Technology and Applications of Microstructured Pigments

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Based on the utilization of embossed foil substrates during vacuum roll coating deposition, a new family of microstructured pigments with specific shapes, containing symbols, gratings or a combination of these features can be obtained.

Special effects diffractive multilayer pigment flakes have been used to create striking color-shifting effects when incorporated into a wide range of paint, molding or coating processes for the decorative markets in segments like the automobile, plastic, cosmetic and textile industries.

Iridescent Optical Variable Image Devices (IOVIDs) have many important anti-counterfeiting applications for the security and authentication markets. Special effect pigments obtained with a combination of technologies that includes diffractive and thin film interference, magnetic properties, specific shapes and personalized symbols/logos offer potentially robust anti-counterfeiting devices with overt and covert features.

II. Introduction

There is a growing demand for new special color effects in every day decorative markets. From paints for exteriors and interiors in the automobile industry to other paint applications such as mobile phones, electronic equipment, etc. Other markets like cosmetic and decorative printing are also looking for extreme new color effects to enhance their market and public attention.

Microstructured pigments can also be used in the inks market, not only to enhance decorative effects, but also to provide protection against fraud, counterfeiting, simulation and copying of important security documents as banknotes, driver licenses, stamps, visas, passports, etc. These pigments are also suitable for the protection of important brand names and in the pharmaceutical industry for packaging and products.

Another important application concerns covert features. In effect, the security and authentication markets are looking for layered solutions to increase the security of the devices applied to the documents or objects to be protected against counterfeiting. Covert features are designed to complement the easily visual recognizable overt features of security devices. Preferentially, covert features should be designed for forensic and in the field detection application.

III. Decorative Pigment Applications

Traditionally, iridescent metallic and pearlescent pigments, based only on thin film interference have been used intensively in the decorative market [1,2,3]. Recently, a new family of pigments based on diffractive interference or in a combination of diffraction and thin film interference has been developed [4].

One can imagine different ways to categorize this new family of pigments. In the present article the pigments will be differentiated as diffractive opaque [5,6] and diffractive semi-transparent pigments [7]. Different special effects are intrinsically obtained with this type of pigments depending on their microstructure. In addition, when selected thin film interference optical designs are superimposed to the microstructure, it can radically change the optical effects obtained. Furthermore, the combination with other absorbing pigments or colorants creates an infinity number of available possibilities for special applications.

III1. Diffraction of Light

When polychromatic light (white light) illuminates a special type of patterned substrate, the reflection from the surface is very colorful. For example, all the color of the visible spectrum can be observed by reflection if a CD is correctly tilt to the incident light.

The light which is scattered, in a controlled manner (diffracted) by the finely periodic grooved microstructure, undergoes a process of constructive and destructive interference to be finally reflected into various discrete directions. Such grooved microstructure is an optical device called a “diffraction grating”. Depending on shape and frequency of the grooves, a grating will diffract white light spreading all or part of the colors of the visible spectrum.

An observer located in a specific region of the space will intercept some of the diffracted waves (colors). If the observer changes his position, the grating is tilted, or the angle of illumination is varied, the observer will intercept a different set of colors.

The diffraction of light created by a grating is described by the grating equation [8]:

$$Gm\lambda = \sin \alpha + \sin \beta$$

where $G = 1/d$ is the groove frequency, λ is the wavelength of the considered light, α and β are respectively the angles between the incident light and the diffracted beam with respect to the normal and m is an integer called the diffraction order.
For $m = 0$, β is equal to α for all wavelengths. For this condition, the grating acts as a mirror and the light is no longer dispersed. This is called specular reflection or zero order diffraction.

This equation shows that a grating with a frequency of 1400 l/mm, illuminated with white light at normal, spreads all the colors (400 -700 nm) of the spectrum of the visible light symmetrically. As illustrated on Figure 1, an observer located at 79º or -79º with respect to the normal sees mainly the red component. For this position, only the red wavelength (~700 nm) follows constructive interference; the other color components are out of step and cancel each other (destructive interference). For a different viewing angle (i.e. 45º or -45º) only the green component, following constructive interference for this geometry, is oriented towards the observer.

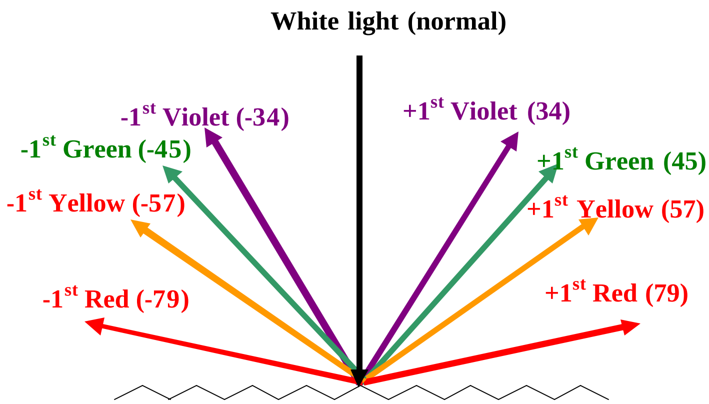

Figure 1. Spectral distribution of diffractive orders at normal incidence for a 1400 l/mm grating

III2. Opaque Diffractive Pigments

The optical effect in these pigments develops through light interference between light waves reflecting at different angles from the top surfaces of the single or multilayer flakes. Depending on the materials and/or optical coating design, achromatic or chromatic pigments can be obtained.

