'Extending the boundaries - Bismuth Vanadate pigments for the plastics industry'

Cristina Zanzottera PhD, Inorganic Product Manager, DCC
Harry Hamers PhD, Technical Service Manager, DCC
Bruce Howie PhD, Manager - Global Product Management and Marketing, DCC.

Introduction

Bismuth Vanadate (BV) pigments (C.I. Pigment Yellow 184) have increased in importance as their field of application has grown since their introduction in 1985 for use in the paints, coatings and plastics markets. They represent an interesting class of pigments, which extend 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 valid candidates as alternatives to the green shades of the lead chromate and cadmium sulphide pigments.

Innovation has expanded the use of this chemistry particularly in plastics applications. Actually, BV is no longer used only in polyolefins but also in engineering plastics, so bringing an added value as compared to other popular chemistries. Historically, in order to meet the most demanding requirements of the plastics industry, Boric acid has been utilized to improve the heat stability of various pigment formulations. There are various methods employed to introduce Boric acid to inorganic pigments, e.g. by direct treatment of the pigment surface with Silicates and Boric acid or secondly by initially encapsulating the Bismuth Vanadate crystal then introducing Boric acid to the pigment matrix. The heat stability of Boric acid containing BV's is thus dramatically improved, so 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, so avoiding any manufacturing issues and any related polymer hydrolization. Recently introduced Boric acid-free BV pigments have outstanding heat stability, exceptional colour strength and represent a valid new option for the plastics market, with no processing issues. Coloristically speaking, the BVs used in plastics have created greater value in use since less pigment is necessary during processing to maintain the hue and hiding power required, meaning less financial impact on the end product and end customer.

Finally, for plastics fibers specifically, the introduction of a *stir-in* technology to BV manufacture has helped to reduce operating costs by making the BV pigment easier to disperse, therefore reducing pressure rise in the extruder and reducing the number of extruder screen changes required during production, resulting in less manufacturing downtime for our customers.

This paper will illustrate the range of BV pigments with the ability to be incorporated into 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.

Bismuth Vanadate 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 chemical resistant across all shade depths. Additionally, they have outstanding fastness to migration, they do not cause warping and they produce dimensionally stable extruded/injection-moulded articles.

In view of more demanding applications in polyolefins (PE + PP), 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 the technical requirements of those resins. Figure 1 shows the colour positioning in HDPE in full shade at 200°C of the most representative Boric acid-free Bismuth Vanadate 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.

