

# The history of blue pigments in the Fine Arts — painting, from the perspective of a paint maker

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## Abstract

In this text, I will introduce you to the colour blue, how and why we see it and when we, as a species, started to discover and use its various versions. I only cover blue pigments as opposed to dyes. Many of the blues that I discuss are known by several names depending on locality, the age in which they were used and, at times, slight variations of their chemical makeup. I do not look at blue dyes mainly due to their inherent lack of lightfastness (and, therefore, usefulness to the artist).

## Introduction

The largest expanse of colour that any human is likely to have seen, or ever will, is the blue of the sky followed by the blue of the sea. Why then was this colour the last to be named by *Homo sapiens* and one of the least to have been reproduced in paint? “The first new blue pigment discovered in 200 years” (Garfield 2017) — headlines from just a handful of years ago. One has to ask how flight, aeronautics, and nanotechnology have all been discovered in the last 100 years and yet we have only discovered one new blue in twice that time.

Is this recalcitrant frontier a sign that we already know all that there is to know about colour, or are we blissfully unaware of a plethora of unfound hues? An insight into these questions may come from examining the history of blue. To do this, we need to look no further than the discipline of Fine Arts which has unknowingly documented the discovery of blue across the millennia.

## How we see colour

Before delving into the intricate past of human endeavour to produce a likeness of

what was seen daily looking skyward or the mottled hues of the never-ceasing oceans, it is worth understanding just how we see colours.

In much the same way our ears tune in to sound, or we use a radio to tune in to a radio station, our eyes detect different wavelengths of electromagnetic radiation or energy. The various wavelengths falling on our eyes’ rods and cones send a signal to the brain commensurate with the particular wavelengths which, if everything is working correctly, we interpret as colour.

We can gain a better understanding of how colour works by understanding what happens when colours are combined: blue is a primary colour in both Additive and Subtractive colour mixing. In other words, along with red, it is not possible to add other colours together to make blue. As a quick aside, Daniel Nelson asked in 2018, “what two colours combine to make blue?” and hypothesised that cyan and magenta mix to make blue. While this is true, many would counter that cyan is indeed a blue; hence, in mixing magenta with it, one is only chang-

ing the hue of a blue to another blue rather than “making blue.”

Additive colour mixing occurs when different colours of light are immitted from an energy source in the visible spectrum. An example of this is an LCD screen where differing amounts of red, blue and green light are combined to form a vast array of colours. All three colours together produce what we call white light or a light containing all the wavelengths of the visible light spectrum (i.e., sunlight). Subtractive colour mixing can be most easily understood using the example of mixing paints. In the presence of sunlight (i.e., all wavelengths of the visible spectrum or white light), when two colours, such as blue and yellow, are mixed together, their combination will result in a reflection of the resultant wavelengths of the yellow being reduced by the blue, the combination of which produces what we perceive to be green, which lies between yellow and blue on the spectrum.

### Did we always “see” colour?

Now that we know how we see colour, we may wonder why we have so few blues and why it has taken so long to discover a new one. As a matter of fact, it appears that we may not have always “seen” blue, or at least may not have always given it its status as a colour.

It is well known that, as humans, we have far fewer receptors for the colour blue in the eye, compared with red and green. This was thought to be due to the fact that there was very little food coloured blue; hence, we as humans did not need to concern ourselves with this colour that much. Specifically, it is widely believed that early man could only recognise black, white and red and then later yellow and green. In fact, many theo-

ries posit that humans did not really know that blue existed until relatively recently.

Jules Davidoff, who worked with the Himba tribe from Namibia as recently as 2006, found that not only did the tribe not have a name for blue but they also found it very hard to distinguish it. In a series of tests to detect a blue square, when presented with 11 squares, 10 of which were green and one blue, the surveyed tribe members were unable to distinguish the blue square that most people in the “outside” world would readily pick from the line-up (Robertson et al. 2006).

Indeed, when one thinks of it, back beyond 6,000 years ago there was very little that was blue. The blue we see in the ocean is due to the molecules of water absorbing more of the red end of the spectrum and therefore producing what we perceive to be a blue hue, this of course can vary considerably depending on impurities in the water. High iron content can give the water a brown hue, as can tannin from leaves and trees leaching into a water course. However it is not possible to harness the blue of water to tint or colour, for instance, for use in a paint.

One may claim, “Of course the sky is blue!”, yet we can respond, “Hold on: we know that is not true!” — the sky appears blue because the sunlight is diffracted by tiny particles in the stratosphere. Subsequently, some of the sunlight is diffracted into the blue spectrum of visible light by particles which are very close to the same size as the wavelength of blue, which explains why we perceive the sky as blue. Theories for this phenomenon were first described by Lord Rayleigh,<sup>1</sup> Richard Gans, and Peter

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<sup>1</sup> See Rayleigh scattering, [Ed.]

