

# Bismuth Oxychloride – A Multifunctional Color Additive

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A modern cosmetic product is not simply about color and improving appearance. It is a fashion statement. It reflects individuality and, sometimes, spirituality. Cosmetic formulations are becoming more complex and a product is more desirable to the consumer if it is multifunctional. The texture and feel of a product reflects the level of sophistication and renders an up-scale image.

While many new cosmetic ingredients are entering the market, bismuth oxychloride remains a unique material with many advantageous attributes for cosmetic formulations. Bismuth oxychloride is versatile and various grades are available for different cosmetic applications. It survives all the fashion trends because in cosmetic products it provides the fundamentals: classical natural color effects, silky pearlescence, excellent skin feel, enhanced binding and compressibility and good skin adhesion.

In this article, the important properties of bismuth oxychloride are described in detail and a few formulations are presented to illustrate the unique attributes of this ingredient in cosmetics as well as personal care applications.

## Bismuth Oxychloride

Bismuth oxychloride (BiOCl) was the first synthetic non-toxic nacreous pigment. It has been used in cosmetic formulations for several decades. It is practically insoluble under cosmetic and physiological conditions. In fact many antacids contain bismuth salts that neutralize excess stomach acid by forming insoluble and therefore harmless BiOCl.

Because of its nontoxicity and brilliance of luster, it is also becoming more popular in many other noncosmetic applications, for example, as a replacement for lead carbonate to give a high pearlescent luster to buttons, in artificial pearls, printing inks and wood finishing. Also, because it is radio-opaque, it has been used in plastic applications for medical devices.

There are mainly two types of bismuth oxychloride: powder and dispersion. Depending on

the pigment types, bismuth oxychloride can impart high pearlescent luster or shimmering effects to cosmetic products (such as nail enamel or lipsticks), or it can act as a functional filler, which contributes significantly to a smooth skin feel and a high skin adhesion (wearability). Furthermore, bismuth oxychloride powder has very good compressibility, hence it improves the performance of cosmetic powder formulations.

## The Structure of BiOCl

Many of BiOCl's cosmetic advantages are attributable to its crystal lattice,<sup>1,2</sup> which consists of a layer of bismuth and oxygen sandwiched between layers of chlorine atoms (see Figure 1). Because the Bi-O and Bi-Cl bonds are considerably stronger than Cl-Cl bonds and because there are no Bi atoms in between the Cl layers, BiOCl tends to form platelet-shaped crystals. This structure

### Key words

bismuth oxychloride, pigment, color cosmetics, luster, high-luster dispersions, powder pigments, pearlescence, functional filler

### Abstract

Bismuth oxychloride – either high-luster dispersions or powder pigments – offers high-luster pearlescence for lip, nail and hair products, and excellent skin feel and skin adhesion for other color cosmetic and personal care products.