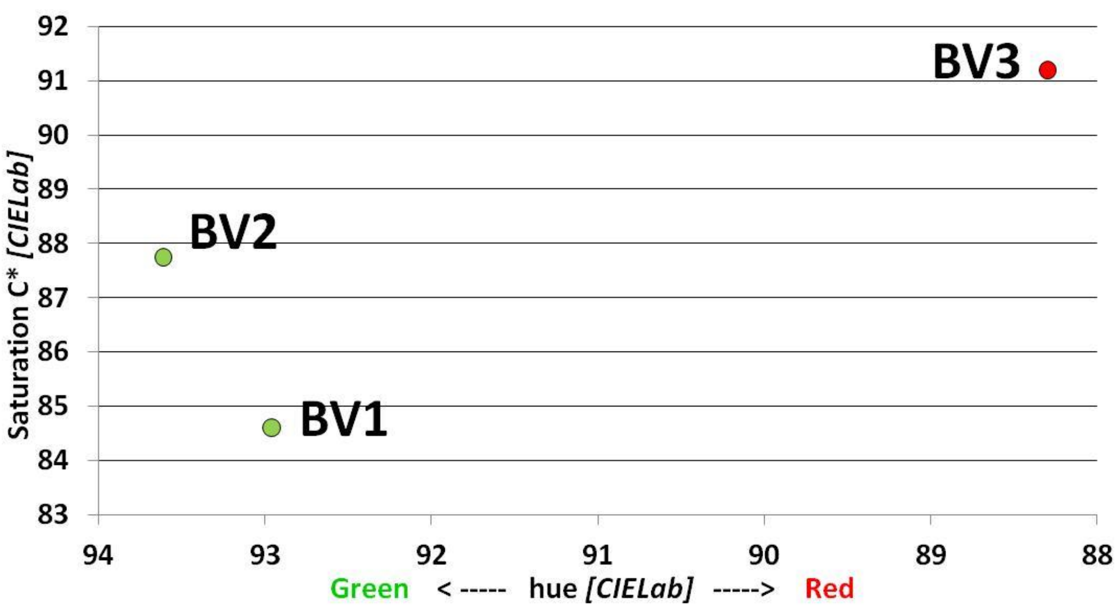

Figure 1: Colour positioning in HDPE (full shade at 200°C).

In the greenish yellow shade area, BV1 and BV2 perform exceptionally well in HDPE and polypropylene due to their excellent heat stability and high relative colour strength in tint. BV's are suitable for extruded products with highly chromatic colors. A valid option in the reddish area is represented by BV3, with improved colour strength in tint against BV2 (Figure 2).

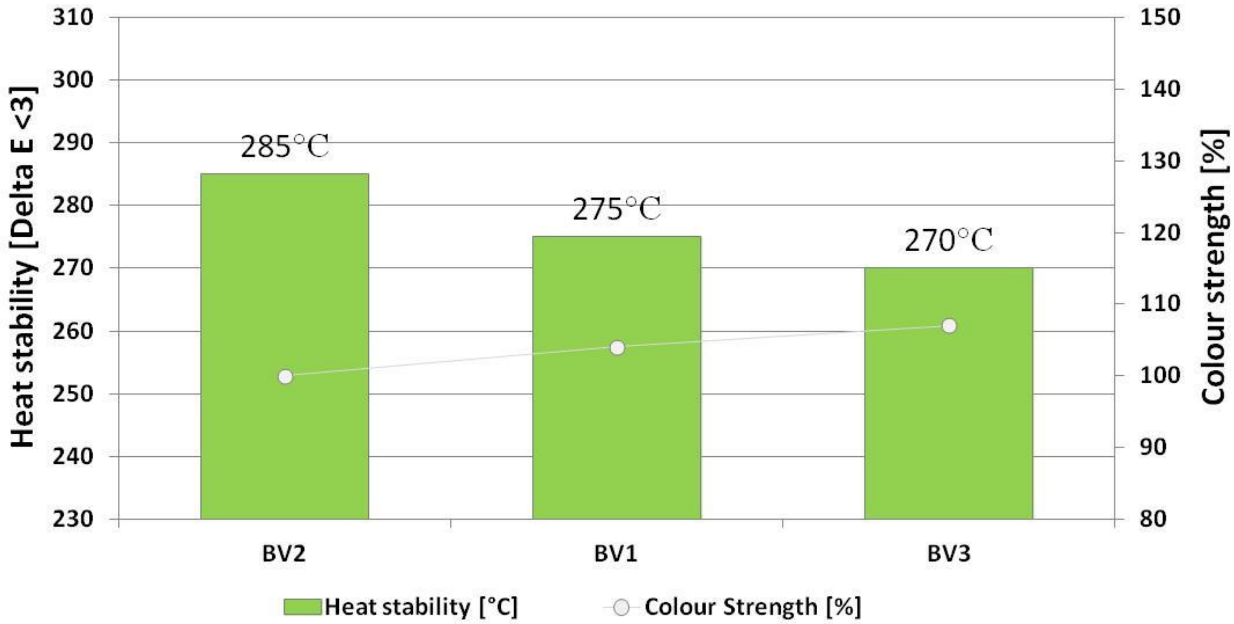

Figure 2: Heat stability (full shade) and colour strength (1:1 tint in HDPE).

