[please note that script in light grey will not be spoken but is left in the text for reference only – Below is the transcript for translation]

Blue is one big accident!

Pablo Picasso said "I don't believe in accidents. There are only encounters in history. There are no accidents"
In my home country of Australia - a blue or to make a blue is to make a mistake or have an accident. It might surprise you to learn that the invention or at least initial discovery for nearly all of our modern blue colourants were accidents?

Hello I am Steven Patterson a second generation colourman with Derivan in Australia here to talk to you about blue pigments from the 18th century to today, we will discuss how they were discovered and how colourmen, otherwise known as paint-makers like me, formulate on them.

PRUSSIAN BLUE
It was not until the very early 1700's that a purely synthesized pigment was recorded as having been made in what we know as Prussian blue
Swiss dye-maker Johann Jacob Diesbach, working in a friend Johann Conrad Dippels Berlin laboratory, was attempting to create Red Florentine lake, carminic acid extracted from cochineal, 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 Dr Alexander Kraft, who believes the most probably year of discovery was 1706, has pieced together more detail from several sources of letters and diaries from the time. Discovering that of one of Dippel's contemporaries, a younger friend Senckenberg, recorded that Dipple had told him on the subject of 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". Dipple'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 - and with his new found colour set about selling it to some local artists un-be-knowns to his friend Dipple – only to find once his source of what he thought to be potash ran out he could no longer make the colour – he reported his problem to Dippel who suggested he use the bovine blood with the potash.

It does make one consider that had Dipple not been aware of the mis-labelling of the jar and exactly what was in it, that the formula may have been lost OR had the jar been labelled correctly Diesbach may not have used it to begin with and may never have discovered Prussian blue and 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 it out in that time – how much longer may 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 were in a time where 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!

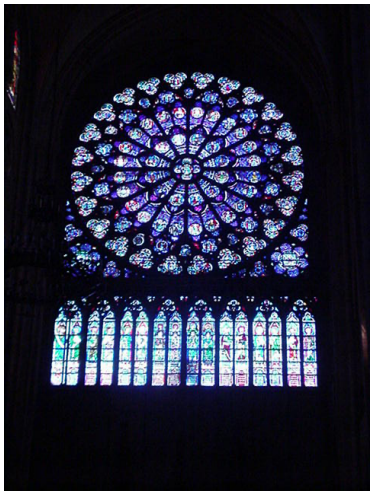
Working by daylight or candle light, a furnace was just that - with little or no idea as to the actual temperature an experiment was being heated to (the first mercury thermometer was not developed until 1714) Even under the most controlled conditions of the time many things were left to chance. One can imagine lab benches with little on them in the way of apparatus, sunlight filtered through smog coated windows 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 - without reading the instructions! And bang here is a brand new colour when you weren't even expecting it! So I guess it is not a surprise to learn Prussian blue was discovered by accident.

Prussian blue is not only interesting for the way is was discovered but also as it has played a role across so many industries, Probably best known for its use in the blue of blue prints,(mid 1800's) where a sheet of paper is coated with a mixture of ammonium iron citrate and potassium ferrocyanide. The original drawing (done on a thin paper like a tracing paper) to be copied is then laid on top of the coated paper and exposed to strong light. The light combines the 2 compounds producing Prussian blue in the exposed areas - the coated sheet is then washed and the unexposed areas show the colour of the paper through - the exposed areas are coated in the combined compound being insoluble Prussian blue. A far easier and more precise way to make copies than was the practice prior to that of tracing them by hand and even when carbon copies and copying machines were invented, large scale technical and architectural drawings were still reproduced 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 World Health Organization's List Of Essential Medicines those considered 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. En Garde!

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 that have come after it. It is a pigment today that can present some issues with flocculation in water-based systems if the correct dispersants are not used when formulating and is not as clean or brilliant as its successors, none the less it is still very much in use by artists and industry alike.

I started with Prussian blue because it really was the first synthesised blue. However the use of the element Cobalt as a colorant dates back to the 8th and 9th centuries when it was used to color ceramics and jewelry but as a colourant in paint it was not commercially produced for another century after Prussian blue - around 1807 in France (discovered in 1802).

It is the effect of cobalt in the now ubiquitous blue and white Ceramics from China, (although apparently early on the blue was seen as too ornamental for local tastes so was not used a great deal for local production but rather more for export).



