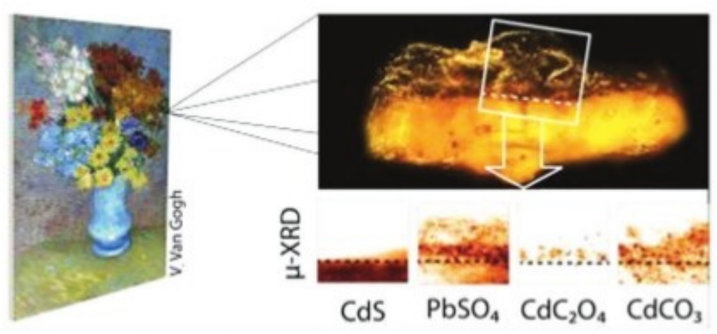
Keeping them bright and yellow

Some cadmium-based paints used by master artists, like Vincent Van Gogh, discolour with age

S ANANTHANARAYANAN


Vincent Van Gogh



Gradual changes in the bright yellow flowers in Vincent Van Gogh's 1887 painting, *Flowers in a blue vase* to an orange-grey colour, have caused grave concern to the Kröller-Müller Museum, which acquired the painting early in the 20th century. The cadmium sulphide paint that Van Gogh had used is known to oxidise in air, getting covered by a slightly off-white, transparent layer and losing colour and luminosity. But what was seen was an orange-grey crust, which could not be removed without damaging the original paint.

The journal, *Analytical Chemistry*, carried a report by scientists of Antwerp, Delft University of Technology and scientists from France and Holland, of a high energy X-ray study of the surface of the painting. The study revealed the nature of the colour changes as being a degradation process at the interface of the cadmium paint and the layer of varnish that is there to protect the paint. The sources of high energy X-ray were the European Synchrotron Radiation Facility at Grenoble, France and the Deutsches Elektronen-Synchrotron at Hamburg, Germany.

Paint and pigment

Modern oil paints are believed to have been formally invented in the early 15th century by the Flemish painter, Jan van Eyck, who mixed mineral pigments with oil, most often linseed oil, which would gradually dry and harden. A series of painting masters perfected the method of mixing minerals and oils or even beeswax. Artists used to grind their own pigments and carefully mix in the oils in the correct proportions. Modern paints use a number of plant-based oils, adjusted for viscosity and modern manufacture ensures consistency, while delivery in tubes even helped with a method of application on the canvas.

Paint gets its colour from small particles of pigment that are suspended in the oily carrier. Mineral oxides, like lead oxide, now replaced by zinc or titanium, give white paint, while cadmium, copper, arsenic, mercury, iron, cobalt, chromium, not just as oxides but in combination with sulphur or carbon, are used for different pastels. Combination of pigments produces a range of shades, while the artist mixes colours on his palette for the final effect. But the colours are basically because of the different-coloured salts and those salts can be affected by heat, humidity and the gases in air.

Cadmium paints

Cadmium is a silvery white metal but the colour of salts of cadmium can be red, yellow or green. Cadmium pigments are usually yellow, orange or red and about half the cadmium produced worldwide is used for making paint, although its use is declining, as cadmium is poisonous. But in the late 19th century, cadmium paints were a newly-discovered medium and were widely used by artists. The cadmium sulphide, yellow pigment used by Van Gogh was one such.

Cadmium sulphide is known to get oxidised to cadmium sulphate, which is dull yellow. Paintings were hence coated with a layer of transparent varnish, to protect the pigments. Van Gogh, himself, produced all his 800 paintings and 700 drawings within 10 short years (till he died, in 1890 at the age of 37) and did not cover any of his painting works with varnish. But with cadmium paints found to discolour, most Van Gogh works were covered in varnish in the early 20th century and the Kröller-Müller Museum did the same with Van Gogh's *Flowers in a blue vase*.

This is the context to the discovery in 2009 that even under the coat of varnish, the yellow flowers in cadmium paint had turned darker. "The removal of the orange-grey crust and discoloured varnish was not possible without affecting the very fragile original cadmium yellow paint on these parts," paintings conservator, Margje Leeuwestein from the Kröller-Müller Museum says. As ordinary methods did not seem feasible, the museum extracted two microscopic paint samples from the affected parts of the painting and sent them to Koen Janssens from the University of Antwerp for analysis.