Polyamides and engineering polymers demand even higher heat stability. Historically, this has technically been achieved by formulating Bismuth Vanadate pigments with Boric acid, as discussed previously. Table 1 reports an update of 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%.

The introduction of Boric acid into Bismuth Vanadate pigment formulations brings a major benefit in terms of the improved heat stability of the pigment, 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 new generation of Bismuth Vanadate pigments that have greater compliance with today's demanding regulatory restrictions.

Country	Regulatory update
Europe	• REACH registered; 01-2119486683-25-xxxx; • 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/m^3 • 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 <u>and</u> present > 0.1% (w/w). • July 2015: 6^{th} Proposal for inclusion Annex XIV (= Authorisation list): ▪ 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	• 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: o Inhalation: product is irritating to the nose, throat and respiratory tract o Skin contact: Boric acid may cause symptoms of skin irritation such as reddening, swelling, rash, scaling, or blistering o Eye contact: this product may cause mild, transient irritation • Workplace exposure limit (ACGIH TLV, short term exposure): 6 mg/m^3 (As borate compounds) • Regulations exist to limit the amount of Boric acid in some products that Canadians use. Specifically: o cleaning products o pool and spa chemicals o creams, lotions and other cosmetics o 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 insure 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	• 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.

Table 1: Boric acid (CAS:10043-35-3/EC 233-139-2 - Index 005-007-00-2) regulatory update.

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°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 masstone and tint

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

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.

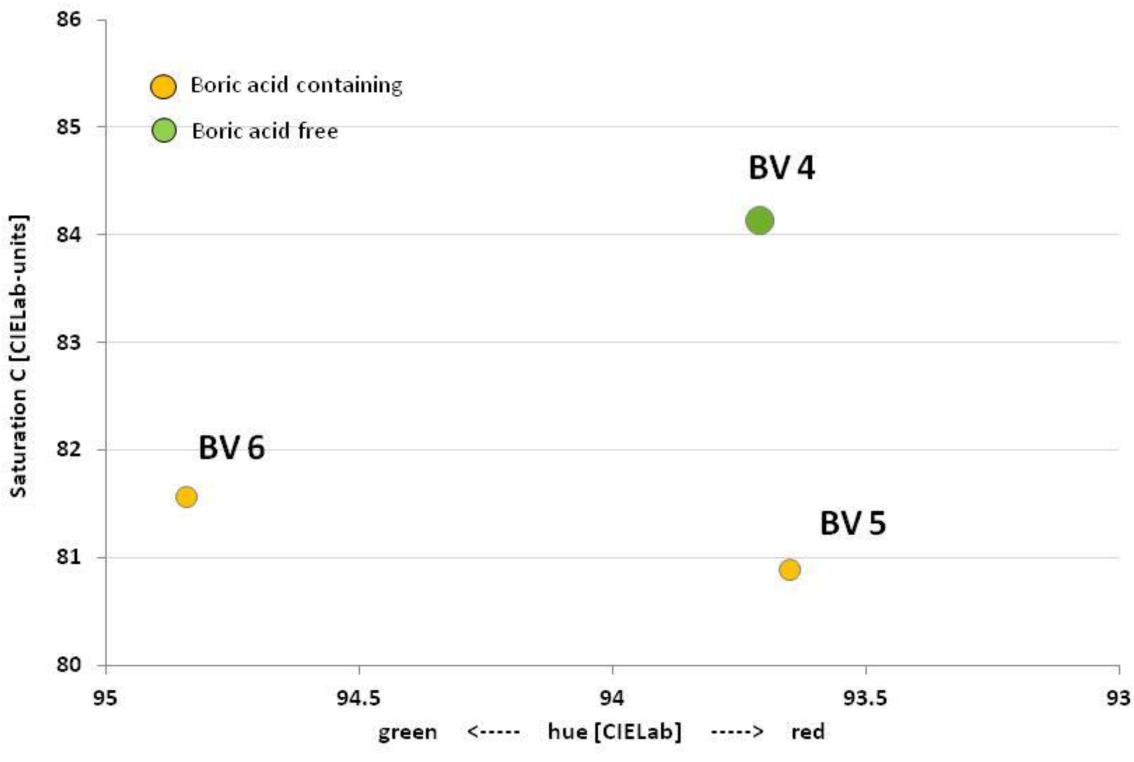

Figure 3: Colour positioning in Polyamide (full shade).

