'Extending the boundaries: Bismuth-based pigments for the plastics industry'

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Abstract

The versatile solid-state chemistry of Bismuth allows for a variety of coordination complexes and the generation of new and robust inorganic pigments as a result.

Bismuth has been used in combination with a few inorganic elements, and is most readily found as complexes containing amines and amides, alkoxides, carboxylates, thiocyanates, thiocyanates, thiocyanates, halides. Bismuth Nitrate is amongst one of the most common starting materials for synthesizing Bismuth complexes, and from this starting material the first Bismuth Vanadate pigments (PY.184) were formulated in the mid 1970s [1,2]. There has been continued innovation in this pigment chemistry over the years, and in 2015 a groundbreaking Bismuth orange with a unique color index, PO.86, was launched (proprietary technology of DCC).

Since their commercial introduction in 1990 (first production for Ciba, The Netherlands) into the coatings & plastics markets, Bismuth Vanadate pigments have increased in importance as their field of application has grown. These bright yellow, highly saturated pigments are characterized by their outstanding opacity/hiding power, chemical resistance, excellent weathering and durability. DCC’s 3rd innovative generation of Bismuth Vanadate pigments have expanded the limitations of this chemistry to cover a wider color gamut from greenish-yellow to orange hues. Advances such as improving the heat stability has increased the utilization of Bismuth Vanadate products in engineering resins e.g. Nylon 6. Increasing the color strength has created value in use for many customers who want to use less pigment whilst maintaining the hiding power within their system. Moreover, introducing Stir-In technology has helped to reduce operating costs by making the pigment easier to disperse, therefore reducing pressure rise in the extruder and reducing the number of extruder screen changes required during production. Improvements in our manufacturing technologies have allowed DCC to attain the most demanding and specific performance attributes such as heat stability & dispersibility.

Through intensive research DCC has been able to introduce an exciting new inorganic pigment into the market, based on Bismuth and identified by a new color index: PO.86 [3]. This clean yellow shade inorganic orange has outstanding hiding power, typical of inorganic pigments and represents an excellent starting base for orange colour matches. Additionally, PO.86 is non-warping and has very good heat stability (up to 250 °C): it is therefore strongly recommended for use in polyolefin based plastics, and architectural, industrial, powder, automotive & coil coating applications. There are only a few options for formulators in this shade area (most of which are based on organic starting materials), but none of these alternatives have the same level of durability and opacity as PO.86.

This paper will illustrate how Bismuth Vanadate and Bismuth Orange pigments compare to other colorants in the green shade yellow to orange shade areas, with particular reference to performance attributes such as heat stability, dispersibility, weather-fastness, warp resistance and reference how these products perform in different polymer systems. This presentation is thus ideal for those who work & formulate with color and would like to develop a greater understanding of how PY.184 and PO.86 pigments influence the plastics they work with.

Introduction

Bismuth Vanadate (BV) pigments (C.I. Pigment Yellow 184) have increased in importance as their field of application has grown since their initial development in the 1980’s for use in the paints, coatings and plastics markets. They represent a captivating class of pigments, which extend beyond the familiar range of yellow inorganic pigments (iron oxide yellow, lead chrome yellow, chromium titanate yellow, cadmium yellow and nickel titanate yellow).
These bright yellow, highly saturated pigments are characterized by their outstanding opacity/hiding power, chemical resistance, excellent weathering and durability. They are also excellent candidates as alternatives to the green shades of the lead chromate based and cadmium sulphide pigments.

Innovation has expanded the use of this chemistry, particularly in plastics applications. BV brings added value compared with other popular chemistries, as it is now being used not only in polyolefins, but also in engineering plastics.

Historically, in order to meet the most demanding requirements of the plastics industry, Boric acid has been utilized to improve the heat stability in various pigment formulations. There are various methods employed to introduce Boric acid onto inorganic pigments, e.g. by direct treatment of the pigment surface with Silicates and Boric acid or by initially encapsulating the BV crystal then introducing Boric acid to the pigment matrix. The heat stability of Boric acid containing BV’s is dramatically improved, broadening their relative use in engineering plastics.