The term achromatic is used here to indicate that the colors under diffuse light conditions, from now on called the "background" color, do not present any specific hue. In opposition, chromatic (i.e. colored) diffractive pigments that are also obtained with single or multilayer designs show a specific hue. The color observed is dominated by the inherent color of the materials by absorption or by the color obtained from optical thin film interference.

In diffuse light (e.g. overcast day), the color (or absence of color) is dominated by the background color. In the presence of a point source (e.g. the sun), the color observed is a combination of the background color and the diffracted light.

Silver and black diffractive pigment (SDP and BDP) with metallic silver and black backgrounds respectively are examples of achromatic diffractive pigments. These pigments are different in the sense that the achromatic background is of high lightness in the case of SDP in opposition to BDP having a dark shade in lightness without any substantial hue characteristic.

The structure of SDP is essentially composed of a high reflecting aluminum layer. The Al layer can be sandwiched between transparent dielectric layers (e.g. MgF2). When added to the design, the dielectric layers protect the Al layer and provide rigidity to the flakes for better mechanical properties, avoiding the curling or folding tendency typical of a thin, pure aluminum flake. These dielectrics do not introduce significant changes in the optical response of the design.

Black diffractive pigments can be produced using a material that inherently absorbs all the wavelengths of the visible light (e.g. carbon) or by a Fabry-Perot thin film interference structure of the type absorber/dielectric/reflector/dielectric/absorber. In the case of a Fabry-Perot structure, the dielectric playing the role of a spacer, should be thin enough to assure that all the wavelengths of the visible follow destructive interference before exiting the flake [9].

In this work a SDP was produced by coating a 1400 l/mm grating with the following three layer design:

4QW MgF2 @ 550 nm /100 nm Al/4QW MgF2 @ 550 nm

For a BDP, a 2000 l/mm grating was used with the following five layers optical design:

8 nmCr/ 1QW MgF2 @ 300 nm/ 100 nm Al /1QW MgF2 @ 300 nm / 8 nm Cr

The characterization of the diffractive effects was obtained with a point source illumination at -45º incidence and -33º to 80º receiving angle. Figure 2 shows the color trajectory in the a*,b* color space for pigment drawdowns of the SDP 1400 l/mm pigment. The trajectory covers almost one full circle showing that all the colors of the visible spectrum are diffracted for this geometry.

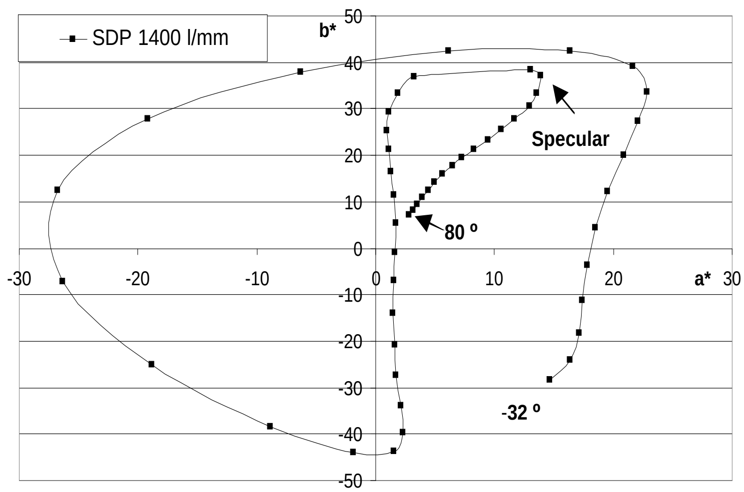

Figure 2. Color trajectory of a Silver Diffractive Pigment (SDP). Frequency = 1400 l/mm

The color trajectory for the BDP 2000 l/mm pigment is shown in Figure 3. Compared with the SDP 1400, the color trajectory of BDP 2000 l/mm is more restricted, mainly to the 2nd and 3rd quadrants of the graph. These results are in good agreement with the calculated position of the visible wavelengths using the grating equation for 1400 and 2000 l/mm frequencies.

