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Angle-Dependent Optical Effects Deriving from Submicron Structures of Films and Pigments

Gerhard Pfaff and Peter Reynders*

Merck KGaA, Pigments Division, 64271 Darmstadt, Germany

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I. Introduction

A. General Introduction

Angle-dependent optical effects can be found in various industrial products and consequently in different end-user applications. These effects are used for functional purposes, such as security printing and optical filters, and for decorative purposes, as in cosmetics and car paints.

In the security field, the user takes advantage of the fact that the angle-dependent optical effect cannot be easily copied with conventional copier machines or photographic techniques. Forging is only possible if similar products are utilized, which makes forging much more complicated and expensive. Consequently, pearlescent and optical multilayer pigments are used on bank notes by many countries.

Multilayer films or films containing pearlescent pigments reflect a certain portion of the visible light. Therefore, they are increasingly being used in greenhouse applications to influence the light that shines onto the plants and, hence, influences their growth.

In the decorative applications, three major advantages are seen from the use of angle-dependent optical effects. The first is the illusion of optical depth, which is, for example, created by the gradual angle-dependent color changes observed of pearlescent pigments in car paints. This illusion is especially strong when extended areas are profiled as in automotive fenders. Pearlescent pigments can be found in the lacquers of more than 40% of the cars in the United States and 30% in Europe.

The second advantage is the subtle to startling eye-catching effect of an angle-depending color. A consequence of this is that pearlescent pigments are often used in packaging for their aesthetic and promotional eye-catching appeal. The third field is the ability to imitate the effect of natural pearls in buttons, plastic bottles, and many other objects.

B. Scope of the Review

Angle-dependent optical effects can be achieved by using extended films, for example, wrapping paper; extended coatings, for example, glass dip coatings; or coatings that contain special effect pigments.

In this review, a special focus is set on the angle-dependent optical effects found in particles, e.g., pigments, because they can be used in a broader set of applications than extended optical films and coatings. Similar products are used for functional purposes, for example, conductive pigments. These are not a subject of this review.

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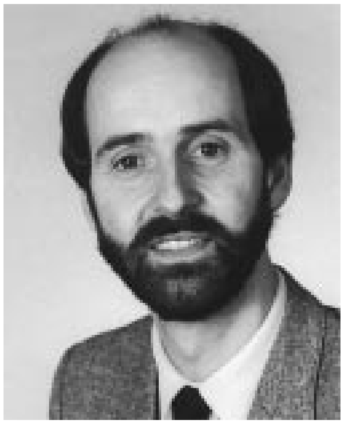

Gerhard Pfaff was born in Meiningen, Germany, in 1953. He received his diploma in chemistry (1978) and Ph.D. (with A. Feltz) from the Friedrich-Schiller-University of Jena (1983). His postgraduate research was in the field of solid-state chemistry and ceramic materials at the University of Jena. He was a postdoctoral fellow at the C.N.R.S. Institute of Solid-State Chemistry of Bordeaux, France (with J. P. Bonnet), in 1987. In 1991, he joined Merck KGaA, Darmstadt, Germany, as a research manager in the R&D department of the Pigments Division. Since 1994, he has been the head of product development for effect pigments in this division. In 1997, he received the habilitation in the field of inorganic chemistry at the Technical University of Darmstadt (with R. Kniep), where he is now also a lecturer. His research interests include synthesis, structural investigation, and application behavior of effect pigments, materials with advanced optical and electrical properties, and perovskites.

Peter Reynders was born in Bad Gandersheim, Germany, in 1958. He received his diploma in organic chemistry from the University of Göttingen (1984) and his doctoral degree in physical chemistry at the Max Planck Institute of Biophysical Chemistry, Göttingen, Germany (1988). In the following years, he worked in the field of industrial nanochemistry at Lucent Bell Laboratories, NJ. He is currently Research Manager in the Pigments Division at Merck KGaA, Darmstadt, Germany. His research interests include the synthesis, sintering, and characterization of nanocrystalline oxides and surface modification and coloristics of industrial pigments.

II. Theory of Angle-Dependent Optical Effects

Due to the importance of interference pigments and films, the theory of interference colors is presented below. The background of dichroism and holographic effects is discussed together with the products.

A. Interference at Single Layers

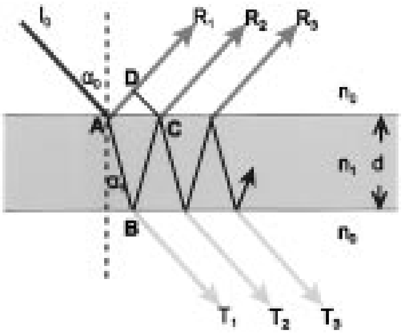

Figure 1. Splitting of a light beam at a thin layer. Reflections occur at both interfaces of the film.

The physical background of optical interference effects has been the subject of many publications.[1] The literature, however, deals either with the theory for idealized thin films[2-5] or with the measurement and characterization of pearlescent pigments in application media.[5,6] A theory for interference pigments that includes the optical effects of the particles boundaries is not yet developed.

When a beam of white light strikes a thin film with a thickness on the order of the wavelength of visible light, interference colors can be detected. The color observed depends on the viewing angle.

The basis of the interference theory is the Fresnel equations, which give the amplitudes r of reflected electromagnetic waves as

$$r_s = \frac{n_0 \cos \alpha_0 - n_1 \cos \alpha_1}{n_0 \cos \alpha_0 + n_1 \cos \alpha_1}$$

$$r_P = \frac{n_1 \cos \alpha_1 - n_0 \cos \alpha_0}{n_1 \cos \alpha_1 + n_0 \cos \alpha_0} \tag{1}$$

n_0 and n_1 are the refractive indices of the two media. The indices S and P refer to the orientation of the electromagnetic field vector relative to the plane of incidence: perpendicular = S-polarized light, parallel = P-polarized light.

The intensity R of the light is closely related to its amplitude

$$R_S = r_s^2$$

$$R_P = r_P^2 \tag{2}$$

The geometry of the light pathway within the two media conforms to Snell's law (eq 3) and the reflection law that the incident angle is equal to the reflecting angle. According to these terms, an incident light

$$n_0 \sin \alpha_0 = n_1 \sin \alpha_1 \tag{3}$$

beam of intensity I_0 and amplitude A_0 splits up into reflected and a transmitted portions, see Figure 1. The amplitudes R_i of the reflected light beams coming from single and multiple reflections can be calculated using the Fresnel equations

$$\mathbf{R}_1 = r_1 \mathbf{A}_0$$

$$\mathbf{R}_2 = t_1^2\, r_2 \mathbf{A}_0$$

$$\mathbf{R}_3 = t_1^2\, r_1 r_2^2\, \mathbf{A}_0, \text{ etc.} \tag{4}$$

with t as the amplitude of the transmitted light. The reflection at the upper and lower surfaces gives rise to different pathways of the particular beams. This difference of the traversed distances, G, is represented by the following terms, see Figure 1

$$G = 2n_1\overline{AB} - n_0\overline{AD} \tag{5}$$

Combined with Snell's law (eq 3), the angle-dependent form is obtained

$$G = 2n_1 d\sqrt{(1 - \frac{n_0^2}{n_1^2}\sin^2\alpha_0} \tag{6}$$

The phase difference angle δ follows as

$$\delta = \frac{2\pi}{\lambda}G = \frac{4\pi n_1 d}{\lambda}\sqrt{(1 - \frac{n_0^2}{n_1^2}\sin^2\alpha_0} \tag{7}$$

The superposition of the reflected beams must be performed for amplitude and phase, see eq 4

$$\begin{aligned}\mathbf{R} &= \mathbf{R}_1 + \mathbf{R}_2 + \mathbf{R}_3 + ... \\ &= r_1 + t_1^2 r_2 e^{-i\delta} - t_1^2 r_1 r_2^2 e^{-2i\delta} + t_1^2 r_1^2 r_2^3 e^{-3i\delta} - ... \\ &= r_1 + t_1^2 r_2 e^{-i\delta}(1 - r_1 r_2 e^{-i\delta} + r_1^2 r_2^2 e^{-2i\delta} - \\ &\qquad r_1^3 r_2^3 e^{-3i\delta} + ...)\end{aligned} \tag{8}$$

This geometrical series can be transformed to

$$\mathbf{R} = r_1 + \frac{t_1^2 r_2 e^{-i\delta}}{1 + r_1 r_2 e^{-i\delta}} \tag{9}$$

The optical impression for the human eye is directly related to the reflected light intensity I_r, which is obtained by multiplication of **R** with its conjugated complex value.

For nonabsorbing media ($r^2 + t^2 = 1$; $I_r + I_t = I_0$) and using eq 7, we obtain the following expression for the intensity of the reflected light I_r

$$I_r = \frac{r_1^2 + r_2^2 + 2r_1 r_2\cos\delta}{1 + r_1^2 r_2^2 + 2r_1 r_2\cos\delta} \tag{10}$$

and for the intensity of the transmitted light I_t

$$I_t = \frac{(1 - r_1^2)(1 - r_2^2)}{1 + r_1^2 r_2^2 + 2r_1 r_2\cos\delta} \tag{11}$$

For a thin film in a homogeneous medium we can set $r_1 = -r_2 = r$ and obtain

$$\mathbf{R} = \frac{1 - \cos\delta}{\frac{1 + r^4}{2r^2} - \cos\delta} \tag{12}$$

Table 1. Refractive Indices n_D of Important Transparent Coating Materials

substance	refractive index n_D (550 nm)	max reflected intensity of thin layer (%) in air	in Lacquer of $n_D = 1.5$
glass	1.5	15	0
natural muscovite	1.58	18	0
Al_2O_3 corundum	1.77	27	3
natural pearl essence	1.91 (perpendicular) 1.78 (parallel)	32	6
basic lead carbonate	2.0	36	8
BiOCl	2.15	42	12
TiO_2 anatase	2.3	47	16
TiO_2 rutile	2.7	58	28

When the incident angle is variable, the amplitude r has to be replaced by the Fresnel expressions of r_s and r_p (eq 1). In the case of perpendicular incidence of light, these equations collapse to

$$r_s = r_p = \frac{n_0 - n_1}{n_0 + n_1} \tag{13}$$

In eq 12, the reflected light intensity R reaches a maximum value for $\cos\delta = -1$. This is realized for distinctive wavelengths and distinctive optical film thicknesses $n_1 d$

$$\lambda_{max} = \frac{4n_1 d}{2m + 1} \text{ for } m = 0, 1, 2, 3, ...$$

$$n_1 d = (2m + 1)\frac{\lambda_{max}}{4} \tag{14}$$

At these wavelengths we observe the maximum reflection R which exclusively depends on the refractive index n_1 of the platelet according to

$$R = \left(\frac{n_1^2 - n_0^2}{n_1^2 + n_0^2}\right)^2 \tag{15}$$

This is the well-known equation for maximum reflectance of perpendicular incidence on a thin film. Values for the refractive index of the most important coating materials are shown in Table 1.