X-ray study

The changes in the nature of the coat on the canvas were not at the level of particles or specks of pigment to make any microscopic analysis possible. The changes were at the atomic level and analysis required probing by X-rays of short and controlled wavelengths. X-ray beams are scattered by individual atoms and the scattering pattern reveals how the atoms are oriented and what atoms they are — in other words, the internal, atomic structure of the grey-brown crust at the place where the cadmium paint and the varnish made contact.

The scientists were surprised to find that even if the cadmium sulphide had oxidised, no crystals of cadmium sulphate, or its compounds were present. But, "it emerged that the sulphate anions had found a suitable reaction partner in lead ions from the varnish and had formed anglesite (lead sulphate)," says DESY scientist Gerald Falkenberg. Anglesite is an opaque compound that was found nearly everywhere throughout the varnish. The sulphate had arisen from the cadmium sulphide pigment and "the source of the lead probably is a lead-based siccative (thickening agent) that had been added to the varnish," adds Falkenberg.

"The research into this hitherto unknown degradation process of varnished cadmium yellow oil paint allows to better understand the current appearance of the painting," explains Leeuwestein. Joris Dik from TU Delft adds that "it also provides information on how later-applied varnish layers may contribute to the decline of certain pigments of a painting. In the future, this degradation process can hopefully be inhibited or even prevented thanks to novel preservation and conservation techniques."

Whether removing the varnish and crusts from paintings with this type of degradation is possible or appropriate is not yet fully understood. Leeuwestein adds that "in every similar case of a possible varnish and crust removal, it should always be considered that this varnish and crust contain original material from the cadmium yellow oil paint. The possible removal of original material from a painting during a conservation treatment is of course undesirable."

"Many of Van Gogh's French period paintings have been inappropriately varnished in the past and removal of these non-original varnish layers is one of the challenges facing conservators on a world-wide basis today. The type of information provided by Janssens and his team is vital to support the difficult decisions that conservators often have to make regarding such complex cleaning treatments," says Ella Hendricks, head of conservation at the Van Gogh Museum in Amsterdam.

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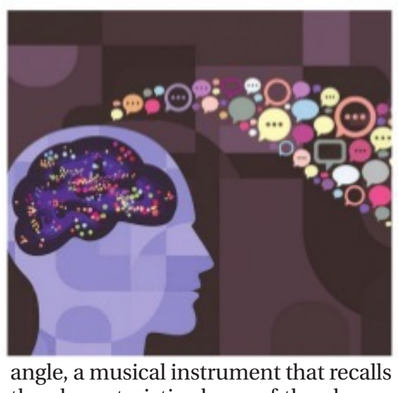
Manipulating all senses at once

Multisensory marketing is becoming big business and it really does work

MARIANNA BOLOGNESI & FRANCESCA STRIK LIEVERS



We're so bombarded with commercial messages every day that creating an ad that actually sticks in the mind is an increasingly difficult task. Research shows that one way to make advertised products more memorable is to engage consumers' feelings and emotions by stimulating multiple senses at once.

And advertisers are now more consciously using this approach in what you'd typically think of as a visual-only medium — print images.

Marketing has undergone what researchers have called a multisensory revolution. Browsing the shops around Christmas time, for instance, is typically a multisensory experience, and that's no accident. Shops combine ambient Christmas music and Christmas-related scents to influence consumers' behaviour and increase sales.

Video advertisements also resort to the multisensory strategy. McDonald's ads, for example, display the famous red and yellow logo that triggers a representation of the brand stored in our mind through the sense of sight, together with a now well known tune that triggers a representation of the brand stored in our mind through the sense of hearing.

The brand is encoded in our memory by means of both visual and audio elements. This establishes immediate and subconscious associations between the different sensory stimuli — the images and sounds — and the advertised product.

Multisensory marketing has also made its way into print advertising. To convey a multisensory message within a medium that is chiefly experienced by sight, advertisers use language and images to evoke the other senses.

