Optical Coatings for Special Effect Pigments

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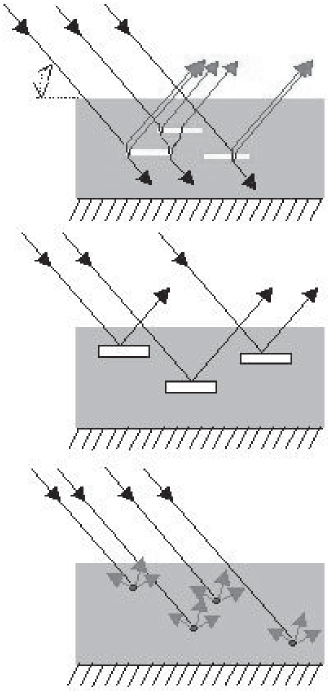
ABSTRACT

Special effect pigments based on the layer-substrate principle belong to the group of high-performance pigments. These pigments, with their special luster and interference characteristics, are very important for the generation of new and unique effects when used in automotive and industrial paints, plastics, printing inks, and cosmetic formulations. Color effects such as pearl luster are produced by light reflection, interference, and absorption. Coloration of application systems with special effect pigments fulfills the highest aesthetic requirements. On the other hand, some of these pigments were developed especially for functional applications (bright electroconductive pigments, pigments for laser marking of polymers, and pigments with special spectral characteristics). Most of the special effect pigments consist of nanostructured, optical metal oxide layers coated on thin mica platelets. They are produced by a complex multiple step process including mica preparation, controlled deposition of transparent metal oxides with high refractive indices (titanium and iron oxide) and calcination. The color of the pigments is determined by the thickness of the metal oxide layers. Besides mica, newly developed substrate materials of silica and alumina flakes can be used for achieving innovative optical effects. Coated with metal oxides, these materials can be used for generating strong angle-dependent (optically variable coatings) and high chroma crystal effects. Deposition techniques for the deposition of special effect pigments include wet chemical deposition, web coating, crystal growth techniques, and the CVD process.

INTRODUCTION

Special effect pigments are synthetic pigments, standing out with their luster, brilliance and iridescent color effect, based upon optically thin layers. This visual impression develops by reflection and scattering of light on thin multiple layers in the pigments.

Figure 1 illustrates the various optical principles of conventional pigments (absorption pigments), metal effect pigments, as well as pearl luster pigments, a main class of special effect pigments. In the case of absorption pigments, the interaction with light is based upon absorption and/or diffuse scattering. A completely different optical behavior can be observed with the group of effect pigments, including special effect and metal effect pigments. Metal effect pigments consist of small metal platelets (for example aluminum, titanium, copper) which operate like little mirrors and almost completely reflect the incident light [1,2].



Pearl Luster Pigments: specific color, luster and color flop due to **interference** (reflection and refraction) of light

Metallic Pigments: metallic gloss due to **reflection** of light

Absorption Pigments: specific color due to **absorption** of light

Figure 1: Optical principles of pigments.

Special effect pigments consist of alternating transparent layers with differing refractive indices. This difference in refractive indices, arising equally on the interface between air/oil film or oil film/water, is a prerequisite for the well-known iridescent color images in these media. Small highly refractive platelets of special effect pigments align themselves parallel in optically thin systems such as paints, printing inks, or plastics. Interference effects develop when the distances of the various layers or the thicknesses of the platelets have the right values.

The breakthrough for special effect pigments came with the invention of mica coated with metal oxides. Mica-based effect pigments now account for > 90 % of the world market. Special effect pigments are used to obtain pearl, iridescent (rainbow), or metallic effects, and in transparent color formulations to obtain brilliance or two-tone color, luster flops, and color travel effects (changing with viewing angle). The most important applications are plastics, industrial coatings, printing inks, cosmetics, and automotive paints.

Table 1 shows an overview of effect pigments. These pigments can be classified as metal platelets, oxide coated metal platelets, oxide coated mica platelets, oxide coated silica, alumina, and glass flakes, platelet-like monocrystals, comminuted PVD-films, and polymer films (e.g. liquid crystal polymer platelets). Aims of new developments are new effects and colors, improvement of hiding power, more intense interference colors, increased light and weather stability, and improved dispersability. Of special interest are pigments which are toxicologically safe and can be produced by ecologically acceptable processes.

Table 1: Overview of effect pigments [3].

