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(54) **Inorganic pigments and process for their preparation**

(57) Yellow pigment based on monoclinic bismuth vanadate containing, as diluent, orthorhombic barium sulphate in an amount from 10 to 90% by weight. The pigments exhibit optical and pigmentary properties similar to those of traditional yellow pigments, e.g. chromium, cadmium and cadmiopone yellows.

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SPECIFICATION

Inorganic pigments and process for their preparation

- 5 This invention relates to inorganic pigments and to a process for their preparation. In particular the invention relates to yellow pigments based on bismuth vanadate. 5
- The most widely used yellow pigments are chromium yellows, cadmium yellows and cadmiopone yellows. However, since these traditional pigments contain lead and hexavalent chromium or cadmium they are suspected of being toxic.
- 10 There are alternative pigments of the same colour, based on nickel titanates $\text{TiO}_2\text{-NiO-Sb}_2\text{O}_3$. However, these pigments do not have properties comparable with those of the aforementioned traditional pigments as far as colour saturation and tinting strength are concerned. 10
- It has been suggested to use bismuth vanadate BiVO_4 with a monoclinic crystalline structure as an alternative yellow pigment. This product possesses optical and pigmentary properties similar to those of "primrose" chromium yellow although its cost is commercially unattractive due to the high price of the raw materials, namely vanadium and bismuth compounds used for its preparation. 15
- United States Patent Specification No. 4 026 722 has suggested the use of bismuth vanadate based pigments, diluted with SiO_2 and Al_2O_3 , in which the content of BiVO_4 may be reduced down to 44% by weight. However, these pigments show a lowering of the colour saturation and a considerable drop in hiding power and tinting strength with respect to pure bismuth vanadate (and thus also with respect to the traditional yellow pigments). 20
- It is an object of this invention to provide new yellow pigments which are free of lead, chromium and cadmium, and exhibit optical and pigmentary properties similar to those of the traditional yellow pigments. 25
- Therefore according to the invention there is provided yellow pigment based on monoclinic bismuth vanadate containing, as diluent orthorhombic barium sulphate in an amount from 10 to 90% by weight.
- It has been found that the presence of BaSO_4 , within the above limits of concentration by weight, allows pigments to be obtained with optical properties (colour saturation and reflectances on green, amber red and blue filters) and with pigmentary properties (tinting strength and hiding powder) absolutely comparable with those of the traditional yellow pigments. 30
- With increasing quantities of BaSO_4 , the tinting strength and the hiding powder will decrease. Thus, it is possible to obtain products that will be comparable, as far as these properties are concerned, with the light cadmium yellows (using about 30% of BaSO_4) with the "primrose" chromium yellows (using about 50% of BaSO_4) and with the cadmiopone yellows (using about 70% of BaSO_4). 35
- With increasing quantities of BaSO_4 , there is also a decrease in the colour saturation although the economical aspect of the products is increased.
- 40 As described above, the quantity of BaSO_4 may vary from 10 to 90% by weight. These products may thus be represented by the formula: 40
- $$\text{BiVO}_4 \cdot x\text{BaSO}_4$$
- 45 in which x (expressed as a molar ratio) varies from 0.15 to 12.5. 45
- These products generally have a colour saturation (P%) of at least 60% and a reflectance on green ($R_V\%$) of at least 60%. These minimum values are referred to the products with the highest content in BaSO_4 .
- Preferred products are those containing between 30% and 70% of BaSO_4 ; in the formula 50 $\text{BiVO}_4 \cdot x\text{BaSO}_4$, x varies from 0.59 to 3.24. In this range of products are those having optical and pigmentary properties similar to those of cadmium yellows, "primrose" chromium yellows and cadmiopone yellows. These products have a colour saturation P% of at least 70% and a reflectance on green $R_V\%$ of at least 70%. 50
- The products that are most widely preferred are those containing 30 to 50% of BaSO_4 ; in the 55 formula: $\text{BiVO}_4 \cdot x\text{BaSO}_4$, x varies from 0.59 to 1.4. These are the products having the higher optical and pigmentary properties; their properties are of the same level as those of the best traditional yellow pigments, i.e. cadmium yellows and chromium yellows, while they are superior to those of the cadmiopone yellows. These products have a colour saturation P% of at least 75% and a reflectance on green $R_V\%$ of at least 75%. In the best products the colour 60 saturation attains about 80% while the reflectance on green is about 80%. 60
- In the products according to the invention, which have less than 30% by weight of BaSO_4 , the colour saturation and reflectance on green tend to increase further, as also do the pigmentary properties. However, it is preferred to use at least 30% of BaSO_4 in order to contain the cost of the product.
- 65 In the products according to the invention, which have more than 70% of BaSO_4 , the optical 65

