WHAT HAPPENS TO CERAMIC PIGMENTS DURING INK MICRONIZATION? A TALE OF PHASE COMPOSITION, GRINDABILITY, MICROSTRUCTURE AND OPTICAL PROPERTIES

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ABSTRACT

Nowadays, ceramic decoration is being industrially carried out mainly by inkjet printing (IJP). The advent of digital decoration has changed the technological requirements of pigments and the way they are obtained. Ceramic pigments must be micronized (median particle diameter d50 ~300 nm) to fulfil IJP and shelf-life requirements. Particle size distribution plays a crucial role for ink compatibility and the final application. In this respect, pigment grindability is a key parameter which has strong repercussions on tinctorial strength, mechanical properties, and degree of amorphization of the pigment crystal structure. The reasons behind different pigment behavior during milling are still unknown. In order to deeply investigate the relationship between crystal properties and milling effects, five pigments with distinct physical properties and different phase compositions (zircon, spinel, malayaite, olivine, and eskolaite as the main constituting phase) were selected. Model inks, characterized by a different starting particle size, were prepared and underwent lab-scale stirred media milling reproducing industrial micronization conditions. Milling evolution was followed by determining particle size distribution (laser diffraction) and energy demand (mill electricity consumption). The effect of the process on phase composition and crystal structure parameters was followed by XRPD-Rietveld analysis. Furthermore, to define the changes in color saturation, micronized pigments were characterized by optical spectroscopy (DRS).

Finally, to point out the possible involvement of different mechanisms during the milling process, a detailed microstructural characterization was performed (SEM). Every pigment exhibits a distinct grindability with non-linear trends of comminution rate and specific energy consumption with particle size. Regardless of the amount of energy involved, only a limited amorphization is observed, and a correlation between the crystallite size and microstrain is highlighted. Optical spectra suggest a specific effect of milling for each pigment, sometimes entailing the formation of new chromophore environments (e.g., in Cr-doped malayaite and Co-olivine). Microstructures hint at different mechanisms acting during comminution, with particle shapes proper of brittle fracture versus plastic deformation or fragments agglomeration. Preliminary results draw a complex dependence of grinding efficiency on the pigment mean bulk modulus, with a different relationship of particle size reduction, optical properties and tinctorial strength on milling cycles.

INTRODUCTION

The decoration step is a key aspect in the ceramic production process, which is strongly affected by the market-driven rapid changes in terms of required colors and motifs. The amount of colorants globally used in ceramics, only for tile production, represents over 80% of the global demand for ceramic pigments and dyes, making the sector a driving force in colorant manufacturing research [1]. Inkjet printing technology (IJP), thanks to its production flexibility, has almost totally replaced the traditional ceramic decoration technology [2]. Furthermore, the introduction of IJP has deeply changed the technological pigment requirements [2,3]. A micronization degree which ensures that >99% of the pigment particles are less than 1 μm in diameter is a necessary requirement for IJP technology [3]. Comminution of ceramic pigments is a key issue for ink production that has strong repercussions on several aspects, such as the tinctorial strength, mechanical properties, and degree of amorphization of the pigment crystal structure, modifying aesthetic performances as well. For this reason, the pigment micronization process plays a crucial role in defining final product performance, also affecting yield and cost of inks production. In the case of ceramic pigments, the studies dealing with their micronization are limited [4-8]. Key points for a better comprehension of pigment behavior during the comminution process, besides the technical solutions, are the pigment crystal structure, the degree of pigment amorphization, as well as the possibility to predict and control the energy consumption.

Furthermore, the effect of the feed size and particle evolution – in terms of size and shape, as well as occurrence of plastic deformation or particle agglomeration – needs to be fully understood. The goal of this work is to disclose the mechanisms occurring during ink micronization for various pigments having different phase composition, and the effect of these mechanisms on the coloring performance, in order to modulate the milling process and better match the industrial decoration requirements.