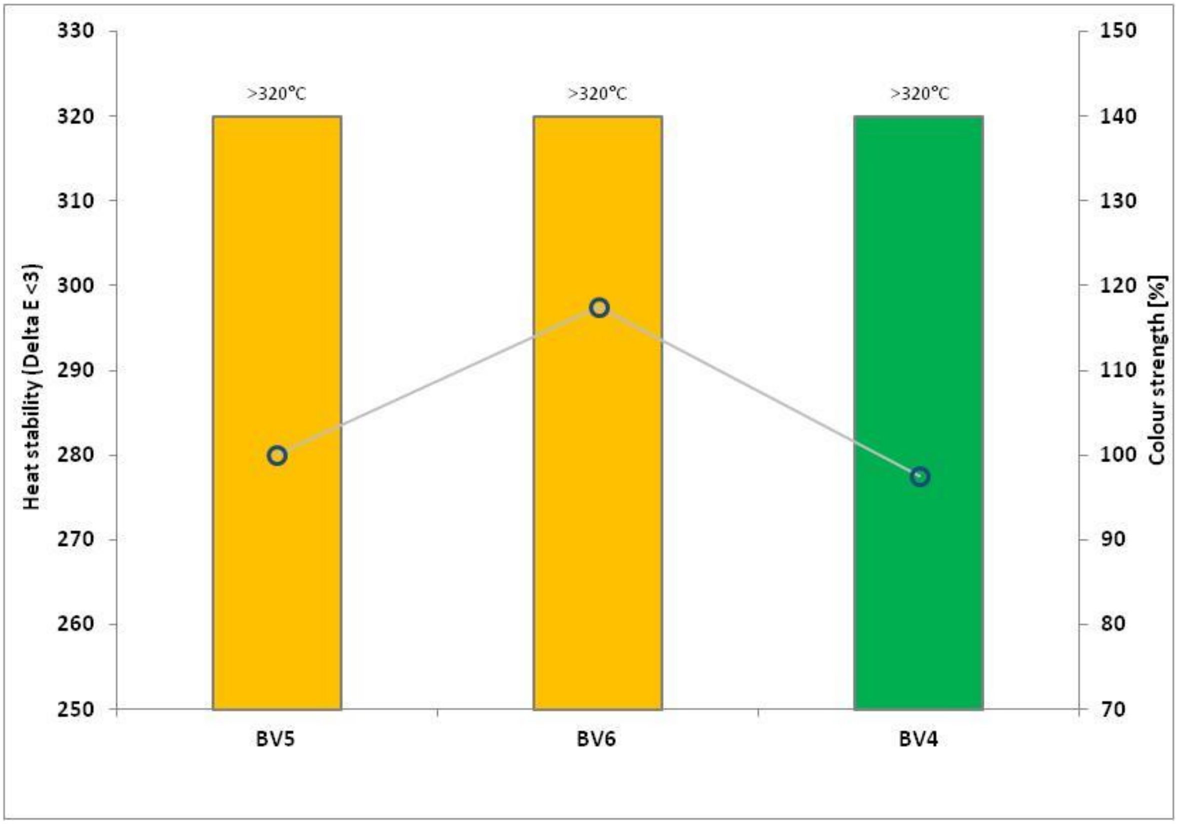

Figure 4 Overview Heat Stability (full shade) and Colour Strength (1:10 tint) in Polyamide.

