed, the PB15 identification was often achieved by using FTIR in combination with Py-GC-MS (Pyrolysis-Gas Chromatography-Mass Spectrometry) and/or XRD (X-Ray Diffraction).

XRD is a structural analytical technique efficient for identifying crystalline compounds, such as phthalocyanine pigments. PDFs (Powder Diffraction Files) related to PB15 may be found in the ICDD (International Center for Diffraction Data) database. Sonada *et al.*<sup>37</sup> pointed out the interest of XRD as a complementary technique for the PB15 identification in the samples taken from paintings by Klein, Dubuffet and Rancillac. More recently, Corbeil *et al.*<sup>34</sup> identified the pigment in two Riopelle's paintings by using XRD and FTIR. Brostoff *et al.*<sup>67</sup> were not enthusiastic regarding the detection of CuPc pigments in paint samples by means of the XRD method and in Lomax<sup>68</sup> the diffraction method led to the PB15 identification in three mock-ups out six. Another study has shown that in the diffractograms obtained for commercial artists' paints; the number of CuPc diffraction peaks varies from two to ten<sup>59</sup>. These differences may be explained by the PB15 concentration, the other components present in the paint system and the orientation of the PB15 crystals in the paint film. Obviously, when the number of PB15 diffraction peaks is sufficient, XRD remains the most reliable non-destructive method for discriminating the CuPc polymorphs.

For identifying phthalocyanine blue in paint layers, unmixed or mixed with other pigments, several authors have proposed the use of visible reflectance spectrophotometry<sup>41, 55, 69</sup>. After detecting copper by XRF, Berns *et al.*<sup>41</sup> have identified the CuPc blue and the CuPc green in *Dionysius* by Barnett Newman thanks to the obtained visible spectral reflectance curves.

In addition, destructive methods, such as Py-GC-MS, LDI-TOF-MS (Laser Desorption Ionization- Time of Flight- Mass Spectroscopy)<sup>38</sup>, MALDI-TOF-MS (Matrix assisted Laser Desorption Ionization - Time of Flight- Mass Spectroscopy)<sup>40</sup>, TLC (Thin Layer Chromatography)<sup>70</sup> and DTMS (Direct Temperature-resolved Mass Spectrometry) may be also helpful for identifying PB15 in paint samples<sup>37, 66</sup>. The efficiency of micro-chemical test using sulfuric acid described in De Keijzer<sup>64</sup> largely depends on the size sample and the PB15 concentration in the mixture<sup>72</sup>. The actual test has worked for the paint samples taken from a fake painting signed Ensor and another one signed Pechstein.

#### 4 PB15 and conservation treatments

Nowadays, conservators have to deal with more and more frequent arrivals of painted works of art containing PB15 in their studio. Most often, the conservation issues posed by modern organic pigments are related to their poor lightfastness and/or their sensitivity to certain solvents. CuPc blue pigments are high performance pigments, they possess a remarkable lightfastness and are insoluble in most of solvents. However, it is of common knowledge that they are partially soluble in aromatic solvents<sup>1</sup>. According to technical and patent literature, the application of aromatic solvents on a painted surface containing the PB15:0 type involves a risk of color changes, resulting from crystallization defects. The mechanism of crystallization depends on the slight, but still significant solubility of CuPc in aromatic solvents<sup>73</sup>. This one consists on the transformation of the unstabilized  $\alpha$ -form into crystals of the  $\beta$ -form with a strong tendency to grow in size. Crystal growth leads to a reduction of tinctorial strength and to a sliding of the blue hue towards green. Crystallization defects occur especially in presence of toluene (methylbenzene) and xylenes (meta-, ortho and para- isomers of dimethylbenzene)<sup>73-75</sup>.

Such solvents are present in various synthetic adhesives, inpainting materials and varnishes employed for conservation treatments of easel paintings<sup>76-78</sup>. For example, the synthetic varnishes based on Paraloid B72 or Laropal A 81, are prepared by dissolving the resin in toluene and/or xylene. In addition, for oil-based paintings, the use of aromatic solvents remains a possible option for varnish and overpaint removals. A preliminary investigation has shown that cleaning and varnishing tests using aromatic solvents, which have been performed on various PB15:0 based paint films, did not cause crystallization defects, irrespective to the nature of the binding medium<sup>2</sup>. Nevertheless, the same study has shown how PB15-based paint films, before and after accelerated aging, are highly solvent sensitive and sometimes even water sensitive, irrespective to the CuPc polymorph present in the paint system. Further investigations should be conducted in order to estimate the influence of PB15 on the pH and glass transition (T<sub>g</sub>) of such paint films.

