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Journal of the European Ceramic Society 26 (2006) 1599–1603
www.elsevier.com/locate/jeurceramsoc

The effect of milling and percentage dissociation of plasma dissociated zircon on the colour of Pr-yellow and V-blue zircon pigments

E. Snyders [a,1], J.H. Potgieter [b,2], J.T. Nel [c,*]

[a] *Department of Chemical and Metallurgical Engineering, Tshwane University of Technology, Private Bag X680, PRETORIA 0001, South Africa*
[b] *School of Process and Materials Engineering, University of the Witwatersrand, Private Bag X3, Wits, 2050, South Africa*
[c] *South African Nuclear Energy Corporation Limited, PO Box 582, PRETORIA 0001, South Africa*

Received 27 October 2004; received in revised form 21 February 2005; accepted 5 March 2005
Available online 27 April 2005

Abstract

The effect of milling and percentage dissociation of plasma dissociated zircon (PDZ) on the colour of Pr-yellow and V-blue zircon pigments were investigated. A solid-state reaction process was used to produce zircon pigments and the Pr-yellow and V-blue pigments were calcined at 1050 and 950 °C, respectively in a conventional muffle furnace. Using pre-milled PDZ material, prior to the calcining process, the influence on the colour intensity of the pigments after application on a ceramic tile were compared to that of a PDZ material with no prior pre-milling before the calcination stage. Pr-yellow and V-blue zircon pigments produced from PDZ with different percentages dissociation, were also evaluated in this study. The different percentages dissociation of the PDZ material was achieved by only changing the zircon feed rate through a non-transfer arc plasma system, keeping all the other plasma parameters constant.

The colour of the pigment samples was characterized on the grounds of the Commission Internationale de l'Eclairage (CIE) standard procedure (CIE L^* a^* b^* measurements) after application on a bisque ceramic tile.

Keywords: Milling; Grain size; Colour; Optical properties; Pigments; $ZrSiO_4$

1. Introduction

The most common method of obtaining colour in a ceramic material is to disperse in that material a coloured crystalline phase, which is insoluble in the matrix. This crystalline phase, or pigment, imparts its colour in the matrix. Pigments based on zircon ($ZrSiO_4$) are widely used in the ceramic industry because it is capable of withstanding high temperatures and corrosive environments. The colour of these pigments is obtained by doping the zircon crystal lattice with guest metal species, such as praseodymium for the yellow pigment, vanadium for the blue pigment and iron for the pink pigment.[1–4]

The first zircon pigments produced were zirconium-vanadium blue pigments and Booth and Peel[5] describe examples of the preparation of this stain and several variants of it. The first study to show that a clean and bright yellow pigment could be produced from a praseodymium oxide, free from other rare-earth impurities, was done by Kato and Takashima.[6]

Although the crystal phase of the final pigment is zircon, it is important to note that zircon pigments cannot be produced directly by mixing the dopant oxides (praseodymium, vanadium or iron ions) with the mineral zircon itself.[7,8] The colouring ion must be present at the time the zircon crystal structure is formed by the reaction: $ZrO_2 + SiO_2 \rightarrow ZrSiO_4$.

Doped-zircon pigments may be prepared by calcining mixtures comprising of zirconium and silicon oxide (or compounds capable of yielding these materials on calcination) in

* Corresponding author. Tel.: +27 12 3053134.
E-mail addresses: ettiennes@peldev.necsa.co.za (E. Snyders), hermanp@prme.wits.ac.za (J.H. Potgieter), jtn@peldev.necsa.co.za (J.T. Nel).
[1] Tel.: +27 12 3053238, fax: +27 12 3053197.
[2] Tel: +27 11 7177546.

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doi:10.1016/j.jeurceramsoc.2005.03.237

the presence of a dopant oxide and one or more mineralizer components, the proportions of zirconium oxide and silica in the mixture being such that zirconium silicate is formed on calcination. Vanadium (as ammonium metavanadate or vanadium pentoxide) is used as dopant oxide for blue pigments, and praseodymium (as oxide, carbonate or oxalate) is used as dopant oxide for the yellow pigments. Common mineralizers, whose function it is to reduce the temperature required for the reaction or to catalyze the reaction itself, include the alkali metal halides, especially fluorides. After the calcining step, the raw product is ground, washed free of soluble salts, dried and pulverized to pigment industry standards ready for application onto a ceramic body, i.e. ceramic tiles.

