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Micronizing ceramic pigments for inkjet printing: Part I. Grindability and particle size distribution

Gülşen L. Güngör[a,b], Alpagut Kara[a,b], Magda Blosi[c], Davide Gardini[c], Guia Guarini[c], Chiara Zanelli[c], Michele Dondi[c,*]

[a]SAM, Seramik Araştırma Merkezi (Ceramic Research Center), 26470 Eskişehir, Turkey
[b]Department of Materials Science and Engineering, Anadolu University, Iki Eylül Kampus, Eskişehir 26555, Turkey
[c]CNR-ISTEC, Istituto di Scienza e Tecnologia dei Materiali Ceramici, Via Granarolo, 64, 48018 Faenza, Italy

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Abstract

Inkjet printing is increasingly used to decorate ceramic tiles, with pigmented inks in most cases. These inks are manufactured by micronizing conventional ceramic pigments down to median diameters of 0.2–0.6 μm. Although such a size reduction theoretically offers significant advantages in terms of the optical and fluid mechanical properties of the pigment particles, still unanswered questions concern color strength and the efficiency of the milling process. The present study aimed to elucidate how micronizing influences the pigments' particle size and shape, and the specific surface area. For this purpose, industrial pigments were selected to represent crystal structures of different density, hardness, cleavage and fracture toughness, i.e. rutile, spinel and zircon. The pigments were micronized in a pilot plant, controlling carrier, solid load, dispersant type and concentration, rotation speed, amount and size of grinding media, temperature and milling time. The pigments were characterized by particle size distribution (laser diffraction and dynamic light scattering) and morphology (SEM). The results revealed a different behavior of the pigments during micronization, with changes in particle size and shape partially consistent with the literature. The pigments' grindability differed: zircon $>$ rutile $\geq$ spinel.

Keywords: A. Milling; B. Grain size; B. Microstructure-prefiring; C. Colour; D. Transition metal oxides

1. Introduction

Drop on Demand Ink-Jet Printing (DOD-IJP) is increasingly used worldwide to decorate ceramic tiles. The method's rapid and widespread diffusion stems from several advantages of digital technology, e.g. non-contact decoration, rational ink management, the opportunity to print textured surfaces, high-quality images, a more efficient management of the decoration department, greater control over the production line, space savings and lower costs (shorter time to market, no need for screens, less wastage of inks and additives, etc.) [1,2]. In December 2010 the total number of digital printing machines installed around the world was 538, but this figure had risen to 1054 by the end of 2011, and to 1537 by the end of 2012 (with an average increase of 500 units a year). Then another 1367 were added in 2013 alone, bringing the total up to 2904 by early 2014 (+89% in 13 months). The number of countries adopting digital decoration in tilemaking increased from 24 in 2010 to 48 in 2013. The countries that turned to this technology early on, such as Spain (with over 300 printers currently in use) and Italy (more than 250 printers), can now be considered more or less "saturated", so the technology's exponential growth is now concentrated in non-European countries, particularly in Asia [3,4].

The inks used in DOD-IJP generally contain ceramic pigments as colorants, together with carriers and additives to improve their performance and stability over time [5–7]. Research and development have made ink manufacturing an extremely dynamic sector, and carriers belonging to various chemical families have been used to formulate ceramic inks. Cooperation with solvent

*Corresponding author. Tel.: +39 546 699728; fax: +39 546 46381.
E-mail address: michele.dondi@istec.cnr.it (M. Dondi).

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and additive suppliers led to ink manufacturers converging towards similar technological solutions in terms of carriers. These solutions changed several times in the space of a few years, from naphthalenes to paraffin oils, to glycol ethers, to fatty acid esters, to mixed carriers (oil + ester and recently organic solvents + water). Each range of products includes a main solvent and low- and high-viscosity cosolvents (for modulating the ink's physical properties), dispersants, and cleaners. The strong competition is encouraging print head manufacturers to make substantial changes to the types of print head used to decorate ceramics so that they can apply large quantities of ink. The present goal is to enable the use of high-polarity liquids, thereby considerably expanding the range of materials available. The ultimate target is a completely water-compatible ink that is eco-sustainable and can be deposited in relatively thick layers for decoration and glazing [4,7].

