Comparison of methods for colour shift effects

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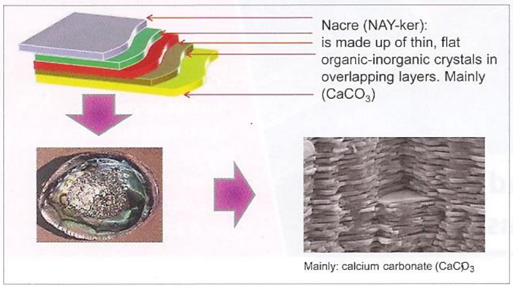
In industrial applications various methods have been employed to reproduce colour shift effects to prevent counterfeit or optical reasons. Each methods has its pros and cons, and there is a most suitable solution for each and every application.

Colour shift effect is produced in nature by different mechanisms including pigments, light absorption and interference and by a mechanism called photonic crystals. In industrial applications various methods have been employed to reproduce such effects. These methods rely on physical, chemical, and mechanical principles. This includes optical absorption, emission (LED), interference, micro-structuring and scattering, In our recent work we have developed a colour shift effect on a flexible film without the use of structural embossing, inks or pigments. The process exhibits an aesthetically appealing colour shift effect from red to green depending on the angle of viewing. This process is more cost effective than that in which structural embossing or pigments are used.

Figure 1 (top): Colour in Flowers is caused by pigments and in Peacock's tail feathers by structural colouration

Figure 2 (bottom): Mother of Pearl Structural Iridescent Colouration



Introduction

Colours with brilliant lustres found in nature have long attracted scientific interest. Such colours can be observed in flowers, pearls, jewels, butterflies, peacock tails, beetles and fishes (Figure 1). Natural colour lustres are caused by different mechanisms including pigments, light absorption and interference and by a mechanism called photonic crystals. To reproduce such colours in the laboratory scientists have used various physical, chemical, and mechanical principles including optical absorption, emission (LED), interference, micro-structuring and scattering. The 'structural' colour produced by micro-structuring the surface of a substrate is a type of coloration originating from the variation at a length scale comparable to the optical wavelength.

In nature the Mother of Pearl Structural iridescent Colouration is produced by the multi-layered structure of Nacre (NAY-ker) which is made up of thin, flat organic-inorganic crystals in overlapping layers, mainly ($CaCO_3$) (Figure 2).

In order to reproduce such coloured lustres for commercial use, vacuum web metallizing technique has been employed. This technique is a powerful and flexible tool that has so far been used successfully to metallize flexible films and papers with aluminium for packaging applications. It is also used to reproduce structural colours by metallizing embossed films with aluminium or high refractive index material. Vacuum web metallizing offers faster and cost effective method for producing colour lustres as compared to other works which have been carried out using slow and ultimately un-scalable physical or chemical processes. Vacuum web metallizing can provide a manufacturing opportunity to increase production throughput of iridescent or colour shifting products at high speeds and low cost.

This article will outline some industrial processes used for the production of colour lustres and will discuss the physics of iridescent colour shifting effect.

Production of iridescent colours

Iridescent colours are commercially produced via interference and diffraction of light passing through or reflected from surface which is structured by various mechanisms. The interference reflects one or more spectral bands or lines and transmits others, while maintaining a nearly zero coefficient of absorption for all wavelengths of interest.

One of the methods employed in industry is to use natural spheres of Opal which is composed of silica spheres (100–300 nm in diameter) forming a hexagonal or cubic close-packed lattice. Iridescent glittering materials are also used for cosmetic, decoration and paints applications. Glittering materials are based on the use of nacreous pigments to produce pearl-like light interference. Most pigments used in cosmetics contain low refractive index mica (1.5 to 1.6) coated with semi-transparent high refractive index titanium oxide (2.4-2.7). The light interference wavelength can be controlled by the thickness of the titanium oxide (Figure 3). When pigments such as iron oxide, chromium oxide or carmine (pigment of bright red colour) are added to TiO2-mica, the product is called a 'coloured nacreous pigment'.

Such pigments are used to produce *Pearl lustre inks*, or *mother-of-pearl inks* to create shiny, pearl-like shimmering effects which change colour with the angle of view. It is used for security documents such as passports or identity cards.

Another method of producing colour shift or iridescent colours is to apply a stack of dye free multi-

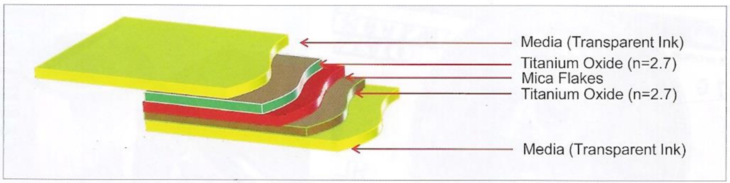


Figure 3: Pearl-Like Interference Effect

layers of polymers with different refractive indices on a flexible substrate such as Polyester. This requires a precise control of the polymer thickness and uniformity to achieve blue, green or red colours due to light interference.

