Chapter 4
Meet the Future: The Creation of New Pigments

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4.1 Introduction

In the world of colour science, the creation of new pigments is extremely rare, but in the beginning of the twenty-first century chemists were successful in discovering four pigments. The synthetic inorganic yellow pigments rutile tin zinc oxide and niobium tin pyrochlore can be of special interest to replace the chrome yellows (PY 34) and cadmium yellows (PY 35) in the near future. The pigment YInMn blue was discovered accidentally and could be an alternative to the existing blue inorganic pigments, because the properties of this modern blue pigment are much more durable. The most recent discovery is Vantablack, whose use as an artists' paint will be very limited, due to its limited availability and extraordinarily high price.

As these pigments are hardly described in the published literature, this article has been compiled on the basis of numerous websites; the most important ones are cited in the text. This contribution is meant to be a follow-up on two articles published by the author on twentieth century synthetic inorganic [5] and synthetic organic artists' pigments [6].

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4.2 Chrome- and Cadmium Yellows: Legislation, Prohibition and Alternatives

Stable yellow and orange-yellow pigments are highly valued in the art world. Environmental and health concerns, market demands and regulating requirements have placed increasing pressure on some pigment groups to find alternatives, especially for the chrome – and cadmium yellows.

The toxicity of the element lead and the carcinogenicity of hexavalent chromium are of particular concerns for the chrome yellows. For several decades the use of chrome yellows (PY 34) has not been permitted in artists' pigments, in coatings for toys and consumer goods, including food contact applications and packaging and have been labelled as 'only for industrial purposes'. Since 2015 its industrial production and use has ceased worldwide.

Yellow pigments with a high chromaticity are made from cadmium sulphide (PY 35). Since the 1980s the use of cadmium in containing consumer goods has been forced back. In 1981 Sweden prohibited the use of the cadmium pigments for ecological reasons and around 1990 the European Committee and Switzerland banned them for their main use, the colouring of plastics. As a result, many industries have cut down or entirely eliminated the use of these colorants. Even in the automobile industry their use declined. In the industry the yellow, orange and red cadmium pigments have already been largely replaced by synthetic organic pigments discovered in the second half of the twentieth century, like the perylenes, quinacridones, diketopyrrolo-pyrroles, the improved Hansa-Yellows and benzimidazolones. These synthetic organic pigment groups offer suitable alternatives, because their properties are sufficiently similar to cadmium pigments in some respects, and even superior in others [6, 8].

For artists' colours and ceramic products the cadmium pigments are still permitted. Only 5–7% of the total cadmium pigment production is used in the manufacture of artists' materials. If these trends continue, application of cadmium pigments in artists' colours will become difficult, and may be impossible due to the lack of availability [1]. However, substitutes for the pigment for use in artists' paints have recently become available.

4.3 Substitutes for Cadmium Pigments in Artists' Paints

The orange and red diketopyrrolo-pyrroles (DPPs) (PO 71, PO 73, PR 254, PR 255, PR 264, PR 272), discovered in the early and produced in the middle of the 1980s, are suitable alternative options for the cadmium reds (PR 108) and cadmium oranges (PO 20) as artists' pigments. They possess excellent properties, but disadvantages are their transparency and their high price. However, after the expiration of the first DPP patent in 2004, several products of European and Asian competitors caused a drop in prices since.

Substitutes for the cadmium yellows are harder to find. The synthetic inorganic yellow pigment bismuth vanadate (PY 184), introduced to the artists´ palette in the middle of the 1990s, is a candidate, but due to the toxicity of the metals bismuth and vanadium it offers little benefit over the cadmium yellows.

A potentially good substitute is from the synthetic organic pigment group of improved Hansa-Yellows, namely Permanent Yellow GX (PY 74), discovered in 1957. Its hue is between cadmium yellow light and cadmium yellow medium and has a relatively high opacity and an excellent light-fastness.

The best alternative nowadays seems to have been the synthetic organic pigment Benzimidazolone Yellow H3G (PY 154). Since it entered the pigment market in 1975, its use is reflected in many international artists' paint catalogues. The only disadvantage is its high price.

4.4 New Developments in the Twenty-First Century

Still, there is need for yellow substitutes that meet the colour characteristics of both (lead) chromate and cadmium yellows. Two developments in the inorganic pigment field can be of interest in replacing these pigments, the first one is the recent commercialization and improvement of the rutile tin zinc oxides (PY 216 and PO 82). The other is the new patented complex inorganic colour pigment class of yellow pigments named niobium tin pyrochlore (NTP). NTP Yellow (PY 227) has recently gained the regulatory approval for commercial sale.

