



Gerhard Pfaff

Special effect pigments in cosmetic applications

An amazing development for a bright future

GERHARD PFAFF*, MIRIAM BECKER

*Corresponding author

Merck KGaA Frankfurter Str. 250 Darmstadt, 64293, Germany

ABSTRACT: The history of special effect pigments dates back to the 17th century. A real breakthrough was achieved with the development of pigments using layer-substrate structures 50 years ago. Platelet-like particles of natural and synthetic mica, silica, borosilicate, and alumina are used today as templates for thin high-refractive metal oxide layers forming attractive pigments with special effects like pearl luster, angle-dependent interference color, sparkle, or multiple reflections. The specific properties of transparent and semi-transparent effect pigments make them unique in a wide range of cosmetic applications – from color cosmetics to personal care products.

INTRODUCTION

What makes modern cosmetics so attractive? It is not only the scientific claim that may be included, often the optical appearance and skin feel triggers the consumer's decision. Appearance and skin feel of cosmetic products can be enhanced by the use of pearlescent pigments and their broad range of stunning effects. Effect pigments differ from conventional pigments in their special coloristic properties. They are used alone or together with other colorants and also fillers in a wide range of applications such as cosmetic formulations, industrial and automotive coatings, plastics and printing inks.

The cosmetic industry is constantly looking for new coloristic effects, which optically attract consumers. Besides colour and effect, the pigments should also provide advantageous skin caring properties as well as ease of application.

Effect pigments can be divided into the two basic classes: special effect pigments, the most important examples of which are pearlescent pigments, and metal effect pigments. All effect pigments are characterized by a platelet-shaped geometry of their particles. These have a diameter, which lies generally between 5 and 200 μm and a thickness showing a dimension below 1 μm . The aspect ratio can therefore reach values of up to 200.

In contrary to metal effect pigments made up of thin metal platelets (typical are aluminium and copper-zinc alloys) and leading to metallic and hiding effects in the application system, pearlescent and other special effect pigments are partially transparent. Although the platelet surface of these luster pigments reflects some of the light, parts of it pass

through the particles. The reflection of the light results in a pronounced luster effect, which is softer than that of metallic pigments and appears to come from the depth of the application medium. Thus, optical effects are created comparable to those associated with natural or artificial pearls. It is decisive that the light is not solely reflected from the high-refractive surface of the particles, but also from inner and outer boundary surfaces of the pigment particles.

Naturally occurring mica and some other materials are important constituents of pearlescent pigments acting as platelet-shaped substrates for high-refractive, metal oxide layers. By the deposition of extremely thin layers of metal oxides (such as titanium dioxide or iron(III) oxide) on the substrate platelets, the layer-substrate principle is used to form effect pigments. The metal oxide layers are in the range of a millionth of a millimetre thick. The optical properties of the so-achieved pigments particles range from transparent to semi-transparent. They can be used in application media to produce a pearl-like luster. The choice of metal oxide, and thereby the refractive-index level of the optically active layer, as well as the correct film thickness allows the creation of interference phenomena, which then show a broad variety of luster effects.

Pearlescent pigments can be classified into various effect groups: silver white-, interference-, gold-, metallic colour luster-, colour luster-, colour travel- or black colour pigments. By varying the size of the pigment particles, a range of effects can be achieved from silky-gloss to sparkling or from transparent to strongly hiding (1-3).

CLASSICAL EFFECT PIGMENTS AND FILLERS FOR COSMETICS

The history of transparent effect pigments goes back to 1656 in France when Jaquin isolated the silvery substance of the inside of fish scales and developed a suspension with silver luster (4). The so-prepared pearl luster suspension showed a brilliant lustrous effect and was called "Essence d'Orient". It contained most probably the two purines guanine and hypoxanthine, and therefore those substances, which were several hundred years later called natural fish silver (natural pearl essence) in this combination. One can assume that the early fish silver was already used in cosmetic applications (5). An early description of the manufacture of pearlescent materials starting from natural sources is given in an encyclopedia published in the 18th century (Figure 1) (6). Today produced natural fish silver consists of 75-97 percent guanine and 3-25 percent



Figure 1. Historical literature showing the early interest in nacreous materials in the 18th century (6).

hypoxanthine. Both substances tend to crystallize in thin, optically high-refracting platelets yielding to the desired pearlescent effects in cosmetics. They are brought into isopropyl alcohol and nitrocellulose lacquer for their use in cosmetic formulations. Natural pearl however is difficult to produce and therefore expensive, which limits its application scope in cosmetic products.

