CCJ
China Coatings Journal

中国涂料工业
China Coatings Journal

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A CHINACOAT Publication
「中国国际涂料展」指定会刊及宣传刊物

主题 Special Feature

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China Coatings Journal

奇妙的金色及蓝色颜料
The Marvels of Gold and Blue Pigments


林珑教授
Prof. Long Lin

今天早上，我得悉这个月，香港新冠肺炎死亡率达全球最高之一。这个消息让我很难过，这不仅是因为我对香港有特殊的感情，因为香港是我去过而且爱上的少数的几个地方之一。我希望，在新冠病毒感染人数在全球「零容忍」和「零限制」国家中都不断上升的境况里，本期《中国涂料工业》杂志能给读者带来一些安慰。确实，读者会发现本期呈现了一些非常有趣的论文和报告。

Manolikakes 先生一篇题为「软和硬——手感触觉」（第 4 页）的论文详细描述了一种 100% UV 可固化涂料系统，该系统既不含溶剂又不含微粒，能够生成具有触感柔软，但耐刮擦和防指纹的涂层。这篇文章让我想起了我与浙江大学王立教授的合作研究工作（Hu, J. et al., *Preparation of UV-curable hyperbranched polyurethane acrylate hard coatings*, Progress in Organic Coatings, 2020, 144）。

执行编辑易丽仪继续在可持续发展栏目中发表一些关于这一日益重要主题的行业信息，本期她分享了一些新涂料系统的信息，这些系统由全球环境法规收紧而推动创新（第 9 页）。

Procopio 博士通过其题为「油漆和涂料流变控制添加剂」（第 27 页）的文章，对流变学、涂料流变学和用于控制涂料流变学的添加剂的基础知识进行了出色的介绍。不熟悉流变学的读者可能会发现阅读这篇文章很有帮助。

本期三月刊还介绍了两篇关于颜料的论文，每篇论文都涉及我最喜欢的一种颜色（金色和蓝色），我对此感到特别高兴，因为三月恰好是我的出生月份。我怀着极大的兴趣阅读了 Huber 博士关于「新型颜料，获得多种金色色调的新途径」（第 18 页）的论文。在他的文章中，Huber 博士向读者介绍了黄金的迷人历史和黄金的独特特性，这些之前我不知道或没有足够注意。不熟悉仿金颜料的读者可能也会对 Huber 博士提及的仿金颜料历史、超薄颜料（UTP）技术以及此类颜料的各种光学特性的介绍感兴趣。令人着迷的是，在 Rosenthal 茶杯上使用含有 UTP 仿金颜料的涂层系统生成的条纹在视觉上与使用金色金属生成的条纹几乎没有区别（第 22 页）。

在题为「蓝色——几乎不自然，更像人造！」（第 24 页）的文章中，Cramer 博士介绍了蓝色颜料的历史。这篇文章让我想起了我过去在基于卟啉（*生命的颜色*）的生物资源颜料领域中的研究。至此，我希望读者非常享乐阅读本期。

林珑教授 Prof. Long Lin
编辑 Editor, CCJ

I read this morning that Hong Kong has clocked one of the higher Covid fatalities in a month. Such news saddens me, not the least because that Hong Kong is one of the few places that I have visited and held a great deal of affection for. I hope that, amidst rising Covid infections across the globe in both 'zero tolerance' and 'zero restriction' countries, this issue of China Coatings Journal brings readers some comfort. Indeed, readers will find that this issue presents a few very interesting papers and reports.

Mr Manolikakes' paper entitled "Soft and Hard – Hand in Hand" (p. 4) described, in detail, a 100% UV curable coating system, which is free from both solvent and microparticle, that is capable of generating films that give a soft haptic feeling when touched but yet is scratch resistant and fingerprint-proof. The article reminds me of my collaborative research work with Prof Li Wang at Zhejiang University (Hu, J. et al., *Preparation of UV-curable hyperbranched polyurethane acrylate hard coatings*, Progress in Organic Coatings, 2020, 144).

The Managing Editor, Miss Sally Yick, has continued her column on the ever increasingly important theme of sustainability, this time sharing information on a few novel coating systems resulting from innovations driven by tightening global environmental regulations. (p. 9)

Through his article entitled "Additives to Control the Rheology of Paints & Coatings" (p. 27), Dr Procopio provided an excellent introduction to fundamentals of rheology, coating rheology and additives for the control of coating rheology. Readers new to rheology will likely find this article useful to read.