At present, most of the new developments avoid using pigments to prevent fading due to chemical reactions and to make the product environmentally friendly. However, some colour-shifting ink may utilize a unique type of pigmentation that changes colour depending on the angle of the light. A more advanced type of colour –shifting ink utilizes vacuum metallizing to produce multi-layers of high and low refractive indices. An example, is in the authentication of the newer US$100 banknote to give an orange/green colour shift (Figure 4).

Iridescent colours by holographic embossing

Iridescent colours can be produced by holographic embossing for authentication and decorative applications. In this process microstructures are embossed on base coated flexible substrates such as Polyester to produce structural colours. By controlling the size of the embossed microstructure the holograms can be used for security applications to prevent counterfeiting (Figure 5).

In the Packaging technology, holographic embossed iridescent colours are utilized to give a visually appealing effect for products. This can be in the form of holographic foils, stickers, labels and holographic films.

The physics of colour shifting

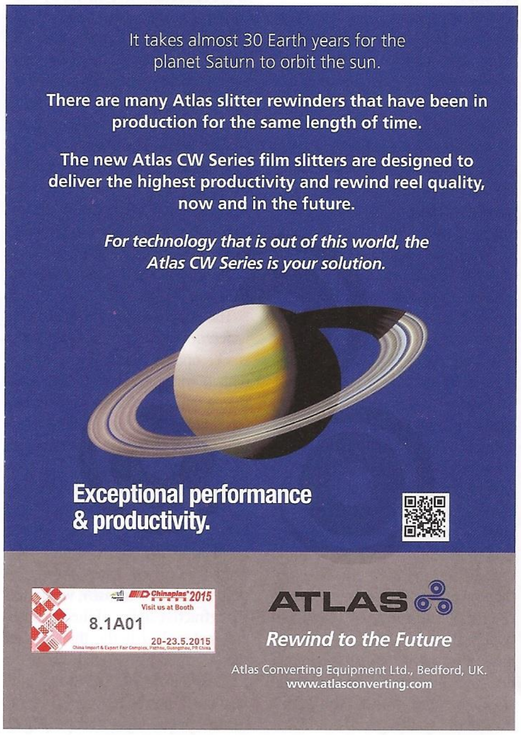
Colour Shifting by Fabry-Perot Structure

Optical coatings consisting of one or more films of dielectric or metallic materials, are widely used in applications ranging from mirrors to eyeglasses and interference filters. Many conventional dielectric coatings rely on Fabry–Perot-type interference, involving multiple optical stacks of transparent layers with thicknesses of the order of the wavelength to achieve functionalities such as anti-reflection, high-reflection and interference. The Fabry-Perot interferometer was designed in the late 1800s by Charles Fabry and Alfred Perot.

Opaque, inorganic based colour shifting Fabry-Perot structures have been used for many years and have excellent colour shifting effects. Typically, structures of this type are made by depositing upon a substrate, a reflector layer, followed by a dielectric layer followed by an absorbing layer. Such products appear highly reflective from one side due to the presence of a reflector layer and appear highly reflective with a colour that changes in an angle dependent manner when viewed from the opposite side due to the Fabry-Perot structure. Iridescent Flakes used in paints and inks can be obtained from symmetric Fabry-Perot structures of the type Absorber/Dielectric/Reflector/Dielectric/Absorber, where two single Fabry-Perot structures share same reflector, by stripping off the deposited layers in the form of Flakes from the substrate , and subsequently dying the Flakes. Such Flakes can be made opaque or transparent and are used to make colour shifting paints and inks.

Types of interference structure

There are two types of distinguished refractive interference structures: refractive –type multilayers and Bragg-type multilayers.



An example of a multi-layer structure is the peacock feather that consists of alternate layers of melamine and keranine as shown in figure 1 on page 18.

a) Refractive -type multilayers- These consist of a limited number of deposited layers (from 3-9) with large differences in refractive index to render the stack of high reflection. An example is the optically variable ink. When the average refractive index of the coated stack is sufficiently low, the refractive -type interference structure combines a considerable reflection with a strong iridescent colour shift. This can be done by either having the all dielectric stack which consist of high and low refractive index or the metal-dielectric stack which is opaque. The metal-dielectric stack combines dielectric and metal layers (e.g. Al or Cr). This combination can be used to produce optically variable ink with high reflectance colour shift effect (Figure 6). This ink is currently used on the Euro50 banknote.

b) Bragg-type multilayers: These consist of many tens to hundreds of layers that slightly alternate in refractive index, together rendering a high iridescent reflection. An example is the co-extruded thermoplastic layers used in the packaging industry and shop-window designs. Iridescent effect produced by co-extrusion consist of alternating low index layers of polypropylene (n=1.49) and slightly high index material such as polycarbonate (n=1.59). The low refractive index makes these foils strongly iridescent. However, the iridescent colour distribution over the foil surface is non- uniform.