Debye and, more accurately, by Gustav Mie. Intriguingly, their work was based on earlier work carried out by Horace-Bénédict de Saussure and Alexander von Humboldt who developed and used a “cyanometer,” which consisted of squares of paper dyed in graduating shades of Prussian blue (mixed with white or black) and laid out on a circle that was then held up at a particular distance from the viewer and used to compare to the colour of the sky at that specific place and time.

Looking wider afield, peacock feathers appear to have blue in them; once again, this is not caused by a pigment absorbing and re-emitting particular wave-lengths as a colour, but rather by diffraction, or the slight bending of light waves known as structural colour. The wings of a blue-winged wasp and the wings of the blue morpho butterfly are all light diffractors, which can be best thought of as acting a little like layers of slits or grates that diffract the light to produce a blue. I will discuss this further with reference to phototronic pigments.






### A timeline of blue pigment discovery

While there is evidence of very early use from around the world of naturally occurring ochres and earths of red and Yellow. Blacks made from charcoal as a result of fire and whites in the form of calcium carbonate and other compounds. All colourants that were readily found or easily dug up. These “pigments” are found in caves around the world from France to Australia and date back millennia. However we can see from above that there were no naturally occurring blues that were able to be found and easily ground into a paste and applied to a cave

wall.<sup>2</sup> We will now look at when the first blues were found and how.

Listed below, for completeness, are the blue pigments in general use over time. They are listed according to their Colour Index pigment number, which is a general classification of colour by chemical type. A more detailed list, maintained by The Society of Dyers and Colourists (UK) and The American Association of Textile Chemists and Colourists (US), provides more specific five-digit numbers.

### Ancient blues

	Lapis lazuli
	Egyptian blue
	Azurite
	Han blue
	Smalt

### *Lapis lazuli PB29 and Egyptian blue — PB31*

Some of the earliest existing examples of the use of blue for adornment is provided by the Egyptians, who used lapis lazuli for ornaments and ceremonial artefacts. The original ultramarine blue made from lapis lazuli (Italian *oltremarino*; ultra: beyond, *marino*: sea) was so called as the lapis was transported from Afghanistan literally “beyond the seas” (from a Eurocentric perspective, of course), and it was originally

<sup>2</sup> There are no blues in the Indigenous art works presented in B. J. Gillam, Figure-ground and occlusion depiction in early Australian Aboriginal bark paintings, *JProcRNSW* 152: 251–267, 2019. <https://royalsoc.org.au/images/pdf/journal/152-2-07Gillam.pdf> [Ed.]

employed by the Egyptians in solid form for ornamental use in jewellery. But there is no record of them having successfully formulating it into a paint, which was left to the clever Italians many centuries later. Due to the processes of collection and manufacture through a series of manual kneading, washing and filtering, it proved to be a highly expensive pigment. There are many stories in later years of well-known artists not finishing pictures or saving their tiny amounts of ultramarine for the final application and only on especially important icons.

Although the Egyptians were never able to incorporate lapis lazuli into a paint successfully, there is little question that it was they who first manufactured a blue pigment, using a chemical reaction. This pigment, now known as Egyptian blue, was used in paint in artwork and ornaments, and the Egyptians indeed referred to their discovery as artificial lapis lazuli: “The term for Egyptian Blue in the Egyptian language is *ḥsbd-irjt* which means artificial lapis lazuli (*ḥsbd*)” (Pagès-Camagna 1998).

I argued that this is the first record of a manufactured blue, yet this applies if one does not consider the incredible amount of work that goes into refining lapis lazuli. As recorded in the 15<sup>th</sup> century by Cennini (who devotes a several pages to detail its precise handling extensively, including who should do the work), “You must know also that it is rather the art of maidens than of men to make it because they remain continually in the house and are more patient and their hands are more delicate. But *beware* of old women.” (Cennini, 1899). On a more serious note, the manufacture of lapis lazuli is mainly mechanical, as it involves taking a semi-precious stone and crushing and purifying it.

Egyptian blue is the earliest blue pigment that we are aware of whose formation is definitely based on a chemical reaction. This reaction takes place when silica (sand) is heated in the presence of a copper compound and an alkali for several hours. Egyptian blue, when studied at a microscopic level, consists of blue crystals, with impurities of unreacted quartz and small particles of glass. Some people thus refer to Egyptian blue as a frit.

Egyptian blue’s reaction can thus be described as  $\text{Cu}_2\text{CO}_3(\text{OH})_2 + 8 \text{SiO}_2 + 2 \text{CaCO}_3 \rightarrow 2 \text{CaCuSi}_4\text{O}_{10} + 3 \text{CO}_2 + \text{H}_2\text{O}$

As we will see with many other blues, the colour is derived from copper. However, looking at the formula, the starting compound is highly similar to that of azurite, which was also to be found in those times.