4.5 Rutile Tin Zinc Oxides (RTZ)

Rutile tin zinc oxide is a mixed crystal compound of oxides of titanium, tin and zinc with the chemical formula $(Sn,Zn)Ti_xO_y$. Synthetic oxide pigments containing two or more different metals are named *complex inorganic colour pigments* (CICPs). Coloured pigments are created by substituting titanium atoms in the rutile crystals with different metal atoms. The discovery of the CICPs dates back to 1934. Nickel titanium yellow (PY 53) and chrome titanium yellow (PBr 24), are the most important pigments of this class [23].

Rutile tin zinc oxide (PY 216) was developed in the 1980s. This yellow complex pigment was patented by the chemists John Ward Jenkins and John Wolstenholme of the British Johnson Matthey Public Limited Company (see Table 4.1). In 2003 this firm, now called Rockwood Pigments, introduced three yellow pigments under their trade name Solaplex®: Rockwood Solaplex® Yellow 34H1001R, Rockwood Solaplex® Mid Yellow 34H1002 and Rockwood Solaplex® Orange 34H1003.

In the period 2006–2010 improvements have been brought to the product class by increasing the colour from a red-shade yellow to a more orange hue. Recent modifications have enabled the achievement of a true orange shade (PO 82), such as

Table 4.1 Patents and applications of rutile tin zinc oxide

Yellow pigment	Discoverers and patents		Industrial production and *occurrences as an artists' paint*	
Rutile tin zinc oxide PY 216 Rockwood Solaplex® Yellow 34H1001R Rockwood Solaplex® Mid Yellow 34H1002 Rockwood Solaplex® Orange 34H1003	1984	John W. Jenkins, John Wolstenholme; Johnson Matthey Public Limited Company, Great Britain, U.S. Pat. 4.448.608, Colored inorganic complex for use as a pigment and compositions containing it	2003	Introduction to the pigment market by Rockwood Pigments, trade name: Solaplex®
	1987	John Ward Jenkins, John Wolstenholme; Johnson Matthey Public Limited Company, Great Britain, European Pat. 0.113.229, Farbiger anorganischer Komplex welcher als Pigment benutzt wird und Zusammenstellungen die ihn enthalten	2009	Yellow shades (PY 216) oil, watercolour paints Orange shades (PO 82)
Rutile tin zinc oxide PO 82 Rockwood Solaplex® 34H1004 BASF Sicopal® Orange L2430 Shepherd's RTZ Orange 10C341	1987	John Ward Jenkins, John Wolstenholme; Johnson Matthey Public Limited Company, Great Britain, German Pat. 3.373.488, Coloured inorganic complex for use as a pigment and compositions containing it	2009	*H. Schmincke & Company, Germany, Norma catalogue* *Chrome yellow hue light,* *Chrome yellow hue middle,* *Chrome yellow hue deep,* *Schweinfurt green hue*
	1987	John Ward Jenkins, John Wolstenholme; Johnson Matthey Public Limited Company, Great Britain, Austrian Pat. 29.511, Farbiger anorganischer Komplex welcher als Pigment benutzt wird und Zusammenstellungen die ihn enthalten	2015	*Winsor & Newton, UK, watercolour catalogue:* *Turner's Yellow hue*
	2006	Ghila Lanzendörfer, Heidi Riedel, Lynn Viehmeyer, Volker Kallmayer, Sophie Viala, Nicole Mocigemba; Beiersdorf AG, Germany, German Pat. 102005007467, Kosmetische Zubereitungen zur dekorativen Anwendung enthaltend anorganische Gelbpigmente auf der Basis von Titan-, Zinn- und Zinkmischoxiden	2016	*Kremer Pigmente, Germany, Hokkaido-Orange, PY 216*
	2006	Ghila Lanzendörfer, Heidi Riedel, Lynn Viehmeyer, Volker Kallmayer, Sophie Viala, Nicole Mocigemba; Beiersdorf AG, Germany, European Pat. 1.690.523, Kosmetische Zubereitungen zur dekorativen Anwendung enthaltend anorganische Gelbpigmente auf der Basis von Titan-, Zinn- und Zinkmischoxiden		
	2008	Norbert Mronga, Kirill Bramnik; BASF SE, Germany, WO 2008/083897, Pigments containing titanium, zinc, tin, rare earth and optionally alkali earth oxides		
	2009	Kirill Bramnik, Norbert Mronga; BASF SE, Germany, Chinese Pat. 101583567		
	2009	Norbert Mronga, Kirill Bramnik; BASF SE, Germany, European Pat. 2.125.622, Titan-, Zink-, Zinn-, selterend-, sowie wahlweise Erdalkali-Oxide enthaltende Farbkörper		
	2010	Norbert Mronga, Kirill Bramnik; BASF SE, Germany, U.S. Pat. 7.837.781, Colorants comprising tin and rare earth elements		

BASF's Sicopal® Orange L2430, Rockwood's[1] Solaplex® Bright Orange 34H1004 and Shepherd's Orange 10C341.