Another process which has been used to produce a interference colour shift effect is the Photo-polymerisation of liquid crystals. The molecular structure of cholesteric liquid crystals is such that layers are created with a periodicity of one half wavelength. Cholesteric liquid crystals are pressure sensitive and thermochromic and tend to be chemically unstable. By photo-polymerisation the liquid crystals can have the right temperature and pressure to be stabilised in the desired state and form a thin, fragile iridescent layer (Figure 7).

Figure 4 (left): USD 100 banknote with orange/green colour shift effect

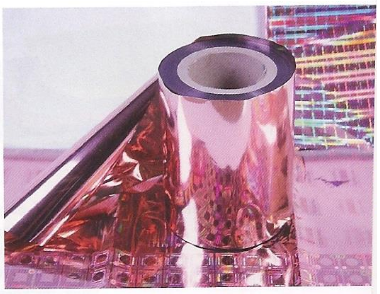


Figure 5 (right): Copper metallization on embossed PET film

The physical principles of thin film interference

Interference effects occur when two optical waves constructively or destructively combine after reflecting from two parallel surfaces. If the optical path of the two surfaces is a multiple of exactly one full wavelength, the two waves will constructively interfere and there will be a strong reflection at that wavelength.

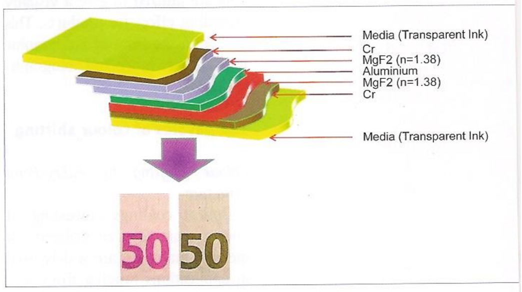
If, on the other hand, the phase of the reflected wave differs by one-half wavelength or an odd multiple of one-half wavelength, then the reflected waves will be completely out of phase; destructive interference will occur at that wavelength. In the latter case, the reflected wave will be weak, and therefore maximum in transmission. The phase of the two waves depends on the thickness and refractive index of the media separating the two surfaces, the wavelength of the light and angle at which light strikes the surfaces.

The simple form of thin film interference consist of a three layer stack; opaque metal layer coated with a transparent dielectric layer then a semi transparent layer on the top (Figure. 8). When a monochromatic beam of light is incident upon the first semi-transparent layer, its amplitude will split or divided by partial reflection. The reflected wave will propagate towards the observer whilst the second transmitted beam will travel an optical path length of $2nd\cos\O r$, where n is the refractive index of the transparent material; d is the thickness of the transparent material; $\O r$ is the angle of refraction. The transmitted beam will then be reflected from the metal opaque layer and propagate towards the observer. If the two reflected light (or partial amplitudes) exit the stack with the same phase then they constructively interfere, thus enhancing the reflectivity of the stack at that wavelength. In this case, the path difference between all corresponding points on the two wavefronts must equal some integer multiple, p, of the incident wavelength.

It can be seen from Figure 8 that if the reflective phase shift is the same then the condition of constructive interference is: $m\lambda= 2\ nd\ \cos\beta$. If the path difference between the two wavelengths is equal to an odd multiple of half wavelength (i.e. $\chi= [(m+1/2)\lambda]$, then they will destructively interfere. This will reduce reflectance at that wavelength. For high quality iridescent reflection the constructive and destructive interference should be optimised to achieve a high degree of luminosity and spectral selectivity. Also, the peak reflective wavelength, i.e. the colour of the stack should change as the observer changes the viewing angle. This will produce a clear colour shift or interference when the optical stack is tilted by a certain degree.

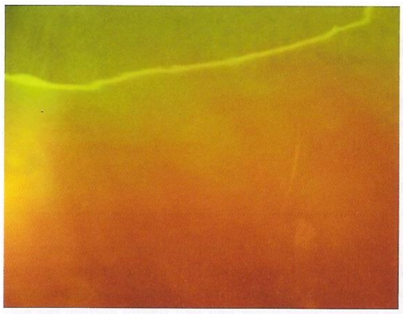
The types of dielectric materials utilized to fabricate interference

Figure 6: Principles of Optically Variable Ink (OVI)



films depend on the application. In general, such dielectrics are non-conductive materials having a specific low or high refractive index. Materials such as zinc sulphide (n=2.6), Titanium oxide (n=2.7), or Aluminium oxide (n=1.76), Silicon oxide (n=1.54) and sodium aluminium fluoride (Cryolite) have been used. However, some of these materials are hygroscopic and must be insulated from the environment by a protective coating. In addition, the zinc and Cryolite salts suffer from temperature instability, which further reduces their performance, even though they are simple and relatively cheap to manufacture. After deposition of the dielectric salt layers, a final layer of silicon oxide or a protective polymeric coat are applied on top of the multi-layered stack for protection.