#### *Azurite — PB30*

Like lapis lazuli, azurite is a naturally occurring mineral, and, when ground and washed, it produces a light blue powder reminiscent of a clear blue sky. Azurite was most likely also used when lapis lazuli was not on hand, namely earlier than Egyptian blue; however it does not appear as highly prized as lapis lazuli, as it is a light blue rather than the rich dark blue of lapis. It was still used in painting between the 14<sup>th</sup> and the 17<sup>th</sup> centuries in China, Japan and Egypt and was a major blue pigment in the Middle Age in Europe. Verditer blue and blue bice are synthesised versions of a basic copper carbonate, similar in chemical composition to azurite. It is believed that these blues superseded azurite predominantly due to cost (Bristow 1996).

#### *Han blue*

Han blue was a manufactured barium copper silicate pigment found since the Chinese

Han Dynasty (208 BC–220 CE). It is similar in chemical makeup ( $\text{BaCuSi}_4\text{O}_{10}$ ) to the Egyptian blue  $\text{CaCuSi}_4\text{O}_{10}$ . It has also been referred to as Chinese blue, but the name Han blue is preferred to avoid confusion with other more common blues recognised as Chinese blue. Synthesised Han blue has a similar chemical makeup to the rare mineral effenbergerite. (Eastaugh et al. 2004)

Subsequently, if we are to believe modern pigment history, there was somewhat of a hiatus between the Egyptians' discovery of *hsbd-irjt* (Egyptian blue) earlier than 3,000 BC, Han blue by the Chinese around 200 BC and the next blue in more modern times over 2,000 years after that. Or was there?

### Other possible early blues

Thomas Katsaros, in his 2019 lecture at the Symposium on the History of Technology and Research of the Colour Blue at the Herakleidon Museum in Athens, argued that in ancient Greece there was at least knowledge of other blues as found in the records of Theophrastus of Eresos — the successor to Aristotle at the Lyceum — who wrote on stones in 315 BC listing, among other things, the colours of the painters of his time and recorded three types of cyanus (blue): Cypriot, Scythian and Egyptian. While it was generally accepted that Chrysopastos (Cypriot) cyanus was lapis lazuli, doubt remains as to what the Scythian cyanus was: possibly sapphire? While there is no certainty as to the exact meaning, the jury is still wondering what blues Theophrastus was referring to; Thomas Katsaros posits that at least the Greeks believed that there was more than just lapis lazuli and Egyptian blue at that time (azurite being included with Egyptian).

### Vivianite

Vivianite is also known as blue ochre and earth iron blue. Its molecule is a phosphate of divalent iron with a significant amount of water:  $\text{Fe}^{2+}_3(\text{PO}_4)_2(\text{H}_2\text{O})_8$ . Vivianite has been used for millennia by artists although sparingly due to its scarcity in an agreeable blue state and its known propensity to change colour unavoidably. It is sometimes confused with azurite because it too changes colour over time, but, unlike azurite that changes into the green of malachite, vivianite tends to continue its process past the green and through to a deep blue-black (as described below). It is found in many places around the world — specifically, in ancient wetlands or where deposits of peat are now found, rich in organic matter but lower in oxygen and calcium concentrations.

As is evident from his 1921 book *The Manufacture of Earth Colours*, Josef Bersch understood vivianite's chemical composition and was cognizant of its ability to oxidise; however, he still thought it to be stable. Eastaugh et al. (2004) touch on the pigment altering to a yellow, which produces an overall green pigment (p. 266); however, the changing colour of vivianite is best explained by Alfredo Petrov (2008) in *A Scientific Study of the Absorption of Evil by Vivianite*, where he describes the various states of vivianite and how it transmorphs into metavivianite:

Some people think vivianite darkens by oxidation — absorbing oxygen from the atmosphere — and then flakes apart along the cleavages by “drying out,” i.e. losing some of its 8 waters. They optimistically hope that both of these processes can be hindered by a thin coating of lacquer (which is why some specimens in old collections were varnished), or by dipping

in oil, or sealing it in a glass jar. They are correct that both oxidation and water loss are taking place, but not in the way they imagine and not in any way that could be prevented by a coating of lacquer no matter how thick! To somewhat oversimplify and paraphrase the process, when photons (particles of light energy) enter a transparent vivianite crystal, they can knock a proton (a hydrogen nucleus) out of one of the 8 water molecules, which converts the water into a hydroxyl ion (OH) which has a negative charge. This extra negative charge is balanced by oxidation of one iron atom, whose valence state changes from 2+ (ferrous) to 3+ (ferric). Notice that no interaction with the atmosphere was involved — no oxygen entered the structure from outside, and no water molecule escaped to the outside — we are dealing with a completely internal reaction (oxidation by deprotonation). The liberated hydrogen (the proton) easily migrates through the crystal lattice, as in other species of proton-conducting crystals (which are currently undergoing intense study for potential industrial uses like fuel cells). No coat of lacquer is going to prevent this.

