Materials : Colouring judgment on colour

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When Mattel recalled millions of toys in 2007 because there was lead in the paint, it left them red-faced. It also coloured our judgment of the safety standards in place in some manufacturing plants and begged the question just how many other toys went unchecked by toy companies with less stringent safety standards. The recall was costly, not only in financial terms; reputations were damaged too. But what could have been the cost in human terms if this went unchecked?

Lead is toxic – a poison that affects many body organs and interferes with the nervous system – and can lead to permanent learning difficulties, seizures and even death. So what does lead do and why is it in paint in the first place? The answer is simply to add colour – which is rather perverse considering we colour these items to appeal to children, luring them to want to play with them, and in the process expose them to a potential killer toxin.

As designers and manufacturers, we often specify colours, but do we actually consider what is in the pigments and paints we chose?

From a materials perspective, regular household paint can have thousands of chemicals in it. Paint consists of a pigment (the colour), a binder, solvents and some other specialist additives such as UV stabilisers, biocides, emulsifiers, flatteners and materials that create particular textures. The binder in the paint is typically a synthetic resin such as acrylic, polyester, epoxy, or an oil-based medium, and it is this material that adheres to the surface being painted and also constitutes the gloss level of the finish. The way in which these materials cure, or dry, is of note – many contain solvents that evaporate, and the solvents can pose a health risk. Solvents and other constituents of paint are often referred to as Volatile Organic Compounds, or VOCs, and thankfully environmental legislation now regulates their use. Even so, paint can still contain hundreds of toxins and harmful substances.

This article could not do adequate justice to the exploration of all the harmful chemicals in paints, but instead explores some of the more intriguing aspects of colourants and pigments.

A colourful and chequered past

We owe a lot to Michael Vernon, the Australian consumer activist, who campaigned for lead to be banned from use in children's toys through the latter part of the 20th Century. He also got cadmium banned from paints, but these are not the only highly toxic materials that have been used to colour our world.

Take yellow for instance. Sweets that can be fatal if swallowed sounds like the basis for a macabre tale befitting of Edgar Allan Poe, yet the reality is that up until the late 19th Century, lead chromate was used to colour confectionary bright yellow. We now know of the extreme toxicity of both lead and hexavalent chromium that makes up lead chromate and that it can be fatal if swallowed or inhaled, and is also carcinogenic. *Alice's Adventures in Wonderland* (1865) has the famous line paid homage to in *The Matrix*, "you take the blue pill and the story ends … you take the red pill and you stay in Wonderland". Perhaps Lewis Carol should have added "…you take the yellow pill and you come to an end."

Other toxic yellows include arsenic sulphide, lead antimonite, and cobalt and cadmium-based pigments. Cadmium was widely used not only for its brilliance of colour – particularly yellows, oranges and reds – but also its ability to withstand the high temperatures of plastic processes such as injection moulding. Cadmium pigments have largely been replaced by azo pigments, which are cheaper and are deemed to be non-toxic, although some studies suggest that some of these pigments can be mutagenic. The term 'azo' derives from the French for nitrogen (azote), the key chemical in this group of pigments.

There are some more peculiar tales of how pigments have been derived. The Dutch artist Vermeer was renowned for his use of expensive pigments. Of particular note is the use of Indian Yellow to paint the, *Girl with a Pearl Earring*. Indian Yellow is derived from the urine of cows that have been fed solely mango leaves (I wonder whether he told the model that she was being painted with cow urine). Another rather bizarre origin of colour involving urine and leaves is a blue dye produced by dyers who would binge drink and then urinate on woad leaves – the alcohol-enriched human urine would then help the leaves ferment and produce the blue pigment. And then there are the purple makers, who had a particularly labour-intensive and smelly job of extracting the mucus from sea snails.

How mankind came to discover such things begs belief, but perhaps our curiosity and fascination with the natural world, how it works, how we can manipulate it, and how we can learn from it are important traits that remain with us still. We are perhaps a little more sophisticated in how we are learning from nature and applying its lessons. Scientists and designers are re-looking at nature to shed new insight on colouring our world.

From butterflies to moths' eyes

Butterflies come in the most beautiful array of colours … or do they? The colouring of many butterflies is not necessarily a pigment in the wing, but rather a naturally occurring nanostructure that distorts and filters particular wavelengths of light to create a colourful illusion. The South American Morpho butterfly, for instance, appears in a range of beautiful metallic blues or greens, yet up close the wings are semi-transparent.

We know this phenomenon as iridescence, where the structure of the material or surface reflects light at different wavelengths, and it occurs elsewhere in nature, such as in opals, nacre (mother of pearl, abalone shells), golden stag beetles, and oil or soap films. In industry we have tried to replicate iridescence either through a nanostructured coating or the addition of nanostructured elements to materials. The most obvious of the latter would be pearlescent coatings, often seen on custom car paint jobs, where tiny reflective platelets are suspended within the coating giving the effect of a change in colour as the viewing angle changes.