This March issue also presents two papers on pigments each dealing with one of my favourite colours (gold and blue), with which I am particularly pleased as March happens to be my birth month. I read Dr Huber's paper on "Novel Pigments, a New Approach to Achieving the Many Colour Shades of Gold" (p. 18) with great interest. In his article, Dr Huber introduces readers to the fascinating history of gold and the unique properties of gold, which I did not know or had not paid enough attention to. Readers who are not already familiar with gold-imitating pigments will also likely find Dr Huber's introduction to the history of gold-imitating pigments, the Ultra-Thin Pigment (UTP) technology, as well as various optical properties of such pigments of interest. It is fascinating to learn that stripes created using a coating system containing a UTP gold-imitating pigment on a Rosenthal teacup was visually virtually indistinguishable from stripes created using gold metal. (p. 22)

In his article entitled "Blue – Hardly Natural, More Artificial" (p. 24), Dr Cramer introduces us to the history of blue pigments. This article reminds me of my past research into the realms of bio-resourced pigments based around porphyrin – *the colour of life*. With this note, I wish readers a very enjoyable reading of this issue.

蓝色——
几乎不自然，更像人造！
Blue – Hardly Natural, More Artificial!

任何看过中国花山岩画、西班牙阿尔塔米拉或阿根廷库埃瓦德拉斯马诺斯的洞穴和岩画的人都会看到许多画作涂有红色、黄色和黑色（颜料）。

—— Werner Rudolf Cramer, Germany 德国
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为了绘制这些图片，人们使用了他们在周围环境中发现的颜料。这些主要是黄赭石、红赭石或木炭。可以磨碎并用作绘画颜料的蓝色矿石几乎不存在。但在早期，中国人学会了用重晶石（钡）、孔雀石（铜）或蓝铜矿（铜）和石英砂的混合物生产合成汉蓝。有证据表明，这种混合矿物在中国已经存在3,000多年。

或者埃及蓝，由石英砂、石灰石和铜矿石制成。为此，将这些材料加热到超过1,000℃数小时。然后将熔融物质研磨并再次加热。

在中世纪，青金石被用为蓝色颜料，用于具价值的图画，这种来自阿富汗或埃及的半宝石，并经过精心打磨和净化。

直到1706年，第一个无机蓝才被合成。它是一种与汉蓝颜色相似的铁氰化物络合物。

1828年首次合成了无机颜料群青。它由高岭土（Al_2O_3、SiO_2）、钙化合物、硫和活性炭制成。高岭土 / 高岭土（拼音gāolǐngtǔ —「来自高岭的矿土」）源自中国地名高岭 / 高岭，gāolǐng —「高山之上」）。这是中华人民共和国的一个村庄的名字，位于中国江西省西北部，景德镇县级市浮梁县境内。

1927年，科学杂志Helvetica Chimica Acta首次报道了有机颜料铜酞菁的合成。这种有机配合物由一个卟吩环组成，其中掺入了铜离子。由于其最佳性能，铜酞菁是当今最重要的蓝色颜料之一。也可从碱性物质生产绿色铜酞菁。有趣的是，铜酞菁在化学上与血红蛋白和叶绿素有关。代替铜离子，血红蛋白有一个铁离子，叶绿素有一个镁离子。

蓝色颜料行列中的一个新成员是钇铟锰颜料（YInMn

Anyone who has ever taken a look at the cave and rock paintings in Huashan on Hua Mountain (Huāshān yánhuà 花山岩画) in China, in Altamira in Spain or, for example, in the Cueva de las Manos in Argentina, will see the many pictures painted with red, yellow and black colours (pigments). To paint these pictures, people used pigments that they found in their surroundings. These were mainly yellow ochre, red ochre or charcoal. Blue stones that could be ground up and used as pigments for painting were almost non-existent. But early on, the Chinese learned to produce the synthetic Han blue from a mixture of barite (barium), malachite (copper) or azurite (copper) and quartz sand. There is evidence that this mixed mineral has existed in China for over 3,000 years.

Or Egyptian blue, which was made from quartz sand, limestone and a copper ore. For this purpose, these materials were heated to over 1,000°C for hours. The molten mass was then ground and heated again.

In the Middle Ages, lapislazuli was used as a blue pigment for particularly valuable pictures. This semi-precious stone from Afghanistan or Egypt was ground up and purified in an elaborate process.

It was not until 1706 that the first inorganic blue was synthesised. It was an iron-cyanide complex similar in colour to Han blue.