Bismuth oxychloride (BiOCl) effect pigments and fillers are produced by hydrolysis of acidic bismuth salt solutions in the presence of chloride ions since the 1960s. The chosen reaction parameters (concentration, pH-value, reactor geometry, addition of surfactants) have a significant influence on the properties of the formed monocrystalline BiOCl platelets, especially on colour, particle size and thickness, scaly shape and density (1). The usual tetragonal dipyrimal geometry of the crystals can be flattened to platelets with high aspect ratio (Figure 2). Bismuth oxychloride variations are mainly used as functional fillers in cosmetic

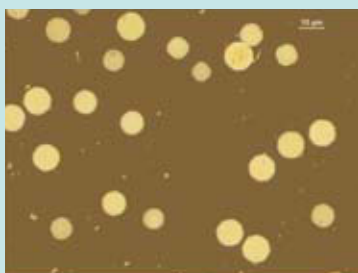


Figure 2. Micrograph of BiOCl crystals showing the monocrystalline platelets.

products because of their unique properties. They provide smoothness to the formulation, good skin adhesion and even application. The wear properties of make-up products are improved due to the hydrophobicity and skin affinity of BiOCl. In compressed powders and anhydrous application systems, bismuth oxychloride acts as frequently used filler with the advantages of excellent compressibility and low oil absorption. The RonaFlair® series of specialty fillers comprises several BiOCl types for cosmetic applications (7). As an example, RonaFlair® ESQ is a matte highly transparent bismuth oxychloride powder offering all the advantages of BiOCl effect pigments but without the luster typically characteristic for them. RonaFlair® LF-2000, on the other hand, offers an optimum balance of optical properties, e.g. luster and opacity, and has a sensational skin feel. Bismuth oxychloride is also applied as traditional pearlescent pigment for silverwhite effects.

SUBSTRATE-BASED EFFECT PIGMENTS

Further evaluation of new materials for the use as pearlescent pigments with improved properties led to the class of the substrate-based effect pigments. Such pigments are based on substrate platelets acting as the mechanical support of thin

optical layers. The platelet also acts as a template for the formation of these thin layers. The material of the optical layers can be chosen predominantly from metal oxides such as titanium dioxide (both rutile and anatase), iron(III) oxide, mixed titanium-iron oxides, silicon dioxide (as low-refractive layer in multilayer systems) and others.

If the thickness distribution of the substrate platelets becomes narrower, the substrate itself will start to act as an optical layer and becomes part of an optical three-layer or multilayer system (1, 2). The most important substrate materials used for effect pigments are natural and synthetic mica, aluminium oxide (alumina), silicon dioxide (silica) and calcium aluminium borosilicate.

EFFECT PIGMENTS BASED ON NATURAL MICA PLATELETS

Mica-based effect pigments were first described in 1942 (8). Their commercial success started in the 1970s. Examples for the use of metal oxide mica pigments for decorative cosmetics are shown in Figure 3.



Figure 3. Example for the use of substrate-based effect pigments from a promotional brochure of 1978 (source Merck KGaA).

Compared to the other substrates – all of them are synthetic – natural muscovite mica is rather inexpensive and available in large quantities in nature. It fulfils all chemical and physical requirements for a highly suitable substrate for effect pigments. Consequently, today natural mica is the most important substrate for pearlescent pigments by far. Due to its crystal structure as a layered silicate, it can be cleaved to thin flakes of a mean thickness of typically 200-500 nm. The diameters of the mica flakes used for the manufacture of effect pigments for cosmetics are mostly in the range from 5-150 µm. Silver white, interference, gold, metallic, and colour luster pigments are possible dependent on the metal oxide coating on the substrate. Timiron® and Colorona® pigments based on natural mica are typical representatives of these effect pigments for cosmetic applications (7).

