HISTORY OF COLOUR IN PLASTICS

Lucy Gibbons and Helen Skelton, DCC Lansco, Toronto, Canada

Abstract

Colour is essential to human experience. From pre-history, through ancient civilization into the modern era, cultures have strived to create colour in the objects around them. Early peoples exploited natural resources to create images from their surroundings, such as red earth, black soot and white chalk. With time people developed more sophisticated techniques to refine minerals to generate a wider palette with blue, green, bright red and yellow. Often toxic in nature, these early inorganic pigments formed the skeleton of the pigment manufacturing industry. With the discovery of coal tar in the 1800s, and the ensuing rapid industrialization of synthetic chemistry, an explosion of colour transpired, leading to the modern chemical industry.

The historic generation of plastics followed a parallel path, beginning with use of natural materials such as ivory and tortoiseshell. Progression to processing of natural materials such as rubber, cellulose and shellac to generate more functional plastics, evolved to a place where coal tar chemistry provided a natural next step. This culminated in the discovery of Bakelite, the first fully synthetic plastic in 1907, which ignited the imagination for plastic materials, and the widespread production of consumer and industrial items accelerated. Colour and plastic developments went hand in hand, as by the 1950s the desire for brightly coloured, functional items sky-rocketed. Pigment chemistries were re-imagined with this new era in mind and from this point colour effects were generated specifically for plastic functionality. Textile fibers, automotive parts, plastic bottles, packaging and film; all un-thinkable now, without the effect of colour.

Pre-History

The earliest examples of pigment use date from around 40,000 BC in the form of cave paintings. Pre-historic people tried to represent aspects of the environment in paintings or carvings, and these often depict deer or bison, which were hunted for food. These images appear to have been created in a ritual way, many being overlaid one upon the other, and reflect the fascination of humans to create coloured images. Good examples of such European Paleolithic art can be found in Lascaux in Southern France. These cave paintings have been carbon dated at around 15,000 BC. The pigments used were taken directly from the natural environment, and vary depending on the area of the world in which they are found. Black was obtained from soot of charred bones or wood. Yellow, orange, red and brown could be obtained from earth; iron and manganese oxide pigments in various states of hydration were used. White was obtained from chalk and clay deposits, and green earth was sometimes used from the minerals celadonite and glauconite. The pigments were applied by mixing with animal fats as early paint, or by blowing dry pigments onto surfaces with hollow tubes. It is likely that a much wider palette was used with plant dyes and stains, but archaeological evidence for these has not survived. Early people were also employing natural "plastic" materials from their environment, such as, horn and ivory or bone which has been found carved into decorative and functional objects. The pre-historic use of colour and materials was limited only to natural materials.

Antiquity

The ancient Egyptian dynasties had one of the longest unified histories of human civilization, extending from around 4000 BC to 300 AD. This period saw many developments in technology, engineering, agriculture and society. People began to settle in organized communities around the Nile and form agricultural settlements, and the stability gained by this lifestyle allowed for advancements in technology and left space for formalized religion, art and technology. In 3100 BC Egypt was unified and ruled by the first pharaoh, Narmer. The earliest examples of Egyptian art, pottery and hieroglyphs date from this period, and a distinct style of art was developed, that can be instantly recognised as Egyptian. As a result, pigment technology was developed to generate a wider, brighter shade palette than the natural earth shades. A wider range of natural mineral pigments were employed using rarer, precious materials with more complex chemistry; green malachite, blue azurite and lapis lazuli, bright red cinnabar and bright yellow orpiment. The high value placed on these minerals led to the development of trade routes with other countries, Orpiment coming from Syria and Lapiz from Afghanistan. Malachite and azurite are both copper carbonate minerals that can be ground and washed to give blue and green pigments. Lapis lazuli is the natural mineral form of the modern pigment ultramarine blue, and is a sodium alumino-silicate mineral, that could be ground and washed to give a much more intense blue pigment. Cinnabar is intense red, mercury sulphide mineral that has a waxy texture and could be carved directly into decorative objects such as beads, statues and vases and also used as a bright red pigment. Orpiment is brilliant yellow arsenic sulphide mineral that was crushed to make a golden yellow pigment. It was known to give off fumes and bad odour, although this doesn't seem to have reduced the usage.