And in 1828, the inorganic pigment ultramarine blue was synthesised for the first time. It is made from kaolin (Al_2O_3, SiO_2), calcium compounds, sulphur and activated carbon. Kaolin (Chinese 高岭土 / 高岭土, Pinyin gāolǐngtǔ - "earth from Gaoling) is derived from the Chinese place name Gaoling (高岭 / 高岭, gāolǐng - "high mountain range"). This

Pigment)。它由钇、铟和锰的熔体组成。它非常耐光，不溶于水和油。

在一系列实验中，研究了各种蓝色颜料的颜色特性。这些在粘合剂中加工并涂在画纸上。它们是使用具有定向照明的分光光度计测量的在45°照明下和在0°测量下（正常情况下）。评估反射值和颜色值。

蓝色颜料操纵入射光以在蓝色光谱范围内反射更多。与所有颜料一样，蓝色颜料会在整个光谱范围内反射。与蓝色和绿色颜料不同，黄色和红色颜料具有反射率平台，即它们的反射在较长波长的光谱范围内增加并保持在该反射率水准。另一方面，绿色和蓝色颜料具有最大值。

在更短的波长范围内，蓝色与蓝紫色相邻，在其最大值的另一侧为绿色。这个区域还表现出蓝色的细微差别：它可以是绿色的，也可以是红色的。与几乎所有有色颜料一样，蓝色颜料不是颜色中性的，而是倾向于一个颜色方向。

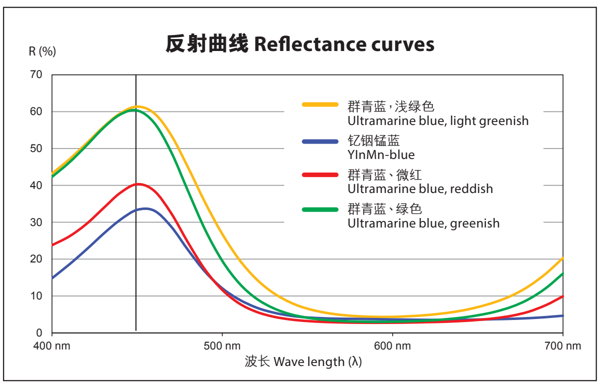

图1：不同颜色颜料的反射曲线
Figure 1: Reflectance curves of different coloured pigments

is the name of a village in the People's Republic of China in the northwest of Jiangxi Province, in Fuliang County of the county-level city of Jingdezhen.

In 1927, the synthesis of the organic pigment copper phythalocyanine was reported for the first time in the scientific journal Helvetica Chimica Acta. This organic complex consists of a porphin ring in which a copper ion is incorporated. Copper phthalocyanine is one of the more important blue pigments today due to its optimal properties. One can also produce a green copper phthalocyanine from the basic substances. Interestingly, copper phthalocyanine is chemically related to haemoglobin and chlorophyll. Instead of the copper ion, haemoglobin has an iron ion and chlorophyll a magnesium ion.

A new addition to the ranks of blue pigments is the YInMn pigment. It consists of a melt of yttrium, indium and manganese. It is very lightfast and insoluble in water and oil.

In a series of experiments, the colour properties of various blue pigments were investigated. These were processed in a binder and applied to painting paper. They were measured using a spectrophotometer with directional illumination: under 45° illumination and under 0° measurement (in the normal). Both the reflection and colour values were evaluated.

Blue pigments manipulate incident light to reflect more in the blue spectral range. Like all pigments, blue pigments reflect in the entire spectral range. Yellow and red pigments, unlike blue and green coloured pigments, have a reflectance plateau, i.e. their reflections increase in the longer wavelength spectral range and remain at this reflectance level. Green and blue pigments, on the other hand, have maxima.

Towards the shorter wavelength range, blue borders on blue-violet and on the other side of its maximum on green. This neighbourhood also shows the nuances of a blue: it can

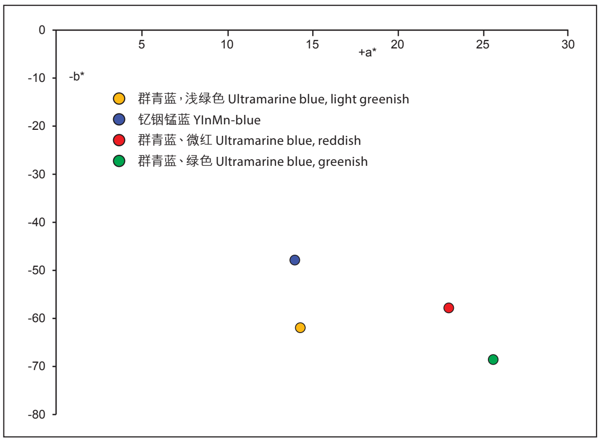

图2：从测量结果中，a*b* 图的颜色值
Figure 2: From the measurement results, colour values shown in the a*b* diagram