If the refractive index of the thin film is higher than that of the medium, which is normally the case, a phase shift of 180° occurs for the portion of the light which is reflected at the upper surface of the film. This phase shift is already taken into account by eq 1.

According to eq 11, R is extinguished for $\cos\delta = +1$. The condition for this is

$$\lambda_{min} = \frac{4n_1 d}{2m} \text{ for } m = 1, 2, 3, ...$$

$$n_1 d = m\frac{\lambda_{min}}{2} \tag{16}$$

For eqs 13–16, we have restricted the model to perpendicular incidence. If this restriction is lifted,

Table 2. Current Producers of Oxidic Effect Pigments (1998)[a]

company	product range	remarks
Merck KGaA (in the U. S.: EM Industries)	full range of metal oxide/mica pigments, pearlescent pigments on silica and alumina flakes, BiOCl	
Engelhard Corporation	full range of metal oxide/mica pigments, BiOCl, natural pearl essence, basic lead carbonate	bought pearlescent pigment business from Mearl in 1996 and from Semo in 1997
BASF	metal oxide/aluminum pigments, limited range of metal oxide/mica, produced by CVD	
Eckart Werke	limited range of metal oxide/mica pigments, metallic pigments	bought pearlescent pigment business from Kemira in 1998
Flex Products	multilayer pigments by CVD, mainly for security printing	subsidiary of OCLI
ISP Van Dyk	BiOCl	formerly Mallinckrodt
Shiseido	titanium suboxide/mica	
Sudarshan	limited range of metal oxide/mica pigments	partly owned by Dainippon Ink

[a] There are some smaller producers that cover approximately less than 2% of the world market.

the relation of the interference color with the incident and viewing angle α makes the equations more complicated, due to the angle dependence of the phase difference δ. Equation 16 then becomes

$$\lambda_{\max} = \frac{4n_1 d}{2m+1}\sqrt{1 - \frac{n_0^2}{n_1^2}\sin^2\alpha} \quad \text{for } m = 0, 1, 2, 3, \ldots \quad (17)$$

This equation shows that the maximum reflectance shifts to a shorter wavelength when the viewing angle is increased. A thin film illuminated by white light can, for example, show traveling colors from red to blue when the observer changes his position toward a flatter viewing angle. A flatter viewing angle corresponds to a longer path through the layers or, respectively, an increased layer thickness. Figure 2 shows the reflectivity spectra of a series of pearlescent pigments consisting of mica platelets with increasing rutile layer thicknesses.

From eq 17 it is also seen that a broader distribution of the thickness d would lead to a less defined color and could finally wipe out the interference maximum. This is the case for ground natural mica which is used as a substrate for the production of pearlescent pigments, see below. It consists of platelets whose thickness vary from particle to particle, typically in the range of 100−1000 nm. Therefore, the single mica particles show interference colors but not the ensemble of particles.[1] In contrast to mica, the alumina and silica substrates mentioned below have a constant thickness and show interference colors. This is also the case for bismuth oxychloride and basic lead carbonate pigments.

The optical layers can also be built up by materials that absorb light such as iron oxides or chromium oxides. In this case, the mass tone is combined with the angle-dependent interference color. For the calculation of the optical characteristics of such layers, the real refractive index in the equations above is replaced by the complex refractive index $n_i = n - ik$, where k is the extinction coefficient, which is of course also a function of the wavelength of the incident light.

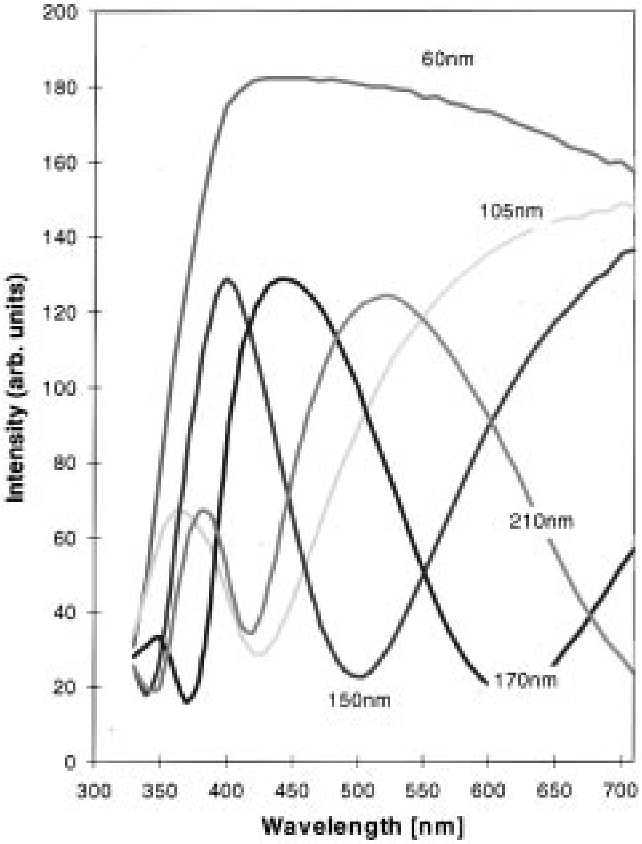

Figure 2. Reflectivity of pigmented nitrocellulose lacquer films containing commercial mica-based pearlescent pigments with rutile layers of various thicknesses indicated in the figure: 60 nm corresponds to a silverwhite, 105 nm to a golden, 150 nm to a red, 170 nm to a blue, and 210 nm to a green interference color.

B. Interference at Multiple Layers

When several thin films of different refractive indices are combined, multiple reflections occur.[7] As a consequence, stronger and better defined interference colors can be achieved, see Figure 9. This multilayer technique is found in nature as the deep iridescent colors of beetles exocuticles,[8] butterfly wings, bird feathers,[9] and plants[10] as well as the nacreous appearance of natural pearls and sea shells.[11] The well-known TiO_2−mica pigments consist of a three-layer system, as shown in Figure 3. Every pigment particle shows the stronger interference color of a three-layer TiO_2−mica−TiO_2 system. How-

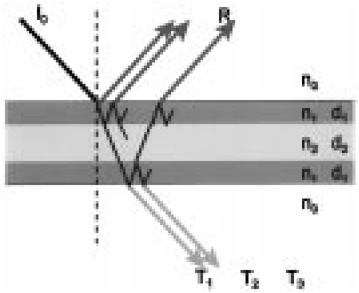

Figure 3. Splitting of a light beam at a three-layer system. Multiple reflections occur at the various interfaces.

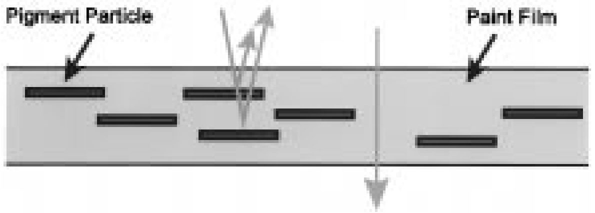

Figure 4. General scheme of platelet-shaped pigment particles in a paint film. Typical thicknesses of the film are between 5 (offset printing), 30 (automotive coatings), and 120 μm (powder coatings). The mean thickness of the pigment particles is about 0.5 μm.

ever, due to the broad thickness distribution of the mica platelets, the ensemble of particles has nearly the same optical characteristics as a single TiO_2 layer on mica.[1] New pearlescent pigments based on synthetic substrates are true three-layer systems and show, therefore, an improved appearance, see below.

If materials are used with a smaller difference in the refractive indices, it becomes necessary to use many more layers to achieve a reasonable interference effect. There are commercial products which are based on organic polymers such as polystyrene and polyethylene and consist of up to 1000 layers.[12]

The interference color effects of multilayer films cannot be calculated in a simple way. It would go beyond the scope of this review to show the theoretical background; therefore, it is referred to in the literature.[13,14] However, as for the single layer, the intensity of the reflected light depends strongly on the differences between the refractive indices.

C. Basic Requirements for Pearlescent Pigments

Pearlescent pigments must fulfill many requirements to be successful in the market place. First of all, they should show a strong pearlescent effect. As outlined above, a high difference in the refractive indices is essential for this goal. The choice of coating materials is limited to, for example, titanium oxides, iron oxides, and chromium oxides and the choice of substrates to silicium dioxide, silicates, and aluminum oxide. The layers of the coating material should also be as dense as possible to avoid the "dilution" of their refractive index, see eq 18 below. The materials used should also be environmentally safe and globally approved for the use in the field of the desired application.

Since the pearlescent effect is a directed reflection, unfavorable diffuse reflection should be reduced to a minimum to suppress a milky diffuse background. This means that, for example, side precipitation during the coating process and crack formation in the coating layer during calcination should be avoided. The edges of plate-shaped particles also give rise to diffuse light scattering. As a consequence, larger particle surface dimensions (diameters) lead to stronger pearlescent effects as the edge scattering effect is greatly reduced. However, the single pigment particles become distinguishable by the naked eye when their diameter reaches 60 μm, and the effect changes from a silky to a sparkle appearance. This is generally not desired for car paints and cosmetics, although there are applications for the sparkle effect like snowboards and toothpastes. Typical particle diameter fractions are in the range of 0−15, 5−25, and 10−40 μm.