A step change in pigment technology took place in ancient Egypt as the first pigments were made by processing of natural minerals to form new materials; examples of the first chemical processes. Smalt is a surviving example of this new technology. It is manufactured blue glass made by heating sand, copper, copper ores, which also contained calcium carbonate, and alkali, such as caustic potash extracted from fire ashes. The mixture was heated in an earth kiln to 850-905°C to form the blue glass, which was used for making beads, ceramic glazes, glasses and for grinding into blue pigment.

The technologies developed in ancient Egypt continued and as Egypt became more open to the outside world around 500 BC, the ancient Greeks adopted many of the ideas and discoveries. The Greeks left a legacy of documentation from scholars such as Pliny, with many of the advances described in detail. The new concept of using natural resources to manufacture colour and chemical processes was expanded, as a cultural revolution was taking place in the city state of Athens, with the concepts of democracy, philosophy and medicine beginning to flourish. The Greeks added to the natural pigments with Sepia from octopus or cuttlefish ink sacks, which was pasted with alkali and then precipitated with acid to give a brown pigment. Gold was used as a pigment by grinding into a fine powder for painting, and the natural green copper silicate mineral crysocolla, was ground and washed from rock to make a green pigment. In addition, the Greeks developed synthetic processes for a number of pigments that are still in use today, although not many physical examples of the pigments survive, detailed documentary processes have left a critical record of the manufacturing processes.

White lead, or basic lead carbonate, is an excellent white pigment compared with chalk, and was used from Greek times up until the advent of titanium dioxide in the 20th century. The Greeks made white lead by a stack process that was described in detail by Pliny. In a small building lead strips were placed in clay pots suspended in racks, above vinegar. The pots were stacked together, and the gaps between them were filled with animal dung. The building was then sealed up for about 3 months, and the action of acetic acid, oxygen and carbon dioxide caused fermentation of the dung, forming basic lead carbonate on the metallic lead strips. The white lead could then be scraped off the strips and ground for use as a pigment.

Two other lead pigments were manufactured: yellow lead monoxide, or Massicot, and red lead. Massicot was made by continuous stirring of molten lead in an open furnace to oxidize it to a yellow powder. This was milled to separate the lead monoxide from metallic lead, and could be further calcined to form red lead Pb_3O_4. The processes for making both materials are very similar today, with red lead being widely used as a protective pigment in coatings.

The green pigment Verdigris was made from copper and vinegar to form basic copper acetate. Pliny describes this process as using sour red wine poured into an earthenware pot, with copper plates being placed above the wine on racks between layers of grape stalks that allowed the acidic wine fumes to circulate. The vessels were sealed up for a week or so, then plates were turned and exposed again. At the end of the process the plates were sprinkled with sour red wine, and pressed between weights. The green pigment Verdigris was then scraped off to be used.

A step change in pigment technology took place during this time as the first synthetic version of a natural pigment was made. The mercury sulphide pigment Cinnabar was manufactured artificially as Vermillion by heating a mixture of mercury and sulphur together in a narrow-necked flask. The mercury sulphide sublimed and condensed around the flask neck, where it could be scraped off and prepared by grinding to develop the bright red shade.

The people of antiquity also began expanding their knowledge and use of early "polymeric" materials, with tree resins and gums to make binders and resins for colour and to make decorative items. Egg tempera paints used egg yolks as an emulsion polymer, shellac resin from beetles was described in India more than 3000 years ago, and lacquer from the Chinese lacquer tree was used for making lacquerware items from more than 5000 BC, but was prevalent in the Shang dynasty around 1500 BC.

Renaissance

The Italian Renaissance was another cultural milestone in the chemical history of Europe, with profound change of culture, thought and lifestyle taking place. Technological change went along with the cultural revolution, and many developments were added. Natural plastic like materials were being used in more sophisticated ways for hair combs and carved ornamentation from bone, horn and ivory. And the thermoplastic properties of tortoiseshell were exploited to make shapes that would hold permanently after the application of heat, for boxes, spoons and other items.