4.6 Properties and Applications of the Rutile Tin Zinc Oxides

The colours of the rutile tin zinc oxides are ranging from bright yellow to orange. The pigments possess an excellent light- and weather-fastness, a high colour strength and a high hiding power. They present an excellent chemical resistance, are extremely heat-resistant, being stable to c. 320 °C. The yellows are already established in road marking, interior and exterior architectural paints and suitable for food packaging and toys. The orange ones like BASF's Sicopal® Orange K2430 and Shepherd's Orange 10P340 are applied in plastics, outdoor applications, such as garden tools, patio furniture and playground equipment. BASF's Sicopal® Orange

[1] In 2014 Rockwood Holdings was bought by the Huntsman Corporation.

L 2430 and Shepherd's Orange 10C341 are especially recommended for coating and paint applications. The difference in these pigments lies most probably in the different surface treatments [15].

4.7 Rutile Tin Zinc Oxide in Art

The Solaplex pigments have already been introduced in the oil – and watercolour techniques as alternatives for the chrome yellows. Rutile tin zinc oxide (PY 216) has been listed in 2009 in the finest artists' oil colours catalogue Norma® of Schmincke as a substitute for different hues of chrome yellow. *Chrome yellow hue light* is made by mixing rutile tin zinc oxide with nickel titanium yellow (PY 53); *chrome yellow hue middle* and *chrome yellow hue deep* only contain the yellow RTZ pigment. Schmincke's *Schweinfurt green hue* is a mixture of rutile tin zinc oxide (PY 216) with cobalt blue (PB 28), cobalt green (PG 19), viridian (PG 18) and nickel titanium yellow (PY 53). Winsor & Newton uses rutile tin zinc oxide (PY 216) in their watercolour product *Turner's Yellow hue*. In 2016 the firm Kremer Pigmente puts PY 216 on their pigment list as *Hokkaido-Orange*, named after the orange Hokkaida pumpkin (*Cucurbita maxima*).

4.8 Niobium Tin Pyrochlore (NTP)

The most recent innovation in the yellow field is niobium tin pyrochlore (PY 227) with the chemical formula $Sn_2Nb_2O_7$. It is a mixed crystal compound of oxides of niobium and tin produced by high temperature calcination. Research in the early 1950s by the scientists W.R. Cook Jr. and Hans Jaffe raised interest in the pyrochlores [3]. Some niobates exhibit ferroelectric properties, but unfortunately the best one contains the element lead in the pyrochlore structure. Since the industrial use of lead poses environmental problems, it is of interest to replace this element by a less toxic one.

In 2000 the Portuguese chemists Cruz, Rocha and Pedrosa de Jesus of the University of Aveiro together with the French chemists Savariant of the CEMES-CNRS in Toulouse and Jumas of the ESA 5072 CNRS at the University of Montpellier attempted to replace lead by tin. Several lead niobates with the pyrochlore structure are known, while only two tin niobates $SnNb_2O_6$ and $Sn_2Nb_2O_7$ have been reported. Their research gave an insight into the synthesis, the structural characterisation of the tin niobates and that the colour of tin niobate, nominally $Sn_2Nb_2O_7$, can range from yellow to red depending on the Sn: Nb – ratio [4].

Between 2005 and 2010, Shepley Booth of the Johnson Matthey Public Limited Company together with Dann and O'Brien of the Loughborough University patented production methods of yellow to red hues based on a modified pyrochlore structure (see Table 4.2). However they had limited success by improving the products of the Portuguese and French scientists and they found it difficult to produce reliable coloured compounds.

In the U.S. patent 7.594.961 the chemists proposed and disclosed the use of this NTP class as a pigment and reported that the invention could be of importance for replacing the cadmium sulphides (cadmium yellows) or cadmiumsulfoselenides (cadmium reds and cadmium oranges). The pigments are particularly suitable for the coloration of glasses and plastics, but they can also be used in paints and inks.