Silver white pigments on natural mica are characterized by titanium dioxide layers with thicknesses of about 50 nm. The particle size can range from < 15 µm (Timiron® Supersilk MP-1005) to 10-150 µm (Timiron® Diamond Cluster MP-149). Depending on the particle size distribution, the pigments display different silver white effects from silky to extremely brilliant and sparkling (7).

Interference pigments show different colours based on an optical effect caused by light interference. The interference colour depends on the thickness of the titanium dioxide layer on the mica. Relevant interference colours for effect pigments used for cosmetics are gold, copper, red, purple, blue, turquoise, and green. In some cases multilayer arrangements of alternating metal oxides – typically consisting of titanium dioxide and silicon dioxide – are used to achieve interference pigments with higher chroma such as the Timiron® Splendid Colours (7).

Gold pigments consist of mica flakes coated with titanium dioxide and iron oxide. They provide highly intense and lustrous gold effects. The particle size distribution as well as the ratio of the two metal oxides is mainly responsible for the characteristics of a single gold pigment. Two examples of this group of effect pigments are Colorona® Bright Gold (10-60 µm) and Colorona® Fine Gold MP-20 (5-25 µm). Colorona® Precious Gold with particle sizes in the range from 10-60 µm gets its strong golden chroma from an additional silicon dioxide layer (7).

Metallic pigments based on natural mica display highly lustrous warm earth-colour shades of different hues for various cosmetic applications. They consist of mica coated with iron(III) oxide. The thickness of the iron oxide layer is the decisive parameter for the colour properties of the pigments. Transparency and coverage respectively are controlled by the particle size distribution of the mica, which ranges from 5-25 µm up to 10-150 µm. Some representatives of this group are Colorona® Copper Fine (5-25 µm), Colorona® Bronze (10-60 µm), and Colorona® Copper Sparkle (10-125 µm) (7).

Finally, colour luster pigments display a colourful fan of various colour shades. In this case the mica platelets are coated with titanium dioxide and an additional layer of an organic or inorganic pigment. The resulting combination of an interference pigment and an absorption pigment results in significantly more brilliant colour effects, in contrast to the simple mixture of the two components. The mass tone of the added colorant is enhanced by the reflection of the interference pigment leading to very intense colour shades. The particle size distribution of these pigments is mostly in the range of 10-60 µm. Examples of this group of effect pigments are Colorona® Carmine Red with a carmine layer on TiO₂ and Colorona® Dark Blue with iron blue as the absorbing component (7).

Effect pigments on natural mica are typically produced by the deposition of metal oxide layers on the mica in aqueous suspension followed by a calcination step (1). Titanium dioxide containing pigment types are manufactured starting from TiOCl₂ (titration process) or TiOSO₄ (homogeneous hydrolysis). TiO₂ can be formed as anatase, when it is deposited directly on the mica or as rutile, when an intermediate SnO₂ layer is deposited on the mica surface followed by the TiO₂ layer. Whereas the TiO₂ layer thickness of silver white pigments is about 50 nm, the TiO₂ thickness of interference pigments is typically in the range of 80-250 nm on both sides of the mica platelets. The control of the metal oxide layer thickness is one of the most important factors for the reproducible manufacture of these effect pigments. Iron oxide layers are formed on the mica by a comparable process. Iron(II) sulfate or iron(III) chloride are used as starting materials. The scanning electron micrographs in Figure 4 show particles of a TiO₂-mica pigment and a cross section through one single particle with the mica substrate and the TiO₂ layer around the mica.