The amazing blue stained glass that we see in churches and cathedrals across Europe owe their distinctive lightfast blue to cobalt which is funny when you consider that the substance cobalt is derived from the word 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 even lethal fumes. Considering their discovery a humbug they saddled it with the unflattering moniker.
This was around 1500ad. Happily nearly 200 years later a Swedish chemist, Georg Brandt, and professor 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, and separated the metal via fire assay, 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 far as a colorant in paint the early cobalt blue was actually glass containing cobalt (known as Smalt) – and this was ground and used as a colorant (smalt PB32) The earliest recording of its use has been found in paintings by Hans Holbein the younger (1497-1543) This blue smalt is not to be confused with that of the Egyptian's frit – who also used a ground, coloured glass however this derived its colour from copper (known as Egyptian blue PB31) rather than cobalt.
As a synthesized 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. While these discoveries are not recorded as having been an accident - I would certainly like to think they were at the least Surprised!

Cobalt blue is a favorite of Artists although more expensive than copper based blues. Tt gives a vibrant but opaque blue slightly leaning to the green bias and is very stable when formulating and lightfast in use. Used in normal good artist practice it is quite safe as most modern versions have no free soluble cobalt.

CERULEAN BLUE
As cobalt blue was being released to artists in the early 1800's a new blue was in development once again making use of cobalt - the compound originally composed of cobalt magnesium stannate (1789). In antiquity, the word caerulum was used to describe blue pigments in general, particularly mixtures of copper and cobalts, (the main chemicals in azurite/malachite and smalt).Cerulean blue was perfected by a process developed by Andreas Höpfner in Germany in 1805 that roasted cobalt and tin oxides together. However the color only appears available to artists in a catalogue from the 1860's under the name of coeruleum. Cerulean blue is an inert, lightfast pigment that can act as a drier in oil paints. It is quite stable in both water colour and acrylic and is referred to as PB35 cobalt Stanate. PB36 which is a cobalt Chromate also used and sold as Cerulean blue for those who prefer a slightly greener/cooler hue.

ARTIFICAL ULTRAMARINE

So now we have a bit of a throwback in our timeline! - Artificial Ultramarine Blue. The original ultramarine blue made from Lapis lazuli - (Italian Oltremarino - Ultra- beyond, marine -sea) so called as the lapis was transported from Afghanistan literally "beyond the seas" from a euro centric perspective of course! -was originally employed by the venerable Egyptians in solid form for ornamental use in jewelry but there is no record of them having successfully formulating it into a paint,(this was left to the clever Italians many centuries later) - however due to its process of collection and moreover its process of "manufacture" a series of manual kneading, washing and filterings it proved to be a very expensive pigment. And there are many stories of well known artists not finishing pictures or saving their tiny amounts of Ultramarine for the final application and only on very important icons. I have made paint on very high quality lapis and while it is very romantic to produce - it is still very weak in comparison to what was to come and vastly expensive to produce still!

Finding a way to make artificial ultramarine assured its inventor of fame and fortune - and even with the promise of fame and fortune it was still a long time till the birth of Artificial ultramarine blue! Sir Arthur Church recorded "In the year 1814 a blue coloration, subsequently proved to be due to ultramarine, was noticed in the soda (blackash) furnaces of St. Gobain"(there we go - by accident again!). it was not until 1824 when the Societé d'Encouragement offered a reward of six thousand francs to anyone who could develop a synthetic alternative to ultramarine that it was born. But 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 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 prior but—like Gmelin—had opted not to publicize his findings. The committee awarded the prize to Guimet, and the artificial blue became known as "French ultramarine."

This new method of production was based in part upon chemical analyses of natural ultramarine, and in part on a study of the conditions which produced the first observed accidental manufacture at St Gobain. So the 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. Ultramarine blue is a soft pigment that quite often does not need much milling to disperse into a paint formulation. It is a non toxic pigment with generally accepted good lightfastness - however more recently research during restoration of Michelangelo's work in the Sistine chapel is throwing some doubt on the lightfastness of Lapis lazuli in oil paint (Lapis blue and ultramarine are very similar in chemical composition) 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 in my experience there

has been times with some ultramarine pigments that I have observed Sulphur off gassing of formulations. They smell very unpleasant. Clearly this is a space to watch

INDANTHRONE BLUE
Indanthrone Blue. PB22 and PB60 (also known as Indanthrene Blue) is first patented in 1901 by Rene Bohn. It belongs to the class of pigments described as “vat pigments”. It is a very red shade, non-bronzing, flocculation resistant blue to indigo pigment However due to the high cost relative to the artificial Ultramarine pigments, uptake and use has been limited. (and disappointingly no accidents either)