Table 4.2 Patents and applications of niobium tin pyrochlore

Yellow pigment	Discoverers and patents		Industrial production and *occurrences as an artists' paint*	
Niobium tin pyrochlore PY 227 NTP Yellow 10C151	2005	Jonathan Charles Shepley Booth; Johnson Matthey Public Limited Company; Sandra Elisabeth Dann and Duncan Lee	2012	NTP Yellow has gained regulatory approval for commercial sale
	2006	John O´Brien, Loughborough University; Great Britain, WO 2005/052068, Inorganic Pigments	-	*Future: Replacing the chrome yellows and cadmium yellows*
	2007	Jonathan Charles Shepley Booth, Sandra Elisabeth Dann and Duncan Lee John O´Brien; Loughborough University Enterprises Limited, Great Britain, European Pat. 1.694.779, Inorganic Pigments		
	2007	Jonathan Charles Shepley Booth, Sandra Elisabeth Dann and Duncan Lee John O´Brien; Loughborough University Enterprises Limited, Great Britain, Chinese Pat. 1.954.036, Inorganic Pigments		
	2008	Jonathan Charles Shepley Booth; Henley-Upon-Thames; Sandra Elisabeth Dann and Duncan Lee John O´Brien; Loughborough, US 2007/0144402, Inorganic Pigments		
		Jonathan Charles Shepley Booth, Sonning Common; Sandra Elisabeth Dann and Duncan Lee John O´Brien; Loughsborough University, Loughborourgh University Enterprises Limited, Great Britain, German Pat. 602004011107, Anorganische Pigmente		
	2009	Jonathan Charles Shepley Booth, Sonning Common; Sandra Elisabeth Dann and Duncan Lee John O´Brien; Loughsborough University, Loughborourgh University Enterprises Limited, Great Britain, U.S. Pat. 7.594.961, Inorganic Pigments		
	2011	Simon K. Boocock; Shepherd Color Company, USA, Canadian Pat. 2.801.260, Tin Niobium Pyrochlore and Tin Niobium Oxide Pigments		
	2011	Simon K. Boocock; Shepherd Color Company, USA, WO 2011156362, Pigments substitutes à base d'oxyde double d'étain et de niobium		
	2011	Simon Boocock; USA, US 2011/0297045, Substituted Tin Niobium Pyrochlore and Tin Niobium Oxide Pigments		
	2012	Simon Boocock; Shepherd Color Company, USA, U.S. Pat. 8.192.541, Substituted Tin Niobium Pyrochlore and Tin Niobium Oxide Pigments		
	2012	Simon K. Boocock; Shepherd Color Company, USA, Australian Pat. 2011264994, Substituted Tin Niobium Oxide Pigments		
	2013	Simon K. Boocock; Shepherd Color Company, USA, Chinese Pat. 103097299, Substituted Tin Niobium Oxide Pigments		
	2013	Simon K. Boocock; Shepherd Color Company, USA, Korean Pat. 20130083431, Substituted Tin Niobium Oxide Pigments		
	2013	Simon K. Boocock; Shepherd Color Company, USA, European Pat. 2.580.163, Substituted Tin Niobium Oxide Pigments		
	2013	Simon Boocock; Shepherd Color Company, USA, Japanese Pat. 2013528156, Substituted Tin Niobium Pyrochlore and Tin Niobium Oxide Pigments		
	2014	Simon K. Boocock; Shepherd Color Company, USA, Spanish Pat. 2.522.215, Substituted Tin Niobium Pyrochlore and Tin Niobium Oxide Pigments		
	2015	Simon Boocock; USA, USRE 45382, Substituted Tin Niobium Pyrochlore and Tin Niobium Oxide Pigments		
	2015	Simon K. Boocock; Shepherd Color Company, USA, Japanese Pat. 5.778.264, Substituted Tin Niobium Pyrochlore and Tin Niobium Oxide Pigments		

In 2010, the chemist Simon K. Boocock of the American Shepherd Color Company came up with an alternative, slightly different from the original, which he called niobium tin pyrochlore (NTP Yellow). In 2012 the company covered the pigment NTP Yellow by a number of patents around the world (see Table 4.2). In the U.S. patents 7.594.961 and 8.192.541 production methods for niobium tin pyrochlore are described. The products range from yellow through orange to red.

4.9 Properties and Applications of NTP Yellow

NTP Yellow is a bright clean yellow similar in shade to the middle chrome yellows. The colour lies between bismuth vanadate (PY 184) and the orange version of rutile tin zinc oxide (PY 216) and is close to the redder shades of Benzimidazolone Yellow H3G (PY 154). It possesses a higher colouring power than nickel titanium yellow (PY 53) and chrome titanium yellow (PBr 24). NTP Yellow provides high chroma, opacity and durability, does not fade, is of excellent resistance to acids and alkalis, fast to weathering, chemically inert, heat resistant, stable to ultraviolet light, non-migratory and does not contain toxic and carcinogenic materials [16]. The Shepherd Color Company specifically developed NTP Yellow 10P150 for plastics applications, while NTP Yellow 10C151 is tailored for coatings and paints. Hopefully they provide viable replacements for the chrome yellows and cadmium yellows on the artists' palettes in the near future.

4.10 YInMn Blue

YInMn blue (PB 86) is a mixed crystal compound of oxides of yttrium, indium and manganese and its name – pronounced as yin-min blue – is derived from these three chemical elements. The chemical formula of the pigment is $YIn_{1-x}Mn_xO_3$ and is the result of the crystal structure, known as trigonal bipyramidal coordination. It is obtained when Mn^{3+} is introduced into the trigonal bipyramidal sites of the metal oxides [12, 17]. By varying the In: Mn – ratio the intensity of the colour can range from light to dark blue and black (see Table 4.3).