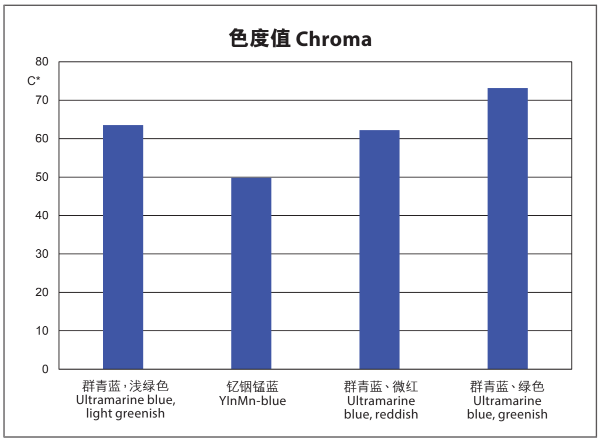

图3：从测量结果中，横条图中的色度值
Figure 3: From the measurement results, the chroma values shown in the bar chart

为这些实验选择了四种蓝色颜料：红群青蓝、绿群青蓝、浅绿群青蓝和蓝色混合颜料 YInMn（钇、铟、锰）。颜料被加入粘合剂中，并一次或多次涂抹在艺术家的纸上。

选择了在低透明度下看起来最强的两倍或四倍色差。所有样品均在 45°/as45°（45°照明 /45°非镜面测量 = 法线）下进行比色测量。从测量结果中，以反射曲线的形式选择反射值，a*b* 图中的颜色值（**图 2**）和横条图中的色度值（**图 3**）。

与其它蓝色颜料相比，这两种绿色群青颜料显示出最高的最大值。微红色群青和钇铟锰颜料的测量显示显著较低的最大值。令人惊讶的是，所有群青颜料在较长波长的光谱范围（即红色）中的反射都略有增加。钇铟锰颜料在此范围内逐渐变弱。

颜色值反映了这些结果：红色和绿色群青的颜色值明显不同于钇铟锰颜料。相比之下，浅绿色颜料更蓝。

色度值显示与群青颜料相比，钇铟锰颜料的色度最低。最高色度值由绿色群青显示。

蓝色颜料用于许多应用。在汽车领域，它们与其它有色颜料以及铝和干涉颜料混合使用。在这里，通常使用酞菁蓝代替群青。根据应用和用途，使用者可以使用不同的蓝色颜料。用户做出正确的选择很重要：美丽的蓝色可能会由于其化学或温度而在应用领域发生变化，这是用户肯定不想要的。

be either greenish or reddish. Blue pigments, like almost all coloured pigments, are not colour-neutral, but tend in one colour direction.

Four blue pigments were selected for these experiments: A reddish ultramarine blue, a greenish ultramarine blue, a light greenish ultramarine blue and a blue mixed pigment YInMn (yttrium, indium, manganese). The pigments were incorporated in a binder and applied to artist's paper single and multiple times.

The 2- or 4-fold spreads that appeared to be the strongest in colour with low transparency were selected. All samples were colourimetrically measured at 45°/as45° (45° illumination/measurement at 45° aspecular = in the normal). From the measurement results, the reflectance values were selected in the form of reflectance curves, the colour values in the a*b* diagram (**Figure 2**) and the chroma values in the bar chart (**Figure 3**).

The two greenish ultramarine pigments show the highest maxima compared to the other blue pigments. The measurements of the reddish ultramarine and the YInMn pigment show significantly lower maxima. It is striking that all ultramarine pigments show a slight increase in their reflections in the longer wavelength spectral range, i.e. in the red. The YInMn pigment tapers off flat in this range.

The colour values reflect these results: The colour values of the reddish and greenish ultramarine are clearly away from the YInMn pigment. The light greenish pigment is bluer in comparison.

The chroma values show the lowest chroma for the YInMn pigment compared to the ultramarine pigments. The highest chroma value is shown by the greenish ultramarine.

Blue pigments are used in many applications. In the automotive sector, they are used in mixtures with other coloured pigments as well as aluminum and interference pigments. Here, phthalocyanine blue is usually used instead of ultramarine. Depending on the application and use, different blue pigments are available to the user. It is important for the user to make the right choice: the beautiful blue colour can possibly change in the application area due to its chemistry or temperatures, which the user certainly does not want.