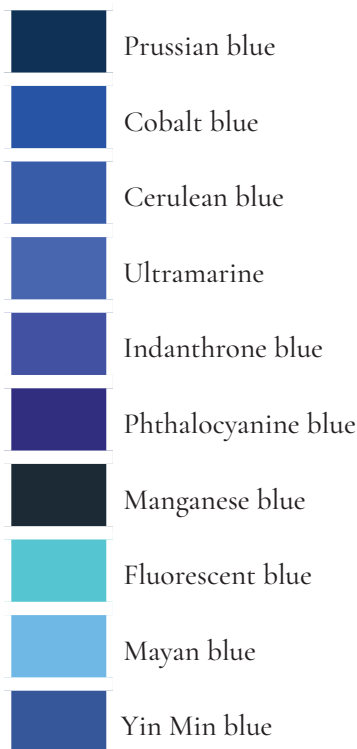
Hence, while this is an intriguing colour, it is not one that is likely to see too many artists wishing to use it due to its inevitable colour shift.

#### *Smalt — PB32*

Concerning colourant in paint, early cobalt blue was actually glass containing cobalt and potassium (known as smalt), which was ground and used as a colourant (smalt, PB32) The earliest recording of its use has been found in paintings by Hans Holbein the Younger (1497–1543).

There are many other examples in China and Japan of blues made from either both copper or/and cobalt — or at least that is what we know now is their main colour constituent. However, following the accepted Western timeline, cobalt blue as a pigment (as opposed to a frit or ground glass) was yet to be discovered. Hence, we move on to Prussian blue, the next blue to be discovered.

#### **Modern blues**



#### *Prussian blue — PB27*

It was not until the very early 1700s that a purely synthesised pigment was recorded as having been made in what we know as Prussian blue. Swiss dye-maker Johann Jacob Diesbach, working in the Berlin laboratory of his friend Johann Konrad Dippel, was attempting to create red Florentine

lake — carminic acid which is extracted from cochineal and precipitated by alum, iron sulphate, and potash.

When Diesbach mixed what he thought was potash with the iron sulphate, instead of the strong red he was expecting, he observed a light pale colour. In attempting to concentrate the product, he first found it went purple, and then a deep blue. Diesbach had unknowingly, and by accident, produced the first batch of Berliner Blau, called many other names such as Paris Blue, Antwerp Blue but what we universally now know today as Prussian blue.

Digging a little deeper into this story, Alexander Kraft, who believes that the most probable year of discovery was 1706, has pieced together more details from several sources, namely letters and diaries from the time. He found out that of one of Dippel's contemporaries, a younger friend named Senckenberg, recorded that Dippel had told him, concerning Prussian blue, that "he was preparing a large amount of a 'sal volatile' by dry distillation of calcined sal tartari (potash) and dried ox blood." Dippel's assistant had not disposed of the remaining mixture but rather stored and labelled it only as sal tartari instead of noting it had other ingredients. This is the "potash" that Diesbach used to make his discovery. Then he set about selling this newfound colour to some local artists unbeknown to his friend Dippel only to find out that, once his source of what he thought to be potash ran out, he could no longer make the colour. He then reported his problem to Dippel, who suggested the use of bovine blood with potash.

This story makes one consider that, had Dippel not been aware of the mislabelling of the jar and exactly what was in it, the formula might have been lost; or, had the

jar been labelled correctly, Diesbach might not have used it at all or discovered Prussian blue, and he would have just continued to make a boring old red! It took nearly another 20 years for the formula to become public, and, even then, both recorded early copies of the process continued to include the superfluous red cochineal dye. It is apparent no one had worked out the true formula in that time: how much longer might it have been before it was discovered?

Spare a thought for these poor guys who really had very little knowledge with which to work, very few books, no internet of things, just a hunch and their observational skills. We can only try to imagine what it would have been like to work in a cold stone building, trying to solve a problem and really not knowing where to start. They lived in a time when the realm of science was the domain of gentlemen who could afford the time and expense to experiment. Today, we might class them as great thinkers or even as lunatics! Working by daylight or candlelight, life was very basic by our standards today, a furnace was just that — with little or no idea as to the actual temperature to which compounds in an experiment were being heated, accuracy would have been very difficult. (The first mercury thermometer was not developed until 1714.)

Even under the most controlled conditions of the time, many things were left to chance. One can imagine lab benches with little on them in the way of apparatus, sunlight filtered through smog-coated windows being the only illumination, and suit-clad menfolk working away, hypothesising and experimenting with no boundaries and very little clue as to what they were doing — a little like a child playing with a chemistry set before reading the instructions! And, bang,

here is a brand-new colour when you were not even expecting it! Hence, I guess it is not a surprise to learn that Prussian blue was discovered by accident.