and pigmentary properties are lower than those of the preferred products; however, these properties on the whole are not inferior to those of the nickel titanates. In fact, their tinting strength and their colour saturation are superior to those of these latter pigments, while their hiding power is inferior.

5 The pigments according to this invention, have usually a dominant wave length λ_D in the range of 573 to 576 nm. The pigments generally have a specific surface from 2 to 15 m²/g. 5

The tinting strength of the pigment is determined by making a film of paint made of one part of coloured pigment with 3 parts of TiO₂ and 3 parts of vehicle, and by then measuring the percentage ratio between the colour saturation of the dilute tone and that of the mass-tone, as will be described in Example 1 hereinafter. 10

The preferred products, containing from 30 to 70% of BaSO₄ have a tinting strength, expressed by the above percentage saturation ratio, of at least 50%. The most preferred pigments, containing from 30 to 50% BaSO₄, have a tinting strength of at least 60%; in certain products the tinting strength attains about 70%.

15 The hiding power of the pigments has been determined through the contrast ratio on green, amber red and blue filters on a film of dry paint, 50 μ thick, spread on Morest cardboards, as will be described in Example 1 hereinafter. The preferred products, containing from 30 to 70% of BaSO₄, have a contrast ratio R_C on green of at least 0.740, on amber of at least 0.680 and on blue of at least 0.950. The most preferred pigments, containing from 30 to 50% of BaSO₄ have a R_C on green of at least 0.880, on amber of at least 0.850 and on blue of at least 0.970. 20 In some pigments R_C attains about 0.950 on green, 0.930 on amber and 0.990 on blue.

The pigments of this invention may be prepared according to the following process.

A solution of bismuth nitrate and barium nitrate in acetic acid having a pH comprised between 0.5 and 1.5 is prepared. Separately, an alkaline solution containing both a sulphate of an alkaline metal or ammonium sulphate, together with an ortho-vanadate VO₄[⊖] or a metavanadate VO₃[⊖] of an alkaline metal or of ammonium is prepared. The second solution is admixed to the first solution with the consequential precipitation of BaSO₄ and BiVO₄. The precipitate is separated from the mother liquor and washed with water, in order to remove the soluble salts. The precipitate is then calcined in the presence of air at a temperature in the range 400 to 700°C, and the calcined product is slowly cooled and finally ground to the desired particle size. 30

It has been found that the presence of CH₃COOH in the solution of Bi(NO₃)₃ and Ba(NO₃)₂ and the solution pH of 0.5 to 1.5, are critical conditions for obtaining a good pigment.

If the pH of the solution tends to be too low, it may be corrected by the addition of an alkaline hydroxide e.g. NaOH or of NH₃. In general, best products are obtained when the pH is from 1.0 to 1.5. The total concentration in moles of Bi(NO₃)₃ and Ba(NO₃)₂ is generally from 0.15 to 0.3 moles per litre of acid solution. The molar ratio Bi(NO₃)₃/CH₃CO₂H is generally from 0.02 and 0.1. 35

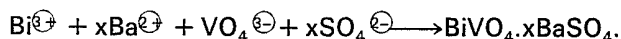
The molar ratio Ba(NO₃)₂/Bi(NO₃)₃ depends on the content in BaSO₄ that is desired in the final pigment.