Pigment type	**Examples**
metal platelets	Al, Zn/Cu, Cu
oxide coated metal platelets	surface oxidized Cu-, Zn/Cu-platelets, Fe_2O_3 coated Al flakes
oxide coated mica platelets (analogous with silica, alumina, glass flakes)	non absorbing coating: TiO_2 (rutile), TiO_2 (anatase), ZrO_2, SnO_2, SiO_2 selectively absorbing coating: FeOOH, Fe_2O_3, $FeTiO_3$, Cr_2O_3, TiO_{2-x}, TiO_xN_y, $KFe[Fe(CN)_6]$, colorants
platelet-like monocrystals	BiOCl, $Pb(OH)_2 \bullet 2\ PbCO_3$, α-Fe_2O_3, natural fish silver
comminuted PVD-films	Al, $Cr/SiO_2/Al/SiO_2/Cr$
comminuted polymer films	liquid crystal polymers, holographic polymer platelets

METAL OXIDE MICA PIGMENTS

The dominant class of special effect pigments is based on platelets of natural mica coated with thin films of high refractive transparent metal oxides. The mica substrate acts as a template for the synthesis and as a mechanical support of the deposited thin optical layers of the pigments. Mica minerals are sheet layer silicates. Effect pigments are usually based on transparent muscovite, but some are based on synthetic phlogopite. Although muscovite occurs worldwide, only few deposits are suitable for pigments. Mica is biologically inert and approved for use as a filler and colorant.

Selection and preprocessing of the mica substrate is one of the key factors which determine the quality and appearance of special effect pigments. The aspect ratio of the final pigment depends on the particle size distribution of the mica platelets, which have a thickness of 300-600 nm and various diameter ranges (e.g., 5-25, 10-50, 30-110 µm). Since light is regularly reflected from the planes of the metal oxide coated mica and scattered from the edges, brilliance and hiding power are inversely related to each other.

The development of the mica-based pigments started with pearlescent colors. This was followed by brilliant, mass-tone colored combination pigments (i.e., mica TiO_2, and another metal oxide) with one color (interference color same as mass tone) or two colors (interference and mass tone different) that depend on composition and viewing angle. In the 1980s further development was made by coating mica particles with transparent layers of iron(III) oxide.

Titanium Dioxide-Mica

The first multilayer pigments were marketed in the 1960s as TiO_2-coated muscovite micas. Two different processes are used for coating mica in aqueous suspension on a commercial basis:

1) Homogeneous hydrolysis

$$TiOSO_4 + \text{mica} + H_2O \xrightarrow{100°C} TiO_2\text{-mica} + H_2SO_4$$

2) Titration

$$TiOCl_2 + 2\ NaOH + \text{mica} \longrightarrow TiO_2\text{-mica} + 2\ NaCl + H_2O$$

The pigments are then dried and calcined at 700-900°C. The titration (chloride) process is preferred for interference pigments with thick TiO_2 layers because it is easier to control. Chemical vapor deposition in a fluidized bed has also been proposed:

$$TiCl_4 + 2\ H_2O + \text{mica} \xrightarrow{>100°C} TiO_2\text{-mica} + 4\ HCl$$

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.

Rutile has a higher refractive index and yields a stronger luster and pearlescence than anatase. Therefore, processes have been developed to create a rutile layer onto mica: A thin layer of SnO_2 is precipitated as a continuous layer onto the substrate, and then the TiO_2 layer is created using the usual process. $SnCl_2$ or better $SnCl_4$ can be used as precursors for the SnO_2 precoating. SnO_2 acts as a template because its lattice parameters are close to those of rutile.

The desired interference color determines the thickness of the titania layer. For a silver white pigment 50 nm of anatase is needed and for a blue interference color about 120 nm. The sequence of interference colors obtained with increasing TiO_2 layer thickness agrees with theoretical calculations. A cross section of a TiO_2-mica pigment is shown in Figure 2. The complete process for the manufacture of metal oxide mica pigments is shown in Figure 3.

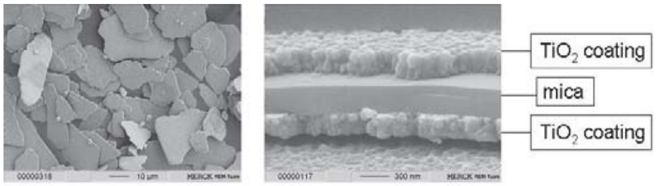


Figure 2: Scanning electron micrographs of a TiO_2 mica pigment.