In 2009 a team of chemists, led by Professor Munirpallam A. Subramanian in the materials science laboratory at the Oregon State University (OSU) tried to find new materials with electromagnetic properties that could be used in electronics applications, such as computer hard drives. For one series of tests they mixed black manganese(lll) oxide with other chemicals and heated the grey mixture in a furnace to nearly 1200 °C. Instead of a new, high-efficiency electronic material one of the samples turned out to be a brilliant blue.

The scientists Subramanian, Arthur W. Sleight and Andrew E. Smith of the OSU patented the invention in October 2012 (see Table 4.4). The U.S. patent 8.282.728

Table 4.3 Different colours of YInMn blue

Composition	Colour
$YInO_3$	White
$YIn_{0,95}Mn_{0,05}O_3$	Sky blue
$YIn_{0,90}Mn_{0,10}O_3$	Bright blue
$YIn_{0,85}Mn_{0,15}O_3$	Bright blue
$YIn_{0,80}Mn_{0,20}O_3$	Bright blue
$YIn_{0,75}Mn_{0,25}O_3$	Royal blue
$YIn_{0,70}Mn_{0,30}O_3$	Royal Blue
$YIn_{0,65}Mn_{0,35}O_3$	Navy blue
$YIn_{0,60}Mn_{0,40}O_3$	Navy blue
$YIn_{0,55}Mn_{0,45}O_3$	Navy blue
$YIn_{0,50}Mn_{0,50}O_3$	Dark navy blue
$YIn_{0,25}Mn_{0,75}O_3$	Black
$YIn_{0,10}Mn_{0,90}O_3$	Black

Table 4.4 Patents and applications of YInMn blue

Blue pigment	Discoverers and patents		Industrial production and *occurrences as an artists' paint*	
YInMn blue PB 86 Blue 10G513	2012	Munirpallam. A. Subramanian, Arthur W. Sleight, Andrew F. Smith; Oregon State University, USA, U.S. Pat. 8.282.728, Materials with trigonal bipyramidal coordination and methods of making the same	2011	*Rebecca Shapiro: Purify*
			2011	*Rebecca Shapiro: Summers Eve*
	2015	Exclusive license between the Oregon State University and the Shepherd Color Company, USA	2015	*Madelaine Corbin: OSU Memorial Union Facade*
	2017	The Shepherd Color Company has received regulatory approval for commercial sale of YInMn blue, known as Blue 10G513	2015	*Carol Chapel: CaMas001*
			2017	*Derivan, Australia, Matisse acrylic paint: Oregon Blue*
			2017	*David Brinsden painted his guitar with Oregon Blue*
			2018	*Crayola LLC, USA, blue crayon named Bluetiful inspired by YInMn blue*
			2019	*Kremer Pigmente, Germany, YInMn Blau*

describes the synthesis, and the individual processes for the manufacture of YInMn blue, such as drying, mixing, pelleting and calcining.

Three years later, in 2015, the OSU reached an exclusive licensing agreement with the Shepherd Color Company for its industrial manufacture and since 2017 the blue pigment is commercially known as Blue 10G513 used in industrial coatings and plastics [13].

4.11 Properties and Applications of YInMn Blue

YInMn blue possesses unique characteristics, which makes it a special material for commercial companies and artists. The synthetic inorganic pigment has a brilliant blue colour, a high colour strength, a very good covering power and is non-toxic. The pigment is more durable than the existing blue inorganic pigments, as it is stable, lightfast, resistant to UV-light, organic solvents and has a good acid, alkali, and heat resistance.

One of the interesting characteristics of YInMn blue is that it reflects a large amount of infrared radiation. The pigment has an infrared reflectivity of about 40 percent, which is much higher compared to other blue pigments, such as synthetic ultramarine blue (PB 29) and cobalt blue (PB 28). The heat-reflecting properties indicate that the pigment is a suitable candidate for energy efficiency and contributes to energy savings. It can find use in a variety of exterior applications, like outdoor paints to paint roofs to keep buildings and cars cool [18].

4.12 YInMn Blue in Art

Before 2017 YInMn blue was not on the market as an artist's pigment, because the pigment had not received regulatory approval for commercial sale. Nevertheless, it has already found its way into the art world. Subramanian has sent out samples to artists, allowing them to experiment creatively with the vivid blue in various techniques, e.g. oil painting, watercolour and dry-point (a form of engraving). In 2011 Rebecca Shapiro used YInMn blue in her paintings *Purify* and *Summers Eve*. Four years later, in 2015, Madelaine Corbin applied it in many shades in her artwork *OSU Memorial Union Façade* and in the same year Carol Chapel made her art-object *CaMas 001* with YInMn blue using dry-point printing. In the aquarel *Mount Hood* by Rajeevi Subramanian except the white, all blue and black colours are derived from the YInMn blue family [2, 10]. Even for art restorers YInMn blue can be of interest, because while the colour is very close to synthetic ultramarine blue (PB 29) and cobalt blue (PB 28), the pigment is more durable, especially with regards to acid resistance.