The pigment substrate (core), e.g., mica, acts as a mechanical support and is often necessary as a template for the synthesis of the high-refractive layers, which will be discussed below. However, if the substrate particles have a wide thickness distribution, they become optically inactive as shown above[1] and dilute the optical effect. In this case, the substrate should be as thin as possible but still thick enough to be mechanically stable. Typical mean values of mica substrate thicknesses are in the range of 200−600 nm.

D. Computer-Aided Simulations and Their Limitations

Computer programs are commercially available for calculation of the optical appearance of monolayer, multilayer, and absorbing systems.[15] They give excellent results for nonabsorbing continuous dense layers which were, for example, produced by physical or chemical vapor deposition (PVD, CVD). For the calculation it has to be kept in mind that the refractive index depends on the wavelength of the incident light, an effect that is particularly strong for titanium dioxide. Often calculation of absorbing layers does not agree well with the practical measurements. The reason is that the extinction coef-

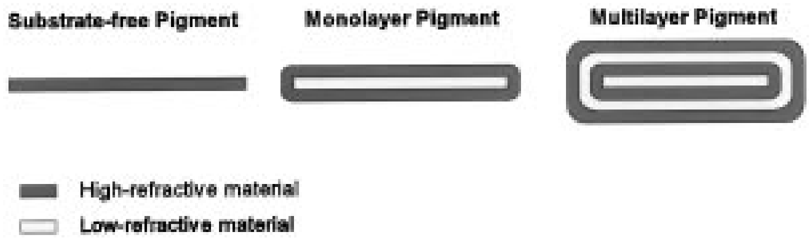

Figure 5. General scheme of substrate-free, monolayer, and multilayer pigments.

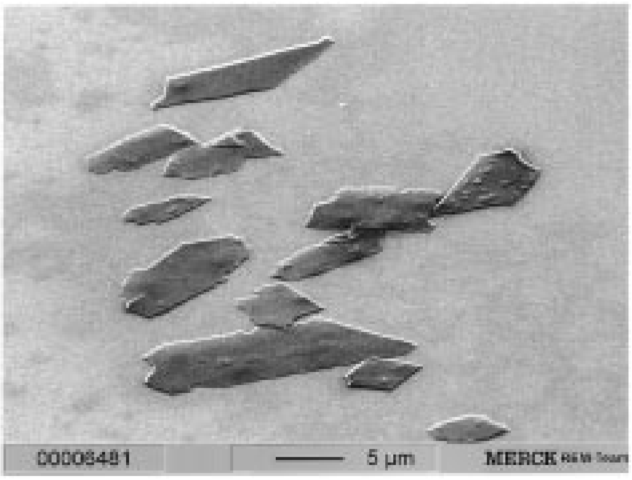

Figure 6. SEM photo of pigment particles isolated from natural pearl essence (fishsilver).

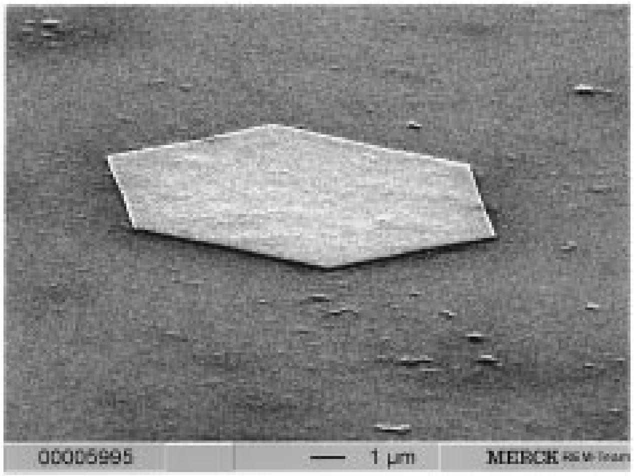

Figure 7. SEM photo of a basic lead carbonate pigment particle with a thickness of 46 nm and a yellow interference color.

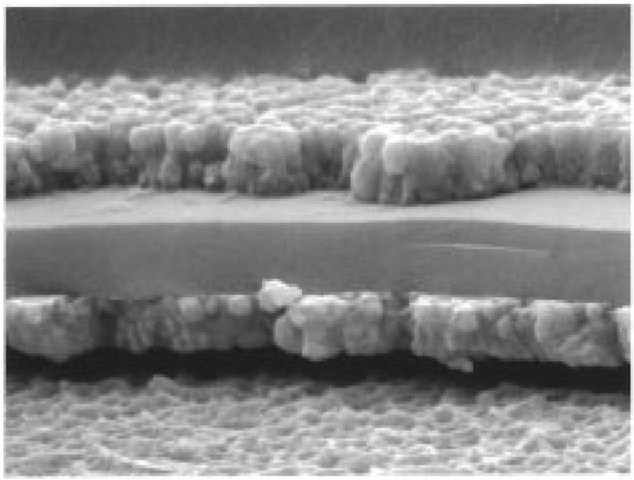

Figure 8. SEM photo of a cross-section through an anatase/mica pigment particle. The anatase layers are precipitated to yield an average thickness of 140 nm on each side of the mica substrate for a blue interference color.

ficient of all light-absorbing layers, e.g., iron oxides and chromium oxides, depends strongly on the grain size, grain shape, dopants, impurities, and preparation.[16]

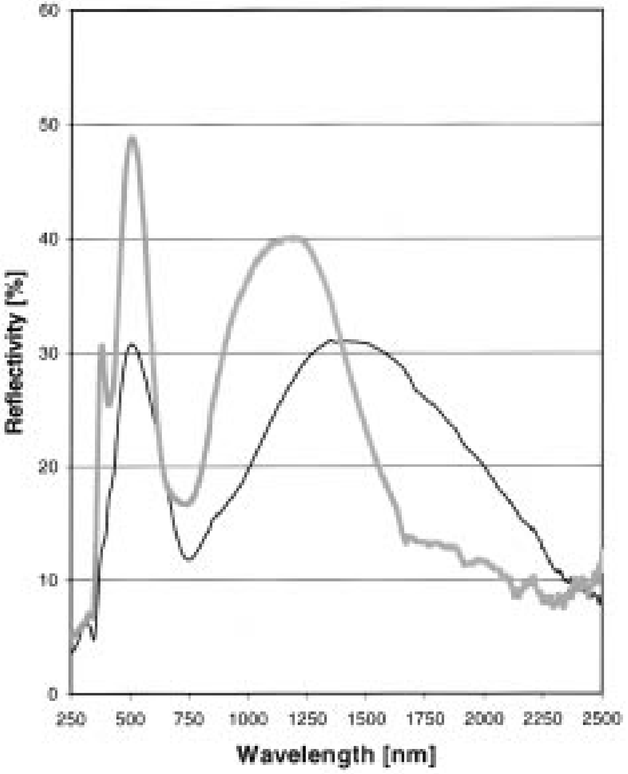

Figure 9. Total reflectivity of two green interference pigments consisting of mica flakes coated with a single layer of 160 nm anatase (thin line), respectively, a three-layer system of 160 nm anatase, 85 nm SiO_2, and 160 nm anatase (bold curve) (see Figure 4). The thickness distribution of the mica flakes is broad enough to decouple the top and bottom coatings.[1] Measurements were carried out on nitrocellulose lacquer films, containing approximately 2 wt % pigment in an Ullbricht integration sphere.

Real systems show a porosity in the optical layers that "dilutes" the bulk refractive index, yielding an effective refractive index of the film. This can be taken into account by using the so-called Lorentz–Lorenz or Clausius–Mosotti equation[17]

$$\frac{n_f^2 - 1}{n_f^2 + 2} = \frac{n_m^2 - 1}{n_m^2 + 2} P + \frac{n_w^2 - 1}{n_w^2 + 2} \alpha(1 - P) \qquad (18)$$

where n_f = the effective refractive index of the film, n_m = the refractive index of the bulk, n_w = the refractive index of the material filling the pores, α = the relative proportion of pores filled with said material, and P = the film packing density (relative density).

The porosity of TiO_2 films has been extensively investigated.[18] Liquid-phase or gas-phase deposition leads to a significant porosity, often more than 25% of the layer. Dense layers can only be prepared using high-energy ion plating techniques. The porosity leads to a reduction of the reflected light intensity, which can be calculated by putting the effective refractive index from eq 18 into eq 15. The Lorentz–Lorenz equation also explains the fact that interference pigment powders show an unusual shift of the interference color when their pores are filled with small amounts of liquid such as water or lacquer.

However, there are limitations due to the fact that the calculation does not take into account the particle characteristics of a pigment. First, the edges of the pigment particles lead to diffuse scattering, resulting in the addition of a diffuse background to the optical spectra. Second, in a typical application, for example, a lacquer coating, the pigment particles do not cover the whole area, see Figure 4. Third, there is also a contribution to the reflection from particles that lie underneath, see Figure 4, leading to a higher reflection intensity. Fourth, the alignment of the platelets could not be optimal, leading to a less pronounced angle-dependence of the reflection. A good parallel alignment is often achieved by the flow characteristics of the platelets themselves, due to their high aspect ratios. The thickness reduction during drying of a lacquer film normally leads to a good orientation. However, when the random orientation of the pigment particles is quenched by high-viscosity or ultrafast curing or when the structure is disturbed by excessive media shrinkage or pigment agglomeration, the parallel orientation of the pigment platelets can be less pronounced.

III. Extended Interference Films

Extended films were the subject of a short review published in 1992.[19]

A. Inorganic Films by Gas-Phase Deposition

Angle-dependent optical effects can also be generated on flat surfaces using evaporation techniques. Commercially used methods are (1) high-vacuum evaporation, also with electron guns,[20] (2) physical deposition processes such as magnetron sputtering, ion plating, ion-assisted evaporation,[21] (3) chemical vapor deposition (CVD) such as low-pressure CVD and plasma-enhanced CVD.[22]

Since most of the substrates, such as glass, show a low refractive index, the coating must possess a higher refractive index than the substrate. It normally consists of titania or zirconia. ZnS and Ta_2O_5 are also used. Very often multilayer coatings are applied that contain SiO_2, Al_2O_3, or MgF_2 as low-refractive layers next to the high-refractive materials and optional transparent or semitransparent metal layers. Mixed oxide layers are also feasible as long as the evaporation is consecutive. Very often small amounts of doping material reduce crystallization and increase, therefore, the homogeneity of the films.