EXPERIMENTAL

For this study five different pigments were selected (praseodymium-doped zircon (tetragonal), Zn-Fe-Cr-Al based spinel (cubic), chromium-doped malayaite (monoclinic), olivine (orthorhombic) and eskolaite (trigonal) as the major phases for each pigment) and used to prepare oil-based inks. The inks were designed to replicate typical industrial formulation, with ethers of fatty acids as carrier and a solid load variable according to the pigment. The micronization process was carried out by a circulation type agitator bead mill (Netzsch, Labstar) using Y-ZrO_2 media. At different times, set to obtain the same particle size for all pigments, several ink fractions were collected. Reference milled sizes were selected at about 0.59, 0.40, 0.35 and 0.27 μm. Particle size was measured by laser diffraction (Fritsch, Analysette 22). Milling energy consumption was measured during the whole process, considering the different milling steps. In order to characterize the pigments, the organic fraction was removed from inks by calcination at 500°C. Complete combustion was verified by TG/DTA analysis. The residual inorganic part was characterized and compared with the starting system.

X-ray powder diffraction was performed on a Bruker D8 Advance diffractometer working in Bragg-Brentano geometry and equipped with a LynxEye XE silicon strip detector set to discriminate Cu $K\alpha_{1,2}$ radiation. Data were collected in the 5-90° 2θ angular range with step size of 0.02° 2θ and a counting time of 1 s per step. Qualitative phase analysis was performed by means of the Bruker AXS EVA software (v.5), while each collected X-ray powder diffraction pattern was Rietveld refined by means of the fundamental-parameter approach (TOPAS v.5.0). All the identified phases were modeled by carrying out multiphase refinements in which only the scale factor, unit-cell parameters, and the crystallite size were varied.

The pigment microstructure evolution was observed by a scanning electron microscope (FEG-SEM, Zeiss, Sigma).

Chromatic appearance was assessed by adding the pigment into glazes (10 wt%), dry mixing and uniaxial pressing. The obtained specimens were fired at 1200 °C using a fast industrial-like cycle and evaluated by diffuse reflectance spectroscopy (HunterLab Miniscan MSXP4000, 400–700 nm, D65 standard illuminant, 108 observer, white glazed tile reference x = 31.5, y = 33.3) and expressed as CIE-Lab coordinates: L* (100 = white, 0 = black), a* (+ = red, - = green), b* (+ = yellow, - = blue).

UV–vis–NIR spectroscopy was performed on both pigments and pulverized fired ones by diffuse reflectance with integrating sphere (Perkin Elmer, Lambda 750) in a variable range between 1800 and 2500 cm^{-1}, using $BaSO_4$ as reference.

RESULTS

PARTICLE SIZE AND MORPHOLOGY

In figure 1, the variation of the median particle size (A) and the energy consumption (B) during the milling process are reported for each investigated pigment. Spinel and eskolaite exhibit an initial particle size (feed size) that is coarser than the other pigments, depending on the specific industrial practice followed for every colorant (Fig 1A). Regardless of feed size differences, the comminution proves to be intrinsically dependent on the crystal structure of the micronized pigments.