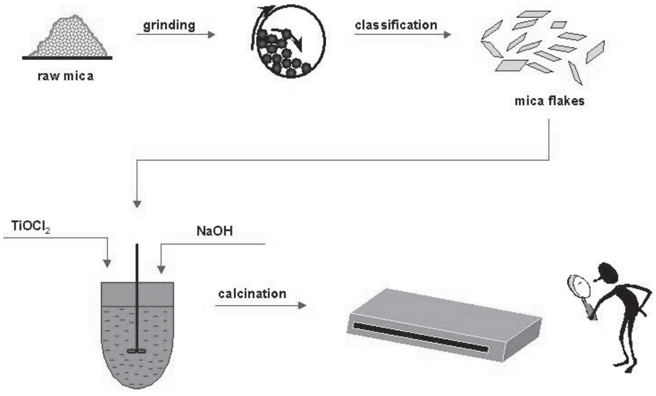


Figure 3: Production process for TiO_2 mica pigments.

TiO_2-mica pigments are used in all color formulations of conventional pigments where brilliance and luster are required in addition to color, i.e. in plastics, coatings, printing, and cosmetics.

Iron Oxide-Mica

Like titanium dioxide, iron(III) oxide is suitable for coating mica platelets. It combines a high refractive index (metallic luster) with good hiding power and excellent weather resistance. Commercial Fe_2O_3-mica pigments are produced by precipitation of iron(II) or iron(III) ions in aqueous mica suspensions and calcination of the resulting coated particles at 700 - 900 °C:

$$2\ FeCl_3 + mica + 3\ H_2O \longrightarrow Fe_2O_3\text{-}mica + 6\ HCl$$

It is also possible to produce iron oxide-mica pigments by a direct CVD fluidized bed process in which iron pentacarbonyl is oxidized and Fe_2O_3 is deposited on the mica surface.

Independent of the synthesis route, iron(III) oxide crystallizes in the α-modification (hematite) after calcination. Brilliant, intense colors are obtained with 50-150 nm layers of Fe_2O_3 (hematite) on muscovite. Absorption and interference colors are produced simultaneously and vary with layer thickness. The red shades are especially intense because interference and absorption enhance each other.

Combination Mica-Based Pigments

One possibility for attractive combination pigments is the coating of TiO_2-mica pigments with an additional layer of an inorganic or organic colorant. The thickness of the TiO_2 layer is decisive for the brilliance or interference effect under regular viewing conditions, whereas the transparent colorant dominates at all other viewing angles. A deep, rich color with a luster flop at all angles is attained when the colorant and interference color are matched. If the interference color and the mass tone of the colorant are different, a color flop (two-tone pigments) is seen in addition to the luster flop.

Iron(III) oxide is the most important metal oxide for combination with titanium dioxide on mica flakes. Brilliant golden pigments result and can be applied for several purposes. Two routes are used to synthesize these pigments, and different structures are formed. In the first, a thin layer of Fe_2O_3 is coated onto the surface of a TiO_2-mica pigment. The overall interference color is the result of both metal oxide layers. The mass tone is determined by the Fe_2O_3 layer, and interesting gold pigments (e.g., reddish gold) are possible. In the second case, co-precipitation of iron and titanium oxide hydroxides on mica particles followed by calcination leads to greenish gold pigments. Interference and mass tone can be explained as above. The mass tone in this case is, however, further modified due to the additional formation of the highly refractive yellowish iron titanate phase Fe_2TiO_5 (pseudobrookite). Other inorganic colorants used (instead of iron oxide) for combination pigments are Cr_2O_3 (green), iron blue, cobalt blue, Fe_3O_4 (black), and $FeTiO_3$.

Mica platelets can be coated with a variety of other compounds to produce additional pigments [4]. The calcination of metal oxide mica pigments in the presence of inert (e.g., N_2, Ar) or reactive gases (e.g., NH_3, H_2, hydrocarbons) allows the formation of phases which are not producible by working in air. Table 2 contains a summary of pearlescent mica pigments with special coloristic properties.

Table 2: Examples of mica-based pearlescent pigments with special coloristic properties.