Because of cost considerations these types of processes are only used for optical lenses, filters, laser mirrors, eyeglasses, and communication. Of increasing importance are nonclassical coatings such as electrochromic and transparent conductive coatings.

B. Inorganic Films by Liquid-Phase Deposition

Extended optical layers are very often generated from the liquid phase. The following methods can be used: (1) dipping processes, for large surfaces, the most economical and easily applicable; (2) spreading out the liquid film by centrifugally spinning the wetted surfaces (spin-coating), only applicable for small circular objects; (3) spraying processes.

To produce homogeneous layers, the coating solutions must have the following characteristics: (1) adequate solubility of the initial compounds, and a minimal tendency toward crystallization during the evaporation of the solvent; (2) sufficiently small contact angles between substrate and solution to obtain a good wetting; (3) easy transformation of the deposited gel film into a solid homogeneous film layer without the appearance of cracks or hazing.

The liquid-phase preparation as well as the optical effects of the resulting films have been well-known for some decades and are covered by an older review article.[23] The liquid-phase deposition processes are today widely used for glass coatings.

Reversible electrochromic and photochromic effects have been observed with thin films made of WO_3, SnO_2 and TiO_2.[24]

C. Organic Films

Angle-dependent optical effects can be generated by organic multilayer films.[25] Because the refractive indices of organic materials differ much less than those of inorganics, such films usually contain more than 70 layers, sometimes even up to 1000 layers to achieve a strong interference effect. The difference of the refractive indices should be, nevertheless, at least 0.06.

The individual layers are normally 50−400 nm thick. As outlined in the theoretical part above, the quantity of the reflected light and the chroma[26] depends on the difference of refractive indices, the number of layers, the ratio of the optical thicknesses of the layers, and the uniformity of the thicknesses.[27]

The multilayer organic films can be produced by a chill-roll casting technique using a conventional single manifold flat film in combination with a feedblock that collects the melts from two or more extruders (co-extrusion) and arranges them into the desired layer design. The low-refractive index polymer is usually polymethacrylate, polymethacrylate−polyester, polypropylene, ethylene vinyl acetate, or polyether glycol (all having n_D of 1.48−1.50). The high-refractive index polymer is often chosen to be poly(ethylene terephthalate) and poly(butylene terephthalate) and their copolymers (1.55−1.61), polystyrene (1.60), or polycarbonate (1.59). The organic films can contain colorants and/or pigments.[28]

At the moment it is not possible to achieve a uniform interference color throughout the whole film. The production process generates a slight thickness variation leading to different color patches, for example, green and blue, that appear very close to each other. Therefore, these films are not widely used with the exception of gift wrapping materials.

IV. Pearlescent Pigments

Special effect pigments with angle-dependent optical effects have a growing economic significance. The total worldwide annual market volume is about 15 000 tons for metallic and 14 000 tons for oxidic pigments.[29] Pigments can be produced by synthesis of pigment particles or by grinding a film that already shows the angle-dependent optical effects.

The field of pearlescent pigments has been reviewed in 1988 by L. M. Greenstein[3] and in 1992 in *Ullmann's Encyclopedia of Industrial Chemistry*.[29] There is also a book[30] about pearlescent pigments which covers marketing and popular aspects and a book about special effect pigments and their applications.[31]

Pearlescent pigments can be grouped into two fields: (1) particles that consist of basically one optically homogeneous material; (2) particles that have a layered structure on a substrate, see Figure 5. Substrate-free pigments can be single crystals such as BiOCl or polycrystalline flakes such as TiO_2 flakes, see below. Their optical thickness is often chosen to be on the order of one-fourth of the wavelength of visible light so that the inference color is at its maximum and the absorption is as low as possible. However, this means that they are often very thin. Therefore, the mechanical stability is usually lower than for substrate-based pigments.

Only a few substances can be forced to crystallize as thin platelets. Therefore, thin platelets are used as so-called substrates or templates onto which materials of high refractive index can be precipitated. The best known examples are the pearlescent pigments that are based on TiO_2 precipitated onto platelets of natural mica, see below. Pigments based on transparent substrates, such as the mica-based products, can be easily combined with absorption pigments even in thicker coatings. They create the impression of optical depth due to their smooth and gradual change of reflection and/or chroma. On the other side, pigments with metallic substrates have advantages in very thin coatings due to their strong hiding power. Mixtures of mica pigments and metallic pigments are often used in car paints.[32]

For outdoor use, especially for car paints and architectural applications, the chemical and photochemical reactivity of the metal-oxide-containing pigments is normally reduced by an additional treatment.[33]

A. Substrate-Free Pigments

1. Natural Pearl Essence

Natural pearls and nacreous shells have been used since ancient times for decorative purposes. In 1656, the French rosary maker Jaquin isolated a silky lustrous suspension from fish scales and produced the first pearlescent pigments.[34] This suspension is often called natural pearl essence. The pigment particles are platelet-shaped with a very high aspect ratio ($0.05\ \mu m \times 1-10\ \mu m \times 20-50\ \mu m$, see Figure 6) and consist of 75−97% guanine and 3−25% hypoxanthine.[35]

To date there is no commercial synthetic process for producing similar platelet-shaped products of such brilliance. One is, therefore, limited to a process based on the natural supply: An aqueous suspension of white fish scales is treated with organic solvents in a complicated washing and phase-transfer process to remove proteins and irregular guanine crystals.[36] One ton of fish yields less than 250 g of guanine. The pigment particles show a high tendency to agglomerate and are, therefore, only handled as dispersions.

Natural pearl essence is very expensive but shows some advantages over synthetic pearlescent pigments: it shows a high but soft luster ($n_D = 1.79$ (parallel) to 1.91 (perpendicular)). It is not brittle and has a relatively low density of 1.6 g/cm^3, which reduces settling in liquid formulations. It is almost exclusively used in expensive cosmetic applications.[37] The world production of natural pearl essence in 1998 is estimated to be well under 50 t.

2. Basic Lead Carbonate

The first commercially successful synthetic pearlescent pigments were hexagonal lead salt crystals, especially basic lead carbonate $Pb(OH)_2{\cdot}2PbCO_3$. Basic lead carbonate[3,38] is precipitated from aqueous lead acetate with carbon dioxide under carefully controlled reaction conditions. The resulting platelets are less than 0.05 μm thick and show hexagonal dimensions of about 20 μm, yielding an aspect ratio of >200, see Figure 7. Due to their high refractive index of 2.0 and their even surface, they exhibit a very strong luster. If the thickness of the platelets is increased by slightly modified reaction conditions, interference colors can be obtained.

The crystals are very fragile and are handled only in dispersions. They settle very fast because of their density of 6.14 g/cm^3. The use of basic lead carbonate is also limited by its low chemical stability and toxicity of its byproducts as well as toxicological concerns in its application areas. Today less than 1000 t of basic lead carbonate pigments are produced annually worldwide.

3. Bismuth Oxychloride

Bismuth oxychloride is produced by hydrolysis of very acidic ($pH < 1.0$) bismuth solutions in the presence of chloride. The crystal quality can be varied by careful adjustment of bismuth concentration, temperature, pH, pressure, reactor geometry, and addition of surfactants. The usually tetragonal bipyrimidal structure can be flattened to platelets with a high aspect ratio. Products with an aspect ratio of 10−15 show low luster and a very good skin feel and are used as fillers in cosmetics.[39] Crystals with higher aspect ratios show an exceptional luster and are mainly used for nail polish.

The low light stability, the fast settling caused by the high density of 7.73 g/cm^3, and the lack of mechanical stability limit the use of BiOCl in technical applications. Therefore, it is mainly used in cosmetics, but also in buttons and jewelry. The light stability can be improved to some extent by cerium doping[40] and UV absorbers. The current world market is about 400 tons per year.

4. Micaceous Iron Oxide

Micaceous iron oxide consists of pure or doped hematite (α-Fe_2O_3). In nature it is found already in the form of platelets,[41] for example, in large quantities in Kärnten, Austria. Its density is 4.6−4.8 g/cm^3; its natural color is dark gray with low luster. Natural micaceous iron oxide is nearly exclusively used in corrosion protection coatings.

Micaceous iron oxide can also be obtained by hydrothermal synthesis in alkaline media. However, the dull dark color is as unappealing as that of the natural product. If substantial amounts of dopants are incorporated,[42] the aspect ratio can be increased up to 100, resulting in a much increased luster. The color can be also shifted to a more attractive reddish brown so that the products can be used for decorative purposes.

The most important dopants are Al_2O_3, SiO_2, and Mn_2O_3. They can enforce a spinel structure. SiO_2 yields thin small platelets, Al_2O_3 yields thin larger platelets, and Mn_2O_3 reduces the thickness.[43] The addition of ZrO_2, B_2O_3, P_2O_5, SiO_2, or additional Al_2O_3 reduces the agglomeration in application. Chromates, molybdates, wolframates, permanganates, and titanates can be used to create different color shades.

The starting material $Fe(OH)_3$ or better FeOOH is heated in an alkaline suspension together with the dopants to temperatures above 170 °C, typically 250−300 °C. Ferrates are probably formed as intermediates.[43] After several minutes to hours, platelets of doped iron oxide are obtained. In a second reaction phase, the pH is further increased so that platelets grow and form flat basal faces.

5. Titanium Dioxide Flakes

Titanium dioxide flakes are produced by breaking down a continuous film of TiO_2. The most efficient process is therefore is a web-coating process involving a thermal hydrolysis of $TiOCl_2$ on the web.[44,45] Alternative procedures are the application of titanium alkoxide on a smooth flat surface and cracking the resulting film into flakes by steam treatment,[46] the application of a TiO_2 sol on a glass surface and scratching off the resulting film,[47] the application of $TiOCl_2$ solution onto a gelatin film and dissolving the gelatin film, vacuum deposition,[48] the treatment of potassium titanate fibers with acid and subsequently with heat,[49] or creating and breaking hollow TiO_2 particles from a surfactant−TiO_2 sol mixture.[50] Using the latter process, often concave shell-type flakes are obtained.