One problem is the price of YInMn blue which is approximately six to seven times higher than the already expensive pigments cobalt blue (PB 28) and ceruleum blue (PB 35). This is largely due to the rare chemical element indium. The Shepherd Color Company offers test samples of YInMn blue at 10 US dollars per 10 grams. For small quantities, the price level is 1000 US dollars per kilogram.

In 2017 the Australian paint supplier Derivan was the first company in the world to make YInMn Blue commercially available to artists. Derivan named its new blue acrylic paint *Oregon Blue*. The Australian David Brinsden used the blue paint to adorn his handmade guitar. In March 2017 the firm Crayola LLC announced that the yellow Dandelion crayon will be retiring and will be replaced by a crayon inspired by YInMn blue. After a contest the new crayon became the name *Bluetiful* and is since 2018 available and expands the Crayola assortment in the USA. From early 2019, YInMn blue is also available by Kremer Pigmente GmbH & Co. KG. The blue pigment can be used in acrylic-, oil-, tempera-, watercolour and gouache techniques.

4.13 Vantablack

So called super-blacks, including Vantablack, consist of carbon nanotubes (CNTs). The discovery of the carbon nanotubes goes back to 1952, when the Russian scientists L.V. Radushkevich and V.M. Lukyanovich of the Physics and Ecology Department published transmission electron microscopy (TEM) images of 50 nanometer diameter tubes made of carbon in the Soviet Journal of Physical Chemistry. This discovery was largely unnoticed, as the article was published in the Russian language, and Western scientists' access to Soviet press was limited during the Cold War [14]. The most famous historical discoveries on the carbon nanotubes between 1952 and 1993 are listed in Table 4.5. In the period 1990–2010, extensive research on the CNTs led to tens of thousands articles.

Table 4.5 Patents and applications of Vantablack

Black pigment	Discoverers and patents		Industrial production and *occurrences as an artists' paint*	
		Discovery of carbon nanotubes		
	1952	L.V. Radushkevich, V.M. Lukyanovich; Physiscs and Ecology Department, Russia, Article: O strukture ugleroda, obrazujucegosja pri termiceskom razlozenii okisi ugleroda na zeleznom kontakte. *Zurn Fisic Chim* 26, 88 - 95, 1952		
	1976	M. Endo, A. Oberlin, T. Koyama; CNRS Orléans, France, Article: Filamentous Growth of Carbon Through Benzene Compostion, Journal of Crystal Growth 32, 335 - 349, 1976		
	1979	J. Abrahmson, P.G. Wiles, B.L. Rhoades; Department of Chemical and Process Engineering, University of Canterbury, Christchurch, New Zealand, Abstract in proceedings of the 14th Biennial Conference on Carbon, June 1979, Reprinted in Carbon 37, 1873 - 1874, 1999		
	1991	S. Iijima; Fundamental Research Laboratories, Nippon Electric Company Corporation (NEC), Miyukigaoka, Tsukuba, Japan, Article: Helical Microtubes of Grahitic Carbon, Nature 354, 56 - 58, 1991		
	1993	S. Iijima, T. Ichihashi; Fundamental Research Laboratories, Nippon Electric Company Corporation (NEC), Miyukigaoka, Tsukuba, Japan, Article: Single-shell carbon nanotubes of 1-nm diameter, Nature 363, 603 - 605, 1993		
	1993	D.S. Bethune, C.H. Kiang, M.S. de Vries, G. Gorman, R. Savoy, J. Vazquez; IBM Almaden Research Center, San Jose, USA, Article: Cobalt-catalysed growth of carbon nanotubes with single-atomic-layer walls, Nature 363, 605 - 607, 1993		
Vantablack Vantablack Vantablack 2.0. Vantablack S-VIS		**Discovery of super blacks, including Vantablack**	2010	*Frederik De Wilde: Hostage, use of NASA's black coating*
	2007	John Hagopian; National Aeronautics and Space Administration Goddard Space Flight Center, Greenbelt, USA, start of the experiments with carbon nanotubes	2010	*Frederik De Wilde: Nanoblack-Sqr#1, use of NASA's black coating*
	2008	Shawn-Yu Lin; Rensselaer Polytechnic Institute, Troy, USA, claiming to have made the blackest black	2014	Surrey NanoSystems Ltd., Newhaven, UK, start of producing Vantablack
	2009	Sembukutiarachillage Ravi Silva, Ben Paul Jensen, Guan Yow Chen; Surrey Nanosystems Limited, Great Britain, U.S. Pat. 2009/0061217 A1, Nanostructure production methods and apparatus	2014	Presentation of Vantablack during the Farnborough International Air Show
	2010	Ben Poul Jensen, Guan Yow Chen; Surrey NanoSystems Ltd., United Kingdom, UK Pat. 2.467.320, Providing gas for use in forming a carbon nanomaterial	2014	*Anish Kapoor starts to use Vantablack*
		Ben Jensen; Surrey Nanosystems Limited, United Kingdom, UK Pat. 2.478.269, Nanomaterials growth system and method	2015	Increase in production of Vantablack due to orders from the military and aerospace
	2011	Ben Poul Jensen, Guan Yow Chen; Surrey NanoSystems Ltd., Great Britain, U.S. Pat. 2011/0311724 A1, Providing gas for use in forming a carbon nanomaterial	2016	Surrey NanoSystems Ltd., Newhaven, UK, start of producing Vantablack 2.0.
	2013	National Physical Laboratory, Enersys' ABSL Space Products Division and Surrey NanoSystems, Great Britain, change in th production process from silicon to aluminium	2016	Surrey NanoSystems Ltd., Newhaven, UK, start of producing the spray-on version Vantablack S-VIS
	2016	Sembukutiarachillage Ravi Silva, Ben Poul Jensen, Guan Yow Chen; Surrey Nanosystems Ltd., Great Britain, U.S. Pat. 9.334.167 B2, Nanostructure production methods and apparatus	2016	*Anish Kapoor secured the exclusive rights for the artistic use of Vantablack*