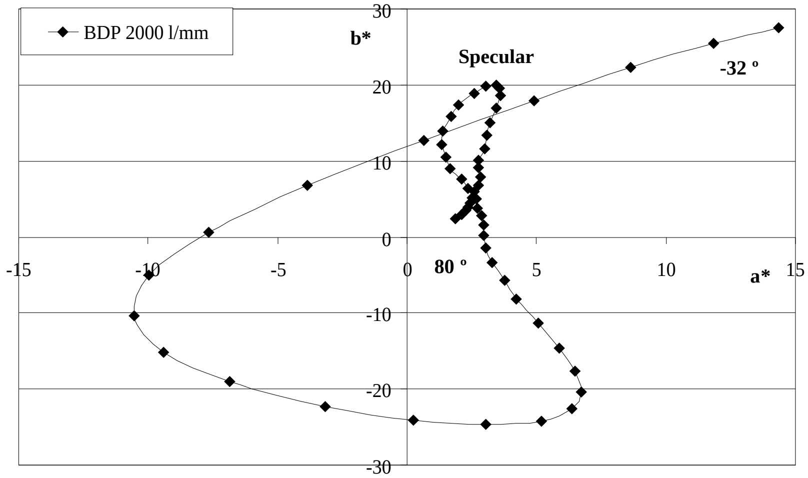

Figure 3. Color trajectory of a Black Diffractive Pigment (BDP). Frequency = 2000 l/mm

Achromatic diffractive pigments are very interesting in the sense that they can be easily combined with other absorbing pigments or colorants. The characteristic color of the absorbing pigment or colorant can be selected to create strong specular or diffuse color effects. The diffractive pigments of the blend contribute to the angular dispersion of light beams in regions of the space otherwise absent of light.

Figure 4 shows the color trajectory for 45º incidence of the SDP 1400 with the addition of increasing amounts of red pigments. The trajectories always follow almost one full circle but are displaced toward the right in the 1st and 4th quadrants.

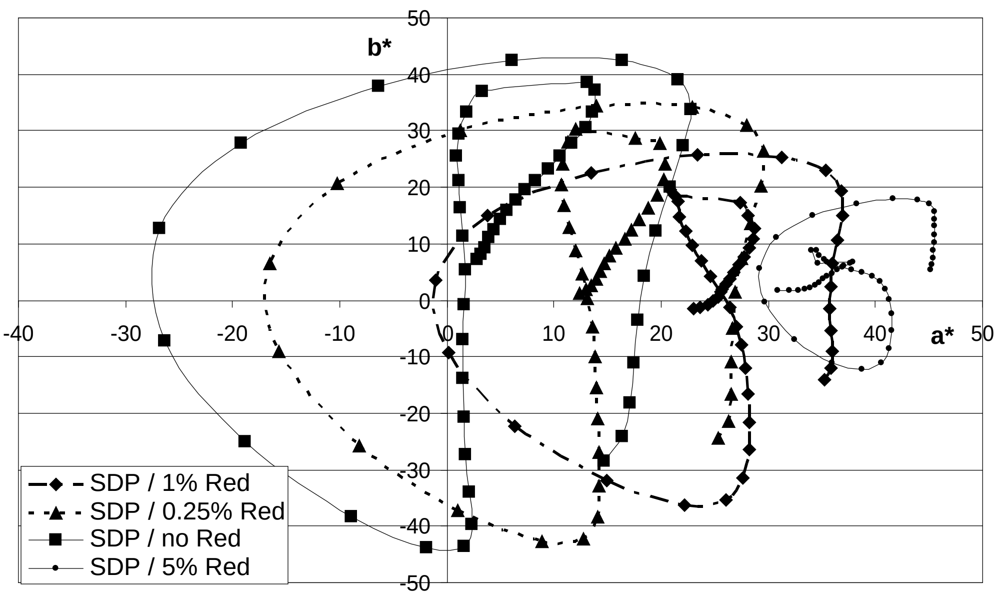

Figure 4. Color trajectory of a SDP with addition of red pigment. Frequency = 1400 l/mm

The background color of opaque chromatic diffractive pigments can also be obtained by the characteristic optical absorbing properties of the material deposited. Layers of Copper, Gold, TiN, etc. are few examples of metals and compounds layers that can be deposited to obtain a specific color background.

Evidently, thin film interference can also be used to create colors that will be superimposed to diffractive interference. As in the case of the BDP, a Fabry-Perot interference design of the type absorber/dielectric/reflector/dielectric/absorber can be used. The dielectric spacer can be chosen to produce any color of the visible spectrum. Further more, if the spacer is a low index dielectric (e.g. MgF2, SiO2, etc), the pigment will show a color shifting background due to thin film interference in addition to diffractive interference. If the dielectric chosen is a high index material (e.g. ZnS, TiO2, etc.), the background color will shift slightly or not at all . This type of interference design produces a color background similar to the color obtained by an absorbing metallic layer.

The following three designs were chosen to illustrate the optical effects obtained.

A/ 2QW ZnS@ 450 nm/ 100 nmCu/ 2QW ZnS@ 450 nm
B/ 8 nm Cr/ 4QW ZnS@ 530 nm / 100 nm Al/4QW ZnS@ 530 nm /8 nm Cr.
C/ 8 nm Cr / 4QW MgF2@ 530 nm / 100 nm Al/4QW MgF2@ 530 nm /8 nm Cr.

Design A, coated on a 2000 l/mm grating, presents a bronze background color. Designs B and C were coated on a 1400 l/mm grating. Design B shows a slightly green shifting background and design C a green to blue color shifting background when viewed close to the specular reflection. All of them also having the diffractive effect superimposed when observed with directional light.