A key pigment technology added during this time was the extraction of natural ultramarine from ground lapis lazuli. A process to remove the grey mineral from the blue pigment was developed using molten beeswax. The ground stone was mixed into beeswax which hardened, and was kneaded under water so that the grey mineral was retained in the dough, and the finest blue pigment was dispersed into the water and could be extracted and dried. This gave the brilliant intense blue pigment that is observed in Renaissance religious paintings and its high value meant it was retained for painting the most important scenes, such as the Virgin Mary's mantle.

The technology of Laking was discovered and described during this time, although may not have been understood in a chemical sense. Laking is widely used in pigment technology today, and is the complexation of a dye colorant with a metal ion to provide greater stability, insolubility and often to precipitate the dye into a pigmentary form. The Italians were precipitating the red dye carmine, extracted from Kermese or Cochineal beetles, as a pigment by Laking with calcium compounds, most likely in the form of chalk, or calcium carbonate. Carmine is still used today as a red lake pigment in cosmetics and food colour, but the more significant contribution was the technology of Laking itself which increases the heat stability of pigments and makes then more suitable for use in plastics processing.

Reformation and the New Worlds of the 17th and 18th Centuries

After the Renaissance, Europe went through many more cultural changes, which inspired technological change alongside. The religious reformation of Martin Luther eventually caused the formation of the protestant church and a splitting of European countries along religious grounds. It triggered the development of the printing press, mass manufacturing of paper, printing ink and greater communication of ideas between people in different countries for advancement. There were a wealth of new materials coming from the Americas and from the East, with the now infamous British East India company and the Dutch East India Company, which were more like private military organizations than trading companies. New colours and natural materials came to Europe and this coincided with a more systematic, organized approach to chemistry which was being investigated as a concern in its own right.

Rubber latex from the rubber tree was being used by the Mayan and Aztec cultures to make rubber balls for their ceremonial ball games, and for impregnating textile fabric to make it waterproof; the first tarps. The rubber latex arrived in Europe in the 1700s and was presented at the French Academy of Science in 1736, which led to the publication of a paper describing this new material. In England Joseph Priestly experimented with rubber and in 1770 noted that a piece of the material was good at rubbing off pencil marks on paper, and he coined the name “rubber” which has stuck.

The development of chemistry moved ahead rapidly in this time, and understanding of elements and their resections became more accepted. Wealthy gentlemen of independent means, dedicated themselves to the pursuit of chemistry and discoveries. Synthetic inorganic pigments began to appear at a more frequent rate, and a key contribution was the discovery of Chromium by French chemist Nicholas Vauquelin in 1770. He realized that a bright orange mineral, called Crocoite, from the Ural Mountains in Russia, could be used in reaction to precipitate bright compounds of yellow, red and green. So, he named the compound “Chromium” from the Greek for colour, and then set about finding a more practical supply of ore. By 1809 yellow lead chromate pigment was being made in small quantities, and later green chromic oxides were also being made. Both these pigments are widely used in plastics processing today, having good stability to both heat and light.

Another notable pigment development which is in widespread use today, was synthetic ultramarine. Analytical experiments carried out at the end of the 18th century showed that ultramarine was composed of soda, silica, alumina and sulphur. By 1806, two French chemists found that a blue impurity occurred in the slag of soda furnaces, which was shown to be chemically similar to ultramarine. This discovery led to The Société d'Encouragement pour l'Industrie Nationale offering a prize of six thousand francs in 1824, to anyone who could make ultramarine pigment for less than three hundred francs per kilo. Four years later the prize was claimed by the French manufacturer Guimet who did not reveal his method. The synthesis of ultramarine was later published by a German chemist named Gmelin, who had discovered the method independently. Full-scale industrial production of the blue pigment was begun immediately, and ultramarine was widely used from that time.