The search for 'world's blackest black' started in 2007, when a team of ten technologists, led by the physicist John Hagopian, at the NASA Goddard Space Flight Center in Greenbelt, Maryland, USA, attempted to develop a super-black coating for aerospace applications by nanotechnology. In 2010 the team succeeded in growing CNTs for stationed optical instruments in space. A breakthrough was the discovery of a method to grow CNTs on a catalytic layer of iron to heat-resistant materials such as silicon, diamond and sapphire. This material was heated in an oven to 750 °C introducing a carbon-containing gas to form the CNTs. In 2014, a first sample of NASA's super-black nano coating was sent to the International Space Station to test its resistance to the harsh space environment.

Unbeknownst to the NASA group, the New York-based Rensselaer Polytechnic Institute (RPI) had initiated a similar effort. RPI announced in 2008 the development of the darkest carbon nanotube-based material ever made by its researchers professor Shawn-Yu Lin et al.. The material had a reflection of 0.045 percent and the Guinness World Records acknowledged the material as the ´blackest black´.

After a few years the technology company Surrey NanoSystems Ltd. (SNS Ltd.) in Newhaven, Great Britain, introduced a new and better manufacturing process, developed by Ben Jensen and his technical department technical department. The new process entailed a high-tech chemical vapour deposition (PECVD) at a relatively low temperature, patented in 2010 and 2011 (see Table 4.5) following this development, a two-year research program (2012–2014) to create a super-black for space applications led to the development of Vantablack in December 2013. In the summer of 2014, SNS Ltd. announced that it had transferred its low-temperature manufacturing process from silicon to aluminium structures [21].

The Vantablack name is trademarked by SNS Ltd. and this complicated production process is registered by several British and American patents (see Table 4.5). The term VANTA comes from the words **V**ertically **A**ligned **N**ano**T**ube **A**rrays and was mentioned for the first time in an article published in 2012 [20]. Vantablack was launched at the 2014 Farnborough International Air Show and first orders were delivered in July 2014. In the following year the production was scaled up for the aerospace and defence sectors. In March 2016, improvements in the process allowed for the introduction of the even darker Vantablack 2.0. In the same year, the coating became also available in a spray-on version, namely Vantablack S-VIS.

The coating is not available to individuals. SNS Ltd. restricted the use of Vantablack exclusively to selected institutions. Only verified companies, research facilities and educational institutions can order a sample of Vantablack. Press releases from SNS Ltd. emphasized that Vantablack has a minimum reflection of 0.035 percent. Although the difference with RPI nano-black is small, soon, Guinness World Records officially announced: Vantablack is the new blackest black.

4.14 Properties of Vantablack

In addition to its exceptionally high light absorption 99.965 percent of light at 750 nm, Vantablack possesses a number of other excellent properties according to the manufacturer. Vantablack is extremely light and hydrophobic. When submerged in water, its optical properties are not influenced. The material has the highest thermal conductivity and conducts heat seven times more effectively than copper and has ten times the tensile strength of steel. Further, it has virtually undetectable levels of outgassing and particle fallout.