Mica pigments with multiple layers of metal oxides show stronger chroma and in some cases also pronounced angle dependent colour effects, if the optical thicknesses of the

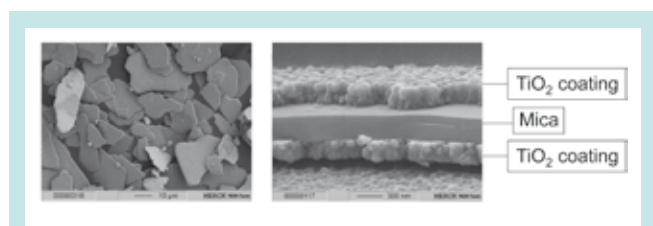


Figure 4. Scanning electron micrographs of a titanium dioxide mica pigment. Left: Overview micrograph. Right: Cross-section through one particle. Layer structure: TiO₂-mica-TiO₂ (1).

layers are carefully chosen. Mica multilayer pigments are, however, much thicker than the later discussed silica flake pigments (e.g., twice the TiO₂-SiO₂-TiO₂ stack plus the optically inactive mica thickness). Examples for pigments of this type are Xirona® Caribbean Blue and Xirona® Volcanic Fire (7).

EFFECT PIGMENTS BASED ON SYNTHETIC MICA PLATELETS

Synthetic mica is used for effect pigments since the year 2000. Pigments based on synthetic fluorophlogopite have similar layer arrangements as those based on natural mica. Silver white pigments based on synthetic mica have a pure white powder colour and display a high brilliance depending on the particle size distribution. The manufacturing process of synthetic mica based pigments can be controlled precisely in respect of both substrate and metal oxide deposition. Fluorophlogopite is manufactured by a high-temperature process. The starting mixture of oxides and salts is heated up to form a melt, which is cooled down slowly to form well-crystalline synthetic mica. The so-formed mica can be cleaved to obtain thin platelets suitable for effect pigments when coated with metal oxide layers. The impurity content can be controlled by the selection of the raw materials for the mica and the metal oxide coating and this presents an advantage over natural mica as a substrate.

Timiron® Synwhite 40 is an example for a synthetic mica based effect pigment. It offers pure white pearl effect together with attractive sparkling behaviour in the cosmetic formulation (7).

EFFECT PIGMENTS BASED ON SILICA FLAKES

Silica flake based pigments were introduced to the market 10 years ago. Coating of silica flakes (SiO₂) with titanium dioxide or iron(III) oxide leads to colour travel pigments that display exciting colour shifting effects depending on the viewing angle.

Thin silica flakes with a very uniform and controllable thickness are manufactured using a specially designed web-coating process (9). The narrow thickness of the flakes together with the adjusted metal oxide layers leads to the desired effects of optimized optical three-layer systems. The very homogenous thicknesses of the SiO₂ flakes used in state-of-the-art processes are in the order of 300 and 400 nm. Some of the available silica-based pigments show colour travel effects such as gold-blue, green-red, red-gold or violet-green. Representatives of this pigment group are Xirona® Magic Mauve (with TiO₂ coating, application example in Figure 5), Xirona® Kiwi Rose (TiO₂) and Xirona® Indian Summer (Fe₂O₃). A very special effect pigment based on silica flakes coated with iron oxide is Xirona® Le Rouge. It is a truly red pearl pigment, displaying shifting nuances from yellow-red to blue-red. In cosmetic formulations it offers a wide range of possible red and pink effects and a unique stability (Figure 6). These properties make this effect pigment superior to common red pigments (such as red organic lakes or pearlescent pigments with organic coatings) as the latter face stability issues towards light, water and pH. The structure of the pure SiO₂ flakes and the TiO₂-coated SiO₂ flakes can be seen in the electron micrographs in Figure 7.



Figure 5. Color travel effect in a nail lacquer with the pigment Xirona® Magic Mauve.

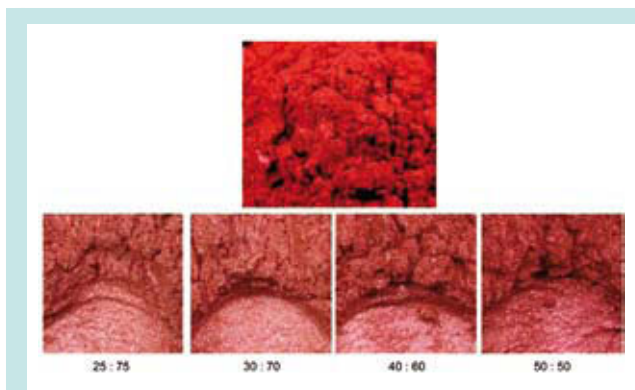


Figure 6. Xirona® Le Rouge as pure powder and examples for creating various pink shades with sparkle effects using this pigment in blends (Xirona® Le Rouge with Ronastar® Red in different ratios).