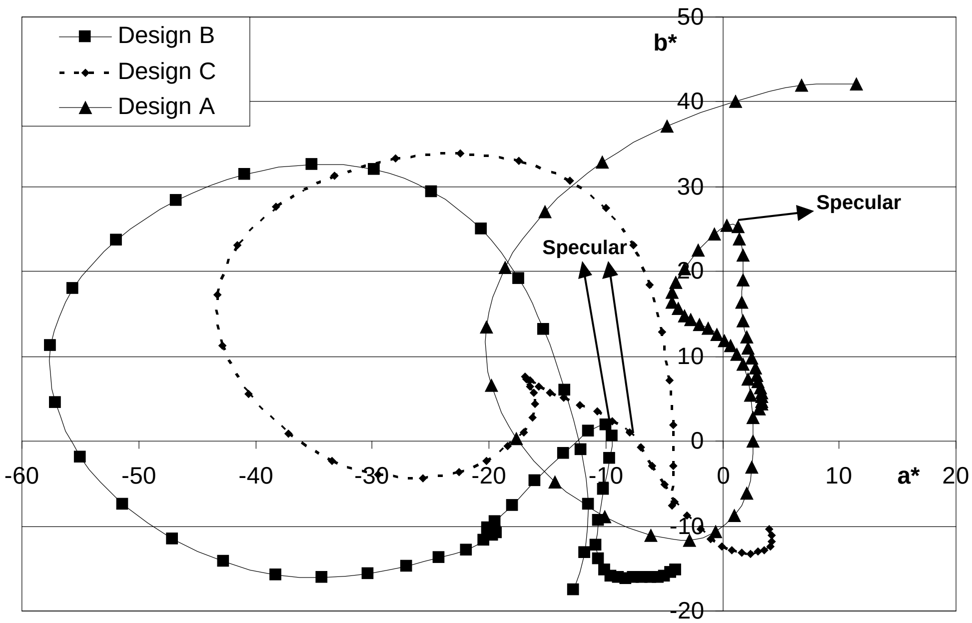

Figure 5. Color trajectory of various diffractive pigments with a chromatic background

Figure 5 shows the color trajectory of these samples when using the 45º illumination geometry explained before. The Gr-Bl CDP and Gr SS samples stay in the 2nd and 3rd quadrants. The bronze design has a goldish specular reflection, the diffractive effects also cover the 2nd and 3rd quadrants, but with less saturated colors.

III3. Semi-transparent Dichroic Diffractive Pigments

For some applications it can be desirable to superimpose a diffractive effect to an object over its background color. Unfortunately, opaque diffractive pigment flakes dull or change the underlying color of the object to be coated.

Unlike diffractive flakes having opaque metal reflectors, semi-transparent diffractive flakes can have reflecting and transmitting colors to be matched to the object they are applied to. These semi-transparent diffractive pigment flakes can be made using alternating layers of dielectric materials in a $(\text{high-low-high})^n$ or $(\text{low-high-low})^n$ design to form an optical interference stack, which is often referred to as a dichroic stack. The color of an image printed with some dichroic diffractive pigment flakes can also color shift as a function of the viewing angle.

The optical effect of dichoic diffractive pigments (DDP) under diffuse illumination conditions is similar to the effects obtained with the well known pearlescent pigments. These pigments have been popular already for some time in the decorative and cosmetic industries. In addition to the standard pearlescent effect, DDP show strong diffractive effects under direct illumination.

Dichroic diffractive pigments can be produced to impart little, and in some cases, essentially no change in the background color of an object. They can also be used as overprinting so that the viewer can see the underlying image or writing through the flakes. In most cases, optical designs of five or less dielectric layers on a grating structure enable strong diffractive effects when the pigment flakes are dispersed in a suitable vehicle or carrier.

To show the optical properties of this kind of pigment, a HLHLH design made of thin film layers with quarter wave optical thicknesses ("QWOT") at 530 nm was used. ZnS was selected as the high refractive index (H) material and MgF_2 as the low refractive index (L) material. The design was centered at 530 nm and coated on a 1400 and 2000 l/mm grating substrate. These pigments do not present a characteristic color tint and were used to obtain a white diffractive effect when applied over a white object. As a result, the object appears essentially white pearlescent under diffuse illumination and diffractive when illuminated with directional light.

Following well know optical thin film interference theory, when the same 5 layer design is shifted from 530 nm to lower or higher wavelengths, the pigment will present a bluish or reddish tint on reflection and yellowish or greenish tint on transmission, respectively. The shifting of the tint obtained is shown in the reflectance plot of Figure 6 for drawndowns made with the 1400 l/mm grating. Figure 7 shows the color trajectory for these three designs. The diffractive effect is observed for all three samples.   However, it is displaced for a trajectory centered on the zero coordinates (white neutral design) to the right and left as corresponding to the tints of the HLHLH thin film interference designs.