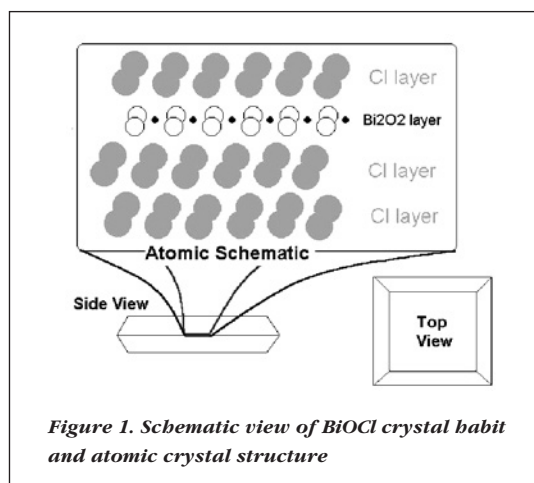


Figure 1. Schematic view of BiOCl crystal habit and atomic crystal structure

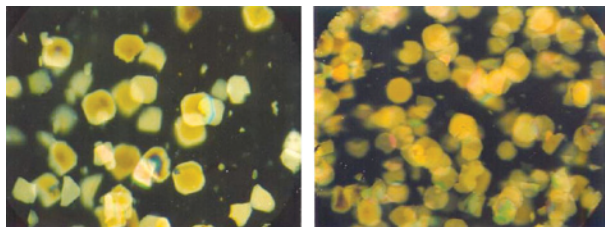


Figure 2. Microscopic pictures of high-luster BiOCl crystals

also accounts for the smooth skin feeling of BiOCl powders because of the relatively facile lateral cleavage of the platelet and the lack of resistance to shear forces as the faces of the plates glide over each other (i.e., a solid-state lubricating effect like graphite and molybdenum disulfide). Furthermore, the high skin adherence of BiOCl is understood because the exposed sheets of Cl layers provide a large planar attachment via Van der Waals bonding.

As mentioned previously, there are basically two types of bismuth oxychloride in use for cosmetic applications: high-luster dispersions and powder pigments (silky-luster powders and matte, low-opacity powder pigments).

## High-Luster Dispersions

The term “high luster” means strongly pearlescent when viewed at a specular or nearly specular angle. High-luster BiOCl dispersion exhibits much stronger pearlescence than regular BiOCl powders that may render a slightly silky effect. The high-luster BiOCl dispersion also shows much higher pearlescence or luster than silver white titanium dioxide-coated mica pigments.

By careful adjustments of the manufacturing conditions it is possible to obtain BiOCl crystals with a very regular shape of high aspect ratio (thickness < 100 nm) and with a very smooth surface and uniform thickness (only a slight taper exists on the edge of the crystal). The well-defined crystal shape and the high refractive index (2.15) combine to provide an extremely high luster. (Pearlescent luster is due to the coherent reflection obtained at the smooth planar interface between a material of very high refractive index and a medium of lower refractive index.) The individual crystals are typically square, vertically contracted bipyramids (Figure 2). The edge-length is usually between 10 and 20  $\mu\text{m}$ . Sometimes the crystals have truncated corners, giving them an octagonal or almost round shape instead of the typical square.

Because BiOCl crystals are fragile and have a tendency to agglomerate when dried, they must be delivered in liquid dispersions. The luster of this type of BiOCl is unsurpassed in brilliance, sharpness (contrast of bright reflection against dark masstone) or depth compared to other transparent pearlescent pigments.

When compared to silver white titanium dioxide ( $\text{TiO}_2$ )-coated mica pigments, the high-luster BiOCl offers one salient feature: the lack of light scattering. BiOCl crystals have no grain structure, unlike the coating of  $\text{TiO}_2$  on mica, so that much more of the light is specularly reflected and transmitted without scattering. This results in substantially more contribution of reflected light from crystals embedded below others. Therefore the luster brightness delivered by BiOCl increases much more strongly as the loading level is increased and does not saturate until much higher loading levels. This presents a definite advantage in formulation to provide consistent levels of luster brilliance.

The luster effect of well-dispersed BiOCl is smooth and continuous. It is not possible to achieve a sparkling effect when formulating with high-luster BiOCl dispersions. The diameter of BiOCl crystals is too small to generate broad-enough glints of reflected light to be discerned under normal visual acuity. High-luster BiOCl shines most brightly in clear and glossy applications. Other pigments or filler particles that reduce gloss will also reduce the luster effect.

BiOCl crystals are very dense ( $7.7 \text{ g/cm}^3$ ), such that highly viscous or thixotropic fluids are necessary to maintain dilute dispersion as homogeneous mixtures. However, it is a simple matter to re-suspend high-luster dispersions with gentle mixing.