40 The alkaline solution of vanadate and sulphate generally has a pH in the range from 7 to 10, preferably from 8 to 9. If the pH tends to be too high, it may be corrected by the addition of HNO₃ or H₂SO₄; in the latter case, care must be taken to respect the stoichiometric ratio between the Ba[⊕] ions of the acid solution and the SO₄[⊖] ions of the alkaline solution.

Suitable starting vanadium compounds include NaVO₃, NH₄VO₃, Na₃VO₄ and V₂O₅ dissolved in NaOH. 45

Suitable sulphates include Na₂SO₄, (NH₄)₂SO₄ and K₂SO₄, as well as H₂SO₄, adjusting when necessary, the pH with an alkaline hydroxide or with NH₃.

In general the total concentration of vanadate and sulphate is comprised between 0.15 and 0.40 moles per litre of solution, and preferably is from 0.20 to 0.35 moles per litre. Generally, the quantities of reactants present in the two solutions are such as to respect the stoichiometry of the reaction: 50



55 It has been found, however, that small variations with respect to the stoichiometry, still yield good products, provided that both the molar ratio Bi[⊕]/VO₄[⊖] and that of Ba[⊕]/SO₄[⊖] are from about 0.99 to about 1.01.

The alkaline solution is admixed under mechanical stirring to the acid solution whereupon a double exchange reaction occurs with the co-precipitation of the BiVO₄ and the BaSO₄. The precipitation temperature of the pigment is generally from 15 to 40°C, but preferably the reaction is conducted at a temperature of 15 to 25°C. 60

The precipitation time varies from 5 minutes to 1 hour and is usually from 15 to 30 minutes.

At the end of the precipitation, the pigment slurry is maintained under stirring, for example, for a period of 15 minutes to 1 hour. The final pH will vary from 0.8 to 3.0, depending on the pH of the precipitating solutions. Operating under the preferred conditions, the final pH will be 65

from 2.0 to 3.0.

The product, separated from the mother liquor, is then washed with water in order to remove the soluble salts, and is then submitted to the calcining treatment. This treatment may be carried out either on the product in the pasty state, that is, on the filtration cake, or on the product previously dried (for example at 100 to 130°C).

The calcining is carried out in the presence of air at a temperature from 400 to 700°C; the duration of the operation is generally from 30 minutes to 3 hours, preferably from 1 to 2 hours. Calcination may be conducted under static conditions but preferably a rotary oven is used in order to ensure a greater uniformity of the temperature inside the mass of the product.

10 Preferably, calcination is carried out at a temperature of from 500 to 600°C. Under such conditions products with a dominant wavelength of from 573 and 576 nm, and endowed with excellent optical and pigmentary properties are obtained.

At temperatures exceeding 600°C, the mass-tones are slightly more yellow or more orange-coloured and the tinting strength and hiding power are inferior. At temperatures lower than 15 500°C, the dominant wave length shifts towards values that are lower than those of chromium, cadmium and cadmiopone yellows, while the pigmentary properties remain good.

In order to obtain good products, it is necessary to cool the calcining product slowly; for example, the calcination product should be brought to a temperature from 200°C to room temperature over a period of 2 to 24 hours.

20 Successively the products will be discharged from the oven and, when necessary, cooled to room temperature, whereafter they are subjected to grinding which will preferably be carried out in the wet state, for example, in a ball mill, a microsphere mill or a sand mill.

When the product is wet ground, it is thereafter dried, e.g. at 100 to 110°C. The product is then subjected to a further dry grinding, for example, in a automatic mortar.