Substrate-free TiO_2 flakes can also be derived from TiO_2−mica pigments[51] or flaky TiO_2−SiO_2 pigments[52] by dissolving the substrate in strong acids and/or strong alkalies.

The titanium dioxide flakes produced by the methods mentioned above are not single crystals but quite porous and, lacking the mechanical support of a substrate, hence brittle. Therefore, they are not used in technical applications in which mechanical stress is exerted. Commercial products are available for the cosmetic market.

The TiO_2 flakes can be reduced to titanium suboxides yielding a dark bluish mass tone in addition to the interference color.[53]

6. Flaky Organic Pigments

Some organic pigments can be forced to crystallize in flake form, such as 1,4-diketo-3,6-diarylpyrrolo-(3,4-*c*)-pyrrole (DPP),[54,55] 2,9-dichlorochinacridone,[56] and metal phthalocyanines.[57] However, the difference between their refractive index and that of typical applications such as lacquer is too small to generate strong interference colors. In most cases, the aspect ratio of these crystals is also much smaller than that of the inorganic pigments mentioned above.

B. Pigments Formed by Coating of Substrates in the Gas Phase

Compared to liquid-phase coatings, gas-phase reactions have the advantage of higher reaction temperatures and a higher tendency for epitaxial growth. Solvents and electrolytes also do not appear as side products that might contaminate the optical layers. Gas-phase reactions allow smooth metal coatings, even as multiple coatings. However, gas-phase processes are, in general, more difficult to handle. One problem is corrosion, for example, by $TiCl_4$, or toxicity of the precursors, for example, of $Fe(CO)_5$. It is also more demanding to fluidize the substrates in the gas phase than it is to disperse them in water.

1. Coatings onto Metal Flakes

Oxide-coated metal flakes can be prepared by atmospheric oxidation at elevated temperatures. Colorful products can be obtained when the surface of titanium flakes is oxidized to titanium suboxides.[58] Iron or iron alloy flakes can be also oxidized.[59] With this technique the resulting surfaces are rather rough, especially for thicker oxide coatings. Only the corresponding oxide can be derived from the metal flake.

It is quite difficult to handle metal flakes in the liquid and especially the aqueous phase because of agglomeration and corrosion. Therefore, gas-phase coating procedures have been developed.

Aluminum flakes can be coated with iron oxide in a CVD process.[60] These are commercially the most important pigments based on CVD. The metal flakes are fluidized in nitrogen gas at temperatures around 450 °C. Then the reagents, $Fe(CO)_5$ and O_2, are injected into the fluidized bed. For a proper coating they must be highly diluted in an inert gas. Sometimes water vapor is added to reduce electrostatic charging. The thickness of the coating is controlled by the reaction time. The only side product is carbon monoxide, which is catalytically oxidized to CO_2.

It is not known yet whether the reagents form an Fe_2O_3 aerosol which then coats the aluminum flakes or whether they react at the hot flake surface.[43] However, the epitaxial growth, the low porosity, and the absence of cracks in the coating support the latter mechanism. The problems with this coating process are to avoid the formation of stack-like agglomerates during the coating process, to fluidize the rather small particles, and to handle the reactive reagents at elevated temperatures.

The aluminum flakes can be coated with aluminum oxide and/or silicon dioxide in the liquid phase before the CVD process[61] to reduce the reactivity of the metal and to create multilayer color effects.

Metal halogenides are difficult to use as gas-phase precursors for the metal oxide coating because of the reactivity of the metal flakes and the corrosion of steel in chloride atmospheres. The use of $TiCl_4$ and water vapor was described[62] about 10 years ago.

However, no commercial products have been introduced as yet.

2. Coating onto Nonmetallic Flakes

Mica flakes can be coated in CVD processes using the same techniques as those discussed for metal flakes. In addition, one can also use metal chlorides as precursors for the oxide coating on mica.[62] However, essentially the same products can be obtained more easily by precipitating the oxides from the liquid phase. Commercially available are iron oxide/mica pigments for which $Fe(CO)_5$ is used as the precursor in a process very similar to the one for Al flakes.

At higher temperatures, golden coatings of TiN on mica can be obtained from $TiCl_4$ and NH_3.[63] Glass flakes can be coated with Si, which is then oxidized to dark SiO_{2-x}.[64] Commercial products that are based on the latter processes are not available yet.

C. Pigments Formed by Coating of Substrates in the Liquid Phase

1. Metal-Oxide-Coated Mica

Today the commercially most important pearlescent pigments are metal-oxide-coated mica particles, see Figure 8. Their synthesis was first published in 1942.[65] However, a commercial use came only after the base patent of Du Pont[66] in the early 1960s and further improvements by Mearl[67] and Merck.[68] The coating of most products is formed with TiO_2, hematite (α-Fe_2O_3), or mixed oxides thereof. But other oxides and inorganic colorants are used to form layers on mica as well: green Cr_2O_3,[51] black Fe_3O_4,[69] ferric ferrocyanide (iron blue),[70] cobalt blue, silver white bismuth oxychloride,[71] SnO_2, ZnO,[72] and ZrO_2.[66]

Coatings of black SiO_xC_y,[73] deeply colored oxide bronzes (wolframates, molybdates),[74] yellow bismuth vanadate,[75] and metal sulfides[76] have also been reported; however, there are no commercially available products yet.

The mica substrate acts as a template for the synthesis and as a mechanical support of the thin optical layer. For nearly all commercial products, muscovite mica is used because the raw material is easily available and can be cleaved to thin platelets of high aspect ratio. However, natural mica contains small amounts of iron (1−2% Fe_2O_3) which cause the slightly yellow mass tone seen in high pigment concentrations. Therefore, a few products have been developed that are based on synthetic fluorophlogopite,[77] which does not have iron impurities but is more expensive than natural muscovite. On the other hand, there are also some products based on natural phlogopite, which is darker than muscovite.

Recently, multilayer oxide coatings have been developed based on a mica substrate. These products have an alternate order of high-refractive and low-refractive oxides precipitated onto mica. The low-refractive oxide layer consists of SiO_2 and/or Al_2O_3. Its thickness is normally adjusted in a way that the layer becomes optically active.[78] Figure 9 shows the stronger reflectivity of such a multilayer pigment that consists of mica coated with 160 nm of anatase−TiO_2, 85 nm of SiO_2, and 160 nm of anatase−TiO_2 compared to the conventional green interference mica pigment with one layer of 160 nm of anatase−TiO_2. When a thin not optically active layer is precipitated, the grain growth of the main oxide layer is started again and a coloristical improvement is observed.[79]

Today TiO_2-coated mica is obtained using the following chloride process: $TiOCl_2$ solution is slowly added to a mica platelet suspension at a pH value of about 2 and temperatures of 60−90 °C. The reactor geometry and mixing conditions have to be carefully controlled. Using this titration process, the oxide layer thickness can be well adjusted to yield defined interference colors, as seen in Figures 8 and 9. An alternative process uses titanium oxysulfate: A suspension of mica platelets in a $TiOSO_4$ solution is heated to undergo a thermal hydrolysis.[66] This process does not allow a precise adjustment of the layer thickness and also shows no significant economic advantages over the chloride procedure. It is, therefore, only used for the generation of thinner silver-white TiO_2 layers, whereas the titanium oxysulfate as a raw material is more available than the chloride.

When TiO_2 is precipitated onto muscovite under reaction conditions unfavorable for side precipitation, e.g., pH >1.5, only the anatase modification is formed. Even after annealing at 1000 °C, no rutilization is found in the layer, whereas the free titania turns completely into rutile at about 700 °C.[80] When the less usual substrate phlogopite is used instead of muscovite, a partial conversion to rutile is observed above 850 °C. Eskelinen sees the reason for this difference in a migration of Al ions from the mica into the anatase layer, which then inhibits the phase transition.[81−85] But the anatase modification is also solely found below 1000 °C, if aluminum-free SiO_2 or alumina itself is used as a substrate instead of mica. The most probable explanation is a considerable constraint in the film which counteracts the volume contraction during rutilization and delays the phase transition.[80,86]

The anatase layers on mica show a preferred crystal orientation when they are very thin,[81,86] e.g., <40 nm. The upper layers then lose the preference. It is also known that uncalcined layers show a deviation from the lattice parameters of bulk anatase, which diminishes after calcination.[86] Both observations support a template effect of the muscovite substrate.

Rutile has a higher refractive index and, therefore, yields a stronger pearlescence than anatase,[87] see section II and Table 1. Therefore, processes have been developed to create a rutile layer onto mica: A thin layer (about 1 wt %) of SnO_2 is precipitated as a continuous layer onto the substrate, and then the TiO_2 layer is created using the usual process. $SnCl_2$[88] or better $SnCl_4$[89] can be used as precursors for the SnO_2 precoating. SnO_2 acts as a template because its lattice parameters $a = 4.737$ and $c = 3.186$ are close to those of rutile, $a = 4.593$ and $c = 2.958$.[90] Instead of the colorless SnO_2 (which is restricted for the use in cosmetics in Japan), Fe_2O_3 can be used to create rutile−mica pigments.[91] However, the necessary amount of iron oxide creates a yellowish mass tone of the resulting pigment. The rutile layers on mica show a little larger preference in the crystal orientation than anatase.[86]

The desired interference color determines the thickness of the titania layer. This relation can be calculated using the equations mentioned above.[5] For a silver white pigment 50 nm of anatase is needed and for a blue interference color about 120 nm. However, these published values are calculated under the assumption of dense layers and are not taking the porosity for which a correction could be applied using eq 18 into account.

The titania in these layers can be reduced to dark-colored titanium suboxides using NH_3,[92] carbon, metals, or metal hydrides[93] as reducing agents. The titanium suboxides are usually accompanied by oxynitrides when NH_3 is used.[92]

The titania layers can be doped with carbon black[94] or organic dyes. They can also be coated with thin layers[95] or dots of metals to create a darker mass tone (with silver,[96] nickel,[97] or mixtures of various metals[98]).