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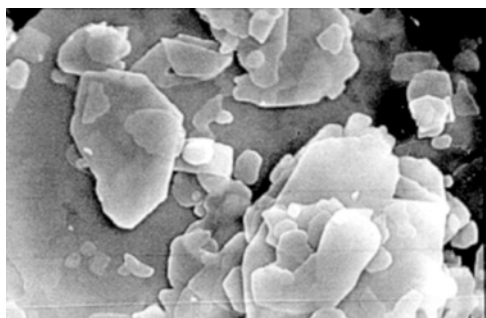


Figure 3. SEM picture of BiOCl crystals from a powder grade

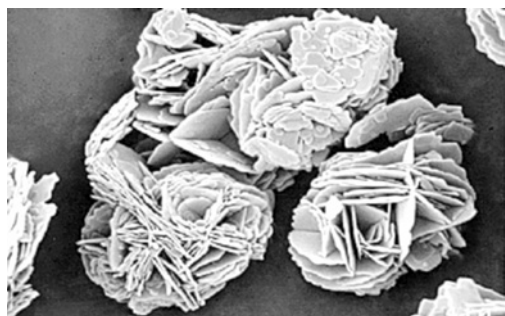


Figure 4. SEM picture of sphere-like crystal clusters from a matte and less opaque BiOCl powder

## Powder Pigments

### *Silky-luster powder pigments:*

Powder BiOCl is comprised of platelet-shaped crystals with irregular edges (Figure 3), typically with a diameter of 5-20  $\mu\text{m}$  and a thickness of approximately 200-500 nm. They are available in a variety of grades. All grades are, by design, much less brilliant than high-luster dispersions.

When applied in a way that orients the BiOCl platelets smoothly over a surface, a silky pearlescent effect is obtained. The weaker brilliance compared to the high-luster BiOCl is attributable to a higher degree of agglomeration and a more irregular surface and crystal habit, which causes increased light scattering. When the powder platelets are dispersed into cosmetic formulations with other particulates such as fillers and colorants, BiOCl tends to provide coverage.

Some variations in particle size (lateral dimensions) and aspect ratio can adjust the powder performance substantially and some alternative grades (with less opacity) are available and will be discussed later.

Besides offering a silky pearlescence, BiOCl powder pigments are also highly desirable because they offer extremely smooth skin feel and adhere very well to the skin, giving products a luxurious feel and good wearability characteristics. In pressed powder applications, BiOCl powders provide good compressibility and contribute significantly to the mechanical stability of, for instance, an eye shadow.<sup>3</sup> In application, the crystal agglomerates slide easily apart under gentle shear force to provide a cushion and lubricating glide; they re-adjust readily to the new state of compaction.

The high density of the BiOCl powder allows it to fulfill the role of unique filler and binder that especially renders cosmetic products, such as pencils and sticks, a tactorial sense of definitive substance and heaviness.

The chemical structure and platelet crystal shape of BiOCl powder particles also exhibit some degree of hydrophobicity. Wetting and dispersibility in water can be enhanced by treating the pigment with a nonionic surfactant (fatty acid type). In oil phases BiOCl powder pigments disperse readily. Powdered BiOCl, like the high luster type and all other platelet-shaped pigments, are of limited mechanical stability. The application of high shear mixing over extended periods of time could yield a product with less luster and higher opacity than expected.

**Matte, transparent powder pigments:** Attempts have been made to produce matte and transparent BiOCl powder pigment. For example, decreasing the particle size creates more edges and thus scatters more light, making the material matte; however, this also results in a higher coverage. Broader particles are possible for higher transparency, but the powders tend to become grayer and too sparkly.

These limitations were overcome a few years ago, when a matte, more transparent BiOCl powder became commercially available<sup>a</sup>. Contrary to traditional bismuth oxychloride powders, the rounded, platelet-shaped crystals of this product are grown together bound at the edges inside of clusters with a diameter of 3-7 micrometers (Figure 4). This sphere-like cluster structure prevents the parallel orientation of crystal surfaces while at the same time the combination of small crystals and hollow cavities results in increased light scattering without making the product too opaque.