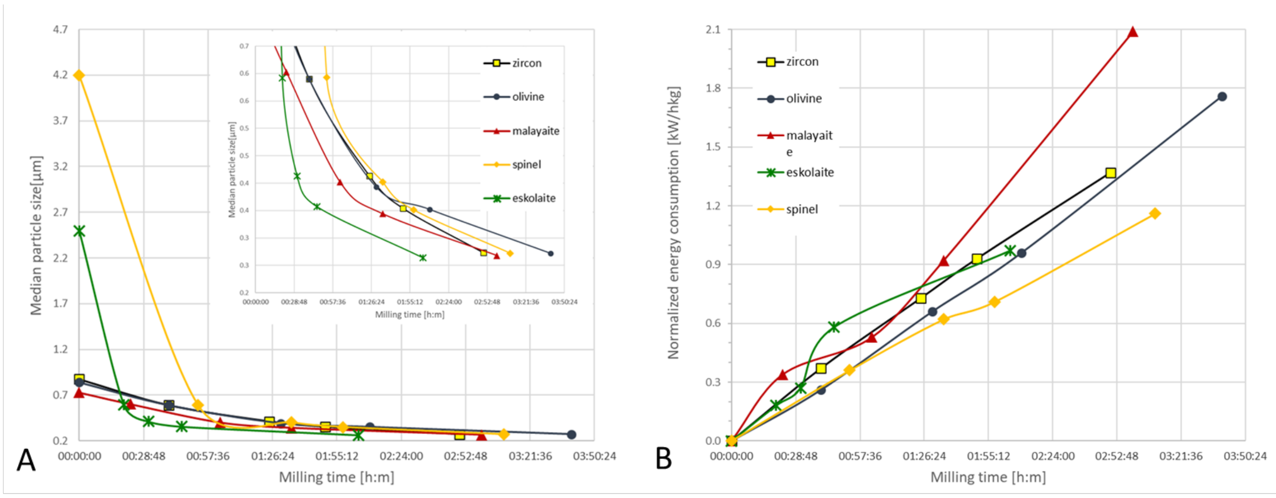

Fig. 1. *Median particle size (A) and specific energy consumption (B) as a function of milling time.*

With the exception of zircon, whose particle size variation scales almost linearly with milling time, the investigated pigments undergo an important size drop down to a particle size between 0.40-0.35 µm (an important change in the milling time *vs*. median particle size curve slope is observed in Fig. 1A), then a slower particle size variation occurs with an extent that depends on the specific system. Such a sudden dimensional change may suggest a variation in the mechanism involved in particle comminution [9]. Looking at the required energy demand as a function of milling time (Fig 1B), sublinear trends are observed for all the investigated systems, emphasizing that time and energy are closely related. About malayaite and eskolaite, a slope rise and a reduction are clearly observed, suggesting the presence of two different phenomena involved in particle evolution.

The microstructural evolution for the different pigments at increasing milling time is reported in Fig. 2. The zircon starting powder shows the presence of coarse, sharp, and irregular particles and smaller fragments, clearly derived from brittle fracture given by the primary milling process [4].

The progressive milling led to a gradual size reduction where irregular and rough shapes are maintained.

In the olivine starting powder, which is characterized by particle sizes finer than zircon, the micronization generated an overall size reduction, and the formation of irregular particles. In regard to malayaite, the feed particle size is similar to that observed for olivine. Differently from previous systems, malayaite seems to undergo some particle agglomeration and plastic deformation of the newly formed fragments. In particular, at the end of the process the presence of flake-like particles can be observed [10]. In the case of spinel, the octahedral crystal habit can be easily identified in the starting system [4]. The progressive comminution led to irregular shapes accompanied by a limited number of flake-like particles, probably attributable to plastic deformation [10]. Also, eskolaite clearly exhibits the rhombohedral crystal habit, which was found in micronized particles as well, along with the presence of irregular fragments.