During this same time period, a new natural thermoplastic material, gutta percha, was found to be of great significance in the plastics industry. This hard, opaque substance was introduced from the Far East in 1843 and a wide range of products were shown in the Great Exhibition in 1851. This “gum-plastic” had specific properties that made it highly useful, such as; hard plasticity, electrical insulating capability and softening at easily attained temperatures. Its major use was for the insulation of submarine cables, which enabled communications around the world. By the nineteenth century, over a quarter of a million nautical miles of telegraph cable was in use, until it was replaced a hundred years later with polythene. Another very different application of gutta percha was the revolution of golf balls in 1848. Prior to this discovery, feathers had been bound in leather, which was a time consuming and expensive method. These would get very damp in wet weather and become unplayable, which was not the case with balls manufactured from gutta percha. Their affordability and reliable performance in different weather conditions impacted golf in many positive ways.[3]

In 1823 another major discovery was made by Charles Macintosh in Scotland. He stumbled upon a new water-resistant material that would forever transform how we dress and relate to our environment. Macintosh ran his own dying plant in Glasgow and it was during his research with naphtha that he discovered a new process, which involved sandwiching a layer of liquid rubber (made with naphtha) between two layers of fabric.[4] This new fabric was not only water-resistant but it also remained flexible. This wearable material made it a perfect fabric for making coats and so the Mackintosh waterproof (the Mac) was born.

Victorian Industrialization in the 19th Century

White zinc oxide came into prominence as a pigment during the late 1800s, although zinc white had been known since antiquity. It was first described in Indian medial texts from 500 BC as a treatment for skin conditions; a use which it still finds today in baby diaper rash creams and sun block creams. The white zinc was made as a by-product from brass manufacture, but the element zinc was not discovered until 1721 when it was identified by Henckle. After the process of making zinc white was understood, an ore could be found to make the pigment cheaper. Zinc white was already being made in India and China, and was introduced commercially into Europe as "Chinese White" in 1834, where it gained commercial status as an alternate to white lead pigments. There were already concerns about the toxicity of lead and had been a number of poisonings from lead fumes at the smelters making basic lead white pigments. The basic white lead was substantially cheaper, so its use continued in parallel with the introduction of zinc oxide.

The formalization of chemistry as a discipline led to the next great step change in chemical history with the discovery of coal tar, and the beginnings of organic chemistry. In 1843 Hofmann identified the organic molecule aniline, in coal tar. He was working as an industrial chemist in Germany at the time, but later became the first director of the Royal College of Chemistry in London. In 1853 Hofmann took William Perking as a student of chemistry, and he showed such natural aptitude that he was quickly promoted to research assistant. Perkin attempted a project to synthesize quinine from aniline, to be used for Malaria treatment for the British in India. The experiments were not successful and were mostly completed by trial and error as molecular structure was not well understood at this time. Instead of synthesizing quinine, he managed to product a black precipitate that gave a bright purple solution in methylated spirits. Luckily, Perkin recognized the potential of this as a colorant and found that he could dye silk an intense purple shade. This was the first organic synthetic colour, and was called "Mauveine". Perkin quickly formed an industrial manufacturing company to start making dyes, and Laking them to make pigments and rode the colour revolution that took place. The new colours were brighter, more intense and of different shades to the natural dyes and inorganic pigments that came before, and they became widely available at lower costs. It is hard to imagine today, a world where bright colour was not widely available, and what a dramatic change this discovery would have caused. The world of colour changed forever, and mass manufacturing and the use of colour in every day consumer items became the new norm. This took place in parallel to the mass expansion of rail networks, which started in the UK, and meant these new manufactured items could be moved more easily to other sites, and used to make consumer items which could easily reach people in cities all over Europe. The availability of new bright dyes spurred a need for textile fibers to make garments, as silk was an expensive rarity. The quest for affordable synthetic silk led to the development of rayon from cellulose, to give a high luster silk like texture.