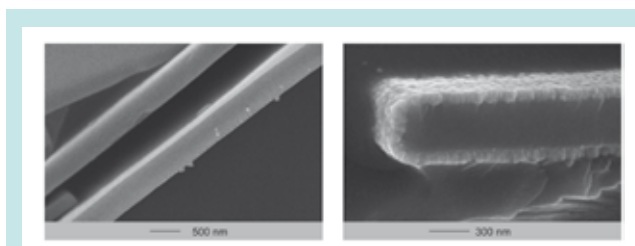


Figure 7. Scanning electron micrographs of pure (left) and TiO₂-coated (right) SiO₂ flakes (1).

EFFECT PIGMENTS BASED ON BOROSILICATE FLAKES

Thin calcium aluminium borosilicate flakes can also act as a substrate for special effect pigments. Using this flaky material, very clean and brilliant colours can be achieved when coated with metal oxide layers. The progress in glass manufacturing technology in the 1990s made it possible to produce flakes thin enough to be suitable for pigments. Effect pigments based on this substrate provide bright colours combined with high transparency. The appearance of these pigments is extraordinarily vivid and goes back to the so-called multi-colour effect (the human eye sees the silver white or interference colour of one pigment in the application and in addition various reflection colours of single pigment particles), typically only for pearlescent pigments based on calcium aluminium borosilicate flakes (10, 11). These flakes are available with different particle size distributions, e.g. from 10-100 µm or 20-200 µm. Dependent on the metal oxide coating, silver white, interference, gold or other pigment types are possible. Examples for effect pigments of this group are Ronastar® Noble Sparks (silver white, 20-200 µm), and Ronastar® Golden Sparks (interference, 20-200 µm) (7). One of the latest pigments of this range is Ronastar® Golden Jewel, which is based on borosilicate flakes with a particle size distribution from 20-200 µm providing a unique combination of clear mass tone, brilliant interference colour, strong sparkle effect and saturated golden colour (Figure 8).



Figure 8. Ronastar® Golden Jewel – a new brilliant golden effect pigment yielding strong sparkle in cosmetic formulations.

EFFECT PIGMENTS BASED ON ALUMINA FLAKES

Alumina (α -Al₂O₃) can be produced in a good optical quality in form of thin flakes using a controlled crystal growth process in molten sodium sulfate (9). The thickness of the flakes can be controlled by doping and special reaction conditions. When coated with metal oxides, the resulting pigments exhibit a distinct directed reflection, often described as sparkling effect. Due to the small particle sizes, the narrow particle size distribution (5-40 µm) and the highly reflective surfaces, pigments based on alumina flakes show a sophisticated glittering shimmer with high luster. Their pure white mass tone clearly differentiates these effect pigments from those on other substrates. An example of an alumina-based pigment developed for cosmetic formulations is Timiron® Glam Silver, a strong sparkling silver white pigment suitable for both personal care as well as colour cosmetics (7).

CONCLUSION

Over the last decades, special effect pigments have found a broad range of applications in decorative and functional purposes like cosmetics but also in paints, printing inks, and plastics. With their unique possibilities to achieve optical impressions such as eye-catching effects, angle-dependent interference colours, pearl luster or multiple reflections, they are used in lipsticks, eye shadow, nail varnish and other cosmetics yielding a constant stream of new and attractive trends and effects.

The use of these pigments is not only restricted to decorative applications. They are also used in personal care products such as shampoos, shower gels, hair care products, body lotions and skin creams to improve the product attractiveness (Figure 9).



Figure 9. Examples for the effect of interference and silverwhite pigments in personal care products (from left to right): Gel with blue dye; gel with blue dye and 0.05 percent Ronastar® Green Sparks; gel with blue dye and 0.3 percent Timiron® Synwhite 40.

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