Processes for the production of doped-zircon pigments using high temperature calcination of oxides in the presence of a dopant oxide or colour inducing metal oxide together with additives are well described. Weber[9] describes a process for the production of zirconium-praseodymium yellow pigments from zirconium silicates. The process entails (a) decomposition of zirconium silicate by heating a alkali-zirconium silicate mixture, (b) an aqueous slurry of the decomposed product is formed by mixing the decomposed product with water together with a praseodymium compound, (c) adding a mineral acid to the aqueous slurry in an amount to solidify the slurry, (d) calcining the solidified mixture to produce a yellow pigment.

Bell[10] describes a process for the production of zircon based ceramic pigments by calcining a mixture of zirconium and silicon oxide in the presence of a dopant oxide and additives to form blue and yellow doped-zircon pigments.

Morriss and Williamson[11] patented an alternative method for the production of zirconium-based pigments. Their method entails the use of plasma dissociated zircon (PDZ) sand for the production of pigments. According to the process the zircon concentrate is fed through a plasma furnace to obtain plasma dissociated zircon. The dissociated zircon is then milled for between 15 and 30 h to a particle size of between 3 and 12 μm in a ball mill charged with water and caustic soda, or alternatively sodium fluoride and hydrofluoric acid, after which the charge is neutralized with hydrochloric acid or sulphuric acid or, alternatively, with caustic soda. The slurry is then dried and pulverized before it is used for the production of doped-zircon pigments.

The above-mentioned processes require chemical treatment and milling of zircon and plasma dissociated zircon before doped-zircon pigments are being produced by means of a solid-state reaction process. The aim of the present work was to study the effect that pre-milling and percentage dissociation of plasma dissociated zircon have on the final colour of the pigment after being applied on a ceramic body. Different Pr-yellow and V-blue zircon pigment samples were produced by varying: (a) the particle size of the plasma dissociated zircon prior to the calcining process and to compare it with no prior milling of PDZ material before the calcining process and (b) the percentage dissociation of the PDZ material used as feed material for the production of V-blue and Pr-yellow zircon pigments.

Although the application of plasma technology is well known in a number of fields, e.g. metals' surface treatments[12,13] and waste treatment[14], no reference could be found in literature describing the production of doped-zircon pigments, as is dealt with in this investigation.

2. Materials and methods

A South African prime grade zircon, which was supplied by Namakwa Sands, was used in this study. The zircon was dissociated in a non-transfer arc plasma system, situated at the South African Nuclear Energy Corporation (Necsa). The process involved the injection of a stream of zircon concentrate through a plasma so that the zircon particles rapidly melt and solidify. The product, referred to as plasma dissociated zircon, is a convenient starting material for the preparation of zircon pigments due to the mixture of ZrO_2 and SiO_2 in a weight ratio of about two to one (equimolecular proportions) which is the normally accepted method to produce zircon pigments. The structure of the PDZ material consists of finely divided crystals of monoclinic ZrO_2 in a SiO_2 matrix. The chemical composition (determined by X-Ray fluorescence spectroscopy) of the prime grade zircon, as well as the dissociated product is given in Table 1. It is evident from the chemical analysis that that ZrO_2 and SiO_2 ratio of the PDZ material compared to the zircon material stays unchanged during the dissociation process within the analytical error of the XRF technique.

PDZ material with different percentages dissociation was produced to investigate the effect of the percentage dissociation on the final colour of the pigment product. This was achieved by applying a slower feed rate of the zircon through the plasma system, which resulted in a higher percentage dissociation of the PDZ material.

2.1. The effect of the particle size of the PDZ material before calcining

PDZ material with a dissociation of 90% was used to investigate the effect that the initial particle size of the feed ma-

Table 1
Chemical analyses of zircon and PDZ

Composition	Zircon	PDZ
ZrO_2 (+HfO_2) (%)	66.7	66.6
SiO_2 (%)	32.6	32.7
TiO_2 (%)	0.12	0.12
Fe_2O_3 (%)	0.06	0.06
Al_2O_3 (%)	0.07	0.09
Cr_2O_3 (%)	<0.01	<0.01
MgO (%)	0.01	0.02
CaO (%)	0.05	0.04
P_2O_5 (%)	0.10	0.09
U + Th (mg/kg)	<500	<500