Pigment composition	**Preparation**	**Remarks**
TiO_{2-x}/TiO_2/mica	TiO_2/mica + H_2 (Ti, Si) T > 900°C (solid state reaction)	grey, blue-grey
TiO_xN_y/TiO_2/mica	TiO_2/mica + NH_3 T > 900°C (solid state reaction)	grey, blue-grey
$FeTiO_3/TiO_2$/mica	Fe_2O_3/mica + H_2 T > 600°C (solid state reaction)	grey (ilmenite pigments)
Fe_3O_4 mica	Fe_2O_3/mica + H_2 T ≈ 400°C (solid state reaction)	black
	Fe^{2+} + O_2 + mica (precipitation)	black

Initially, metal oxide-mica pigments were developed purely for their excellent coloristic properties. Since then, they have also become of interest for functional uses. The composition and thickness of the oxide layer on the mica surface are always responsible for the physical properties like electrical conductivity, magnetism, IR reflectivity, and laser markability of polymers [4]. Table 3 lists data on some functional metal oxide mica pigments.

Table 3: Functional metal oxide-mica pigments.

Pigment composition	**Property**	**Application**
$(Sn,Sb)O_2$/mica $Sn(O,F)_2$/mica	electrically conductive	conductive flooring, anti-static packaging materials, light colored primed plastic surfaces which can be electrostatically painted in further coating process, light colored conducting surfaces in clean room conditions for dust reduction
Fe_3O_4/mica	magnetic	magnetic surfaces
TiO_2/mica	IR-reflective	IR-reflecting plastic sheets, e.g. for domed and continuous roof lights
TiO_2/mica $(Sn,Sb)O_2$/mica	laser sensitive	laser marking of plastics, coatings

SILICA FLAKE PIGMENTS

Instead of mica, SiO_2 flakes can be used as a substrate for special effect pigments [5]. The SiO_2 flakes are produced by a web coating process. 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; with the interference color of those systems 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 the slightly yellow mass tone of natural mica; (3) SiO_2 has a lower refractive index (1.46) than mica (about 1.58) and leads to a stronger interference effect.

The properties available with silica flake pigments can be summarized as follows:

Improved substrate characteristics
- Uniform and controllable substrate thickness
- Smooth and uniform substrate surface
- Transparent substrate with no mass tone color

Improved reflection and refraction of light
- Improved chromatic strength and purity
- New color travel behavior

The silica flakes are manufactured by a web coating process as shown in Figure 4. The web, moving at a controlled speed, is wet with an aqueous solution of a silica compound. The film on the web is dried to form a stable coating layer that can be selected between 50 nm and 1000 nm thick by adjustment of process parameters. The layer is then removed from the web and processed further to generate flakes that are fractionated and coated. The transparent flakes have a relatively low refractive index. However, they provide an excellent substrate for coating with the relatively high index metal oxides, such as titanium dioxide and iron oxide. These metal oxides are applied in a standard precipitation coating process producing high performance effect pigments.

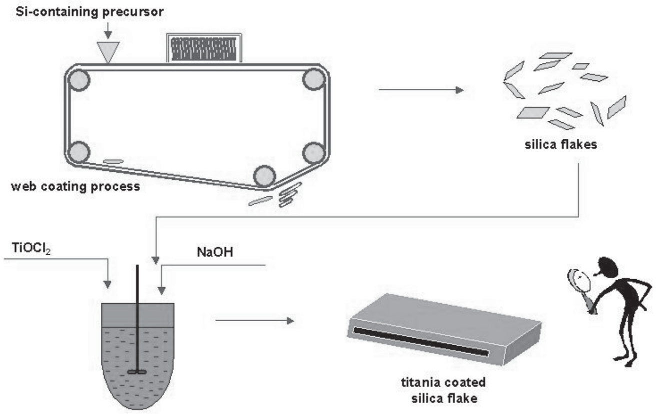


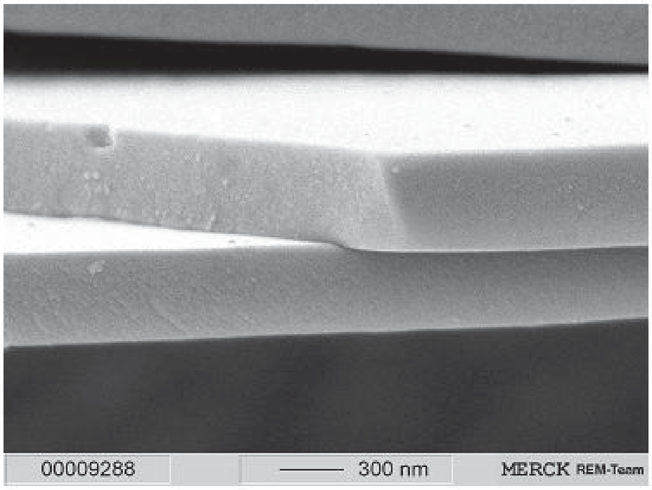
Figure 4: Production process for silica flake pigments.

