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

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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

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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