However, the use of Boric acid in pigment formulations has been curtailed somewhat due to global regulatory restrictions. If Boric Acid free BV’s are used during processing then there is no visible sign of water being released, which avoids manufacturing issues and any related polymer hydrolyzation. Recently introduced Boric acid-free BV pigments have outstanding heat stability, exceptional colour strength and represent an interesting new option for the plastics market, with no processing issues.

Colouristically speaking, the BVs used in plastics have created greater value since less pigment is necessary during processing to maintain the required hue and hiding power. This in turn, means more cost savings for the end product and end customer. Finally, the introduction of a stir-in technology for BV manufacturing has helped to reduce operating costs, specifically for plastics fibers. This is accomplished by making the BV pigment easier to disperse, This translates to more time saved in production (due to less downtime changing extruder screens), and a possible increase in pigmentation level in the masterbatch (brighter colour), ultimately providing downstream cost savings.

This paper will present PY.184 and PO.86 pigment ranges for a variety of plastics applications, along with an update on regulatory considerations in the EU, USA and Canada in terms of the use of Boric acid in pigment formulations and manufacturing.

**BV Pigments for Plastics**

There is a range of thermostable BV pigments currently available today with heat stability in the range of 260-300°C for polyolefins and 280-320°C for polyamides. They are typically greenish yellow in hue with high tinting strength, high chroma and excellent hiding power. They exhibit very good fastness to heat, light and weathering, both in full shade and tint, and are resistant to chemicals across all shade depths.

Additionally, they have outstanding fastness to migration, do not cause warping during processing and produce dimensionally stable extruded/injection-molded articles. In light of more demanding polyolefin (PE + PP) applications where good weather fastness is required along with excellent heat stability, BV pigments represent a valid alternative to other chemistries that are not able to measure up to these technical requirements.

Figure 1 shows the colour positioning in HDPE in full shade at 200°C of the most representative Boric acid-free BV pigments that are recommended for use in HDPE. Interestingly, BV3 is even redder in shade with increased saturation and very good heat stability, which widens the colour gamut from greenish-yellow to reddish-yellow hues.

![Figure 1: Colour positioning in HDPE (full shade at 200°C).](image)

In the greenish yellow shade area, BV1 and BV2 perform exceptionally well in HDPE and polypropylene due to their outstanding heat stability and high relative colour strength in tint. BV’s are appropriate for extruded products with highly chromatic colours. A suitable option in the reddish area is represented by BV3, with improved colour strength in tint compared with BV2 (Figure 2).
Polyamides and engineering polymers demand even higher heat stability. Historically, this has technically been achieved by formulating BV pigments with Boric acid, as discussed previously. The section entitled “Boric acid regulatory update by area” describes the regulatory obligations related to the use of Boric acid in the following areas:

- Formulation of mixtures and/or re-packaging and building and construction work
- Manufacturing of chemicals, mineral products (e.g. plasters, cement), machinery and vehicles, fabricated metal products and metals

No labelling is required on products that have a Boric acid level of \(<5.5\%\). The introduction of Boric acid into BV pigment formulations brings a major benefit in terms of the improved heat stability, therefore broadening their use in plastics. However, the release of water during processing may be difficult to control during extrusion. Additionally, the hydrolization of polymers can take place, particularly in polyester and polycarbonate when a higher concentration (namely \(>10\%\) on the total formulation) of Boric acid is introduced. Therefore, **Boric acid-free** versions with outstanding heat stability and colour strength, represent a contemporary generation of BV pigments that have greater compliance with today’s demanding regulatory restrictions.