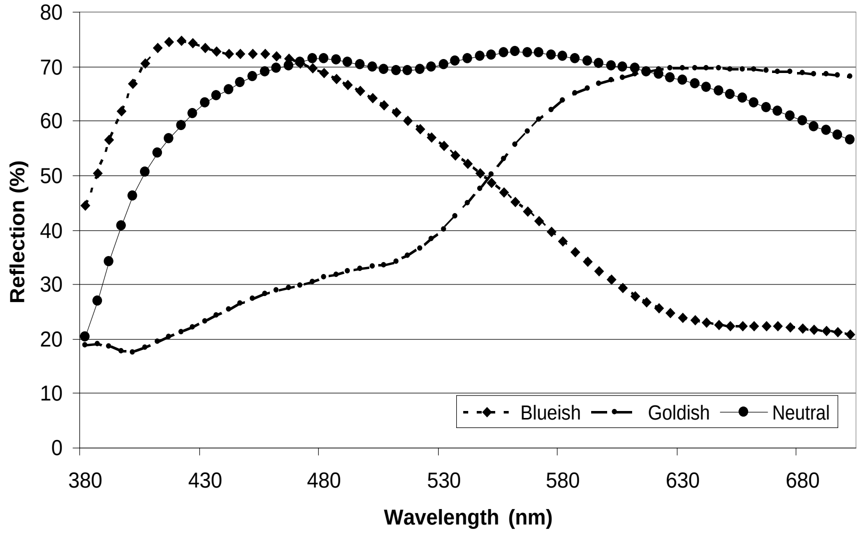

Figure 6. Reflectance under diffuse illumination of various Dichroic Diffractive Pigments

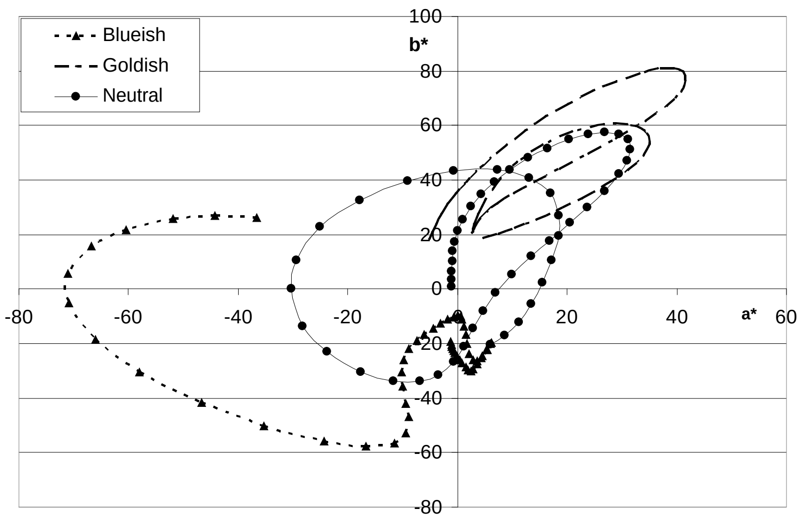

Figure 7. Color trajectory under direct illumination of various Dichroic Diffractive Pigments

It is obvious that the neutral design centered at 530 nm is more suitable as an overcoating on a white background. Other tints (i.e. the goldish or bluish) will match other background color of objects producing almost infinite matching possibilities for practical applications.

Diffractive pigments obtained with high and low index dielectric materials as TiOx, SiOx, FeOx, etc. are particularly suitable for products in the cosmetic market such as nail polish, lipstick, colored powders, etc. They can also be combined with other raw materials in cosmetic formulations.

IV. Security and Authentication Applications

As previously explained, microstructured pigments can create strong visual attractive special effects (overt effects) that are extremely difficult to copy or simulate. In addition, these pigments can also be used as taggants (covert features) in mixtures with other coating to demonstrate the authenticity of the product or to track its origin. Further more, these pigments can provide security with both overt and covert features in the same anti-counterfeiting device.

Independently, if we are looking for an overt or covert feature, the basic requirements are similar. The feature has to be easy to recognize and it can not be alternatives or equivalents that will make the feature easy to emulate. In addition, it is important to use technologies and materials from secure sources to make the feature hard to copy.

IV1. The Combination of Diffraction and Magnetic Orientation to produce DOVIDs

Any ferromagnetic particle immersed in a non-magnetic fluid phase (i.e. ink vehicle) and exposed to an external magnetic field exhibits an orientation that tends to minimize the energy condition for the specific particle/magnetic field system. In effect, when a magnetic field is applied to the particle/fluid system, a torque is exerted on the particle. The particle will be oriented along a certain direction corresponding to its axis of easy magnetization ("Easy Axis") such that its demagnetization energy is minimized. The concept of the "easy axis" is related to the magnetic anisotropy of the particle [10].
It has been demonstrated [11] that in the case of linear grated flakes (Figure 8a), the condition of lower energy is achieved when the particles are oriented with the grooves parallel to the magnetic field since the smallest number of surface poles are separated by the larger distance. (Figure 8b).