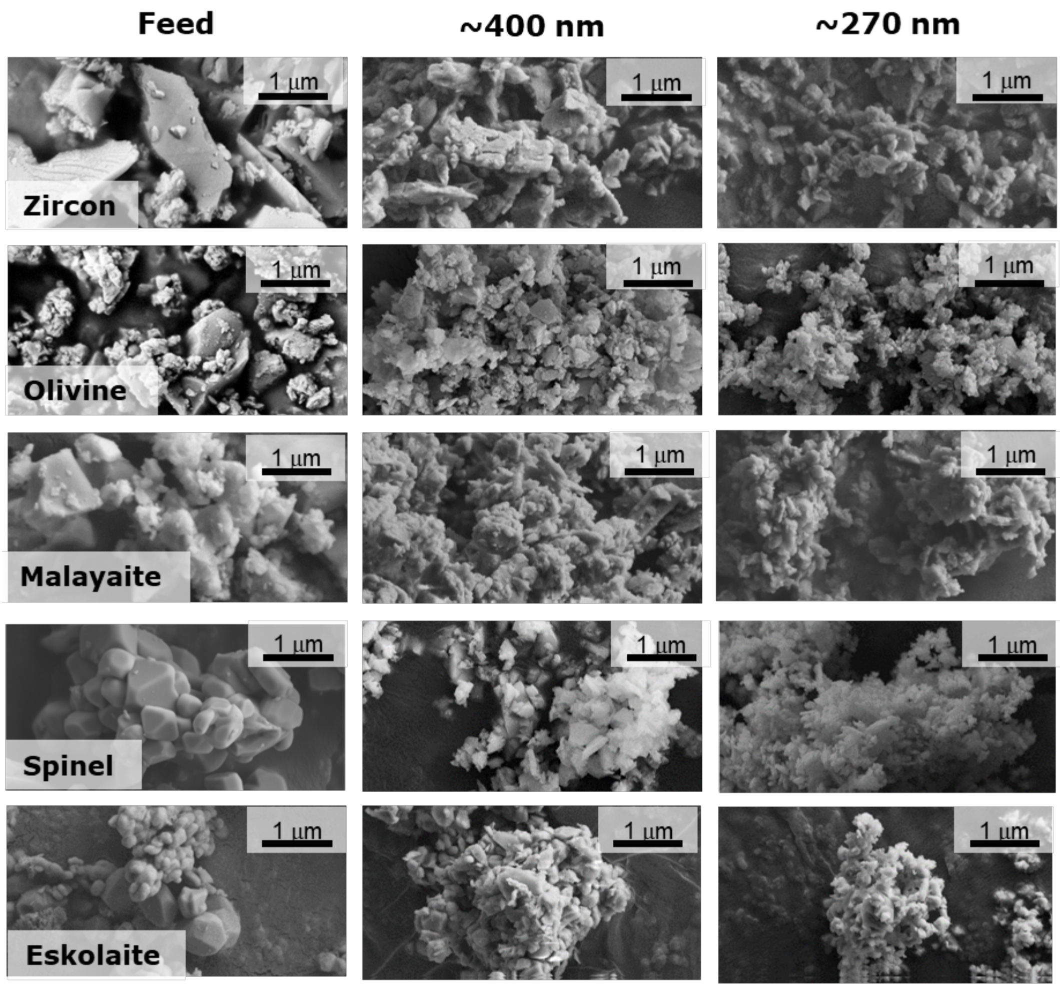

Fig. 2. *Microstructure of pigments for different median particle sizes*

PHASE COMPOSITION

The milling process changed the ink phase composition, modifying the amounts of crystalline and amorphous phases as a function of milling time (Fig. 3). Figure 3A reports the variation of crystalline phases for each pigment during the milling process. It may be noted that every system is polyphasic, except eskolaite (monophasic). This fact is due to the occurrence of some precursors left unreacted after the industrial pigment production. The spinel pigment shows a high and almost constant degree of crystallinity, with a limited increase in amorphous content throughout the comminution process. Zircon and olivine pigments present similar trends, with a reduction of the crystalline phases of about 8 wt%. Regardless of the different starting degree of crystallinity and phase composition, both pigments are characterized by a good compositional stability during the whole milling process. The greatest effect of the micronization process is observed for malayaite, which suffers from a drastic reduction of its degree of crystallinity. In the case of eskolaite, the loss of crystallinity (which pairs with the increase in amorphous content) scales linearly with the milling time (and median particle size reduction).