Ceramic inks are currently prepared by means of a high-energy ball milling process to reduce the size of the particles of pigment from micrometric (a typical jet mill output reaches diameters in the range of 5–10 μm) to submicrometric (commonly involving diameters (d_{50}) of 0.2–0.5 μm). To prevent print head nozzles from clogging, the most important requirement is to ensure that 99% of the pigment particles are less than 1 μm in diameter [5,7]. This demands a very different approach to the comminution stage: from controlling *average particle size* during jet milling (conventional pigments) to ensuring that nearly *all particles* are submicrometric (micronized pigments). The comminution process is known to depend mainly on the specific energy input, which is the total energy supplied to the grinding chamber in relation to the mass of product [8–11]. Other factors influence the outcome of comminution too, such as the size of the grinding media, the use of deflocculants, and agglomeration phenomena, but the emphasis on targeting the 99th percentile of the granulometric curve during milling has turned pigment micronizing into the most energy-consuming comminution process per unit weight of product [11,12].

Despite a thorough understanding of the properties of inks for DOD-IJP (viscosity, surface tension, fluid mechanics numbers) that govern their behavior during jetting, spreading and storage [13,14], little is known about what happens to the pigments during micronization [15]. The behavior of products in suspension in the submicronic particle size range is more influenced by greater particle–particle interactions, which may prompt the spontaneous agglomeration of pigment particles, thereby increasing the ink's viscosity [8,10,14,16,17].

There is a large body of literature on mechanochemical synthesis/alloying by means of high-energy ball milling, including some extensive reviews [18,19]. Most papers deal with metals and alloys, however, while our knowledge of how oxides behave is less substantial [20,21]. Under high-energy grinding conditions, brittle materials like ceramic pigments have different characteristics from metals. The grindability of brittle mineral powders reaches a certain particle size limit, below which further fracturing is impossible [16,22]. It has been suggested that this limit is due to extremely small particles undergoing plastic deformation instead of fracturing and the greater cohesion between finer particles leads to aggregation or phase changes in their surface layers [10,17,22,23].

The aim of the present work was to follow what happens to pigments during micronization, and its effect on subsequent steps in the ceramic tile-making process. The study is divided into two parts: the first deals with particle size distribution and grindability under high-energy ball milling; the second concerns phase composition, and the optical and technological properties of micronized pigments. Three crystal structures were considered as representative of the ceramic pigments used for DOD-IJP: zircon, spinel and rutile. Industrial processing (high-energy ball milling, applying glaze, and firing) was simulated on a laboratory scale, and the pigments were accurately characterized at each processing step.

2. Experimental

Industrial pigments were selected to represent crystal structures with different physical properties relevant during comminution, as density, hardness, cleavage, elastic moduli and fracture toughness (Table 1): zircon (TZ), spinel (BS) and rutile (OR). In particular, vanadium-doped turquoise zircon ($ZrSiO_4$:V) [30,31], a black pigment with composition in the Co–Cr–Fe–Mn–Ni system [32,33] and an orange–yellow pigment doped with chromium and antimony (TiO_2:Cr,Sb) were considered [34,35].

The micronization process was simulated in a pilot plant (Netzsch Labstar LS1) keeping carrier (distilled water), solid

Table 1
Average physical properties of ceramic pigments under investigation.

Property	Unit	Zircon	Spinel (chromite)	Rutile	Source
Cleavage	–	{1 1 0} indistinct	None observed	{1 1 0} distinct, {1 0 0} less distinct	[24]
Fracture	–	Conchoidal	Irregular-uneven, sub-conchoidal	Irregular-uneven, sub-conchoidal	[24]
Density	g cm^{-3}	4.6	4.7	4.1	[24]
Mohs hardness	1	7½	5½	6½	[24]
Vickers hardness	kg mm^{-2}	2090	1036	974	[25]
Fracture toughness	MPa m$^{1/2}$	2.5	1.8	2.3	[26,27]
Bulk modulus	GPa	224	203	216	[28]
Elastic modulus	GPa	200	267	285	[27,29]
Poisson coefficient	1	0.27	0.28	0.28	[27,29]
Bond work index	kW h t^{-1}	40	13	12	[25]