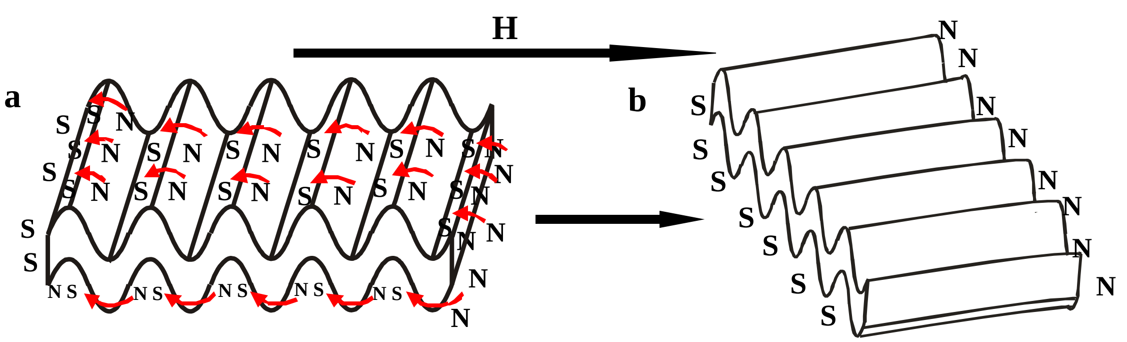

Figure 8. Preferential orientation of a grated particle in the presence of magnetic field H

This property of groove orientation can be used to create a new optical variable diffractive device (DOVID) for security and authentication applications. As an example, Figure 9 shows a simple in plane DOVID using diffractive microstrctured pigments. The outside circle was printed with diamond shaped flakes with a 1400 l/mm grated microstructure (see insert) and the inside arrow with a 500 l/mm unshaped diffractive pigment. The grooves of the circle are perpendicularly oriented with respect to the groove in the arrow. The overt feature in this case can be observed when the device is illuminated with a focal point. Only one of the images lights (arrow or circle) when the incident light is diffracted. This device cannot be replicated by computer scanning, color copiers, photography, or other commonly used forgery techniques.

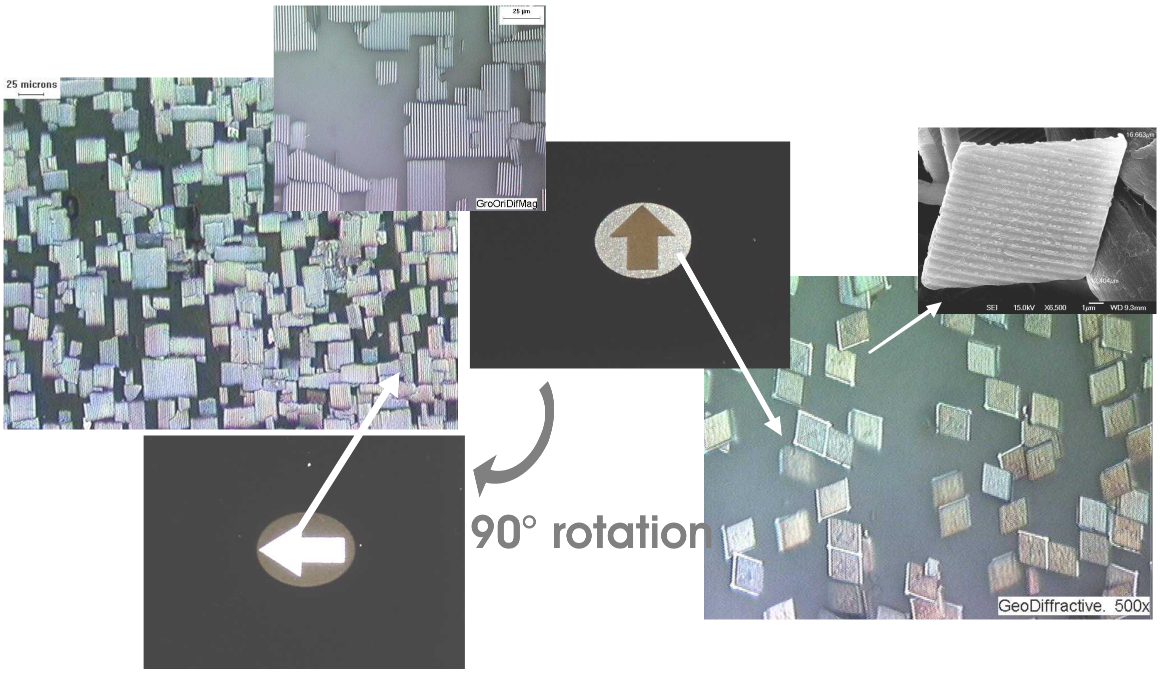

Figure 9. Printed DOVID with the outside circle printed with the grooves oriented 90° with respect to the grooves in the arrow

The technology for printing in the presence of magnetic fields in addition to the grove orientability and the specific shape of the flakes as part of the overall pigment design, adds an extra layer for authentication with a first level covert verification readily identifiable with a simple hand held optical microscope.

IV2. Microstructured Covert Taggants

As mentioned before, microstructured pigments can be used as taggants (covert features) in mixtures with other overt features like optically variable pigments, fluorescent pigments, dyes, etc. The addition of microstructured covert taggants (MCT) is easily achievable by any of the current printing technologies [12].