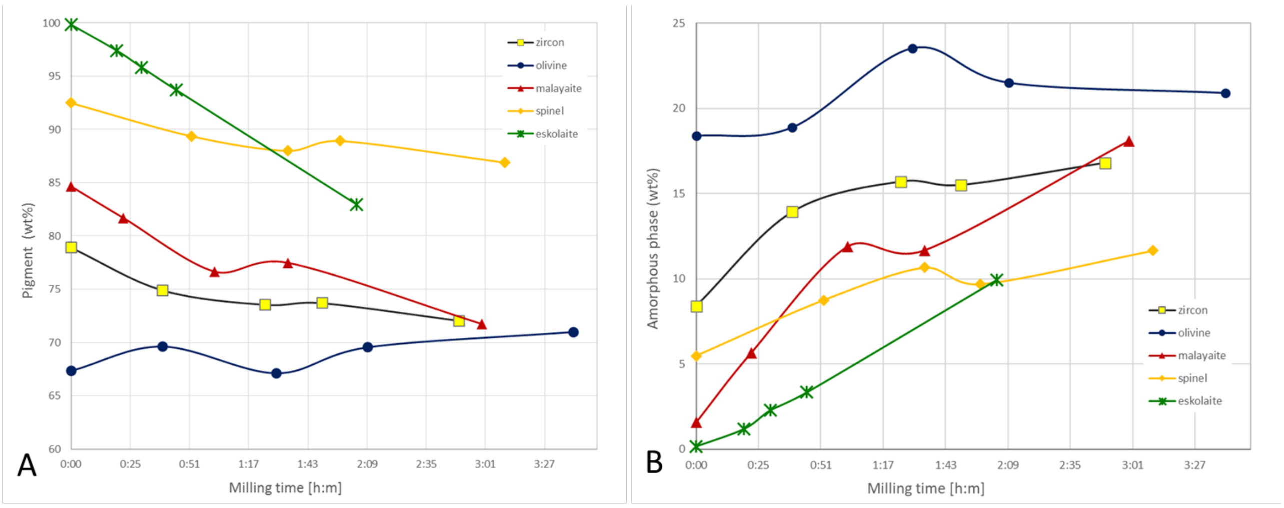

Fig. 3. *Degree of crystallinity (pigment wt%, A) and amorphous content (B) as a function of milling time*

OPTICAL PROPERTIES

The optical absorption spectra for the studied pigments are shown in figure 4, where only the main optical bands responsible for coloration are reported as a function of comminution.

In the case of zircon, a band centered at about 25000 cm^{-1} is observed that can be referred to a metal-ligand charge transfer transition (Pr^{4+}-O^{2-}), which is the main band responsible for the yellow coloration [11].

With the micronization progress, the intensity of the main absorption band gradually decreases and its onset energy shifts from 19900 cm^{-1} to 19600 cm^{-1}, leading to a progressive decrease in tinctorial strength.

In the spinel system, a strong absorbance reduction is observed from the micrometric particle size of the feed to that of the submicrometric milled samples. The bands observed at about 18000 cm^{-1} and 25250 cm^{-1} are attributable to Cr^{3+}, while those at 21550 cm^{-1} and 27900 cm^{-1} to Fe^{3+}, both in octahedral coordination. The recorded band intensities vary in a complex way with the milling process, so that further investigation is needed.