By coating a material with tiny refractive spheres or prisms, when bright light shines on the surface it 'bounces' back thus giving the appearance of luminescence – this phenomenon is exploited in clear coatings on traffic signs and driving licenses and passports. The traffic signs thus look brighter and help warn and inform road users, whilst in the case of driving licenses and passports it is used as a preventative measure against forgery. These coatings are typically referred to as retro-reflective coatings.

An interesting development in anti-counterfitting is the use of nano-scale quantum dots, or Nano-dots, that emit specific wavelengths of light. The quantum dots can be printed onto a surface to create a unique optical 'barcode' or added as a paint coating. Applications include as a security measure to prove authenticity of artworks, or applied to a car's bodywork as an additional security feature to help detect car 're-birthing' (this feature can ensure that the body panels match the engine and chassis number).

Conversely, there are also anti-reflective coatings, often applied to lenses, which interfere with light hitting the surface to minimise reflection. These coatings work in a couple of ways. The most common method is the use of a clear material with a different refractive index from the substrate it is coating and can be applied either as a single layer interference coating or as multi-layer coatings. The other common type is absorbing anti-reflective coatings, which are made up of a thin layer of a material that does not transmit light that well.

Many moths have a nano-structured anti-reflective film on their eyes consisting of a series of tiny hexagonal bumps that are smaller than the wavelength of visible light so light cannot bounce back. This phenomenon inspired the Fraunhofer Institute for Solar Energy, Germany, and a UK company, Autotype, to produce a commercially-available antireflective coating, aptly named MARAG film (Motheye antireflective, antiglare).

Mimicking natures' colour changers

A number of species, such as chameleons and cuttlefish, have the ability to change colour or even produce light, and we now know, in part, how they do so. Chromatophores (from *chromato* – colour and *phore* – bearer, producer) are the cells that contain or produce pigment typically found in cold-blooded animals like fish, crustaceans, cephalopods (cotopus, cuttlefish) amphibians and reptiles, as well as some bacteria. We have been inspired to mimic some of these cells' behaviour in a range of exciting pigments.

Several smart materials are available that reversibly change colour or opacity in the presence of a stimulus, such as light, temperature, electricity, chemicals or mechanical forces. *Photochromic* pigments change colour when stimulated by light. A common example of this is the photochromic material used in sunglasses that cause the lenses to darken or lighten according to the intensity of light. Chromatic Technologies Inc, produces a range of colour-changing materials including photochromic paints and dyes.

Thermotropic materials change their optical properties (opacity) with temperature, whilst *Thermochromic* materials change colour with temperature (think back to the *Hypercolor* T-shirts popular in the 1980's). The thermochromic pigment, a leucodye for instance, is typically encapsulated in a microcapsule that can be bonded to fabric or other materials. Leucodyes need only a few degrees change in temperature to go from their coloured state to clear, and they come in a range of colours and operational temperatures. By utilising more than one leucodye, a range of colours can be obtained. In a similar fashion, *electrochromic* and *electrooptic* materials change colour and opacity when an electrical current is applied. Because these materials can be printed, often onto flexible mediums, there is growing interest in them being used for such purposes as smart packaging, cheap displays, and electronic newspapers. E-INK is one notable demonstration example of this technology.

Chemochromic pigments change colour dependent upon the chemical composition of the environment, and offer great potential as a visible warning and detection system for environmental and chemical hazards (eg, increased CO2 levels or a change in pH). *Mechanochromic*, *piezochromic* and *tribochromic* materials change colour when a force is applied, and again these can be used as remote, un-powered and cheap sensors to alert of stresses and strains in a material (a mechanical component or a civil infrastructure like a bridge for instance).

There are also smart material pigments that not only change colour, but can emit light too. Luminescent pigments emit light when excited by the effects of energy (electricity or light for instance). These pigments fall into two main groups: fluorescent pigments give off light almost simultaneously, whilst phosphorescent pigments have a delay resulting in an afterglow. Phosphorescent paints have been around for quite a while and were commonly seen on glow in the dark watch hands and faces. The early versions were commonly based on radioactive materials such as radium-226, strontium-90 and yttrium-90, and resulted in many people with wrist complaints. Newer phosphorescent materials are much safer and modern pigments can be blended fro different effects The duration of the phosphorescent afterglow can vary significantly: zinc sulphide and magnesium sulphide crystals glow for a relatively short time, whilst persistently phosphorescent materials such as alkaline earth aluminate crystals can give off light long after the stimulus has been removed.

We can learn a lot from the natural world when it comes to colour. In the historical shift from naturally derived dyes and pigments to synthesised chemical-based colourants, an important lesson from nature was forgotten. Bright colours on insects are typically a warning signal to warn off prey and let them know that they are poisonous. We're now learning and applying more sophisticated lessons from nature, but we all need to be better informed in order to more wisely colour our judgement of colour.

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