

Synthesis, Characterisation and Testing of Bismuth Vanadate — An Eco-friendly Yellow Pigment

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Bismuth based pigments are environmentally friendly and can replace more hazardous yellow formulations containing lead, chromium or cadmium pigments. They offer brilliant greenish yellow and orange shades with high opacity and high colour strength. An improved method is developed for the preparation of bismuth vanadate from an aqueous solution of sodium vanadate by adding a solution of bismuth nitrate in the presence of sodium acetate/acetic acid buffer. This avoids the polymerisation of vanadate ion in acidic solution as well as the formation of bismuthyl ion in alkaline solution. The pigment is characterised by measuring its bulk density, particle size, and oil absorption value. Its colour is matched with colours of standard yellow and orange pigments. An XRD study is also carried out which indicates the pigment to be of monoclinic form.

Introduction

Although the two functions of a pigmented coating are to inhibit corrosion and extend useful life of materials, its primary function is to impart an eye-catching colour. The modern coating system requires pigments with outstanding properties which are difficult to obtain without using toxic compounds such as those of lead, chromium or cadmium. Only in 1976¹ attention was focussed on the possibility of producing eye-catching less toxic² brilliant yellow pigments based on bismuth vanadate. Mostly, they find application as leadfree yellow and orange formulations. They are not only less toxic but also offer attractive colour, opacity, and durability of the final product.

Bismuth yellow pigment is an orthovanadate of molecular formula BiVO_4 having three stable polymorphs. The low temperature phase is classified into Zircon (ZrSiO_4) type with tetragonal unit cell³ and the high temperature phase has a monoclinic unit cell⁴. The naturally occurring mineral "Pucherite" is found to be a mixed oxide of bismuth and vanadium⁵. In Western Australia, it occurs as monoclinic

clinobisvanite⁶. The mineral pucherite is reddish brown in colour with a specific gravity of 6.249 at 24.5 °C and has an orthorhombic crystal structure with dimensions: $a = 5.33\text{A}$, $b = 12.02\text{A}$, and $c = 5.06\text{A}$ (ref. 7).

The study attempts a laboratory synthesis of bismuth vanadate, determines its composition, structure, and examines its suitability as a pigment.

Materials and Methods

Preparation of Bismuth Vanadate

The raw materials are highly pure solutions of bismuth nitrate, sodium hydroxide, sodium acetate and acetic acid. One molar solution of sodium vanadate and a buffer of sodium acetate and acetic acid are taken in a reaction vessel. Molar solutions of bismuth nitrate and sodium hydroxide are added simultaneously from two different separating funnels, drop by drop, to the stirred solution taken in the reaction vessel. Complete precipitation of bismuth is tested with 1-2 ml of supernatant liquid by addition of 3-4 drops of ammonium hydroxide. Absence of white precipitate of bismuth hydroxide indicates the completion of precipitation. Stirring is continued for 2 h after addition of the reagents for ageing the precipitates. The slurry is filtered, washed with water,

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and dried at 120 ± 10 °C for 4 h. The dried sample is then calcined at 550-600 °C for 6 h and the final product obtained is pulverised to the desired particle size.

Determination of Vanadium

The sample was dissolved in dilute hydrochloric acid and vanadium was determined by titration against standard ferrous ammonium sulphate solution after addition of syrupy phosphoric acid, using barium diphenyl amine-4-sulphonate as indicator. The iron(II) solution was standardised against standard ammonium vanadate solution.

Estimation of Bismuth

Bismuth was estimated gravimetrically by precipitating it as bismuth phosphate by addition of diammonium hydrogen phosphate solution to a solution of bismuth vanadate in 1.0 N nitric acid. There was no interference from vanadate ion. However, a titrimetric method was developed and the result was verified. The results are given in Table 1.

Particle Size & Surface Area

The particle size distribution of the pigment and its surface area were determined using the "MALVERN" Particle size analyser. The results are shown in Tables 1 and 2 respectively.

Oil Absorption and Bulk Density

The oil absorption and bulk density were measured using standard procedures⁸.

Table 1 — Physical and chemical properties of bismuth vanadate

1 Composition	Bi ₂ O ₃ = 72(71.91) per cent* V ₂ O ₅ = 27.5(28.09) per cent
2 Colour	Matched with ISC-592 (International orange)
3 Absolute reflectance in terms of CIE-values	63.4G, 70.9R and 6.4B G= green, R= red, and B= blue
4 Surface area	2.28 m ² /ml
5 Average particle size	4.08 μm
6 Oil absorption	300-320 ml/kg
7 Bulk density	0.5-0.6g/ml

* In the case of composition the figures in the parenthesis indicate the theoretical values

Table 2 — Particle size distribution of bismuth vanadate.