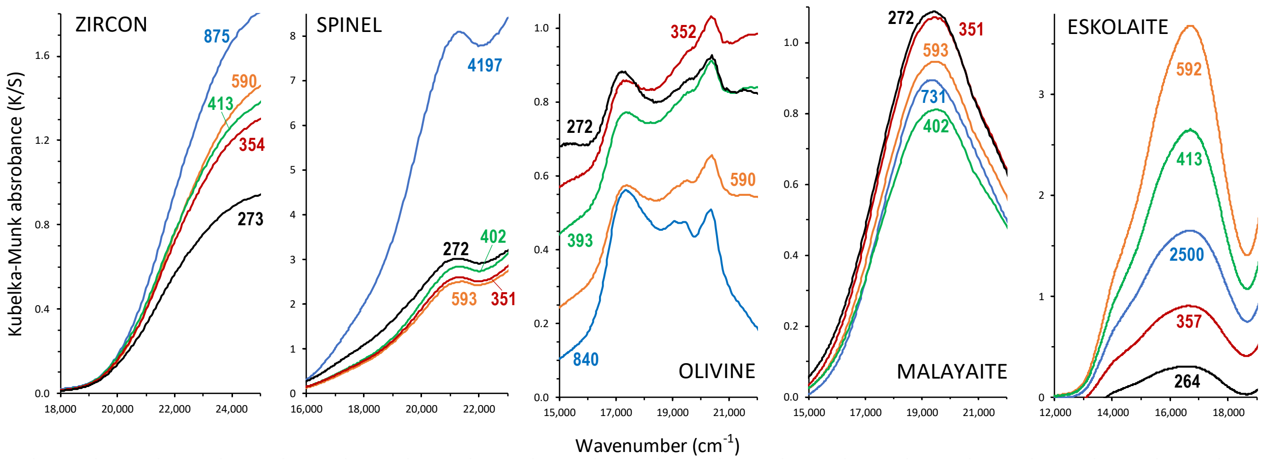

Fig. 4. *Main optical bands of pigments at increasing milling times. The numbers within each graph refer to the median particle diameter (in nm).*

In the case of olivine, the progressive micronization led to an increase in band intensity for multiple bands between 20450 cm^{-1} and 19190 cm^{-1}. Those bands correspond to spin-allowed transitions from $^4T_1(F)$ to $^4T_1(P)$ of octahedrally coordinated Co^{2+} at both M1 and M2 octahedral sites of the olivine structure [12, 13]. The reduction of the d_{50} value from 352 to 272 µm occurred with a decrease in reflectance. In contrast, an increase in band intensity with the milling process is observed at lower energy. In particular, the absorbance related to the $^4T_1(F) \rightarrow {}^4A_1(F)$ transition [14], centered at 17730 cm^{-1}, is enhanced by particle size reduction. Furthermore, the formation of two milling-derived bands in the 15000-16000 and 23000-25000 cm^{-1} ranges is consistent with the presence of Co^{3+} in octahedral coordination, which might be due to oxidation phenomena in the amorphous phase [15].

For malayaite, a linear relationship between particle size and band intensity is missing. Its spectra present an intense band, centered at about 20000 cm^{-1}, which is given by $^3T_{1g}(3F) \rightarrow {}^3T_{2g}(3F)$ Laporte-forbidden and spin-allowed transition of Cr^{4+} in octahedral coordination [16]. The change in intensity of this band along with comminution let suppose a variation of the Cr^{3+}/Cr^{4+} ratio in the octahedral site of malayaite.

The eskolaite spectra of the micronized pigment show a progressive intensity reduction of the Cr^{3+} bands in octahedral environment at 16350 and 21700 cm^{-1}. This effect can be traced also for the tiny peaks at 13900, 14500 and 19710 cm^{-1} that are attributable to the forbidden transitions $^4A_{2g} \rightarrow {}^2E_g$, $^4A_{2g} \rightarrow {}^2T_{1g}$ and $^4A_{2g} \rightarrow {}^2T_{2g}$, respectively.

DISCUSSION

As already highlighted, the relationship between grinding behavior and the pigment properties is not yet fully understood.

In figure 5, the variation of the reciprocal of the particle size after each milling step, expressed as the variation of the median particle diameter d_{50}, is reported. It is evident that the particle size reduction strongly depends on the structural features (i.e., crystal structure and chemical composition) of the micronized ceramic pigments. The different trends are representative of the pigments grindability. Similar to what has been reported in the literature, the particle size variation of zircon pigments scales almost linearly with the milling rounds, while the rate of the particle size variation for spinel pigments undergoes a gradual decrease. Spinel turns out to be more grindable than zircon. It must be taken into account that the energy supplied during the milling process is not only the one required to propagate brittle fractures, but is mainly dissipated in other phenomena, such as elastic and plastic deformations, heat, and other side effects characteristics of the milling process [17]. As already discussed, an abrupt change in the curve slope is observed in correspondence of a particle size range between 0.40 and 0.35 µm.