Table 2
Description of series 1 samples

Series number	Sample number	Description of sample	Particle size—d_{50} (μm)
1	Y1a	PDZ pre-milled before calcining: yellow	3.5
1	Y1b	PDZ pre-milled before calcining: yellow	6.0
1	Y1c	PDZ pre-milled before calcining: yellow	8.2
Ref	Yref	PDZ unmilled before calcining: reference	108
1	B1a	PDZ pre-milled before calcining: blue	3.5
1	B1b	PDZ pre-milled before calcining: blue	6.0
1	B1c	PDZ pre-milled before calcining: blue	8.9
Ref	Bref	PDZ unmilled before calcining: reference	108

terial has on the colour hue of the yellow and blue pigments after application on a ceramic tile. Table 2 shows the first series of pigment samples that was prepared from the PDZ material, which was milled to a mean particle size (d_{50} value) of 3.5, 6.0 and 8.2 μm, respectively for the yellow pigments, and to a mean particle size of 3.5, 6.0 and 8.9 μm, respectively for the blue pigments. Milling was done by means of a wet milling process in a planetary ball mill by using yttria stabilized zirconia as milling media to eliminate any contamination during the milling process. Using the pre-milled PDZ samples as feed material, Pr-yellow and V-blue zircon pigments were produced and applied on a ceramic tile.

For comparison purposes, Pr-yellow and V-blue pigments were produced by using unmilled PDZ material prior to the calcining process with a mean particle size of 108 μm as feed material.

After the calcining process, the pigments were washed with a near boiling HCl/water mixture to remove the excess mineralizers and the dopant oxides that were not incorporated into the zircon crystal lattice. A 6% pigment/glaze mixture was prepared for the yellow pigments (samples Y1a–Y1c) and the blue pigments (samples B1a–B1c), after which it was applied on a bisque ceramic tile by means of a high-pressure spray gun.

The unmilled PDZ material that was used as feed material to produce yellow (Yref) and blue pigments (Bref) prior to the calcining step, Table 2, were subsequently milled to a particle size of 7–8 μm before it was applied on a ceramic tile and the colour assessed on the grounds of L^*, a^*, b^* parameters.

2.2. The effect of the percentage dissociation of the PDZ material

Four samples of PDZ material were prepared with different percentages dissociation to investigate the effect of dissociation on the colour hue of the yellow and blue pigments. Samples were prepared with a 74.7%, 82.4%, 90.0% and 95.7% dissociation. Table 3 shows the second series of Pr-yellow (samples Y2a–Y2d) and V-blue zircon pigments (samples B2a–B2d) produced without any milling of the different PDZ samples prior to the calcining process. After the calcining process, the pigments were washed and milled to a mean particle size of 7–8 μm before application on a ceramic tile. Both the Pr-yellow and the V-blue pigments were then compared with that of industrial zircon pigments commonly used in the ceramic industry.

Table 3
Description of series 2 samples

Series number	Sample number	Description of sample
2	Y2a	PDZ—74.7% dissociation: yellow
2	Y2b	PDZ—82.4% dissociation: yellow
2	Y2c	PDZ—90.0% dissociation: yellow
2	Y2d	PDZ—95.7% dissociation: yellow
2	B2a	PDZ—74.7% dissociation: blue
2	B2b	PDZ—82.4% dissociation: blue
2	B2c	PDZ—90.0% dissociation: blue
2	B2d	PDZ—95.7% dissociation: blue

The samples were demarcated as follows:

- a letter that is relative to the colour of the pigments (Y: yellow, B: blue);
- a number that is relative to the experiments (1: series 1, 2: series 2);
- yellow and blue zircon pigments using unmilled PDZ material prior to calcining process are indicated as Yref and Bref.

The colour of the zircon pigments was assessed on the grounds of L^*, a^* and b^* parameters, calculated from the diffuse reflectance spectra, through the method recommended by the Commission Internationale de l'Eclairage (CIE).[15] According to the method the parameter L^* represents the brightness of a sample; a positive L^* stays for a light colour while a negative one corresponds to a dark colour; a^* represents the green (−) → red (+) axis and b^* the blue (−) → yellow (+) axis.

Particle size measurements were carried out on a Sedigraph 5100 particle size analyser supplied by Micromeritics.