It has an exceptionally high degree of elasticity and is robust against heavy mechanical shocks, loads, long-term vibrations and exposure to high vacuum. It has also a very high thermal shock resistance. Extreme changes in temperature (temperature cycling) (in liquid nitrogen from −196 °C to +300 °C) do not affect the Vantablack properties. Vantablack appears to be sensitive to touch and scratches, but the coating adheres well to the substrate [19].

4.15 Other Applications of Vantablack and Vantablack S-VIS

Vantablack has interesting potential applications in a number of fields ranging from aerospace and military sectors to design. The material was originally developed to increase the sensitivity of precision optical systems, such as optical satellites, imaging and calibration systems for earth observation. The super-black coating is particularly effective in the coating on the inside of telescopes absorbing stray light and obtaining a sharper image.

Further on, the application of Vantablack may be of interest for scientific instruments, such as infrared cameras and sensors. Due to its unique physical and optical properties, the product can be used for cinema projectors and lenses. Aesthetic effects can be obtained for luxury products and design goods, such as watches, jewelry, dashboard displays and smartphones. The ability to absorb light and to convert it into heat is also important for collector elements in solar energy systems, which leads to the creation of more efficient solar panels and solar cells.

Its light absorbing properties make Vantablack applicable for stealth applications for the military in e.g. aircraft, helicopters, and armoured vehicles as well as thermal camouflage, making uniforms appear virtually invisible during nighttime.

The spray-on version Vantablack S-VIS is particularly suitable to cover larger surfaces and complex three-dimensional objects. The main condition is that the surface of the material to be sprayed is resistant to temperatures up to 100 °C, which means that this super-black coating is also suitable for polymers and composite materials.

4.16 Artists' Use of Super-Black Pigments

4.16.1 Frederik De Wilde

The super-blacks not only aroused interest in science, aerospace and defence, but also in the art world. NASA's coating was so black that it attracted the interest of the Belgian artist Frederik De Wilde, who persuaded the NASA group to allow him to use their super-black coating in some of his projects, such as 3D printed sculptures, in the works *Hostage* (2010) and *Nano Black-Sqr # 1* (2014). After the discovery of Vantablack, De Wilde also approached the firm Surrey NanoSystems Ltd. with a proposal for artistic collaboration. However, the company refused, because it had already signed an exclusive agreement with the British-Indian artist Anish Kapoor [7, 22].

4.16.2 Anish Kapoor

Since the summer of 2014 the artist Anish Kapoor has been working with Vantablack. In the beginning of 2016 he secured, for a very high amount of money, the exclusive rights for the artistic use of Vantablack. This led to a great outrage among a number of artists, such as the Belgian Frederik De Wilde, the British Christian Furr and Stuart Semple and the British-Indian Shanti Panchal. They think that Kapoor has given a monopoly on a material which he did not discover and/or patent, so actually it should belong to everyone. Furr, largely known for being the youngest artist to portrait the Queen of England, stated: 'I have never heard of an artist monopolising a material. We (artists) should be able to use it – it is not right that it belongs to one man.' Panchal also criticized Kapoor: 'I have not known of anything so absurd – in the creative world, artists, nobody should have a monopoly.' To date, Kapoor is the only artist in the world given permission to paint with the blackest black [9].

4.16.3 Yves Klein

It is not the first time that an artist has claimed a unique bond with a pigment. In 1960 the French artist Yves Klein (1928–1962) took out the French patent 1.258.418 for his International Klein Blue (IKB) [24]. He developed in collaboration with the Parisian art paint supplier Edouard Adam a deep matt shade of blue, which he used in a series of monochrome blue paintings. Klein experimented with synthetic ultramarine blue (PB 29) and the synthetic resin binder polyvinyl acetate. The French chemical company Rhone-Poulenc developed this synthetic binder and marketed it under the name Rhodopas M60A. The paint mainly consists of synthetic ultramarine blue (PB 29), but it is the matt binder which makes the IKB colour. After drying the paint appeared to hover over the surface creating a rich velvety texture and an unusual appearance of depth. The difference between Klein and Kapoor is that the latter did not invent or patent a material, but just bought the right to use a colour. So, he does not actually own the colour black, he has just an exclusive legal right to that particular material for artistic purposes.

4.16.4 Stuart Semple

In 2016 Stuart Semple has addressed this situation as an art project in the internet by selling his own pigments, like PINK, Diamond Dust and Black 2.0. To buy the pigments the customer is required to make a declaration stating that he or she is not Anish Kapoor, is in no way affiliated to Anish Kapoor, is not purchasing this item on behalf of Anish Kapoor or is an associate of Anish Kapoor. The ongoing colour battle over the artistic rights to Vantablack continues. Semple will ony stop his project, when Kapoor wants to share his super-black with everyone [11].

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