The general equation used to describe the generation of brittle fracture for solid particles during a comminution process is:

$$dE = -K \frac{dx}{x^{f(x)}}$$

where dE represent the infinitesimal energy required in comminution process, dx the infinitesimal size change, x the current particle size and $f(x)$ the exponent. When the particle size falls in the micrometric range, Rittinger's law, for which $f(x) \rightarrow 2$, is considered the most suitable in describing the energy demand involved in comminution process [9]. For size variation in the sub-micrometric range a change in the exponent value is here suggested.

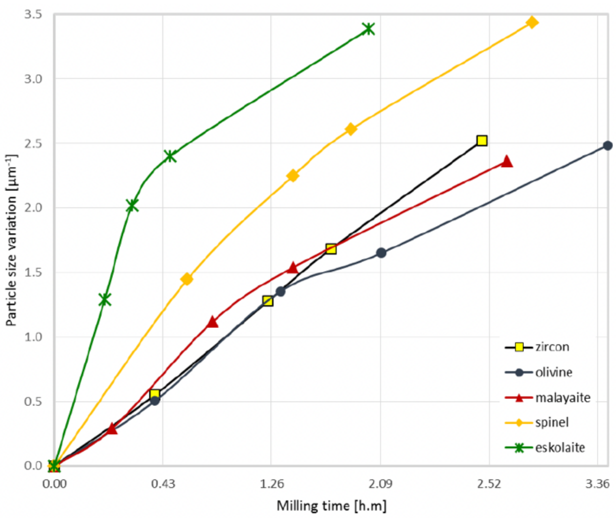

Fig. 5 *Particle size variation as a function of milling time.*

In general, for zircon-based pigment the effect of the milling process is quite clear. Micronization leads to a progressive particle size variation which required a proportional energy demand according to the literature [1]. This behavior suggests a comminution mechanism which mainly involves a brittle fracture mechanism, as qualitatively confirmed by SEM investigation. The progressive loss of Kubelka-Munk absorbance may be due to the physical effect of gradually finer particle sizes, which brings about increasing light scattering. The same effect is clearly observed for the micronized samples of eskolaite and spinel. However, their feeds have a much coarser median size, and a conspicuous change in the optical response occurred passing from the micrometric range to the submicronic field.

On the opposite side lies the case of malayaite, where the increase in milling time brings about a higher energy demand because of an evident particle plastic deformation and amorphization. This is associated to an intensity increase of the main optical band, presumably associated to changes in the oxidation state of chromium. Analogous phenomena seem to occur in the olivine-based inks, where additional bands induced by micronization led to a strong absorbance all over the visible range.

CONCLUSIONS

Inks micronization is a crucial step in matching the technological properties imposed by digital decoration, not only because it is responsible for reducing particle size to a submicronic scale but also because it induces strong changes in all the ink technological performances. In order to clarify the milling effects, a preliminary characterization of ink evolution during a comminution process was performed. The trend of the particle breakdown as a function of milling time mainly depends on the type of crystal structure. With the exception of zircon pigment, for which a linear relation can be identified, it is not possible to describe a common model for all the studied pigments. Plastic deformation and agglomeration mechanisms compete with the comminution process affecting the particle evolution in terms of size and microstructure. More complex and even less generalizable appear the optical properties, for which the mechanism involved in color generation and changes in the crystalline phases act differently for each system. A deeper investigation will be carried out to define the key aspects involved in ink property changes, to predict and control the technological performances by setting the milling process conditions.

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