Another grade of BiOCl was developed very recently utilizing a somewhat different approach to crystal shape modification. This very transparent and matte pigment<sup>b</sup>, which we will call m-BiOCl in this article, is now commercially available. We believe it to be the least opaque BiOCl powder in the market. Unlike other commercially available powder BiOCl, m-BiOCl provides a virtually luster-free effect, but without reducing or disturbing gloss. (Note that gloss is due to the reflection obtained from a smooth interface of the vehicle with air.)

<sup>a</sup> Biron ESQ, INCI: bismuth oxychloride. Biron is a registered trade name of EMD Chemicals Inc.

<sup>b</sup> Biron MTU, INCI: bismuth oxychloride. Biron is a registered trade name of EMD Chemicals Inc.

### Formula 1. Styling gel with a high luster BiOCl dispersion

A.	Oleth-3 (Volpo 3, Croda)	7.00%
	Oleth-5 (Volpo 5, Croda)	4.00
	Oleth-3-phosphate (Crodafos N-3 Acid, Croda)	7.00
	Cyclomethicone (Dow Corning 345, Dow Corning)	10.00
	Paraffinum liquidum (mineral) oil (Blandol, Witco)	10.00
	Bismuth oxychloride (and) ethylhexyl hydroxystearate (Biron Liquid Silver, Rona)	10.00
B.	Water (aqua), deionized	4.50
	Potassium hydroxide (Unichem POHYD, Universal Preserv-a-Chem)	0.50
C.	Water (aqua), deionized	37.00
	Glycerine (Emery 916, Cognis)	7.00
D.	Mica (and) iron oxides (and) titanium dioxide (and) ferric ferrocyanide (Colorona Patagonian Purple, Rona)	2.00
	Propylene glycol (and) diazolidinyl urea (and) methylparaben (and) propylparaben (Germaben II, ISP)	1.00
		100.00

*Procedure:* Blend A and heat to 85-90°C with stirring. Blend B. Blend C; add B to C and heat to 85-90°C with stirring; add to A. Have additional water heated to ~90°C; some slight addition of water may be necessary to compensate for evaporation. Adjust pH to 5.5-6.5 with KOH solution; viscosity will rise as the gel is formed. Mix vigorously until the system is smooth and homogeneous. Add D with mixing; maintain temperature. Package while still hot and fluid (set point ~80°C).

## Applications

High-luster BiOCl is mostly used for high-frost applications, especially in nail enamels, lip and hair products. Several grades of dispersions (with different degrees of luster and opacity) are commercially available. Typical dispersion media are nitrocellulose lacquers (for nail enamels) and castor oil or a cosmetic grade ester (for lip and hair products).

BiOCl powder pigments are commonly used in powder applications, eye shadow, cosmetic pencil, makeup and lipstick formulations (to improve the long-wearing properties). BiOCl powders<sup>c</sup> can substantially increase an eye shadow's mechanical stability, which almost doubled in the dropping test when compared to the formulation without BiOCl powder. Additionally, the matte and transparent grades of BiOCl powders are especially useful when formulating ethnic cosmetic products because they can minimize the light scattering (chalky appearance) and transmit the light to saturated and intense colorants, which is beneficial for ethnic makeup.

Furthermore, the application of BiOCl powder pigments is no longer limited to color cosmetics and can be extended to personal care products, such as antiperspirants, deodorants and personal care powder products, and medicinal creams and ointments because of the excellent lubricity and skin adhesion of BiOCl.

<sup>c</sup> Biron powder pigments. INCI: bismuth oxychloride. Biron is a registered trade name of EMD Chemicals Inc.

To illustrate some of the outstanding properties of BiOCl products, we present three exemplary formulations.

**Styling gel:** Formula 1 illustrates a high-luster BiOCl dispersion<sup>d</sup> in an ester (ethylhexyl hydroxystearate). We'll refer to this dispersion as BiOCl-o. Typical use levels are 5-20%.