Prussian blue is not only interesting for the way it was discovered but also because it has played a role across many industries. It is probably best known for its use in the blue of blueprints (since the mid-1800s), in which a sheet of paper is coated with a mixture of ammonium iron citrate and potassium ferrocyanide. The original drawing (done on a thin paper, such as a tracing paper) to be copied is then laid on top of the coated paper and exposed to intense light. The light combines the two compounds, producing Prussian blue in the areas exposed to light and not protected by the drawn line on the design above. The coated sheet is then washed, and the unexposed areas washed clean to show the colour of the paper through, as the white of the print. The exposed areas are coated in the combined compound being insoluble Prussian blue, resulting in a blue background, thus a blue print. A far easier and more precise way to make copies than was the pre-existing practice of tracing them by hand. Even when carbon copies and copying machines were invented, large-scale technical and architectural drawings were still reproduced in this way for some time.

For anyone who has visited a machine shop, Prussian blue is mixed with oil as “marking blue” or “engineer’s blue” to show high spots or areas that rub when “mating” machine parts.

In medicine, Prussian blue is used to very effectively remove thallium and radioactive caesium from the body. In fact, it is included in the World Health Organization’s list of essential medicines, namely those consid-

ered essential to any basic healthcare system. Strangely enough, while Prussian blue is used as a life-saving antidote to heavy metal poisoning, when combined with acid and a bit of heat, it gives off life-ending cyanide. “By itself it is only slightly toxic; however, it can produce extremely toxic hydrogen cyanide gas in hot acid if heated to decomposition or exposed to strong ultraviolet radiation.” (McCann 1979, p.145)

For those with a technical interest, variations on the hue can be produced by varying the reagents; an example of this is Turnbull’s blue. Prussian blue continues to be used by artists today although not to the extent of other blues which have come after it. There are three variants of Prussian blue, and only one of them will work in a water-based system such as acrylic or watercolour, which still needs to be incorporated in a well-balanced formulation. Many see Prussian blue as not as clean or brilliant as its successors. Nonetheless, it is still highly employed by artists and industry alike, although most paint manufacturers now offer a blend to achieve the colour rather than the original pigment.<sup>3</sup>

### *Cobalt blue — PB28*

I started with Prussian blue because it was the first modern synthesised blue pigment. However, the use of the cobalt as a colourant dates back to the eighth and ninth centuries and, in fact, far earlier when it was used to colour ceramics and jewellery, but as a colourant in paint, it was not commercially produced for another century after Prussian blue: around 1807 in France (where it

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<sup>3</sup> Use of Prussian blue spread quickly around the world, even into Japan, despite its *sakoku* trade policy, where it is seen in Hokusai’s *The great wave off Kanagawa* (1830–1834), as Davies (2017) discusses. [Ed.]



was discovered in 1802). It is the effect of the element cobalt in rich blue in the now ubiquitous blue and white ceramics from China (although, apparently, early on, the blue was seen as too ornamental for local Chinese tastes; hence it was not used much for local production but rather for export). The amazing blue stained glass that we see in churches and cathedrals across Europe owes its distinctive lightfast blue to the element cobalt as well, which is somewhat ironic when considering that the word “cobalt” is derived from “Kobold”, the name of a devilish sprite well known in German folklore for mischief-making. Miners in the Saxony region discovered the silver-like ore which after smelting formed a “useless” lump and produced noxious and lethal fumes. The irritated miners thus dubbed the ore Kobold, and the name stuck. This was around 1500 AD.

Nearly 200 years later, a Swedish chemist, Georg Brandt, at Uppsala University, began researching the rejected substance. Suspecting that the core of the material was in fact a previously unknown element, Brandt tested his theory on an ore from Sweden, separating the metal via fire assay, thus isolating the same substance that the Saxony miners had stumbled upon and discounted. Brandt stuck with the miners’ name for the material and called the newly discovered element cobalt.

As a synthesised pigment, a purer alumina-based version of cobalt blue was discovered by French chemist Louis Jacques Thénard in 1802. Leithner of Vienna is also recorded as having developed a cobalt arsenate as early as 1775. Cobalt blue is a favourite of artists: although more expensive than copper-based blues, it gives a vibrant but opaque blue, slightly leaning to the green

bias, and is very stable when formulating and lightfast in use. Furthermore, when used in standard proper artist practice, it is quite safe, as most modern versions have no free bio-soluble cobalt.

#### *Cerulean blue — PB35 (PB36)*

As cobalt blue was being released to artists in the early 1800s, a new blue was in development, once again making use of cobalt: the compound originally composed of cobalt magnesium stannate (1789). In antiquity, the term “caeruleum” was used to describe blue pigments in general, particularly mixtures of copper and cobalt: the main chemicals in azurite or malachite and smalt. Cerulean blue production was then further perfected by a process developed by Andreas Höpfner in Germany in 1805 by heating that roasted cobalt and tin oxides together. However, the colour only appeared available to artists in a catalogue from the 1860s under the name of caeruleum. Cerulean blue is an inert, lightfast pigment that can act as a drier in oil paints. It is quite stable in both watercolour and acrylic and is referred to as PB35 cobalt stannate. PB36, which is a cobalt chromate, is also used and sold as Cerulean blue for those who prefer a slightly greener or cooler hue.