Size in microns(μ)	Weight in per cent	Cumulative weight in per cent
10.2 - 13	4.1	100
7.88 - 10.2	12.2	95.9
6.15 - 7.88	11.8	83.7
4.83 - 6.15	11.2	71.9
3.80 - 4.83	14.1	60.7
3.02 - 3.80	10.3	46.6
2.41 - 3.02	7.8	36.3
1.94 - 2.41	8.6	28.5
< 1.94	19.9	—

Colour Matching

The pigment was mixed thoroughly with a carrier and painted on a stainless steel plate. Its colour was matched with yellow and orange shades, available in IS-5 "Indian Standard Colours for Ready Mixed Paints". The results are given in Table 1.

The colour properties were also measured in terms of absolute reflectance values with respect to G (green), R (red), and B (blue). For measuring these values the DUCOLOUR model 220 instrument supplied by M/s Neotic, USA, was used. The instrument employs a tungsten quartz-iodine light source, silicon cells, and specially designed glass filters to provide CIE tristimulus values. The results are given in Table 1.

XRD Study

The X-ray diffractograms of the unroasted and roasted samples of bismuth vanadate were obtained using Phillips Diffractometer Model PW-1400. The *d*-values found out corresponding to the 2θ values were compared with those of tetragonal and monoclinic forms of BiVO₄ available in X-ray data file.

Results and Discussion

Preparation

In the synthesis of pigment grade bismuth vanadate two problems are normally faced. The first is that the acidification of colourless alkaline vanadate solution results in the formation of polyanions of vanadic acid as a result of which

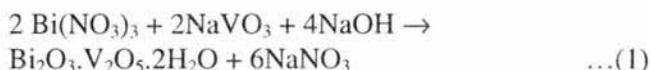
bismuth cations do not get a chance to react with vanadate anions. The second problem is that at alkaline pH bismuth cations react with hydroxide anions to give sparingly soluble bismuth hydroxide. Addition of a buffer of sodium acetate and acetic acid before precipitation of bismuth vanadate maintained the pH at about 4, and suppressed polymerisation of vanadate ion. Since bismuth nitrate solutions contain nitric acid, sodium hydroxide is added to neutralise this free acid and to maintain the pH along with the buffer.

Analysis

Bismuth vanadate is soluble in nitric acid or hydrochloric acid. Most existing methods for determination of bismuth by titration with EDTA are applicable only in nitric acid medium. During such titrations at about pH 2 the bismuth vanadate pigment separates out. Though the pigment was soluble in hydrochloric acid, in this medium many indicators showed no response. Hence, an improved method was used for estimation of bismuth in hydrochloric acid medium which involves the use of α -hydroxy acids, preferably tartaric acid for complexing bismuth. Under this condition, bismuth was not hydrolysed, although the pH was more than 1.5 and xylenol orange could be successfully used as an indicator in its titration against standard EDTA solution. The colour changes at the end point from intense red to yellow. For the determination of vanadium also the pigment is dissolved in hydrochloric acid. Nitric acid is avoided, as it is likely to interfere in the titration with iron(II).

Hue of the Pigment

In the process of preparation of bismuth vanadate, an amorphous hydrated Bi-V-oxide gel is produced. Although this material looks yellow, it is not crystalline and cannot be used as a pigment. The pigment with brilliant hue is formed according to Eq.(2) only when it is subjected to controlled crystallisation between 550 to 600°C.



The necessity for heating the dried material between 550-600°C, in order to develop the pure hue

and other properties, is attributable to the formation of intrinsic crystalline imperfections or vacancies. The incorporation of colour ions into the crystal lattice is likely to take place through solid state reaction in the above range after passing through the steps such as defect formation, disintegration of crystal lattice, and chemical interaction between the initial compounds⁹. The hue of the roasted pigment was found to match with ISC 592 (International Orange).

The reflectance values of the pigment, as measured in the CIE system, are 63.5G, 70.9R, and 6.4B, where G, R, and B represent reflectance of green, red, and blue colours, respectively. The CIE system of colour matching is more objective, since it involves the matching of colour of the pigment with that of a light source, instead of a standard pigment sample. The light source is formed by mixing coloured lights from standard sources.

Particle Size

The particle size distribution of a pigment is important because it influences the optical performance of the pigmented material. The suitable particle size for an ideal pigment is 2-50 μm (range). If the average particle size of the pigment is very small, it exists in the form of dust and hence difficulties arise in handling it. On the otherhand, if the particles are too large, their light scattering efficiency is impaired and the pigmented material will lack brightness.