Titania is deposited as hydrated titanium oxide on the surface of the SiO_2 flakes. The thickness of the layer is monitored and precisely controlled. After drying and calcining, TiO_2 (anatase or rutile) is formed and a specific color is produced corresponding to the film thickness. Rutile can only be achieved by using a thin intermediate layer of SnO_2.

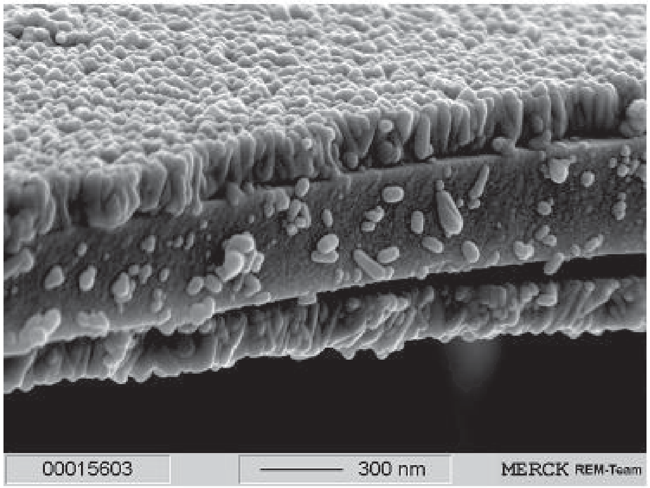
SiO_2 can be coated not only with TiO_2 but also with other metal oxides that are deposited from hydrolysable salts. Iron(III) oxide is deposited as hydrated iron oxide on the transparent silica flakes. Subsequent drying and calcining produces α-Fe_2O_3 (hematite) layers on the flakes. The high refractive index of iron oxide generates strong interference effects and, in conjunction with the mass tone, brilliant red pigments.

Extraordinary optical effects are achieved by the combination of transparent silica flakes selected for precise uniform thickness and controlled depositions of metal oxide coating layers. The color of these pigments exhibits extreme angle dependence, and objects painted with them will change appearance with the direction of lighting and the location of the observer. Color changes from gold-silver to green, to green-blue, to dark blue are seen. The strong color travel is seen even under subdued lighting conditions.

The SEM micrograph in Figure 5 shows a cross section through a TiO_2 coated silica flake. It shows clearly that both the SiO_2 flake and the TiO_2 layer thickness are precisely controlled.



SiO_2 flakes



TiO_2-coated SiO_2 flake

Figure 5: Scanning electron micrographs of silica flakes and of a TiO_2-coated flake.

ALUMINA FLAKE PIGMENTS

Al_2O_3 flakes of a high quality are produced by the following steps, see Figure 6. First, 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 (Figure 7). 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 special effect pigments of very high luster. The advantage over a 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. A very interesting crystal-like effect can be achieved by using alumina flake pigments in application systems, such as car paints [5].