#### *Artificial ultramarine — PB29*

We now have a bit of a backtrack in our timeline!: Artificial Ultramarine Blue. The original ultramarine blue made from lapis lazuli was employed by the venerable Egyptians in solid form for ornamental use in jewellery, as remarked above. Due to the processes of collection and manufacture through a series of manual kneading, washing and filtering, it proved to be a highly expensive pigment. While paint made on

remarkably high-quality lapis is a romantic idea to produce, it was still feeble in strength in comparison to what was to come and vastly expensive to produce even now.

Finding a way to make artificial ultramarine (lapis lazuli) was going to assure its inventor fame and fortune, but, even with that promise, it was still a long time till the birth of artificial ultramarine blue. Sir Arthur Church (1915) recorded that, “[i]n the year 1814, a blue colouration, subsequently proved to be due to ultramarine, was noticed in the soda (black ash) furnaces of St. Gobain.” Artificial ultramarine blue was not born until 1824, when the Societé d’Encouragement offered a reward of 6,000 francs to anyone who could develop a synthetic alternative to ultramarine. It was a troublesome birth. Two men came forward within several weeks of one another: Jean-Baptiste Guimet, a French chemist, and Christian Gmelin, a German professor from the University of Tübingen. The prize was fiercely contested. Gmelin claimed that he had arrived at a solution a year earlier but had waited to publish his results. Guimet countered by declaring that he had conceived his formula two years before, but, like Gmelin, had opted not to publicise his findings. The committee awarded the prize to Guimet, and the artificial blue became known as “French ultramarine.”<sup>4</sup>

This new method of production was based in part upon chemical analyses of natural ultramarine (lapis lazuli), and in part on a study of the conditions which produced the first observed accidental manufacture at St Gobain. This very rich red-blue was developed and revolutionised the way artists could now mix their purples and violets, while also allowing for a full new range of

subdued greens and shadow hues. Modern ultramarine blue is a soft pigment that quite often does not need much milling to disperse into a paint formulation. It is non-toxic, with generally accepted good lightfastness. However, recent research conducted during the restoration of Michelangelo’s work in the Sistine chapel has thrown some doubt on the lightfastness of lapis lazuli in oil paint (lapis blue and ultramarine are very similar in chemical composition). Specifically, it seems that sulphur, which is one of the constituents of the colour, has been moving out of the pigment molecules, resulting in fading. Certainly, most colour chemists would have struck occasions where they have observed sulphur off gassing from formulations, which smells very unpleasant. Clearly, this is a space to watch.

It would be remiss of me not to add in Yves Kline blue here — if only for completeness of the story. Kline’s blue was just artificial ultramarine which was underbound — namely, presenting too much pigment and not enough binder — which gave a striking finish extremely rich in colour and texture, which is how the raw pigment presents. However, it does not take much of an imagination to work out what happened to those works: by producing a coating that did not have enough binder, the resulting colour was not going to hold on well. This still happens today, as there can be found more than one story of gallery staff coming in each day to find more ultramarine pigment on the floor to be cleaned up below a Kline artwork.

#### *Indanthrone blue — PB22 and PB60*

Indanthrone blue (PB22 and PB60, also known as indanthrene blue), was first patented in 1901 by Rene Bohn. It belongs to

<sup>4</sup> See Mertens (2004) for details of this rivalry. [Ed.]

the class of pigments described as “vat pigments.” It is a very red shade, ranging from blue to indigo pigment. However, due to the high cost relative to the artificial ultramarine pigments, uptake and use have been limited.

#### *Phthalocyanine blue — PB15*

Phthalocyanines were discovered in 1907 by Braun and Tchermiac in London. Without understanding the importance of their finding, they noted the results, but did not follow them up. Then, in 1927, the Swiss chemists Von der Weid and de Diesbach (no relation to our Prussian blue inventor that I could find) accidentally obtained a form of copper phthalocyanine whilst trying to produce phthalonitrile. Then, in 1928, at Scottish Dyes Ltd., iron phthalocyanine was found as an impurity during the preparation of phthalimide, a fine white solid produced by reacting phthalic anhydride and urea. A crack was spotted in one of the glass linings of the reactors which was leading to an unwanted blue impurity in what was supposed to be a whiteish end product. The Scottish dyers had the foresight to follow through and find out what was going on. With experimentation, they produced iron phthalocyanine, and, in 1929, Scottish Dyes was granted a patent for the preparation of phthalocyanine produced from phthalic anhydride, a metal salt and ammonia.