PHTHALO BLUE
Phthalocyanine blue PB 15
{According to an article in Paint and Coatings magazine (Jan 2005)} - the word Phthalocyanine is said to be from phthalo from naphtha (meaning oil) and cyanine meaning blue sounds a bit dubious to me - but there you go :
Phthalocyanines were discovered first in 1907 by Braun and Tchermiac in London, without understanding the importance of their finding they noted the results but did not follow it up, then in 1927 by the Swiss chemists Von der Weid and de Diesbach (no relation to our Prussian blue inventor), who obtained a form of copper phthalocyanine whilst trying to produce phthalonitrile (accidentally), Then again in 1928 by Scottish Dyes Ltd., where iron phthalocyanine was found as an impurity during the preparation of phthalimide. Phthalimide, a fine white solid produced by reacting phthalic anhydride and urea. It was found that one of the glass-linings of the reactors had a crack in it and this was leading to an unwanted blue impurity (accidental) - in what was supposed to be a whiteish end product. At least the Scottish dyers had the foresite to follow through and find out

what was going on! With experimentation they produced Iron Phthalocyanine and In 1929, Scottish Dyes were granted a patent for the preparation of phthalocyanine from phthalic anhydride, a metal salt and ammonia

Since then several Phthalocyanine variations have been produced on various metals (and a metal free version) however the most popular of this most popular pigment is the Green tone based on copper, it is used across many industries as it is very light fast incredibly strong in tint strength and very stable in formulations

(it is worth noting that while now days there are many producers around the world it was first marketed by ICI in 1935 under the name monastral blue and this is still available today)

MANGANESE BLUE

A synthetic green blue pigment was 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" first mentioned in the late 1800's Only becoming commercially available in the 1930's {when IG Farbenindustries AG patented it in 1935} - however production appears to have been phased out only recently in the 1990's due it seems to the cost vs other pigments on the market such as cobalts and phthalocyanines, together with the fact that it contained barium and was deemed to be toxic. Therefore now days any artist paint manufactures who offer the colour make a blend to arrive at the same hue.

MAYAN Blues

A fairly recent addition to the modern range of pigments of a very old colour The MayaCrom and Maya Pure blues - PB 82 and PB 84 is an ancient blue pigment composed of palygorskite clay and indigo. It was used by the ancient Mayans throughout Mesoamerica. Research has shown it to be very stable to acids, alkalis, and chemical solvents.

Using multiple modern analysis techniques The chemical make up of the blue was discovered and then re-created by a group at the university of Texas around 2006. Artist colours have been formulated on these re-created pigments and while they are generally not as strong as other synthesized pigments such as the phthalocyanines they do have a wonderful hue for painting. They are a little tricky to formulate on as they are based on clays and of course time needs to be given to wet these out sufficiently so as to avoid post thickening.

YIN MIN

While I could talk all day about this fantastic colour, we are very lucky to have the inventor, Dr Mas Subramanian of Oregon State University here to talk about his discovery and you will hear from him shortly - I will let you know that it is a colour that from a colourmans perspective is very easy to formulate around, is very stable and we at Derivan were the first to produce an artist paint on this pigment. - and I am sure I am not stealing his thunder - to let you know that again this brilliant blue was discovered by accident!

For those of you who are counting we are nearly at the present day!

2 blues left

PHOTOTRONIC

The concept of Phototonic pigments or Structural colours is not new,the wasy we see the sky is a form of structural blue. Birds, Insects and flowers have been using this form of colouring for ever - the wings of the Morpho butterfly being a perfect example of a bright blue caused by light defraction - the bending of light rather than generation or absorption/reflection. The latest iteration of this exciting method of producing colour has been 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 made entirely of silica, an abundant, (photo)chemically stable and nontoxic material, with an ordered, macroporous structure that interacts with incident light to endow the pigments with a color. Theoretically these colours should be very stable, very lightfast - an utter dream for formulators, artists and hopefully conservators alike!

QUANTUM BLUE

Last but certainly not least is Quantum Blue...So it seems after all this talk of accidental discoveries we'll close with this stunning new color whose discovery was definitely not an accident. Quantum Blue was conceived within the imagination of an artist and is intentionally being brought to life by the will and passion of that same artist and her devoted colleagues.

Once again we have an expert, Maria Chatzidakis, who will explain far better than I how Quantum blue came about and just what it is - however I will quickly describe how we have been working with the aforementioned Artist and inventor, Olga Alexopoulou, in developing a commercial version of the colour Quantum blue. Quantum blue does not have a very long life as a colour in an artwork - months at best - In fine art as a general rule, a picture is expected to last for many many decades if not centuries. Therefore we have been working with Olga to manufacture a colour that matches that of the quantum blue that will have a significantly longer life. While modern communications have been able to reduce the time in the process - ultimately we are still limited to having to send

samples from Australia to Greece for Olga to test them. However I am pleased to say we are pretty well there

As for next Blue to be discovered... Well that sounds like an accident waiting to happen! and your next speaker, Dr Subramanian would know better about that than most!!!!.

With thanks to :
Hazel Reyes
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and Countless websites!