Plastic fibres

A recent pioneering ***stir-in technology*** has been introduced to the manufacture of Bismuth Vanadate 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 Bismuth Vanadate 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)

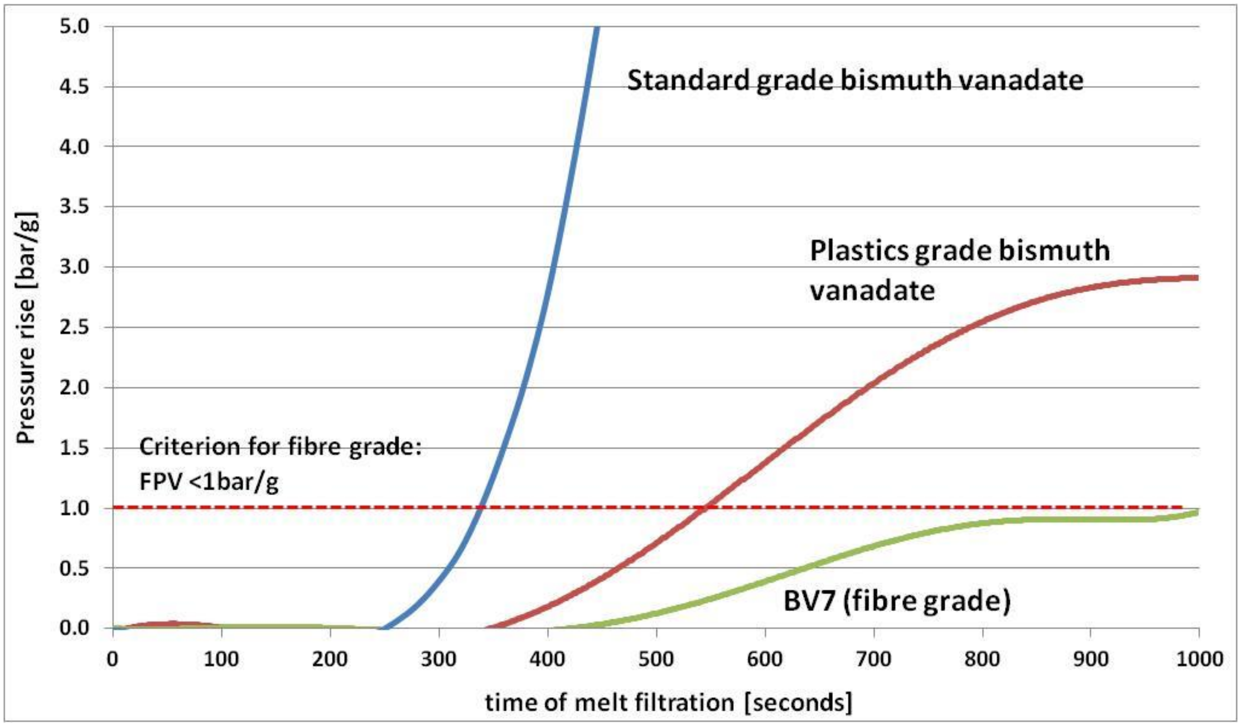

Figure 5 Pressure rise upon melt filtration of Bismuth Vanadates.

Conclusions

Bismuth Vanadate 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. Recently, due to technical improvements they can be utilized in a vast number of resins and plastics applications as a result, even 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 attention from 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 the formulator could use certain dye chemistries. Historically, the best performance in terms of heat stability was reached with Boric acid encapsulated Bismuth Vanadate pigments. However, the release of water during processing, which is very difficult to control during extrusion, the potential hydrolization of polymers and regulatory concerns have been valid reasons for boosting the development of grades of Bismuth Vanadate viable for use in polyamides. Engineered BV4 is the best example of this achievement: a very clean green shade is maintained even when processed at more than 300°C.

Finally, the innovative ***stir-in BV pigment,*** BV7 represents a pioneering technical solution specifically for PP and PES fibres, where excellent dispersion characteristics are absolutely essential.

Acknowledgements

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