25 The invention will now be illustrated by the following Examples.

Example 1

0.077 moles of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was dissolved in 100 cc of 96% acetic acid. To this solution were admixed 0.107 moles of $\text{Ba}(\text{NO}_3)_2$ and the whole was then diluted with water to make 30 1000 ml. The solution was maintained under mechanical stirring until attaining complete dissolution of the salt whereupon a solution of 2N NaOH was added until the pH of the solution was equal to 1. The temperature of the solution was 25°C.

Separately, 0.077 moles of NaVO_3 and 0.107 moles of Na_2SO_4 were dissolved in 700 ml of H_2O and the pH of the solution was adjusted to 8.5 by the addition of 2N NaOH. The 35 temperature of the solution was 25°C.

The vanadate-sodium sulphate solution was dripped over a period of 30 minutes into the solution containing bismuth and barium nitrates in a 2.5 l beaker, fitted with a mechanical stirrer. At the end of the addition, the pH of the slurry was about 1.5.

40 The precipitate was maintained under stirring for 30 minutes at a temperature of 25°C, after which the product was allowed to settle and the mother liquor decanted and discharged. The product was then washed with water in order to remove the soluble salts. Thereafter the product was filtered, dried at 100 to 110°C and calcined in a muffle stove at a temperature of 550°C for 1 hour. At the end of the calcining the product was cooled to room temperature over a period of about 20 hours and was then wet ground according to the following procedures.

45 35 g of small glass balls (having a diameter of 2 mm), 15 g of pigment and 30 ml of water were introduced into a 80 ml container. The container was then sealed and placed on a "Red Devil" (Registered Trade Mark) vibrating stirrer where the product was ground for 20 minutes.

At the end of the grinding operation the product was separated from the grinding elements and was filtered, dried at 100°C and finally ground in a automatic laboratory mortar of the 50 "Pulverisette" type, for 5 minutes.

The pigment thus obtained, analysed by X-rays, proved to consist of monoclinic bismuth vanadate (card ASTM 14-688) and of orthorhombic barium sulphate (card ASTM 24-1035). The pigment exhibited a mean granulometry of about 0.2 μ and a specific surface of 7.2 m²/g.

55 The product contained 50% by weight of BaSO_4 , corresponding to the formula $\text{BiVO}_4 \cdot 1.388 \text{BaSO}_4$. For comparative purposes, there was prepared a bismuth vanadate diluted with SiO_2 and Al_2O_3 , following the procedures indicated in Example 1 of United States Patent Specification No. 4026 722.

60 5.14 g of Bi_2O_3 , 2.58 g of NH_4VO_3 , 4.5 g of $\alpha\text{-Al}_2\text{O}_3$ and 0.5 g of SiO_2 were intimately dry-mixed together in an automatic mortar of the "Pulverisette" type. The mixture was then placed into a porcelain crucible and calcined for 0.5 hours at 900°C. The product was successively crushed and homogenized in the automatic mortar after which it was again calcined for 1 hour at 1100°C and successively wet ground for 15 minutes, following the operational conditions described herein above. The product was then dried and dry-ground, as described above. The product thus obtained contained 58.9% by weight of BiVO_4 .

65 The colorimetric characteristics of the two products were determined on a film of dry paint 50 65

μ thick, obtained by dispersing in a Hoover-type (Hoover is a Registered Trade Mark) mixer two parts of pigment in one part of vehicle of the following composition:

5	Aroplaz 1279 (alkydic resin 68% by weight; soya oil 32%)	76.3 %	5
	FL 30 (boiled linseed oil)	19.0 %	
	Drying mixture	4.7 %	

The drying mixture was of the following composition:

10			10
	Ca-naphthenate	1.77 %	
	Zr-naphthenate	5.31 %	
	Co-naphthenate	6.90 %	
	white spirit	86.02 %	

15

The colorimetric measurements were carried out by means of a differential tristimulus colorimeter Model Ducolor 220 by the Neotec Instruments Corporation. The apparatus gives the values of tristimuli X, Y and Z, and the reflectances R_V , R_A and R_B respectively on a green, amber and blue filter, with reference to a calibrated standard with respect to Mg oxide (standard S/N 22 197 by Neotec Corporation with $R_V = 92.0$, $R_A = 92.0$ and $R_B = 88.6$).