It was also cellulose that provided the raw material for the next great breakthrough in plastics history - the material "Parkesine", named by the British inventor Alexander Parkes, who showcased his patented discovery at the 1862 international exhibition in London.[5,6] This semi-synthetic or chemically modified natural polymer was created when cellulose in the form of cotton or wood pulp was treated with nitric acid and a plasticizer, resulting in cellulose nitrate, which was largely accepted as the first common domestic plastic.[7] Parkesine was extensively used as a convincing imitation of natural substances like tortoiseshell, ivory and horn, which was revolutionary as manufacturing was no longer constrained by the limits of nature. This commonly available and inexpensive plastic was easily dyed, and the range of colours possible was extensive, for things such as dressing table sets and combs, billiard and ping pong balls, knife handles, jewelry, toys, buttons, costume accessories and spectacles.[8,9]

Late 19th Century

People were beginning to encompass thinking about things that couldn't be seen or explained in the traditional ways; molecules, atoms, energy, evolution. The late 1800s were a time of experimentation and new ideas. Charles Darwin published his theory of evolution in 1859 and European art had moved past impressionism to the experimental times of Van Gough, Cezanne and Gauguin. The development of chemistry galloped ahead; Kekule discovered the structure of the aromatic benzene ring in 1865 and this opened the understanding of coal tar chemistry. There were so many developments in this era that it would require a separate paper to describe them in detail. Prominent colour chemistry discoveries of the late 19th century include alizarin red and synthetic indigo, but for the pigment industry the most notable breakthrough was the advent of azo chemistry, which allowed the first true pigments to be synthesized. Azo molecules have a double bonded linkage of two nitrogen atoms, that allows two aromatic organic molecules to be linked together and produces the effect of colour. With Kekule's understanding of the structure of benzene, this led to a whole new way of thinking about designing molecules to specifically try and make pigments, rather than just by trial and error. A vast number of azo pigments were rapidly discovered and introduced, but the first was tartrazine yellow, which is still used as a food colour and in artists pigments today. In 1895 the use of naphthol's in pigment synthesis began. Beta-naphthol analogues were being used to make a series of intense red pigments.

Many of these pigments did not stand the test of time and were later discovered to be fugitive. Analysis of paintings from the time, such as pictures by Van Gough, show a large number of new reds and yellows being used in mixtures with the traditional inorganic pigments, but many of these colours are now not visible in the paintings as they have faded with light exposure.

In the late 1890s shellac was used to press the first rpm gramophone records. The natural raw material for this thermoplastic resin derived from the East Asian Lac insect, a plant parasite that produced an exudate as a protective barrier against predators. This excretion was harvested by the labour intensive process of scraping the hardened deposits from the trees these insects inhabited, adding fillers such as cotton flock, powdered slate or wood flour produced a composition capable of being moulded by heat and pressure.[10] This plastic was brittle, but capable of reproducing very fine detail and was used well into the 1940s.

Casein plastic derived from milk, was introduced at the Paris Universal Exhibition in 1900, not long after the first patent for "plastic compositions" was taken out in Germany in 1899. This thermoset plastic was created from milk curds hardened with formaldehyde and was produced in a vast array of colours including delicate pastel shades, pearls and mottles.[13] Casein plastics were usually opaque but could achieve some translucency when imitating tortoiseshell and horn. Many other decorative effects could be fulfilled with this material, and it could be polished to a brilliant lustre. This material was especially important for the button trade, which was the principal consumer of casein plastics. It was also a popular choice for buckles and knitting needles, and other items such as fountain pens, dress ornaments, knife handles, necklaces, dressing table ware, manicure sets and a wide variety of items generally referred to as "fancy goods".[13]

Early 20th Century

Cadmium was already known as an element in the 20th century, German chemist Stromeyer had discovered yellow Cadmium Sulfide in 1817 and deduced the colour was caused by a new element. Unfortunately, Cadmium was rare and expensive so was not being used in any commercial sense. However, in the early 20th century, building and engineering with iron and steel magnified, and it was discovered that coating these metals with cadmium gave corrosion resistance, so the production of cadmium expanded, and became more available for other industrial uses. In 1921 Cadmium Lithopone's were introduced and these were made by precipitating barium sulfate (blanc fixe) with cadmium sulfide, and a range of other elements, which made a series of bright yellow, orange and red pigments. These were cheaper, heat stable and fast to light and weather, so their use as pigments expanded rapidly, as cadmium had become more available as an element,