BiOCl-o is used in the Formula 1 to provide the styling gel with a highly metallic and mirror-like effect. We believe that at the same pigment loading level, no TiO<sub>2</sub>-coated mica pigments can match the luster and the smoothness that BiOCl-o offers. BiOCl-o can also be used in other products such as lip products, eye products and personal care products in anhydrous or microemulsion systems.

**Nail lacquer:** Formula 2 illustrates a dispersion<sup>e</sup> of BiOCl in nitrocellulose lacquer. We'll refer to this dispersion as BiOCl-n. Typical use levels are 1.6-5% (60% paste) or 4-12% (25% paste).

BiOCl-n is used in the Formula 2 nail lacquer formulation to provide the brightness, highly reflective pearlescence and metallic effect. Compared to nail lacquers with aluminum flakes, these BiOCl-n products offer a brighter shade of finish. Furthermore, to be environmental friendly, all the BiOCl-n products are formaldehyde-, toluene- and phthalate-free.

Note that with Formula 2 a wide range of shades can be made using either silver, gold or interference pigments<sup>f</sup> or colored pigments<sup>g</sup> in combination with the high-luster BiOCl-o dispersions.

**Antiperspirant:** The matte and transparent grades of BiOCl powders improve both the skin feel and the adhesion of the antiperspirant to the skin with no whitening effect.

The antiperspirant in Formula 3 contains the m-BiOCl, a rather matte and transparent BiOCl powder. Typical use levels are 2-10%.

<sup>d</sup> Biron Liquid Silver. INCI: Bismuth oxychloride (and) ethylhexyl hydroxystearate. Biron is a registered trade name of EMD Chemicals Inc.

<sup>e</sup> Nailsyn Dispersions. Various INCI names. Nailsyn is a registered trade name of EMD Chemicals Inc.

<sup>f</sup> Timiron pigments. Various INCI names. Timiron is a registered trade name of EMD Chemicals Inc.

<sup>g</sup> Colorona pigments. Various INCI names. Colorona is a registered trade name of EMD Chemicals Inc.



## Formula 2. Nail lacquer with a high-luster BiOCl dispersion

Ethyl acetate (and) butyl acetate (and) nitrocellulose (and) isopropyl alcohol (and) camphor (and) dibutyl phthalate	qs to 100.00%
Iron oxides and mica (Colorona Sienna Fine, Rona)	1.00-2.00
Butyl acetate (and) bismuth oxychloride (and) nitrocellulose (and) isopropyl alcohol (and) ethyl acetate (and) stearylaluminum hectorite (Nailsyn II C2X or Nailsyn II Platinum 25, Rona)	2.00-10.00

*Procedure:* Add the pigments to the nail lacquer base with stirring (10 minutes @ 1000 rpm).

## Formula 3. Antiperspirant with BiOCl powder pigments

A.	Stearyl alcohol (Crodacon S-70, Croda)	18.00%
	Hydrogenated castor oil (Castor Wax, Ross)	5.00
	Cyclomethicone (Dow Corning 345 Fluid, Dow Corning)	42.90
	Cyclomethicone (and) dimethicone crosspolymer (Dow Corning 9040 Silicone Elastomer Blend, Dow Corning)	2.70
	PPG-3 myristyl ether (Varonic APM, Goldschmidt)	3.00
	Glylaurate (Jeechem MLD, Jeen)	4.00
B.	Aluminum zirconium tetrachlorohydrate GLY (Rezal 36 GP Superfine, Reheis)	20.00
	Bismuth oxychloride (Biron MTU, Rona)	4.00
	Triclosan (Jeechem Triclosan, Jeen)	0.30
C.	Fragrance (Grapefruit Fragrance 26520M, Shaw Mudge)	0.10
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		100.00

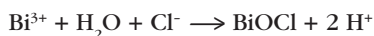
*Procedure:* Blend A; heat with mixing until clear. Add B with mixing. Cool the AB to 60°C and add C with mixing. Package.

### Manufacturing Process

While detailed manufacturing procedures are of course proprietary information, the typical method of production can be disclosed.