Particularly, BV4 has been designed specifically for use in polyamides and other engineering plastics and is able to maintain its clean green shade even when processed at high temperature (\(>300^\circ C\)). The key properties of BV4 are:

- Clean, greenish yellow shade in polyamide resins
- Highest heat stability in polyamide of all Boric acid-free products in the market
- Similar heat stability in polyamide as Boric acid containing products
- No water release during processing, thus preventing polymer hydrolization
- Excellent weather fastness in mass tone and tint

BV5 has been the reference standard for engineering plastics for many years. It can be shaded with complex inorganic coloured pigments and organic pigments according to the end-use requirements. BV6 is suitable for use in most engineering plastics including polyamide, polyester, styrenics and EPL. Boric acid free BV4 is much more chromatic when compared to Boric acid containing pigments due to the new proprietary manufacturing techniques employed. These proprietary manufacturing techniques also give BV4 its exceptional heat stability as well.

Figure 3 and 4 report the colour positioning, heat stability and colour strength (1:1 tint in polyamide), of recommended BVs for polyamides and engineering plastics.

Figure 2: Heat stability (full shade) and colour strength (1:1 tint in HDPE).

Figure 3: Colour positioning in Polyamide (full shade).

Figure 4: Overview Heat Stability (full shade) and Colour Strength (1:10 tint) in Polyamide.
Boric acid regulatory update by area

Europe [4]
- REACH registered; 01-2119486683-25-xxxx;
- March 2010: Inclusion as Substance of Very High Concern (SVHC) - within 6 months after inclusion: ECHA notification obligation for producers and importers of articles containing boric acid if > 1 Ton/Y and present > 0.1% (w/w).
- March 2014: Harmonised classification - Reprotoxic Category 1B; H360FD
- Specific concentration limits for mixtures: C ≥ 5.5 %
- Workplace exposure limit (air): DNEL 8.3 mg boric acid/m³
  - No official decision as to date
  - Sunset date = date of inclusion plus 45 months (3 years and 9 months)
  - Use after sunset date is only allowed if an authorisation request has been approved for that use or has been submitted before the latest application date and no decision made

Canada [5]
- Listed in DSL Inventory
- WHMIS Classification: D-2A: Very Toxic (reproductive toxin). May cause reproductive effects based on studies in laboratory animals. A human study of occupational exposure to borate dust showed no adverse effect to reproduction.
- Potential health effects:
  - Inhalation: product is irritating to the nose, throat and respiratory tract
  - Skin contact: boric acid may cause symptoms of skin irritation such as reddening, swelling, rash, scaling, or blistering
  - Eye contact: this product may cause mild, transient irritation
- Workplace exposure limit (ACGIH TLV, short term exposure): 6 mg/m³ (As borate compounds)
- Regulations exist to limit the amount of boric acid in some products that Canadians use. Specifically:
  - Cleaning products
  - Pool and spa chemicals
  - Creams, lotions and other cosmetics
  - Homemade arts and crafts materials as well as toys
- When Environment Canada and Health Canada suspect that a SNAc (Significant New Activity) in relation to the substance may result in the substance becoming toxic, a notice is issued to ensure that adequate additional information is provided by the notifier or any other proponent who wish to manufacture, import or use the substance for a significant new activity specified by the notice. The additional information will allow Environment Canada and Health Canada to assess the potential environmental and human health risks associated with the new activities.

USA [6]
- Listed in TSCA Inventory
- Reprotoxic Category 1B; H360FD:
- Boric acid is considered hazardous by the OSHA HCS (29CFR 1910.1200)
- Workplace exposure limit (ACGIH TLV, short term exposure): 6 mg/m³ (As borate compounds)
- SARA 311/312: Chronic health hazard
- As being an Inert Ingredients in Pesticide Products: Under the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA), all pesticides sold or distributed in the United States must be registered with EPA.

BV Plastic fibres

A recent pioneering stir-in technology has been introduced to the manufacturing of BV pigments. This ground-breaking new technical solution was specifically designed for PP and PES fibres. Interestingly, whilst maintaining its outstanding durability, hiding properties and opacity, BV7 represents the very first grade of BV that was created for fibre applications.

The results shown in Figure 5 below, used a test method whereby the pigments were dispersed on a two-roll mill at 10% pigmentation in P.P. and subsequently letdown to 5% with P.P. The pressure testing was performed using a single screw extruder with a 500-mesh screen and ¾” screen pack in LDPE.