The chemical and specifically colorant industry was almost entirely focused in Germany at this time, and it seemed natural that this should continue. Chemistry was expanding so fast that it was hard to keep track of developments, and for colorants an early categorization system was developed by Shultz and Julius and ran from 1888 to 1914. This may have continued but the political situation in Europe took a dramatic turn with the outbreak of the Great War which ran from 1914 to 1918. Suddenly the flow of chemicals and production items from Germany was in question, and the sharing of knowledge between countries came to a halt. The British and Americans formed stronger links and recognized the need for an independent English language system of categorizing colorants, and the need to develop their own technology and processing, separate from the Germans. From 1920 the Society of Dyers and Colorists in the UK began categorizing all colorants in a system called the "Colour Index" which is still used as the principal listing of colorants today. The SDC partnered with the America Chemical Society and work together to keep the data on colorants accurate. The war spurred both countries to develop their own chemical technology and production plants and new developments shifted away from Germany and towards other countries.

Part of this "homegrown" development of chemical technology was the formation of ICI (Imperial Chemical Industries) in 1926, from several other companies, including the British Dyestuffs Corporation. An early, but key discovery of ICI was phthalocyanine blue and green pigments in 1928. A blue, insoluble impurity was discovered in reaction vessels at ICI, and was analyzed by Linstead at Imperial College London, and found to be Iron Phthalocyanine. After the structure was understood, it was found that replacing iron with copper gave a much more intense colour, and this was patented in 1932, and began being manufactured in 1935. A few years later the use of halogenation to make green phthalocyanines was introduced, and the shade range we know today was completed. These could be considered the first organic "super-pigments", as they are extremely high in colour strength, intense in shade, highly durable and heat stable, hence they are used in high volumes in many applications and are critical for the plastics industry.

Another key pigment development that took place outside of Germany was the manufacture of white Titanium Dioxide. The white natural mineral was already known and the new element Titanium had been identified by the German chemist Klaproth in 1795. However, a suitable purification method for removing iron from the mineral had not been established that would work industrially. The sulfate process was developed where the mineral was heated with sulfuric acid at 200°C and then hydrolyzed to form a white precipitate of hydrated titanium dioxide, which could then be calcined. Several companies began manufacturing titanium dioxide white in 1916, notably Titan Co. in Norway, and the Titanium Pigment Co. of Niagara Falls NY, in the USA. This white pigment has the highest refractive index of all the white pigments, so was more opaque, which provided great value to all applications needing coverage or hiding. Titanium dioxide began replacing basic lead white in coating applications, but also found use in newly emerging plastics applications of the 20th century.

Chemists at this time had begun to recognize that many natural resins and fibers were polymers, with the potential of phenol-formaldehyde resins being of particular interest.

In 1907, a Belgian-born American, Leo Baekeland invented Bakelite, the world's first synthetic thermosetting plastic and the first to be derived not from plants or animals, but from fossil fuels, which marked the introduction of the abundant Polymer Age.[14]

Baekeland had been experimenting with controlling the temperature and pressure applied to phenol and formaldehyde, trying to find a synthetic substitute for shellac. Bakelite had the electrical insulation performance of shellac, plus other beneficial properties; it was hard, durable, heat resistant, and could be shaped or molded, which led to the marketing slogan, "The Material of a Thousand Uses".[15,16] It was soon used for all non-conducting parts of radios and other electrical devices, such as bases and sockets for light bulbs and electron tubes, supports for any type of electrical components, and other insulators.[17] Furthermore, this new plastic could be molded very quickly, a huge advantage to the mass production processes that manufactured identical units one after the other. In October 1925, the first issue of Plastics magazine featured Bakelite on its cover and included the heading "Bakelite — What Is It?" by Allan Brown.[18] This article emphasized that Bakelite came in various forms and covered an extensive colour range, including "black, brown, red, yellow, green, gray, blue, orange, cream, maroon, and blends of two or more of these" colours. Bakelite soon found a place in almost every area of modern life, from costume jewelry and iron handles to telephones and toothbrushes, it was a constant presence in the growing technological infrastructure.[19]