20 The trichromatic coordinates (x, y) were determined from the tristimuli values X, Y, Z and by means of a graph the values of the dominant wave length (λ_D) and of the colour saturation (P%) were extrapolated.

25 The values thus obtained are reported in Table A which also includes for comparative purposes, the values relative to two commercial yellow pigments: a primrose chromium yellow and a light cadmium yellow.

30 For the determination of the tinting strengths, one part of coloured pigment, three parts of TiO_2 and three parts of the vehicle described previously were blended together. The tinting strength was evaluated through the percentage ratio between saturation (P%) of the dilute tone and that of the mass-tone. The higher said value, the higher the tinting strength of the product. The values obtained are reported in Table A.

The hiding power of the pigments was evaluated both by simple visual comparison of the paint of the pigment under examination with the paint of the reference pigment, as well as by measuring the contrast ratio on the usual three filters.

35 The measurements were carried out on thin films of dry paint, 50μ thick, spread on Mostest cardboards. The paints were prepared according to the following procedures.

10 g of pigment were added to 35 g of small glass balls of about 2 mm diameter and with 15 g of a vehicle of the following composition.

40	50% Resial (Registered Trade Mark) 3118 (consisting of 55% linseed oil, 29% phthalic anhydride, 16% of pentaerythritol and glycols) and 50% white spirit	70.60% by weight	40
	xylol	14.70% by weight	
	white spirit	14.70% by weight.	

45

These mixtures were placed into 80 ml glass containers. The containers were then sealed and placed into a "Red Devil" vibrating mixer, for 1 hour.

Thereafter a further 24 g of a mixture consisting of 70% Resial 5132 (soya oil 65%, phthalic anhydride 20%, pentaerythritol 15%) and 30% white spirit were added.

50 After homogenisation, the paint was subjected to treatment on the vibrating mixer for 5 minutes. The pigment thus dispersed in the vehicle was separated from the small glass balls and then added with further 3% by weight of a drying mixture of the following composition by weight:

55	Ca-naphthenate	1.77 %	55
	Zr-naphthenate	5.31 %	
	Co-naphthenate	6.90 %	
	White spirit	86.02 %	

60 The contrast ratios, determined by colorimetric measurements carried out on a differential tristimulus colorimeter, model Ducolor 220, built by Neotec Instruments Corporation are reported in Table A.

Table A

Product under examination	Reflectance			λ_D nm	Colour satura- tion P%	Tinting strenght- age sat- uration ratio	Hiding power		
	R _V	R _A	R _B				Percentage contrast ratios		
							R _C green	R _C amber	R _C blue
Product of Example 1 BiVO ₄ diluted with SiO ₂ and Al ₂ O ₃ "primrose" chromium yellow light cadmium yellow	80.7	89.4	13.7	573.6	75.0	65.3	0.904	0.868	0.986
	68.9	74.9	12.6	574.7	67.3	52.4	0.622	0.571	0.874
	77.6	87.8	10.3	574.6	80.8	60.1	0.842	0.798	0.972
	78.3	87.8	10.5	573.4	78.5	70.6	0.938	0.910	0.989

Comparing the results reported in Table A, it will be seen that all the properties of the product prepared according to this invention are by far superior to those of BiVO_4 diluted with SiO_2 and Al_2O_3 in spite of the fact that the latter has a greater content in BiVO_4 .

5 The pigment according to the invention displayed properties comparable with those of the two commercial pigments. 5

Examples 2 to 6

The same procedure as in Example 1 was adopted, except that the content of BaSO_4 in the pigment and the calcining temperature was varied. The composition of the pigments, the
10 calcining temperature, the optical properties and the tinting strength are reported in Table B. 10

Example 3 coincides with Example 1 herein above described.