Figure 10 shows the example of diamond shaped aluminum flakes used as covert taggant for a printed device with a red to gold color shifting pigment as the overt feature. These aluminum flakes are easily detectable when observed with an optical microscope. Other optical designs, including designs creating color shifting effects, can be used simultaneously with the shape feature.

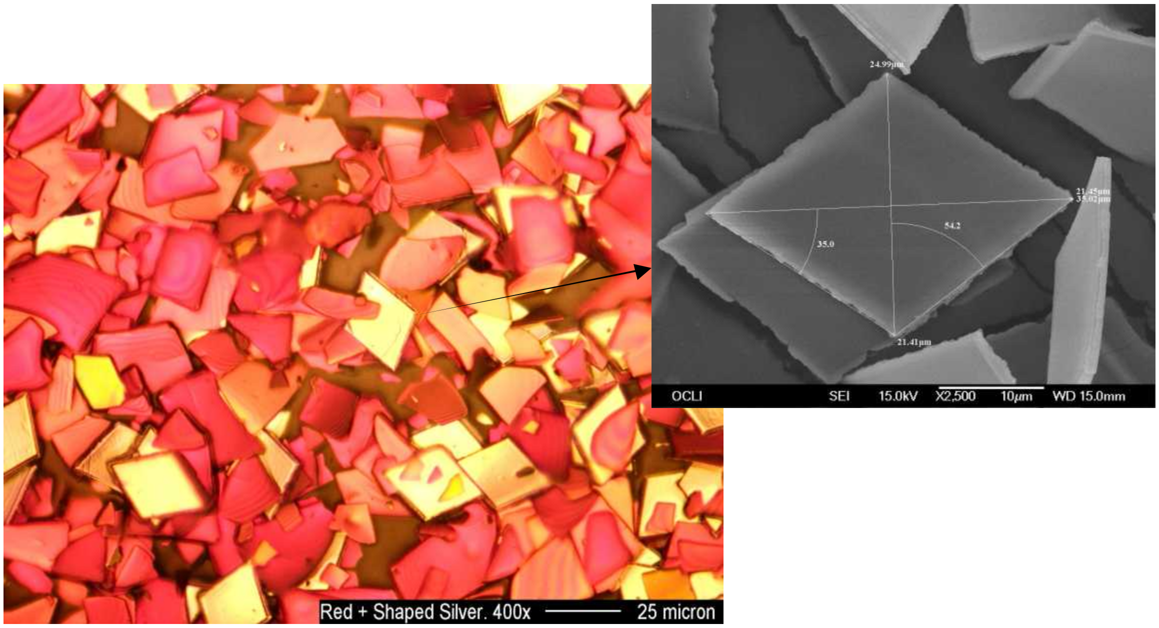

Figure 10. Diamond shaped aluminum flakes in a Red-Gold Color Shifting pigment

Other MCTs can incorporate symbols [13]. Figure 11 shows semitransparent unshaped flakes with a "F" symbol added to a magenta to green color shifting pigment intaglio printed. Compared with the diamond shaped aluminum flakes, these semitransparent flakes are more difficult to spot. Size and separation of the symbols can be easily changed. Figure 12 shows three different semitransparent flakes in a blue to bronze color shifting security device printed by silk screen.