3. Results and discussion

3.1. The effect of the particle size of the PDZ material before calcining

Table 4 reports the CIE L^* a^* b^* parameters of the series 1 Pr-yellow zircon pigments of the PDZ material that was pre-milled to a mean particle size of 3.5, 6.0 and 8.2 μm prior to the pigment calcining step. The yield of the yellow colour is described by the value of the b^* parameter; the more positive the corresponding b^* value, the more intense the colour hues. The results showed that the coarser the PDZ

Table 4
CIE L^* a^* b^* parameters of Pr-yellow pigments—pre-milled PDZ samples

Sample	L^*	a^*	b^*
Y1a	82.9	−2.3	37.1
Y1b	81.6	−1.7	56.9
Y1c	80.4	−1.3	58.5
Yref	78.6	1.8	75.8

material before the pigment calcining step, the higher the corresponding b^* positive parameter. A b^* value of 37.1 of sample Y1a is obtained when pre-milled to 3.5 μm compared to the value of 56.9 for sample Y1b which was milled to 6.0 μm and a value of 58.5 for sample Y1c which was milled to 8.2 μm. Better results, in terms of the hue of the yellow colour, are therefore obtained with a coarser PDZ material prior to the pigment-calcining step. As concerns the effect of no milling of the PDZ material before the calcining step, sample Yref, the advantage can clearly be seen in the much higher b^* positive value of 75.8 achieved. The L^* parameter, which represents the brightness of a sample, decreased from 82.9 for sample Y1a to 81.6 for sample Y1b and to a value of 80.4 for sample Y1c. A value of 78.6 was achieved for the unmilled PDZ sample prior to the calcination stage, sample Yref, which is indicating a lower brightness obtained.

Table 5 reports the CIE L^* a^* b^* parameters of the series 1 V-blue zircon pigments of the PDZ material that was pre-milled to a mean particle size of 3.5, 6.0 and 8.9 μm prior to the pigment calcining step. The yield of the blue colour is described by the value of the b^* parameter, the more negative the corresponding b^* value, the more intense the colour hues. A b^* parameter of −6.9 for sample B1a is obtained when the PDZ material is pre-milled to 3.5 μm compared to the value of −3.8 for sample B1b which was milled to 6.0 μm and a value of −3.6 for sample B1c which was milled to 8.9 micrometer. The b^* parameter of −13.5 for sample Bref is significantly higher which is again indicating the advantage of using PDZ material with no pre-milling prior to the pigment calcining step. The L^* parameter decreased from 67.8 for sample B1a to 67.3 for sample B1b and 63.2 for sample B1c. A significantly lower L^* value of 53.8 was achieved for the unmilled PDZ sample prior to the calcination stage; sample Yref, which is indicating a lower brightness obtained.

3.2. The effect of the percentage dissociation of the PDZ material

Tables 6 and 7 report the CIE L^* a^* b^* parameters of the series 2 Pr-yellow and V-blue zircon pigments of the PDZ material with a dissociation of 74.7%, 82.4%, 90.0% and 95.7%. The pigments were produced by mixing the PDZ material with a mean particle size of 108 μm together with the dopant oxide and the mineralizer, and then calcined in a muffle furnace to produce the raw pigment product. The product was then washed and milled to a mean particle size of 7–8 μm before it was applied on a ceramic tile. No pre milling of the PDZ material took place before the calcining step. For the yellow pigments, a b^* positive parameter of 65.6 (sample Y2a), 68.3 (sample Y2b), 75.8 (sample Y2c) and 82.3 (sample Y2d) were obtained with the PDZ dissociation of 74.7%, 82.4%, 90.0% and 95.7%, respectively. A b^* parameter of 79.1 was obtained for an industrial Pr-yellow zircon pigment after application on a ceramic body which is lower than that of the 95.7% dissociated pigment product, indicating a lower colour intensity. For the blue pigments, a b^* negative parameter of −7.8 (sample B2a), −11.5 (sample B2b), −13.5 (sample B2c) and −17.9 (sample B2d) were obtained with the PDZ dissociation of 74.7%, 82.4%, 90.0% and 95.7%, respectively. Compared to the industrial V-blue zircon pigment, the b^* parameter of the PDZ material with a dissociation of 95.7% resulted in higher value of −17.9 compared to that of −17.3. Better results, in terms of hue of yellow and blue colour, are therefore obtained with an increase in the percentage dissociation of the PDZ material.

The L^* parameter, which is indicating the brightness of the sample, is decreasing from 79.3 for a 74.7% dissociation (sample Y2a) compared to 77.3 (sample Y2d) for a PDZ material with a 95.7% dissociation. This in fact betters the L^* parameter of 78.7 achieved with the industrial Pr-yellow pigment. The same tendency is observed for the blue pigments where the L^* parameter decreases from 57.3 (sample B2a) for a 74.7% dissociation to 50.7 (sample B2d) for a PDZ material with a 95.7% dissociation.