In 1922 a German organic chemist, Hermann Staudinger published his work recognizing that plastics are composed of long chain molecules, which he identified as polymers. Staudinger founded the first polymer chemistry journal in 1940, and received the 1953 Nobel Prize in chemistry for his work. He was known as the "Father of Modern Polymer Science" for paving the way forward in the world of plastics.[20]

During the 1930s, plastics became an industry in its own right with successes such as 'Scotch' tape, the first production of aircraft canopies made from 'Perspex', DuPont patented Nylon leading to the first toothbrushes with nylon tufts, and ICI in the UK accomplished the commercial production of polyethylene and poly(methyl)methacrylate.[2]

Late 20th Century

The outbreak of the Second World War represented a massive upheaval of society in the 20th century and brought about the modern era. Society in Europe changed from a world of rigid social classes and aristocracy dominating culture, to greater flexibility and opportunity for every-day people. During the war for the first time, women went to work in factories and took roles traditionally regarded as "male". The USA became the defining force in western culture and the age of the automobile, rock and roll and consumerism was born. The development of plastics boomed to fit this new age. The production of low-density polyethylene containers caused a rapid expansion of the industry, with common glass bottles for shampoos and liquid soaps being readily replaced, and the launch of Tupperware in the US in 1949 also caused great commercial impact.

Prior to this time all pigments had been developed for coating applications, but now there was a need for pigments of high durability for automotive coating, for high heat stability for the newly developed high-density polyethylene, polyester fibers and polypropylene plastics and for a wider colour range for consumer items. Pigment research looked to more complex polycyclic chemistries to achieve high performance and to heterocyclic chemistries to expand the performance of azo pigments. A new addition to the red, magenta and violet colour range came with quinacridone pigments, which fit this high durability, and bright shade requirement. Quinacridones are synthetic linear heterocyclic molecules that had been known as structures since 1896, but not synthesized in a suitable crystal form until Liebermann studied them in 1935. However, Liebermann did not recognize their potential use as pigments. It was only in 1955, after Struve began working on quinacridones at the DuPont Company, that a commercial process for making pigments was developed, and the key was recognizing the different crystal forms that the linear molecules could make. In 1958 this new class of pigments was introduced into the market, providing high performance magenta and violet shades.

Modernism

Pigment development and synthesis of new chromophores slowed down in the modern era, but development has continued with a different focus borne of its consumerist background, meaning visual effect, styling and branding have come to the fore. Pigments for metallic, pearl and reflective effects have become widely used to create visual interest. Shades of existing pigments have been developed for branding and trade name market recognition, and this has driven a lot of development.

Many cultural icons in plastics were introduced in the late 1950s, some of which are still hugely popular today. The hoop was reinvented using polyethylene as the Hula Hoop by Knerr & Medlin, Wham-O Toy Company,[21] LEGO patented their stud-and-block coupling system[22,23] and the first Barbie doll was unveiled by Mattel at the 1959 New York Toy fair.[24] These examples gained global popularity and demanded branding and marketing of plastic colour trends.

Probably the most important colour pigment development in the modern era, was an accidental discovery of a red impurity that did lead to a new chromophore; Diketopyrrolopyrrole (DPP) pigments. They were discovered by Iqbal working at Ciba and developed around 1974 in secrecy, and patented in 1983. DPP is a heterocyclic molecule and can give bright red and orange colours depending on substitution groups. The original DPP red pigment is now synonymous of Ferrari Red branding. It is a high performance, high durability red that has been gradually replacing other red pigments in use, as its pricing has dropped making it accessible for many applications and widely in plastics.

Future

The trend for pigment and plastic developments in the future are geared towards greater environmental responsibility and understanding of product cradle to grave life cycles. Pigment manufacturers have a strong push to reformulate products at higher purity, with higher durability and a greater degree of technical information available on products. Partly this push is regulatory, such as the REACH program in the EU, but also a drive from consumers and marketing to provide products seen as more environmentally friendly and responsibly manufactured. This drive is also experienced in the plastics industry, as consumers demand plastics to be safer and more sustainable. Therefore, these are likely the trends that will urge development forward in the future.

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