Hematite coatings on mica are usually generated from two different precursors. Solid iron (II) sulfate can be added to a suspension of mica platelets at temperatures above 60 °C. A better control of the coating layer quality is found when $FeCl_3$ solution is slowly titrated to a mica suspension[86,99] in a way very similar to the titanium oxychloride titration mentioned above. The mica platelets can be optionally precoated with a thin layer of titania.

The resulting dried iron oxide layer consists of hematite (α-Fe_2O_3) and sometimes minor amounts of goethite (FeO(OH)). It is formed as nanocrystallites of 20−40 nm diameter which show a strongly preference of crystal orientation due to a template effect of the muscovite.[86] During annealing at temperatures of 700−900 °C, the grainy layer structure sinters to a less porous glasslike crystalline plate.[86] Doping with a borate or phosphate can prevent this sintering. The layer thickness is about 75 nm for a bronze and 85 nm for a red color. As mentioned in section II.D, the interference color as well as the mass tone of these light-absorbing layers are a function of the layer thickness.

Layers of golden Fe_2TiO_5 (pseudobrookite)[100] are formed if stoichiometric amounts of Fe_2O_3 and TiO_2 are precipitated one after another onto mica and then calcined above 800 °C. A coprecipitation reduces the temperature for the conversion to pseudobrookite to some extent. If a mixed iron oxide/titania layer is calcined under a reducing atmosphere, silver gray $FeTiO_3$ (ilmenite)[101] is obtained.

2. Coatings onto SiO_2 Flakes

Instead of mica, SiO_2 flakes can be used as a substrate for pearlescent pigments.[102] The SiO_2 flakes are produced by a web-coating process.[45] Synthetic SiO_2 flakes offer three advantages over the use of natural mica: (1) the thickness of the SiO_2 substrate can be controlled in the preparation so that at the end a pigment with a true optical three-layer system is obtained; the interference color of those systems is stronger than for the conventional mica pigments for which the effect of the mica is “wiped out” by a broad thickness distribution; (2) as synthetic substrates they do not have the small iron impurities that cause slightly yellow mass tone of natural mica; (3) SiO_2 has a lower refractive index (1.46) than mica (about 1.58) and, therefore, leads to a stronger interference effect.

SiO_2 flakes have higher production costs than for mica due to the large area and high rotation speeds needed in the web coating. Silver white pigment are only accessible by mixing batches with different substrate thicknesses. The reason lies in the optical three-layer system that is found when all substrate particles have the same thickness.[1] As a coating, the same oxides and colorants can be used as for mica substrates. Commercially available glass flakes can be coated with metal oxides as well.[103] However, these flakes are generally too thick for an optical three-layer system with a strong reflection.

Multilayer oxide coatings have been created on the base of SiO_2 substrates.[78] They show even stronger and clearer interference colors than the mica-based multilayer pigments due to the fact that the substrate becomes part of the optical system. At the present time, pigments based on SiO_2 flakes are at the beginning of their commercialization.

3. Coatings onto Al_2O_3 Flakes

Thin Al_2O_3 flakes can be obtained by applying an alumina sol on a smooth surface and scratching off the resulting film.[47] However, this process can hardly be used for an industrial production. Thin hexagonal monocrystalline Al_2O_3 flakes can also be produced by hydrothermal processes. The thickness of the resulting flakes is not uniform. Therefore, the resulting coated pigments merely assume a dull pearlescence.

Al_2O_3 flakes of a higher quality are produced by the following steps:[104] An aqueous solution of an aluminum salt is mixed with small quantities of a titanium salt and phosphate. After neutralization, a sol or suspension is obtained, which is then dried and heated to 900−1400 °C. After washing, very thin flakes are found which consist of corundum and show a high aspect ratio, a very narrow thickness distribution, and very smooth surfaces. The thickness can be controlled by the doping and reaction conditions. The resulting flakes are used as substrates in the aqueous-phase processes described above to prepare pearlescent pigments of very high luster. The advantage over the mica substrate lies mainly in the fact that all Al_2O_3 flakes have about the same thickness, which leads to true optical three-layer systems as for the SiO_2 flakes.

4. Coatings onto Other Flaky Substrates

Flaky barium sulfate can be used as a substrate in the preparation of UV-absorbing pearlescent pigments.[105] It can be coated with UV-absorbing zinc oxide and optional TiO_2 and cerium oxide components. The main use of these materials is in cosmetics. Titanium dioxide flakes can be used as pigments themself, see above, but can also be coated with metal oxides[106] or multiple layers of oxides.[107] Because of their tendency for hydrolysis and corrosion, it is difficult to coat metal flakes in the liquid phase. All reasonable attempts were made using organometallic compounds in nonaqueous or wet organic solvents. For example, titanium flakes can be coated with TiO_2 using the well-established sol−gel process based on $Ti(OEt)_4$.[108] Aluminum flakes have been coated with a ZrO_2 layer that was doped with cobalt and iron to create a mass tone.[109] The surface of aluminum flakes can be oxidized in aqueous media, and the resulting aluminum oxide layer is used as an absorbent for organic and inorganic colorants.[110]

V. Pigments and Films Based on Dichroism

Interference and angle-dependent color effects can also be achieved by layers or particles based on liquid crystal polymers (LCP).[111] Such effects can, for example, be produced by small plate-like substances which consist of a LCP material itself or by small platelets which are uniformly coated with a cross-linked liquid crystalline polymer in a chiral−nematic arrangement.[112]

Liquid crystals are organic compounds in a state of matter intermediate between that of an isotropic liquid and an anisotropic crystalline solid.[113] Most liquid crystalline molecules are markedly elongated and rod like. In nematic liquid crystalline materials, the direction of the long molecular axes (director) is arranged parallel to each other. Adding a chiral molecule to a nematic phase causes a superstructure comparable to the steps of a spiral staircase. The structure can be understood as being composed of nematic layers having the director rotated by a certain angle with respect to an adjacent layer, eventually building up a helical array (Figure 10). The thickness of a 360° turn of the director represents the pitch length p of the helix.[111] The color design of LCP pigments in paint films or of pure LCP films has its origin in an interference phenomenon.[111,112] In this case, only incident light with a wavelength equal to the LCP lattice separation interferes and is reflected.

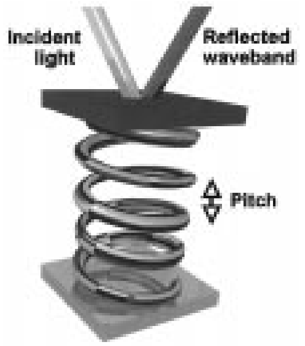

Figure 10. Scheme of a liquid crystal film.

Due to the change of refractive index from layer to layer, the helical structure gives rise to interference effects (Figure 11). When white light is incident normally on a film or an oriented arrangement of platelet-like particles of a cholesteric material with the helical axis perpendicular to the substrate, selective reflection of a finite wavelength band occurs similar to Bragg X-ray reflection. The reflected band is centered about a wavelength l_o, which is related to the helical pitch length p of the phase and its average refractive index n by $l_o = np$.[111,112]

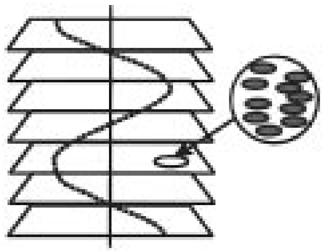

Figure 11. Chiral cholesteric (nematic) liquid crystal structure. The dotted line shows a helical path within the medium. Pitch length $p = 360°$ rotation.

On the other hand, a structure which has a helical superstructure with no change in the refractive index can also reflect light just like cholesteric phases.[114] In this case, it is not so much a change in the refractive index that gives rise to the optical effect but rather the superstructure.

The reflected light is circularly polarized with the same sense of polarization as the helical sense of the liquid crystal phase. Light circularly polarized in the opposite manner is transmitted through the sample together with those wavelengths of light not being reflected. Light experiences a double refraction as a result of the anisotropy of the system. The bandwidth $\Delta\lambda$ of the selectively reflected band is described by the relation $\Delta\lambda = p\Delta n$. The angular dependence for an incident and observed angle Θ is given by $\lambda_\Theta = \lambda_o \cos \Theta$.

The reflected light waves from the layers increase the intensity of the total reflection. The maximum reflectivity of one polarization state requires at least 6 helices or a thickness of about 3 μm.[111] The most efficient reflection is given by layers with a thickness of up to 10 μm.

Cholesteric materials are temperature sensitive and show a thermochromic effect. The reason for this is that the pitch length of the helix and the refractive index are temperature dependent.[111,112,115]

Liquid crystal polymer films are transparent to visible light, including in the form of platelets and coatings on substrates dispersed in a transparent paint film. These films need to be deposited on a dark substrate or in an effect lacquer with a dark base coating. Light is transmitted through the liquid crystal polymer, but some wavelengths are absorbed by the dark substrate or base coating. The liquid crystal polymer will be aligned parallel to the substrate, either as a film coating or on the interference pigment platelets within the paint film. This will then show a particular color in the orthogonal view and another color when observed at an angle. Such angle-dependent color phenomena give a very striking effect, which is of great interest for security applications. Paint coatings incorporating such pigments must be constructed of several layers with the liquid crystal materials in one of the inner layers only.

A number of this type of interference pigments are based on polysiloxanes. They are formed first as a thin cross-linked film of liquid crystalline polymers which are then ground to small platelets. The interference pigments themselves are colorless and transparent. The color effect is based on the regular structure and on the uniform arrangement of the liquid crystalline molecules. This gives rise to the reflection and subsequently interference with light of a particular wavelength. The other parts of the light go through the pigment particles. Very interesting color effects are possible based on these optical principles.