Table B

Example No.	Composition	Calcination temperature °C	Reflectances			λ_D	Colour saturation P%	Tinting strength percentage saturation ratio
			R_V	R_A	R_B			
2	50% BaSO ₄	500	82.0	89.8	15.0	573.3	72.8	66.8
3	50% BaSO ₄	550	80.7	89.4	13.7	573.6	75.0	65.3
4	50% BaSO ₄	600	80.3	90.3	12.5	574.2	76.8	64.1
5	30% BaSO ₄	500	78.6	88.7	12.2	574.4	76.9	69.2
6	30% BaSO ₄	600	74.4	86.6	9.4	575.5	81.0	58.3

Examples 7 to 19

In the following series of Examples were varied: the content of BaSO_4 in the pigment, the molar concentration in cations of the acid solution ($\text{Bi}^{3+} + \text{Ba}^{2+}$) and the concentration in anions of the alkaline solution ($\text{VO}_4^{3-} + \text{SO}_4^{2-}$), as well as the pH of the solutions, the precipitation time, the final pH, and the calcining temperature. In all other respects the procedure of Example 1 were adopted.

Table C reports the above cited operational conditions and Table D the main characteristics of the pigments, i.e. the λ_D , the reflectance on green (R_V), the colour saturation P%, the hiding power and the tinting strength.

Table D also reports the same characteristics for four commercial pigments: a nickel titanate, a light cadmium yellow, a "primrose" chromium yellow and a cadmiopone yellow.

Table C

Example No.	Composition	Acid solution		Alkaline solution		Precipitation time (minutes)	Final pH	Calcining temperature °C
		molar concentration	pH	molar concentration	pH			
7	30% BaSO ₄	0.22	0.8	0.22	8.0	20	2.1	600
8	30% BaSO ₄	0.22	0.8	0.32	8.0	40	2.0	500
9	30% BaSO ₄	0.16	1.3	0.22	8.0	40	2.9	500
10	30% BaSO ₄	0.22	1.3	0.22	9.0	20	2.8	500
11	30% BaSO ₄	0.22	1.3	0.32	9.0	40	2.7	600
12	70% BaSO ₄	0.22	1.3	0.32	8.0	20	2.2	500
13	70% BaSO ₄	0.22	1.3	0.22	8.0	40	2.3	600
14	70% BaSO ₄	0.16	1.3	0.22	9.0	20	2.4	600
15	50% BaSO ₄	0.20	1.3	0.29	8.6	30	2.5	700
16	50% BaSO ₄	0.20	1.3	0.29	8.6	30	2.5	400
17	50% BaSO ₄	0.20	1.3	0.29	8.6	30	2.5	510
18	65% BaSO ₄	0.22	1.5	0.32	8.7	30	2.0	460
19	80% BaSO ₄	0.27	0.8	0.40	8.9	20	2.2	500

Table D

Example No.	λ_D	Reflectance R_V	Colour saturation P%	Hiding Power			Tinting strength percentage saturation ratio
				R_C green	R_C amber	R_C blue	
7	575.2	75.7	80.2	0.886	0.857	0.969	60.8
8	574.2	80.0	76.0	0.952	0.928	0.985	68.8
9	574.0	80.6	76.9	0.950	0.928	0.992	69.6
10	574.7	77.0	77.2	0.953	0.931	0.992	68.9
11	575.7	75.1	80.0	0.943	0.919	1.000	61.2
12	573.4	78.0	71.3	0.747	0.680	0.956	58.9
13	574.4	77.0	75.2	0.823	0.773	0.968	58.0
14	574.7	75.3	74.0	0.785	0.726	0.963	57.8
15	576.2	68.0	83.0	0.729	0.691	0.923	37.3
16	573.5	76.8	71.2	0.824	0.765	0.981	69.1
17	573.5	81.7	75.0	0.892	0.856	0.979	68.0
18	573.4	78.9	72.3	0.780	0.719	0.961	63.0
19	573.0	70.7	65.0	0.743	0.682	0.948	50.0
Nickel titanate	572.5	74.9	55.2	0.890	0.878	0.984	38.4
light cadmium yellow	573.4	78.3	78.5	0.938	0.910	0.989	70.6
primrose yellow	574.6	77.6	80.8	0.842	0.798	0.972	60.1
cadmiopone yellow	574.5	71.4	81.2	0.773	0.710	0.953	57.4