Even though bismuth is a relatively rare metal, there are certain areas of the world (especially in Latin America) with relatively large deposits of the pure metal, its oxide or sulfide. Due to its chemical properties bismuth metal can be obtained in a very pure form (pharmaceutical grade) from these deposits.

The metal is dissolved in acid to yield a bismuth salt solution. In the presence of chloride ions the pH of this solution is adjusted by adding a suitable base (such as sodium hydroxide) so that BiOCl starts to precipitate.



By careful choice of reaction conditions (such as temperature, concentration, pH), crystals with different size and thickness can be obtained, which are subsequently isolated from the mother liquor (by processes such as decanting or filtration). These crystals are washed to remove any remaining acid or salt residues and then either dried (in the case of powders) or transferred from the aqueous suspension to a different solvent or oil system (in the case of high-luster dispersions).

Depending on the reaction conditions, one can produce BiOCl in various grades that differ in luster, opacity and whiteness.

### Chemical Stability, Safety and Regulatory

The chemical stability of BiOCl is very high and there are no reactions with any other cosmetic raw materials known that would limit the use of BiOCl in cosmetic applications. BiOCl has no defined melting point because it decomposes slowly at temperatures above 400°C before melting, forming yellow bismuth oxide. BiOCl is chemically stable at moderately acidic and basic pH-values and becomes soluble only in strong acids at pH-values well below 2. At a pH of 12 or above, it will slowly convert into bismuth oxide or subhydroxide.

Although bismuth metal is high in atomic weight, it is not considered to be a heavy metal in any sense. Technically, BiOCl is a basic (alkaline) chloride salt. The chloride has no chemical resemblance to organic chlorides whatsoever and is as innocuous as the chloride in NaCl, table salt. Toxicity studies have been performed<sup>4,6</sup> and the results confirm a high degree of safety with no danger from accidental ingestion, inhalation or exposure to mucous membranes. The United States Food and Drug Administration has placed no restrictions on use of BiOCl in different bodily areas.

BiOCl is approved for use in all cosmetic applications in the United States, the EU and Japan.

### Light Stability

BiOCl has one disadvantage. It is sensitive to UV light. It slowly turns gray when exposed to sunlight. This darkening effect is partly reversible. If a darkened BiOCl is kept in the dark, it will whiten again, however, not quite to the degree of whiteness it had before the light exposure.

Due to the absorption of UV light, only the very top surface of the BiOCl turns gray. Deeper layers of the crystals or of the cosmetic product are unaffected. The physical/chemical cause for this light-induced graying is not accurately known. It is however suspected that it is caused or propagated by imperfections in the crystal lattice. Therefore it is not surprising that the more regular, better-formed crystals of the high-luster dispersions undergo less of a color change than the more irregular crystals of powder pigment types.

While the regular high-luster types typically can be used in cosmetic formulations without any additional measures, care should be taken in formulating light-colored products with some of the BiOCl powders.

Even though the graying effect is not typically visible on the skin because of the thin or diluted layer or in strongly colored formulations, it may limit the use of clear packaging for light-colored BiOCl-containing cosmetics. Therefore attempts have been made to stabilize BiOCl against the effects of UV light. Some of the applicable methods include doping of the crystal lattice with other materials (such as cerium), high-temperature treatment or the addition of UV-absorbers to cosmetic formulations. These

methods improve the light stability drastically to an acceptable level, however, they can not yield a completely UV-stable product.

Powder grades of bismuth oxychloride with high light stability have been available with traditional coverage and luster performance for many years, but now, in products such as m-BiOCl, they are also available with the unique combination of low luster and low coverage.

## Summary

Bismuth oxychloride was the first synthetic non-toxic nacreous pigment and has been used in cosmetics for many decades. Either high-luster dispersions or powder pigments offer brilliant high-luster pearlescence for lip, nail and hair products, and excellent skin feel and skin adhesion for other color cosmetic and personal care products, depending on the type and grade used.

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