In other optical interference designs, alternating high and low refractive index values are applied on substrates such as flexible films. The critical element of this design is the interface between two dielectric materials of differing refractive index (one much higher than the other), which is responsible for partially reflecting incident light forward and backward through the filter and producing the interference effect that results in wavelength selection. Reflected and transmitted wavelength values are determined by the thickness and refractive index of the interspersed dielectric layers. Even though the thin coatings themselves are transparent, light waves reflected and transmitted by the dielectric materials interfere to produce brilliant iridescent colours that appear to be emanating from the film surface.



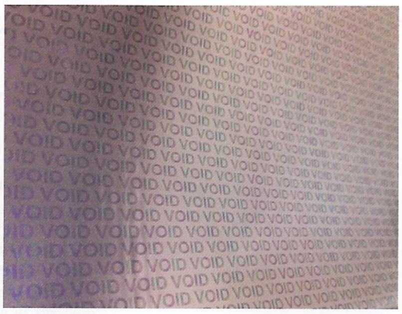
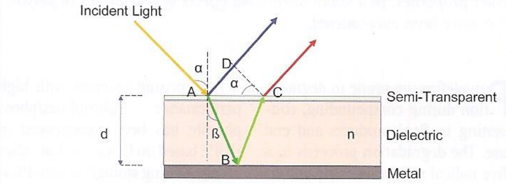


Figure 7 (left): Photo-polymerisation of liquid crystals

Figure 8 (right): The physical principles of interference



Optical Path length Difference; X

$X = n(AB+BC)-AD$

$AB = d/\cos ß$

$AD = (2d \tan ß)\sin\alpha$; $AD = 2d \tan ß(n \sin ß)$

$X = 2\,nd[\,(1/\cos ß) - \tan ß \sin ß$

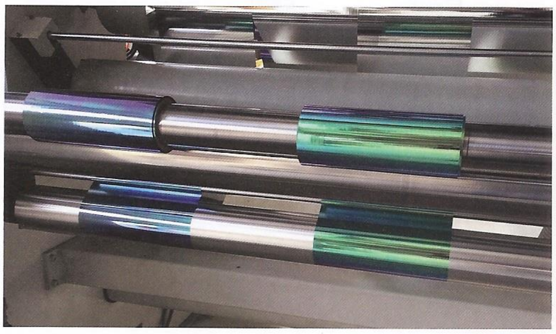
$X = 2\,nd\,[(1-\sin^2 ß)/\cos ß) = 2\,nd \cos ß$

No phase change; constructive; $m\lambda = 2\,nd \cos ß$

Interference effects occur when two optical waves constructively or destructively combine after reflecting from two parallel surfaces. If the optical path of the two surfaces is a multiple of exactly one full wavelength, the two waves will constructively interfere and there will be a strong reflection at that wavelength.

Figure 9: Idvac new colour shift product

Figure 10: Printed texts with colour shift effect using Idvac process



New colour shift effect

Idvac Ltd. has recently developed a colour shift effect on flexible film without the use of structural embossing, inks or pigments. This is a Photonic Crystal Process based on Fabry-Perot optical principles for quick colour switch. It is a combination of dry vacuum metallizing process and low index polymeric coating. The process exhibits an aesthetically appealing colour shift effect from red to green depending on the angle of viewing. This process is more cost effective than the one in which structural embossing or pigments are used (Figure 9).

The metallization process is carried out at fast line speeds and can be done inside a standard vacuum web metallizer without the need for any additional parts or modification. This effect can be combined with holographic embossing images to add an extra security element to a hologram. It can also be used for security threads and decorative packaging including pharmaceutical to add visual appeal to packed products. This colour shift effect can also be printed on films to produce texts, logos and patterns with a quick colour switching between red and green (Figure 10). The effect can also be implemented on a chrome alloy metallized film to produce environmentally durable colour shift films for outdoor applications.

Conclusion

There are various methods that can be employed to produce iridescent or colour shift effects. The selected method depends on the final application and market.

However, the employment of Fabry-Perot principles, which consists of multi-layered optical stack, allows the tuning of the reflected colours according to applications and requirements. This provides good spectral selectivity performance over particular wavelengths to give flexible films unique features such as selective see-through (transparency) with a colour shift effect or a selective visible reflected (opaque) colour shift effect. The product can be used in many applications including packaging and security.