Liquid crystal polymers are side chain polymers which are usually prepared in a procedure, employing the coupling of a H-siloxane main chain with ω-alkenyl bearing mesogenic groups via catalytic hydrosilylation.[116] There is an extension of this concept to different geometric and chemical classes of backbone siloxanes, i.e., linear,[117] cyclic,[118,119] and cage-like siloxanes.[120] Siloxanes with a great variety of substituents are used.[121]

For use as optical films or individual pigment particles, liquid crystalline materials are required which are stable within a suitable temperature range. Thermotropic materials can, therefore, not be used for this purpose. The problem of obtaining mesomorphic structures over a broad temperature range can be overcome in two special ways. First, it is possible to fix the structure in the glassy state, thus requiring a high T_g, or second by cross-linking. Chemical cross-linking is generally done photochemically; this leads to a fast polymerization. Contrary to thermal cross-linking, a wide choice of cross-linking temperatures is possible.

Liquid crystalline siloxanes are limited with respect to the glass transition in comparison to other backbone systems, such as poly(meth)acrylates. Glass transition temperatures of up to 80 °C can be achieved,[121] but there is a limit for the variations of the mesogenic groups. Therefore, cross-linking is the preferred method. The presence of at least some polymerizable moieties within the side chain groups is necessary. Typical examples for these groups are epoxides, cinnamates, or methacrylates.

To obtain cholesteric films with good optical properties, the cross-linkable siloxanes must have a low viscosity. Small molecules containing 3−10 siloxane units are preferred. Cyclic siloxanes as well as linear siloxanes can be used.

There are two ways to introduce the cross-linking moiety to a siloxane backbone:[116] One possibility is to couple an OH-protected unit to the siloxane chain followed by methacrylation of the deprotected OH groups.[122] Another way is to directly couple the methacrylate-bearing unit to the siloxane backbone chain.[123] The second way should be feasible at least for small and medium-sized siloxanes, as the reactivities of ω-alkenes and methacrylates toward hydrosilylation differ by a factor of at least 10, thus minimizing premature cross-links via hydrosilylation.

The reflection wavelength of liquid crystalline layers or particles can be tuned in the region from 390 to 670 nm by mixing suitable cholesteric liquid crystal compounds. The wavelength of reflection I_T is inversely proportional to the concentration of chiral component, yielding the following equation[116]

$$\frac{I}{I_{\mathrm{T}}} = \mathrm{const}\cdot C_{\mathrm{Chiral}} \tag{19}$$

C_{Chiral} is the concentration of the chiral component in the mixture. In some cases, more than one chiral component is used, e.g., C_1 and C_2. Therefore, the relation

$$C_{\mathrm{Chiral}} = xC_1 + (1 - x)C_2 \tag{20}$$

is used, where x is the fraction of C_1 in the mixture. Combining eqs 19 and 20 leads to the relation between the wavelength of reflection and the fraction C_1 in the mixture[116]

$$I_{\mathrm{T}} = \frac{1}{ax + b} \tag{21}$$

The coefficients a and b must be determined and then compared with the experimental data. I_T is dependent on the curing temperature. When cross-linkable cholesteric liquid crystalline siloxanes are cured, two things happen to the helical pitch: It reduces the helical pitch by about 2% due to shrinkage of the material during the curing process, and it becomes fixed to this value. Depending upon the temperature of curing, the reflection wavelength can vary, for example in the red, green, or blue region.

After curing, the I_T becomes virtually independent of temperature up to 140 °C. A very small residual increase (less than 0.2 nm/K) can be attributed to the thermal expansion of the cured polymer.

Several applications were developed to take advantage of the specific properties of the cross-linkable cholesteric liquid crystalline siloxanes. For example, optical filters can be made of cross-linkable and noncrosslinkable liquid crystalline siloxanes.[124,125] Another application is the use of glassy cholesteric materials as meltable paints.[111]

Liquid crystalline polysiloxanes are also suitable for optical write-once storage.[126] A high contrast in reflectivity for data storage is obtained with these materials at wavelength and energies which can be supplied by commercially available semiconductor lasers.

On the other hand, small, insoluble platelets can be used as iridescent pigments.[127,128] Such platelets can be suspended in inorganic and organic media, especially lacquers. The spray technique is mostly used for the application in paint films. The color effects are very strong if black substrates are used to ensure the absorption of the transmitted light. Very interesting colors can be obtained when combined with other effect pigments or in mixtures with conventional pigments.[129]

Interference pigments based on liquid crystalline materials are prepared by a doctor-blade coating of the polymers in the liquid or liquid crystalline state on an even surface. The doctor-blade process leads to a thin film wherein a homogeneous orientation of the molecules takes place. It is only after this orientation process that the film shows an interference color. The films are then cured and crushed by special techniques to yield platelets of liquid crystalline polymers showing interference effects.

VI. Pigments and Films Based on Holography and Gratings

Holography, as a field of optical science in which wave fronts are recorded, stored, and recovered, can be described as the technique of using diffraction to transform one wave front into a second in a prescribed manner.[130] A hologram is generally a two-dimensional mask which contains structures with details on the order of the wavelength of the transformed wave front. The technique of holography may be applied in the entire spectrum of electromagnetic waves (visible, infrared, ultraviolet, X-ray) and non-electromagnetic waves (acoustic waves, matter waves such as electrons).

Mass replication of holograms is commonly accomplished through the embossing of clear or reflective films.[130,131] During a typical embossing process, a master hologram is recorded in a photoresist which, upon development, exhibits a surface relief mapped from the intensity distribution of the holographic interference pattern. The photoresist master is then copied onto a metal stamping master. The stamping master is then heated and pressed in contact with a thermoplastic material, which is then separated from the stamping master and contains a replication of the original hologram structure. Injection molding is used as an alternative. Thousands of impressions may be produced from one stamping master, and the resultant embossed plastic holograms may be reconstructed in transmission or reflection. In the latter case, the plastic is usually coated with aluminum to enhance diffraction efficiency.[130]

Holograms can perform the functions of basic optical elements, e.g., holographic diffraction gratings, holographic multilayer mirrors, diffractive lenses, chirped holograms as scanners, etc.[130,132] Diffraction patterns and embossments, and the related field of holograms, have begun to find wide-ranging practical applications due to their aesthetic and utilitarian visual effects. In recent times, the diffraction grating technology has been employed in the formation of two-dimensional holographic images which create the illusion of a three-dimensional image to an observer. This holographic image technology can be used for the manufacture of very attractive displays. The concept of using holographic images to discourage counterfeiting has meanwhile found wide application.

The holographic exposure may consist of the interference pattern produced between two plane waves, where the period Λ along the surface of the grating is controlled by the exposing wavelength λ and the angles, θ_1 and θ_2, which plane waves subtend with respect to the surface normal.[130] These parameters are connected by the equation

$$\Lambda = \frac{\lambda}{\sin \theta_1 - \sin \theta_2} \tag{22}$$

At the beginning, diffraction gratings were formed by scribing closely and uniformly spaced lines on polished metal surfaces using special “ruling engines”.[133] Subsequently, techniques were developed to reproduce a master diffraction grating by shaping a moldable material against the master diffraction grating surface. The development has led to a technology where thermoplastic films are embossed by heat softening the surface of the film and then passing them through embossing rollers which impart the diffraction grating or holographic image onto the softened surface. Sheets of effectively unlimited length can so be decorated with the diffraction grating or holographic image on a surface. The decorated surface of polymers is sometimes sufficiently reflective that there is an optical effect from the diffraction grating already without further processing, because the incident light is reflected by the facets of the decorated surface.[133] The full optical effects, however, require metallizing of the embossed polymer surface.

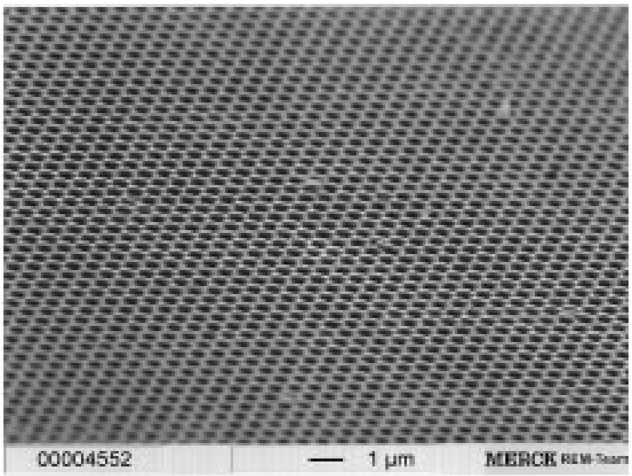

Figure 12. SEM picture of a holographic film made by aluminum metal deposition on a polymer film to be used for the production of holographic pigments. The average distance between the peaks of the structures is about 800 nm.

Diffraction gratings manufactured in this manner are free from so-called “ghosts” caused by systematic ruling errors. They can be produced rapidly with a large aperture. Further, holographic diffraction patterns and embossments can be recorded throughout a volume recording material rather than as a surface modulation. Such volume holograms can be recorded as transmission or multilayer reflection gratings.[130] In the former case, they can exhibit peak diffraction efficiencies near unity and spectral bandwidths of 400 nm.[134] Holographic multilayers can be applied as notch filters with bandwidths on the order of 10 nm and efficiencies of 99.99%.

Grinding of holographic films, when done in a suitable manner, can lead to small holographic particles. These so-called holographic or hologram pigments are relatively new materials for attaining special optical effects in different application media.[133,135,136] A structure of a holographic pigment particle is shown in Figure 12. Generally, any hologram base material on which an interference band corresponding to the wave face of light from a substance is formed as a hologram image may satisfactorily be used with no specific limitation for the production of holographic flake pigments.[135] For practical use, holographic mirrors are preferred for the manufacture of those pigments. A holographic mirror is the simplest reflection hologram. It can be created by splitting a laser beam and recombining the beams at a photosensitive layer on the thermoplastic film (two-beam method).[136] Alternatively, it can be created by projecting a laser beam through the photosensitive layer onto a mirror (single-beam method).