The advantages of processing at lower screen pack pressures with BV7 are:
- Improved overall dispersion in final product
- Yield higher quality products
- Increased throughput through extruder
- Decreased number of screen changes on extruder (less down time and less waste)

![Figure 5: Pressure tests on BVs.](image-url)
Bismuth Orange (PO.86) for Plastics

PO.86 is the cleanest inorganic orange in the market. It is a non-warping grade suitable for polyolefin applications, and can be processed at temperatures up to 250°C (Figure 6).

With a total solar reflectance (TSR) of 58.8%, it is also well suited to be incorporated into cool coating applications for exterior IR reflective systems to help lower the overall temperature of structures while providing exceptional durability.

Figure 6: HDPE chips in mass tone (left) and tint (right); Incorporation: 1%, compound; Processed @ 5 minutes at 200 °C, 220 °C, 240 °C and 260 °C, respectively.

PO.86 has unique colour positioning compared to other orange and red shade yellows (Figure 7). It is cleaner and slightly redder than PO.85 and several units redder than PY.139 and PY.110. It is the reddest Bismuth based inorganic pigment currently available and is cleaner in shade compared to the organic PO.36 pigment.

Figure 7: Colour positioning in HDPE (full shade) of inorganic and organic orange pigments.

PO.86 is also an excellent starting base to create cost-effective orange RAL and brand colour matches (Figure 8). For example, it is now possible to match RAL 2011 by using up to 90% of this inorganic orange, which massively reduces the organic content in the formula and maximises the durability of the final product. This generates many benefits in terms of cost-savings and optimizes the performance of the coating or plastic application it’s incorporated into.

Figure 8: Examples of orange colour matches by using PO.86.
Conclusions

Bismuth-based pigments have exceptional durability and superior functionality that make them well suited for a variety of coatings and plastics applications. They cover a wide colour gamut, spanning from green shade yellows to the recently introduced orange hue.

PY.184 pigments have been used in plastics formulations since their inception, although initially they were somewhat hampered by their limited technical performance in PVC and engineering resins. Due to recent technical improvements, they can be utilized in a vast number of resins and plastics applications as a result, and are becoming the alternative of choice for other heavy metal based formulations.

They are characterized by their excellent weather fastness along with exceptional heat stability in today’s more demanding polyolefin resin based systems. Boric acid-free green and red shade BV solutions are gaining more and more traction at plastic customers, who now have a wider colour palette at their fingertips that allows them to cover a greater number of applications when compared to the past. Additionally, they can also widen their portfolio of regulatory compliant solutions with Boric-acid free alternatives.

Polyamides and engineering polymers can only be formulated with pigments that have outstanding heat stability, or there are also specialized dye chemistries available to formulators. Historically, the best performance in terms of heat stability was reached with Boric acid encapsulated BV pigments. However, the release of water during processing, which is very difficult to control during extrusion, the potential hydrolyzation of polymers and regulatory concerns have been valid reasons for boosting the development of Boric acid free grades of BV viable for use in polyamides. Technologically advanced Boric-acid free BV pigments as illustrated in this paper have the ability to maintain their very clean green shade even when processed at temperatures of more than 300°C.

Finally, the innovative stir-in BV pigment represents a pioneering technical solution specifically for PP and PE fibres, where exceptional dispersibility is absolutely paramount.

PO.86 is a brand-new Bismuth based pigment available on the market. It is the cleanest pure inorganic orange suitable for polyolefin based plastics, and architectural, industrial, powder, automotive & coil coating applications (heat stability up to 250°C). It also gives formulators a unique opportunity to match orange RAL & brand shades whilst using less organic pigments to optimise the performance characteristics of the end application.

The plastics market is evidently trending towards higher performing, Boric-acid free pigments, and thanks to intensive R&D development with the introduction of PO.86 there are now a greater number of inorganic based options available for this application. This presents stylists and formulators with a wider array of colours that can meet the challenging requirements typical of the plastics industry.

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