The detection of CuPc blue in overpaint layers is relevant for dating previous conservation treatments. For the John Hayls' painting, *A portrait of a Lady and a Boy with a Pan* from 1655-59 (Table 1), acquired by the Tate Gallery in 1995, it allowed identifying a 20<sup>th</sup> overpaint and led to the decision of its removal<sup>56</sup>. Phthalo blues

and greens are commonly employed as inpainting materials. The use of modern pigments to retouch paintings made from traditional pigments is sometimes unavoidable, particularly when the pigments used by the artists are toxic, unavailable or prone to a degenerative color change. The imitative retouching is probably the most practiced technique for the inpainting of losses on easel paintings. The degree of the color matching required in the imitative technique may be very difficult to attain, notably in the presence of blue pigments<sup>80</sup>. Moreover, the attained degree of the color match has to be conserved in all conditions of illumination and observation. The inpainting quality largely depends on the similarity of the spectral reflectance curves between the pigments from the locations adjacent to the paint loss and the retouching pigments and, on the low degree of metamerism of the color match. Berns *et al.*<sup>81</sup> have defined a retouching palette that contains a reduced number of pigments and that minimizes metamerism. The authors have selected ten pigments having spectral properties that are representative of the very large number of pigments available to the painting conservators. This restricted palette includes copper phthalocyanine blue and green pigment. PB15 is a good candidate for substituting Prussian blue and other blue pigments whose reflectance remains low towards the red region of the visible spectrum<sup>81</sup> and could be suitable for matching azurite<sup>80</sup>.

Inversely, for matching highly chromatic pigments like CuPc blues and greens, very similar pigments are required<sup>81</sup>. It is not surprising that Donald Judd complained about the color change of his 1965 *Untitled* sculpture, repainted in 1976 with a mismatched purple paint. Whereas the original purple shade resulted from the combination of a quinacridone violet (PV19) and a CuPc blue, the PV19 based paint applied in 1976 lacked of PB15<sup>40</sup>. Furthermore, because the coloristic properties of PB15 strongly depend on the CuPc crystal form, the polymorphic identification could be of great interest for retouching monochromes or pieces with smooth and large surfaces based on PB15, such as those made by S. Francis, B. Newman and R. Lichtenstein. Typical visible reflectance curves obtained for PB15:1, :3, :4 and :6 are illustrated in Perego<sup>20</sup>.

The range of Gamblin Conservation Colors contains two phthalo blue-based paints; *Phthalo Blue* is based on PB15:2 (non-crystallizing and non-flocculating  $\alpha$ -form) whereas *Manganese Blue Hue* is based on PB15:4 (non-flocculating  $\beta$ -form). For both of them, the concentration of PB15 is 25%<sup>82</sup>. In the Kremer Conservation Colors range the phthalo blue-based paints available includes *Phthalo Blue* that is based on PB15:1 (non-crystallizing  $\alpha$ -form) and *Phthalo Blue King Blue* that is based on PB15:3 ( $\beta$ -form). *Primary Blue-Cyan* from the Maimeri Restoro range is also based on PB15:3. Commercial inpainting paints based on PB15:0 and PB15:6 are missing. The absence of the PB15:0 type certainly results from its sensitivity to the solvent(s) generally used in such paints. A reddish blue shade similar to PB15:6 may be achieved by combining an  $\alpha$ -CuPc pigment with a low proportion of Dioxazine Violet (PV23)<sup>1</sup>.

## 5 Conclusions

PB15 was incorporated in artists' paints very soon after the pigment appearance on the market in 1935 and has been adopted by artists since its introduction on their palette. CuPc blue is now the most widespread 21<sup>st</sup> artists' blue pigment. Currently, six types of CuPc blue pigments are manufactured. PB15:3 is the type the most used in artists' paint formulations.

Various destructive and non-destructive analytical techniques are suitable for detecting PB15 in paint layers, but the Raman spectroscopy is by far the most efficient of them. Indeed, CuPc blue pigments exhibit a typical Raman pattern easily distinguishable in spectra recorded on paint samples, irrespective to the PB15 concentration. The distinction of the CuPc polymorphs in paint layers is possible by means of XRD analysis or by combining Raman spectroscopy and LDA. It has been shown that CuPc blue pigments are valuable retouching pigments. On the one hand because they are high performance pigments, on the other hand because they can be used as a substitute of several traditional blue pigments, such as Prussian blue and azurite. Aromatic solvents do not cause the crystallization defects of the PB15:0 pigment crystals, when they are contained in dried paint films. A better knowledge of the factors influencing the sensitivity to solvents of the PB15-based paint films requires further investigations.

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