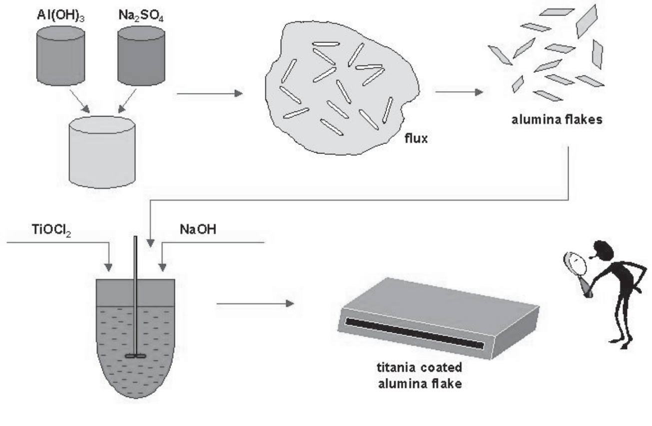
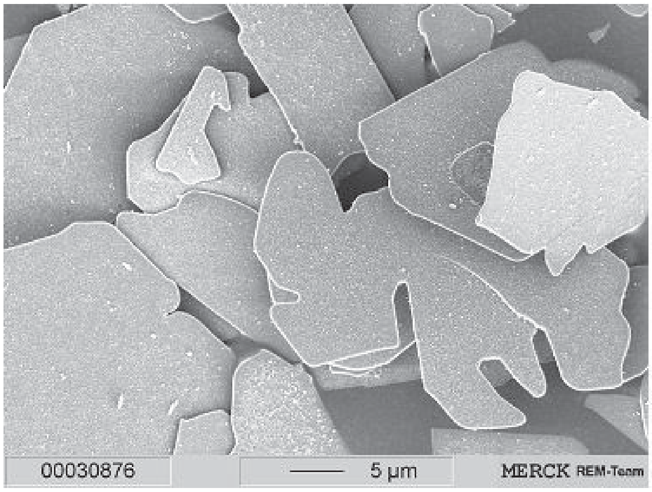


Figure 6: Production process for alumina flake pigments.

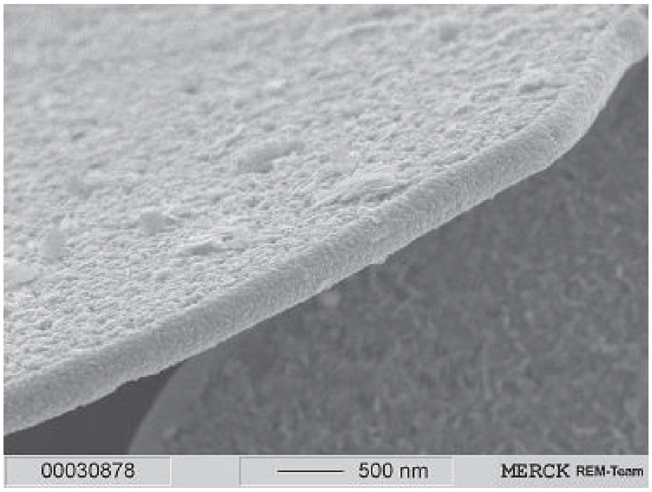
EFFECT PIGMENTS FORMED BY COATING OF METAL FLAKES

Metal flakes, especially aluminum platelets, can be coated with iron oxide in a CVD process [6]. 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. 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. The resulting pigments show golden, orange, and reddish metal-like effects.

The aluminum flakes can be coated with aluminum oxide and/or silicon dioxide in the liquid phase before the CVD process to reduce the reactivity of the metal and to create multilayer color effects. These pigments show strong angle-dependent coloristic effects (color travel). Metal halogenides are difficult to use as gas-phase precursors for 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 about ten years ago. However, no commercial products have, as yet, been introduced.



Al_2O_3 flakes



TiO_2-coated Al_2O_3 flakes

Figure 7: Scanning electron micrographs of alumina flakes and of TiO_2-coated flakes.

PIGMENTS FORMED BY COMMINUTION OF A PVD-FILM

Effect pigments with a metal-dielectric multilayer structure (Fabry-Perot type) can typically be manufactured sequentially in a series of specialized roll-coating machines [2]. 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., aluminum). 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 subsequent step, the formed thin multilayer film is removed from the supporting transfer foil by dissolving the release layer. Transformation into pigment particles is done by comminuting the removed part of the film into small platelets which now show pigment dimensions (thickness of 0.2 - 2 μm, diameter 1-100 μm).

Such types of effect pigments can be used for several applications and are on the market as so-called optically variable pigments (OVP). They have found a broad application, especially in preventing counterfeiting of important documents such as bank notes, stock certificates, visas, passports, or car licenses. When incorporated into security inks and printed on bank notes and other documents of value, the pigments are effective against color copying by printers, copiers, or cameras and unauthorized lithographic reproduction [7].

PIGMENTS BASED ON LIQUID CRYSTAL POLYMERS

Interference and angle-dependent color effects can also be achieved by layers or particles based on liquid crystal polymers (LCP) [2]. 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 comminuted 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 subsequent 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 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, 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.

After polymerization and crushing, the liquid crystal polymer platelets can be used as iridescent pigments. Such platelets can be suspended in inorganic and organic media, especially lacquers. The color effects are very strong if black substrates are used to ensure the absorption of the transmitted light.

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.

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