Since then, several phthalocyanine variations have been produced on various metals, together with a metal-free version, the most popular being the green tone based on copper, which is used across many industries, as it is very lightfast, incredibly strong in tint strength and very stable in formulations. It is worth noting that while at present there are many producers around the

world, this type of blue was first marketed by ICI in 1935 under the name Monastral blue, which is still available today.

#### *Manganese blue — PB33*

A synthetic green-blue pigment is formed “when an aqueous solution of permanganate of potash yields, with baryta-water, a violet mixture which afterwards becomes colourless and deposits a blue precipitate.” (Eastaugh et al. 2004, p.44). This was first mentioned in the late 1800s. Manganese blue only became commercially available in the 1930s when IG Farbenindustries AG patented it in 1935. However, its production appears to have been phased out in the 1990s probably due to the higher cost when compared to other pigments on the market, such as cobalt and phthalocyanines. Furthermore, it contained barium and was deemed to be toxic. Therefore, at present, any artist-paint manufacturer who offers the colour produces a blend to arrive at the same hue.

#### *Fluorescent blue*

Although most artists do not use fluorescent pigments due to their fugitive nature, I will mention them here for completeness and because how they were developed is an interesting story. In the summer of 1933, Rob Switzer had taken a summer job before he started medicine at UC Berkeley. In a terrible twist of fate, he suffered an accident which saw him spend a prolonged period in hospital, followed by doctor’s orders to rest in a dark room. Rob and his brother Joe had a love of magic: during Rob’s time of convalescing confined to darkened rooms, he and Joe found that their parents’ pharmacy provided an Aladdin’s cave of compounds that glowed under black light, which gave

them the idea to enhance their magic show with the addition of fluorescent costumes, which earned them a prize for best illusion at a magicians' convention in Oakland. Rob and Joe were to go on and build the company now known as Day-Glo Color Corp., and in 1957, they were awarded a patent to produce the first commercial fluorescent pigment.

As early as 1944 artists started using fluorescent colours, which were dyes and not very stable (De Winter 2010); however, they became more popular in the 1960s as they became commercially available in more stable paint forms. Blue was not one of the first fluorescent colours developed but did start appearing in catalogues for fluorescent pigments by the late 1960s.

#### *Pearlescent, Iridescent and Interference blue*

Pearlescent pigments are made by coating mica with metal oxides and titanium dioxide and may contain other blue pigments. The pearlescent pigment does not contain any pearl but rather has a lustre similar to that of a pearl that gives it its name. The colour, however, can be considered to be homogenous. This is in contrast to iridescent blue pigments which are produced in a similar way yet appear to the observer to “change” colour around a limited spectrum. Interference colours go one step further and tend to emit two definite homogenous colours, depending on the angle of view.

In each of the above cases, the observer sees colours which are developed through the result of interference between rays of light. The light is reflected off the top and the bottom of particular layers (platelets or flakes) within the pigment, which collide or combine to form particular colours. The

angle at which the pigment is viewed will dictate what colour is observed.

“The development of pearlescent pigments only started in the 20<sup>th</sup> century using mercury and arsenic salts, but there were no substantial advancements until the invention of mica coated with metal oxides in 1963. From that point onward, new discoveries were made in this field, as the production of aluminium-based pearlescent pigments in the 1990s.” (Rossi and Russo).

#### *Mayan blues — PB82 and PB84*

A fairly recent addition to the modern range of pigments, the MayaCrom and MayaPure blues (PB82 and PB84) are a recreation of an ancient blue pigment composed of palygorskite clay and indigo which was used by the ancient Mayans throughout Mesoamerica between the 6<sup>th</sup> and the 8<sup>th</sup> centuries. Research has shown it to be very stable when exposed to acids, alkalis, and chemical solvents. Artefacts recovered from a well at Chichen Itza along with over 100 skeletons gave further weight to the theory that Maya blue was an essential colour in Mayan culture. It is believed that, at some time in the Mayan history, blue was produced by burning incense, which was found to contain palygorskite and indigo, during sacrificial ceremonies and applied to the sacrificial victims just before their still-beating heart was cut out and they were thrown into the well as an offering to the rain god (Arnold et al. 2008).

Using multiple modern analysis techniques, the chemical makeup of the blue was discovered and then recreated by a group at the University of Texas around 2006. Unfortunately, it seems at writing, the company that was to commercially produce the pigments is now defunct. I have formulated

artist colours on these recreated pigments, and while they are generally not as strong as other synthesised pigments, such as the phthalocyanines, they do have a wonderful hue for painting. Formulating can be a tedious process and takes time as they are based on clays and time needs to be given to wet these out sufficiently to avoid post-thickening.