It is observed from Table 2 that about 20 per cent of the particles are smaller than 1.94 μm and about 4 per cent larger than 10.2 μm . The average particle size is 4.08 μm . This particle size distribution is quite suitable. The surface area and the oil absorption of the pigment are both quite low (Table 2). Hence, high pigment loading can be achieved using dispersant to avoid sedimentation.

XRD Study

From the X-ray diffraction study of the unroasted bismuth vanadate (Table 3), it is observed that the peaks are broad and ill defined compared with those of the roasted form. This indicates the unroasted form to be of amorphous character. In the case of crystalline pigment formed by heating between 550-600°C, some of the lines could not be attributed to any known form of bismuth vanadate. It

Table 3 — XRD data of bismuth vanadate.

d-values and intensities of the prepared bismuth vanadate pigment	d-values and intensities of standard monoclinic bismuth vanadate
4.72(25)	4.749(25)
3.42(10)	—
3.35(16)	—
3.26(12)	3.12(30)
3.10(100)	3.10(100)
2.93(33)	2.924(25)
2.76(15)	—
2.65(9)	2.598(12)
2.60(21)	2.546(14)
2.55(23)	2.374(2)
2.28(18)	2.282(6)
2.21(11)	2.250(10)
2.13(21)	2.133(8)
2.11(7)	2.127(12)
2.05(11)	1.995(6)
2.02(13)	1.988(4)
1.99(15)	1.976(6)
1.97(19)	1.97(8)
1.95(34)	1.949(4)
1.92(33)	1.92(16)
1.88(12)	1.82(6)
1.82(21)	1.812(8)

The figures inside the parenthesis indicate intensities

is supposed that the pigment is still in a quasi static condition and it is in the process of attaining specific crystal structure. If the pigment is heated above 600°C the hue is adversely affected. Thus, it should be given prolonged heating at this temperature to ensure satisfactory crystal growth. Hence, it is to be heated at the same temperature for a longer duration.

The prominent lines of the standard tetragonal variety are: 3.65(100), 4.84(45), 2.74(60), and 1.88(50). Of these the line with *d*-value (intensities in parenthesis) 3.65(100) is not found in the XRD of the unroasted pigment. The presence of the strong lines with *d*-values 4.75(44), 2.80(64), and 1.80(69) indicates that tetragonal form is a major component of the unroasted pigment. The prominent lines of the monoclinic form of bismuth vanadate are : 3.10(100), 3.08(95), and 3.12(30). The presence of the lines with *d*-values of 3.10(100) and 3.20(90) indicates that the monoclinic form is also present in the unroasted pigment.

The presence of the prominent lines with *d*-values 3.26(12) and 3.12(100) in the XRD of roasted pigment, indicates that the sample is essentially monoclinic. However the line with *d*-value of 2.76(15), corresponds to the prominent line of the tetragonal form with *d*-value of 2.73(60). Since the intensities are not comparable, this line does not confirm the presence of the tetragonal form. Almost all of the other *d*-values in the XRD of the roasted pigment, correspond to those of the standard monoclinic form except the two with *d*-values of 3.42(10) and 3.35(16). These two lines indicate the presence of some other form of bismuth vanadate which may be converted to monoclinic form by heating for a longer duration.

Toxicity

Bismuth vanadate was the subject of a patent application on medicine¹⁰ in the year 1924 itself. The pigment did not show any acute toxicity in animal skin sensitization tests whereas animal inhalation studies with pigment dusts indicated low effect on lung tissues². The high density of the compound helps in quick settling of the dust and making it safe.

Cost

Its surface area and oil absorption are quite low in comparison with those of organic pigments which means very high pigment loading is possible. Moreover its hiding power is also 4-5 times higher than those of organic pigments². Hence, although it will be costlier than the other environmentally hazardous inorganic yellow pigments such as chrome yellow, cadmium yellow and chrome titanium yellow it will be cheaper than the organic pigments. Eco-friendly nature of the pigment also compensates for its cost.

Conclusions

In the synthesis of bismuth vanadate yellow pigments, the polymerisation of vanadate anions can be avoided by the use of a buffer of sodium acetate and acetic acid. The colour and other properties of the pigment such as suitable particle size, bulk density, and oil absorption, develop only when it is heated for more than 6 h at between 550-600°C. This is a low toxicity and eco-friendly pigment which can replace the hazardous chrome and cadmium yellow pigments.

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