Evoking individual senses in print is relatively straightforward, using words like "smell", "hear", or "yellow", and images of objects that we strongly associate with specific senses, such as a bottle of perfume (smell), or a bar of chocolate (taste). But words and images can also evoke multiple senses within the same ad, and in the most creative ways.

The chief method for making multisensory print ads is employing linguistic synaesthesia. Not to be confused with the neuropsychological condition synaesthesia, this is a type of metaphor created by combining linguistic expressions that refer to different senses — for example, "sweet melody" (taste and hearing) and "soft voice" (touch and hearing).

Print ads often display synaesthetic slogans. For example, the Hogwine food company advertises its potato chips with the slogan "Like sweet banjo music to your tongue". The chips' taste is associated with music, which is in turn described as "sweet", an adjective that primarily relates to taste.

Our recent research shows how synaesthetic associations can also be created by the image only, in what researchers call visual metaphors. For instance, Popclik advertises its headphones by showing them on a comic-like black and white background. Here, only the drawings within the space defined by the headphones are illustrated in colour.

The positive feelings that we tend to associate with colourfulness (as opposed to black and white) are arguably used to convey a positive judgment about the quality of sound that the advertised headphones reproduce. In other words, this advertisement is an example of a visual synaesthesia by which sound is described in terms of colour.

Not only do we have purely linguistic and purely visual synaesthesia — language and images can also interact. The image above advertises Toblerone through the image of a triangle, a musical instrument that recalls the characteristic shape of the chocolate bar. Music is also mentioned in the slogan "Music to your mouth", where it is explicitly connected to the taste of the advertised product.

In other ads, the image seems to visually "translate" synaesthetic combinations that are commonly used in language. For instance, a lemon-flavoured soft drink has been advertised by the image of a lemon wearing a spiked mask. This combines with the slogan "L&P sour lemon. Sharp as. Bit different aye".

Together they provide a visual realisation of the conventional and commonly used linguistic synaesthesia "sharp taste", with the lemon representing the taste and the spikes on the mask the sharpness (touch).

Visual communication is extremely powerful. As these ads show, it allows us to evoke multiple sensory domains and establish creative associations between them by effectively combining words and images. What's not yet clear is whether these synaesthetic print advertisements have the same effects on sales and brand memorability as the complex experiences used in multisensory experiences.

If so, learning how advertisers use these techniques to brand new products can help us to become more aware of our behaviour as consumers.

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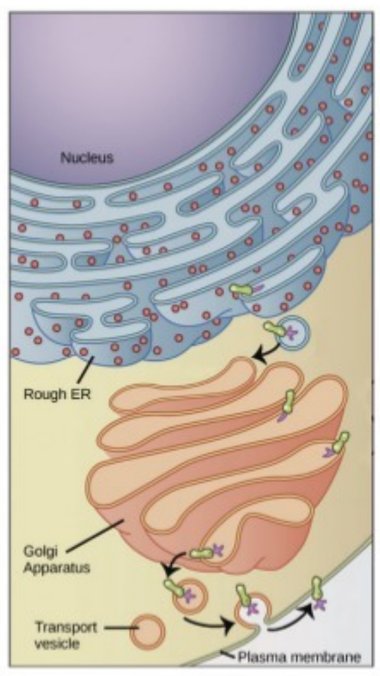
Protein trafficking

Here's a look at the role of the ER and Golgi complex in glycosylation

TAPAN KUMAR MAITRA



Much of the protein processing carried out within the endoplasmic reticulum and Golgi complex involves glycosylation — the addition of carbohydrate side chains to specific amino acid residues of proteins, forming glycoproteins. Subsequent enzyme-catalysed reactions then modify the oligosaccharide side chain that was attached to the protein.

Two general kinds of glycosylation are observed in cells. N-linked glycosylation (or N-glycosylation) and O-linked glycosylation.

Conceptually, one can divide the N-linked glycosylation process into two stages — the initial glycosylation event and the subsequent modification of the carbohydrate side chain. The enzymes that catalyse various steps of glycosylation and subsequent modifications are present in different com-partments, or groups of compartments, of the ER and Golgi complex.