Holographic flake pigments frequently have a band-center wavelength of about 380−1100 nm and an effective bandwidth of about 10−200 nm.[136] The pigment particles have a thickness of about 1−100 μm, an average diameter of about 10−300 μm, and a thickness-to-diameter ratio from about 1:2 to about 1:60.[136] Holograms can be converted to pigment particles of the desired size by any conventional means, such as grinding, ball milling, attritor grinding, or two-roll milling. One possibility that can be used is to cool the hologram below its glass transition temperature, for example in liquid nitrogen, before grinding. It is also possible to grind the hologram in cold water, such as ice water. As an alternative, the grinding equipment can be refrigerated to cool the hologram to below its glass transition temperature.

Holographic flake pigments are useful for the preparation of decorative coatings that can be used to emphasize the lines and contours of a three-dimensional surface. They can also be used for the preparation of exterior finishes for automobiles. Another possibility is the application in molded plastics to provide a decorative appearance, e.g., in tiles.

VII. Pigments Formed by Grinding a Film

Optical coatings that shift color with viewing angle have been adapted into optically variable films, pigments, and inks during the last years. These coatings are based frequently on metal-dielectric multilayer thin structures having large color shifts with angle, high chroma, a large color gamut, and light fastness.

Different colors are produced by precisely controlling the thickness of the multilayers in the coating's structure. To maintain tight color tolerance, the layer thickness must be controlled to within a few atoms. The schematic of the light interference multilayer structure is shown in Figure 3.

The metal layers frequently consist of chromium (semitransparent absorber metal) or aluminum (opaque reflector metal). Silicon dioxide or magnesium fluoride are the materials mostly used for the dielectric layers. In the case of pigment particles, there is a symmetrical arrangement of the layers, as shown in Figure 13, whereas optical coatings can also consist of a system of unsymmetrical layers. All these arrangements are the basis for an optical phenomenon called the Fabry−Perot effect.

Such multilayer interference configurations filter the spectrum into a sequence of high-reflectance regions surrounded by low-reflectance regions and thus lend themselves, in principle, to high-purity color production. The detailed spectral characteristics can be widely controlled by controlling the specific design parameters. The metal-dielectric multilayer systems consist of a structure which can be written in the form $(M_1 - \alpha D)^q - M_2$, where M_1 and M_2 are the metal components (generally different), D represents a dielectric layer, α is the unit of quarterwave optical thickness of the dielectric layer, and q is the number of periods in the stack.[137] There are many variations which are obtainable within this framework by varying parameters, such as refractive index, thickness ratios, number of periods, etc. Additionally, a number of variations and extensions of the designs can be obtained by using multicomponent periods, altering the period makeup to consider symmetrical periods, etc.

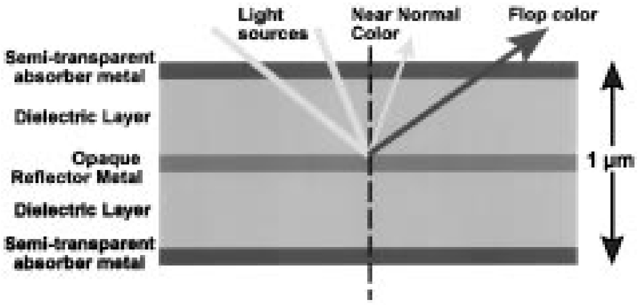

Figure 13. Scheme of the design of optically variable pigments (OVP).

The metal-dielectric stack, in its simplest form of a three-layer combination can be regarded as a Fabry−Perot reflection-type interference filter.[137] Such a design will be of the form $M_1 - \alpha D - M_2$, where M_2 is a highly reflecting, essentially opaque metal layer and M_1 is a rather thin metal film with high absorption properties. A sequence of high- and low-reflectance wavelength regions can be realized corresponding closely to the conditions that give rise to the nodes and antinodes of the standing wave electric field established by the reflector M_2. In the vicinity of an antinode wavelength position, where the electric field intensity is a maximum, induced absorption can be shown to occur in the thin metal layer M_1 resulting in a low reflectance. At a node position, M_1 has little effect on the reflectance of M_2 and the overall reflectance remains high. The separations between the node and the antinode wavelength locations and thus between the low- and high-reflecting regions correspond to quarterware optical thickness changes in the dielectric layer D. The basic reflectance profile for the three-layer metal-dielectric design as described here will be essentially retained in design employing additional periods of $(M_1 - \alpha D)$.[137]

For obtaining optimum performance in optically variable articles using a metal-dielectric design, one would take for M_2 the highest reflecting metal consistent with overall good durability properties, for D the lowest usable refractive index material, and for M_1 a metal with high absorption properties. High potential absorption properties occur for metals with a high product $n \cdot k$ (n refractive index, k absorption coefficient). For example, instead of using chromium for the semitransparent absorber metal layers M_1, materials such as nickel and Inconel could also be

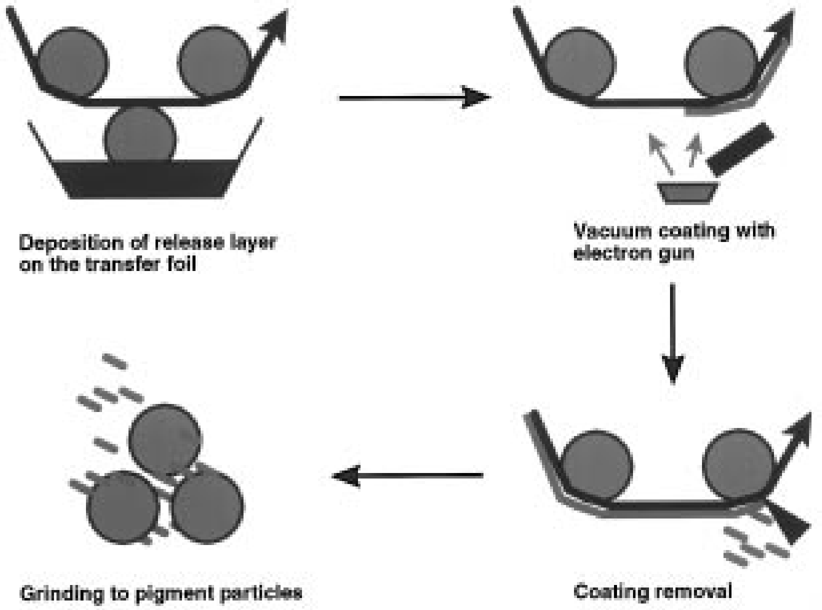

Figure 14. Scheme of the production of optically variable pigments (OVP).

utilized. Instead of silicon dioxide or magnesium fluoride for the dielectric layers *D*, materials such as aluminum oxide or indium oxide could also be used. Finally, instead of aluminum as the opaque reflector metal, layer materials such as gold, copper, and silver could be used for this purpose.[138]

In the foregoing discussions, it has been already described that for flaky pigment particles, a symmetrical arrangement of the layers is necessary. A minimum of five layers and for some optical purposes more may be required. The need for many layers tends to make such a design relatively impractical in any high-volume coating production. Therefore, for practical use, only the five-layer arrangement plays a role.

The pigment flakes can typically be manufactured sequentially in a series of specialized roll-coating machines.[139] In the first machine a carrier film, the so-called release layer, is deposited on a moving polymer web (transfer foil). This release layer is soluble in organic solvents to remove the later formed multilayer film from the web at the end of the process. After depositing this release layer, the transfer foil is placed in a vacuum deposition roll coater and the first metal layer (e.g., chromium) as the semitransparent absorber metal is deposited followed by the first dielectric layer (e.g., magnesium fluoride) and the opaque metal layer (e.g., chromium). The second dielectric layer and the second semitransparent absorber metal layer follow by the same deposition process. After this symmetrical multilayer interference coating has been deposited, the coated foil is removed from the vacuum chamber. In a next step, the formed thin multilayer film is removed from the supporting transfer foil by dissolving the release layer. The transformation into pigment particles is done by grinding the removed part of the film into small platelets which show now pigment dimensions (thickness of 0.2−2 μm, diameter 1−100 μm). The whole process is shown schematically in Figure 14.

Besides the here described metal-dielectric multilayer pigments, there is also another group of color-shifting pigment called all-dielectric thin-film pigments.[140,141] The optical effects are partially different because of the transparency of these multilayer structures without metal layers. Both color-shifting pigment types, the metal-dielectric as well as the all-dielectric thin-film designs, can be used for several applications and are on the market as so-called optically variable pigments (OVP).[141] Such pigments can be applied in automotive paints, plastics, and packaging, mostly as color-shifting optical coatings. A broad application field has been found for prevention of counterfeiting of valued documents such as bank notes, stock certificates, visas, passports, or car licenses.[141,142] The pigments, when incorporated into security inks and printed onto bank notes and other documents of value, are effective against color copying by printers, copiers, or cameras and unauthorized lithographic reproduction.

VIII. Concluding Remarks

Angle-dependent optical effects are broadly used in industrial products. The effects are achieved using different techniques. Some of them are just at the beginning of their commercialization, such as the liquid crystal applications and the new substrates for oxide layers. Although the optical physics background of thin extended layers is mostly understood, there are hardly any attempts to incorporate the particle characteristics of pigments into the calculations. Also, the coating processes and the constrained sintering of thin oxide layers still wait for a thorough investigation.

IX. List of Abbreviations

α = relative proportion of pores filled with said material
δ = phase difference angle
A_0 = amplitude of incident light
C_{Chiral} = concentration of the chiral component
CVD = chemical vapor deposition
I_0 = intensity of incident light
I_r = intensity of reflected light

I_t = intensity of transmitted light
LCP = liquid crystal polymers
n_0, n_1 = refractive indices
n_f = refractive index of film
n_D, n_m = refractive index of bulk
n_w = refractive index of material filling the pores
OVP = optically variable pigment
P = film packing density
p = helical pitch length
PVD = physical vapor deposition
r, r_P, r_S = amplitudes of reflected electromagnetic waves
r_1, r_2, r_3 = amplitudes of reflected electromagnetic waves from multiple reflections
R, R_P, R_S = intensities of reflected electromagnetic waves
R_1, R_2, R_3 = intensities of reflected electromagnetic waves from multiple reflections
t_1, t_2, t_3 = amplitudes of transmitted electromagnetic waves from multiple reflections
T_g = glass transition point (of liquid crystals)

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