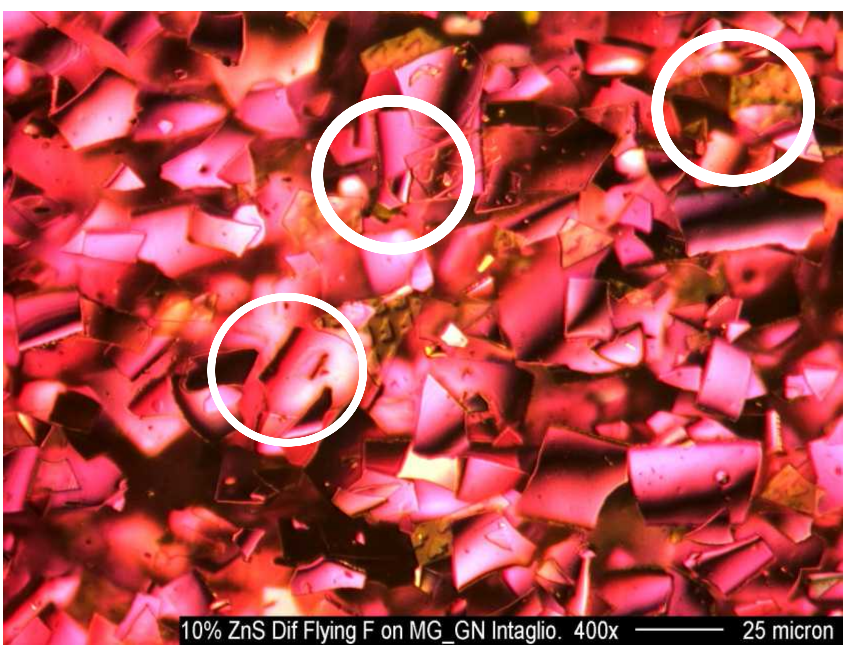

Figure 11. Semitransparent unshaped flakes in Mg-Gr color shifting pigment

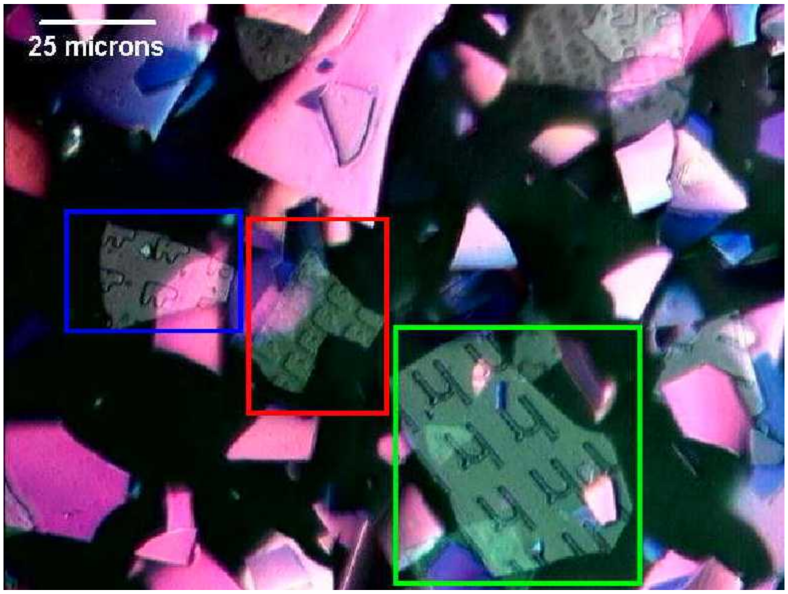

Figure 12. Semitransparent unshaped flakes in Bl-Rd color shifting pigment

As another microstructure variation, symbols and logos can be incorporated in shape flakes. Figure 13 shows a 24 microns square aluminum flake with a company logo added as covert feature to a rose to green color shifting UV flexo printed label. The flakes are easily detected and the logo easily readable with a low/medium magnification hand held optical microscope counting for the authentication of the product.

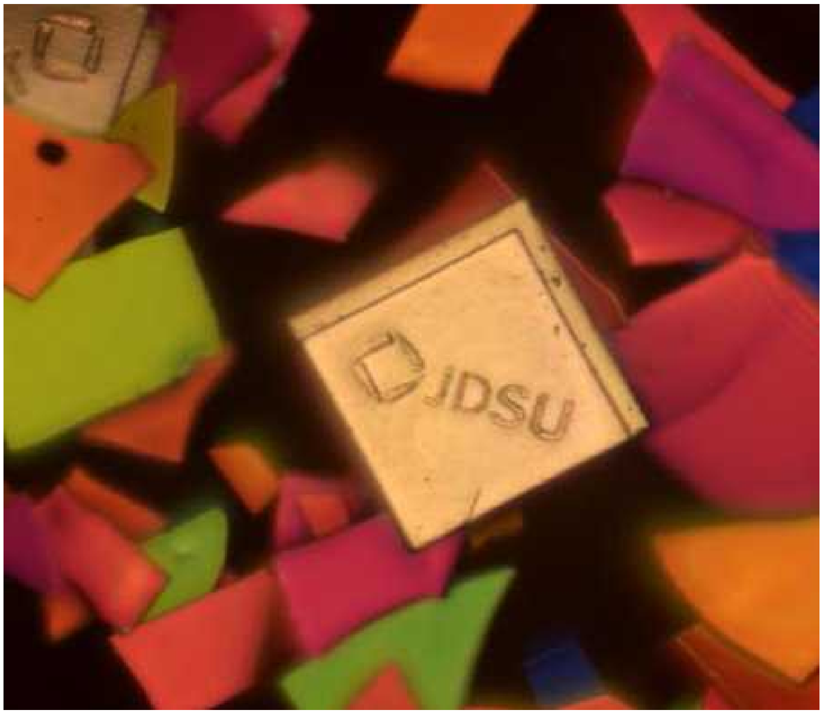

Figure 13. Square shaped aluminum flake with personalized company logo in Ro-Gr color shifting pigment

Of course as in the case of other microstructured pigments previously described, different optical designs can be used to match specific applications and functionalities to the devices to be protected, providing in some cases not only covert features but interesting combinations of covert and overt features extremely difficult to counterfeit or simulate.

Conclusion

The combination of materials with different functional properties in addition to engineered microstructures have generated a whole new family of special effect pigments that found a large number of applications in important markets such as product decoration, cosmetic, document security, authentication, brand protection, etc.
For some applications these pigments can combine thin film and diffractive interference to create strong iridescent effects in different illumination conditions.
For other markets, such as security and authentication, new devices need to be constantly developed as barriers to counterfeiting. Layering multiple technologies in addition to easily recognizable covert and overt features in a single device offers an efficient way to prevent counterfeiting.

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