Table 6
CIE L^* a* b^* parameters of Pr-yellow pigments—percentages dissociation

Sample	Dissociation	L^*	a^*	b^*
Y2a	74.7%	79.3	0.3	65.6
Y2b	82.4%	79.6	0.6	68.3
Y2c	90.0%	78.6	1.8	75.8
Y2d	95.7%	77.3	4.8	82.3
Ind. yellow	–	78.7	1.3	79.1

Table 7
CIE L^* a* b^* parameters of V-blue pigments—percentages dissociation

Sample	Dissociation	L^*	a^*	b^*
B2a	74.7%	57.3	−18.2	−7.8
B2b	82.4%	55.0	−18.9	−11.5
B2c	90.0%	53.7	−19.9	−13.5
B2d	95.7%	50.7	−20.3	−17.9
Ind. blue	–	49.0	−21.9	−17.3

Table 5
CIE L^* a^* b^* parameters of V-blue pigments—pre-milled PDZ samples

Sample	L^*	a^*	b^*
B1a	67.8	−17.1	−6.9
B1b	67.3	−16.9	−3.8
B1c	63.2	−17.9	−3.6
Bref	53.8	−19.9	−13.5

4. Conclusions

Pr-yellow and V-blue zircon pigments were prepared by the direct use of plasma dissociated zircon sand. The effect of milling and percentage dissociation of plasma dissociated zircon on the colour of Pr-yellow and V-blue pigments has been established. The CIE L^* a^* b^* parameters showed that pre-milling of the PDZ material prior to the pigment calcination stage had a negative effect on the final colour of the yellow and blue zircon pigments after application on a ceramic tile. Better results, in terms of the hue of the yellow and blue colour, are obtained with a coarser PDZ material prior to the pigment calcination stage. The study has highlighted the advantage of using coarse PDZ material as feedstock for the production of yellow and blue zircon pigments. No pre milling of PDZ material prior to the calcination stage are therefore necessary for the production of high quality Pr-yellow and V-blue zircon pigments.

It was found that the percentage dissociation of the PDZ material was a very important parameter influencing the colour of the zircon pigments. Figs. 1 and 2 show that better results, in terms of hue of the yellow and blue colour, were obtained with an increase in the percentage dissociation of the PDZ material. This is due to less undissociated zircon material that is present during the calcination stage, which adversely affect the colour intensity of the zircon pigments. This work has highlighted that PDZ used as feed material with a dissociation of not less than 94% for the yellow and 95% for the blue zircon pigments, is comparable in terms of the brightness and colour hue with that of industrial Pr-yellow and V-blue zircon pigments commonly used in the ceramic industry.

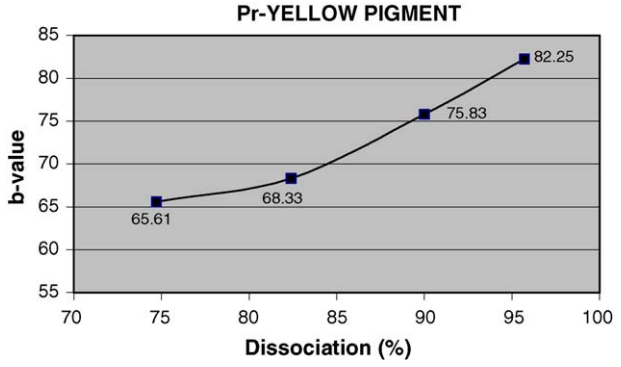

Fig. 1. Influence of the percentage dissociation of PDZ on the colour of Pr-yellow pigments.

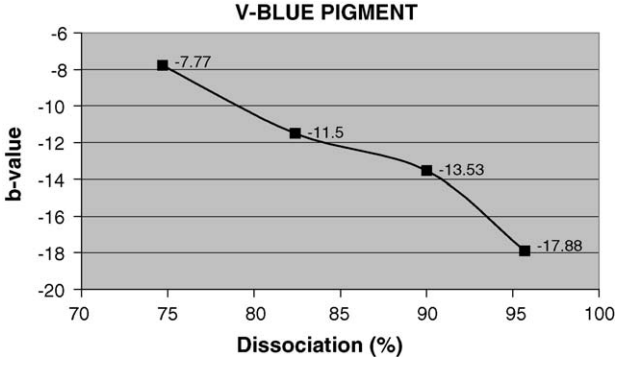

Fig. 2. Influence of the percentage dissociation of PDZ on the colour of V-blue pigments.

Acknowledgements

The authors would like to express their gratitude to the Innovation Fund of the National Research Foundation of South Africa for the funding of the project. The assistance of Mr. J.L. Havenga and the Plasma Technology group at the South African Nuclear Energy Corporation (Necsa) with regard to the experimental work on the dissociation of the zircon is gratefully acknowledged.

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