The first stage of N-glycosylation, called core glycosylation, takes place in the ER. Invariably, the carbohydrate directly linked to asparagine is N-acetylglucosamine (GlcNAc). Early steps of the process occur on the cytosolic side of the ER membrane and later steps occur in the ER lumen. Typically, the core oligosaccharide is added to the protein as the polypeptide is synthesised by a ribosome bound to the ER membrane.

During the second stage of N-glycosylation, the core oligosaccharide is trimmed and modified. In this process, several additional ER proteins interact with the newly synthesised glycoprotein to ensure its proper folding. One of two ER proteins known as calnexin and calreticulin can bind to the monoglucosylated glycoprotein and promote disulphide bond formation by forming a complex with the glycoprotein and a thiol oxidoreductase known as ERp57.

Glycosylation occurs only on the lumenal and not the cytosolic side of the ER and Golgi complex membranes. The glycoproteins and glycolipids assembled in these organelles are therefore additional factors that contribute to membrane asymmetry. Following biosynthesis, the glycosylated proteins and lipids face the lumens of the ER and Golgi complex.

As vesicles bud from these organelles and fuse with other cellular membranes, the asymmetry established during glycosylation is carried over to the other membranes.

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PLUS POINTS

Where they belong

The British Museum is returning a collection of 5,000-year-old antiquities, which had been looted from an ancient site in Iraq shortly after the 2003 US-led invasion and then seized from a dealer in London. The eight objects were confiscated by Scotland Yard during a May 2003 operation, after they were suspected of being looted and the dealer failed to produce proof of ownership for them.

The British Museum said the dealer then ceased trading and the objects, which include jewellery, inscribed cones, a decorated seal and a mace-head, were passed to the Crown and then on to the British Museum for analysis earlier this year. Identification of the origins of the objects was aided by three items carrying cuneiform inscriptions — one of the earliest systems of writing — invented by the Sumerians. The Sumerian text indicates they came from the Eninnu temple in the ancient city of Girsu, now known as Tello, in southern Iraq.

Iraq's ambassador, Salih Husain Ali, praised the museum's staff for their "exceptional efforts" in identifying the antiquities. "Such collaboration between Iraq and the United Kingdom is vital for the preservation and the protection of the Iraqi heritage," he said, "The protection of antiquities is an international responsibility and in Iraq we aspire to the global cooperation to protect the heritage of Iraq and to restore its looted objects."

The group of eight artefacts consists of five Sumerian inscribed objects, two Jemdet Nasr stamp-seal amulets in the form of a reclining sheep or showing a pair of quadrupeds facing in opposite directions, and an Achaemenid stamp-seal showing a reclining sphinx.

The independent

Between crab and wave

Periwinkles, struggling to survive the seashore battleground, have developed a genetic "toolkit" to help them adapt to different environments, a new study shows.

A team of researchers from the University of Sheffield, in the UK, and the University of Gothenburg, in Sweden, investigated hundreds of rough periwinkles, collected from seashores on the west coast of Sweden. They noted their shell form and exact position on the shore, and then analysed their genomes to try to find out how these adaptations occurred to give the snails the best chance of survival.

The results, published in *Evolution Letters*, showed the snails' characteristics changed significantly at the point on the shore where the crabs disappear and the wave action gets stronger. Anja Westram, postdoctoral researcher at the University of Sheffield, who led the analysis, explains, "Either side of the habitat transition, the snails look like different species. Snails on the boulder shore have thicker shells, which are a better defence against crabs. The smaller, cliff shells have a wide opening, so the snail's foot can attach more securely to rocks, to defend against waves. And across 10 to 20 metres of shore in between these areas, we found all kinds of intermediate forms."

But when the team analysed the periwinkles' genetic data to try to discover how these changes occurred, they uncovered some surprising results. They identified around 1,000 genes that differed between snails in the "crab" and "wave" environments but instead of being spread throughout the genome, most of them were clustered in specific regions across just three chromosomes. The researchers concluded that the chromosomes were holding together sets of genes to help the snails adapt to different environments.

Professor Roger Butlin, of Sheffield's department of animal and plant sciences who led the study, says, "Rather than many genes having to respond separately to natural selection, this creates a ready-made 'toolkit' on these three chromosomes that has allowed the snail to adapt more rapidly."