### *Yin Min blue*

In 2009 the discovery of Yin Min blue, the first truly new blue pigment in two centuries, was the result of a happy accident in the research for new materials that could be used in electronic applications. In the course of research by an Oregon State University team led by chemistry professor Mas Subramanian, his then-graduate student Andrew E. Smith took manganese oxide mixed with other compounds — yttrium (Y) and indium (In) — and heated it at high temperatures to test for structure. They noticed that one of their samples turned out into a very vivid brilliant blue colour. Despite not being specifically developed for artistic purposes, the characteristics of this newly created inorganic pigment undoubtedly make it possible for it to have applications in art.

One of the most remarkable structural characteristics of this pigment is that it absorbs red and green wavelengths of light while at the same time only reflecting the blue wavelengths in the light spectrum. This new inorganic pigment has been described as an intense blue colour with high solar radiation (IR) reflecting properties. As has been observed, the resulting vibrant blue appears to be very durable, and its core compounds are said to be so stable that “the colour does not fade” (Subramanian 2018). The initial application and use intended for

this pigment may concern a variety of commercial products, such as paint coatings for buildings and roofs. Specifically, the coat of paint would help to keep buildings cool by reflecting infrared light.

In artistic terms, Yin Min blue (or YInMnBlue, as it is quoted in research notations) has a brilliant, almost shimmering look with a, maybe, very slight red undertone. Research notes from evaluation testing of samples indicate a higher optical reflectance (vividness) than other blues in the colour spectrum due to the compounds in the structure of the pigment particles. Another crucial factor to consider, and in direct relation to health and safety, is that none of this pigment’s compounds is toxic, which cannot always be said for copper or cobalt. Yin Min Blue has just as vivid an appearance, providing an alternative to ultramarine blue with the added benefits of refracting infrared wavelengths, which makes it highly lightfast, in archival terms, with no toxic compounds — specifically, a very safe pigment to use either in paint form or dry. Yin Min has gone through initial approval in the US to be used in artist paints only in bound form in July 2020.<sup>5</sup>

### Forthcoming blues?



Quantum blue

### *Deepwater blue*

Presently, I have no more information than the one referenced below from Ruth Siddall’s article; however, I have made contact with Professor Dobson and, on his return from hiking in Scotland (whilst socially distancing I am sure), I hope to find out

<sup>5</sup> To read further, see Kupferschmidt (2019). [Ed.]

more about his discovery, however I find this quote from a recent article very exciting. “Here in UCL Earth Sciences, we are attempting to develop synthetic structures which mimic the unusual ferric iron structure of ringwoodite but which are stable at atmospheric pressure. So far we have shown that we can make blue pigments from iron-bearing oxides and are now investigating how much  $\text{Fe}^{3+}$  the structures can take before they become unstable. That will determine just how blue we can make them. The prospects are bright ... blue.”

#### *Phototonic blue*

The concept of phototonic colours, a colour produced through the modulation of light pigments a form of structural colours, is not new; as discussed previously, the way we see the sky is a form of structural blue. Birds, insects and flowers have been using this form of colouring forever — the wings of the morpho butterfly being a perfect example of a bright blue caused by light diffraction, which is the bending of light rather than generation or absorption and reflection or generation or reflection. The latest iteration of this exciting method of producing colour has been reported in 2019 as taking place at Wageningen University in the Netherlands where they have produced photonic pigments, which they refer to as suprapigments — free-standing water-dispersible spheres entirely made of silica, an abundant, (photo)chemically stable and non-toxic material, with an ordered, macroporous structure that interacts with incident light to endow the pigments with a colour. Theoretically, these colours should be very stable and very lightfast — an utter dream for formulators, artists and hopefully

conservators alike. In theory; they could be a real game changer!

#### *Quantum blue*

From his lecture at the Symposium on the History, Technology and Research of the Colour Blue at the Herakleidon Museum in Athens in 2019, Jason Hartlove, CEO of Quantum Dot Leader Nanosys put the question: “What if paint pigments could actively emit light instead of merely absorbing it? A new type of nanotechnology called Quantum Dots is changing the way artists work with colour and light. Quantum Dots are tiny nanocrystals — 10,000 times narrower than a human hair — that can be tuned to actively emit light at any colour in the visible spectrum. This exciting new material is enabling artists to explore a new mode of expression — painting with light. Light-emitting pigments open new artistic possibilities for unique colour combinations and surprising perceptual manipulation through additive light mixing.”

Artist Olga Alexopoulou is already working with quantum dots. It will be interesting to watch how quantum dots evolve over time and just how the artistic community will embrace and use them to create work we cannot probably even imagine at present.

#### **Conclusion**

Ancient or Modern blue pigments — one does not need to be a paint maker or an artist to appreciate how we see them or indeed the various ways they came into use. An understanding of the development of one of the three basic primary colours, however, is a window into human development over the ages. With hopefully more to come.

It seems that we are not at the end of the discovery of all things blue, but partway

along the course; therefore, next time you look up at a never-ending blue sky or across the vast plain of the ocean, your inner artist will realise that you are not really seeing blue ... or are you?

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