Comparing the results reported in Table D it will be seen that the product having 30% BaSO₄ (Examples 7 to 11) having a hiding power in general higher than that of the light cadmium yellow and at any rate always better than that of the "primrose" chromium yellow and cadmiopone yellow. The tinting strength of the products of Examples 8, 9 and 10 is comparable with that of the light cadmium yellow, while that of Examples 7 to 11 is superior to that of "primrose" chromium yellow. In all cases the tinting strength is greater than that of the cadmiopone yellow.

The products having 70% BaSO₄ (Examples 12 to 14) usually have a hiding power and a tinting strength greater than that of the cadmiopone yellow.

10 A product containing 80% of BaSO₄ (Example 19) has a colour saturation and a tinting strength that are superior to those of nickel titanate; however, its hiding power is inferior. 10

Examples 20 to 22

15 Pigment containing 50% of BaSO₄ was prepared adopting the same procedures as those in Example 1, except that the calcining was carried out at 600°C and the nature of the starting vanadate was varied. The nature of the vanadium compound and the optical properties of the products thus obtained, have been reported in Table E. 15

Table E

Example No.	Vanadium Compound	Reflectances			λ_D	Colour saturation P%
		R _V	R _A	R _B		
25 20	NH ₄ VO ₃	81.6	90.7	12.7	573.8	76.6
21	Na ₃ VO ₄	81.9	90.3	13.1	573.4	75.9
22	NaVO ₃	80.3	90.3	12.5	574.2	76.8

30 CLAIMS 30

1. Yellow pigment based on monoclinic bismuth vanadate containing as diluent, orthorhombic barium sulphate in an amount from 10 to 90% by weight.

2. A yellow pigment as claimed in Claim 1, having a colour saturation of at least 60% and a reflectance on green of at least 60%.

35 3. Yellow pigment as claimed in Claim 1 or Claim 2, containing from 30 to 70% of barium sulphate. 35

4. Yellow pigment as claimed in Claim 3, having a colour saturation of at least 70% and a reflectance on green of at least 70%.

40 5. Yellow pigment as claimed in Claim 1, substantially as herein described with reference to any one of the Examples. 40

6. A process for preparing a yellow pigment in which a solution of a bismuth nitrate and barium nitrate in acetic acid having a pH comprised between 0.5 and 1.5, is admixed with an alkaline solution containing a sulphate of an alkaline metal or ammonium sulphate and an orthovanadate or a metavanadate of an alkaline metal or of ammonium, to cause precipitation of BaSO₄ and BiVO₄, the precipitate being separated and washed with water in order to remove the soluble salts, the washed precipitate is then calcined in the presence of air at a temperature in the range from 400 to 700°C, and the calcination product is slowly cooled and finally ground to the desired particle size. 45

7. A process as claimed in Claim 6, in which the product is calcined at a temperature of from 500 to 600°C. 50

8. A process as claimed in Claim 6 or Claim 7, in which the pH of the solution of bismuth nitrate and barium nitrate in acetic acid, is in the range from 1 to 1.5.

9. A process as claimed in any one of claims 6 to 8 in which the temperature of the mixture at which precipitation occurs is from 15 to 40°C.

55 10. A process as claimed in any one of claims 6 to 9 in which the grinding of the calcination product is conducted by a wet grinding method. 55

11. A process for the preparation of yellow pigment as claimed in Claim 6 substantially as herein described with reference to any one of the Examples.