The Porcelain Tile Dry Colouring Process

Variables Involved and Influence on Tile Properties.

Introduction

Porcelain tile has as a principal characteristic its very low apparent porosity (water absorption below 0.5%), which has led to the creation of a new product group (Blu) in standard ISO 13006. Among the different types of products included in the generic name porcelain tile, glazed porcelain tile has witnessed the greatest production growth in recent years [1-2]. This is due to its excellent technical properties, as well as to the relative ease of manufacture in conventional facilities intended for the fabrication of other glazed tiles (stoneware and earthenware tiles), compared with the greater investments required for unglazed porcelain tile manufacture, in which tile decoration takes place mainly in the pressing stage, and, in addition, an important part of tile production is polished.

One of the most widespread decorating techniques in the manufacture of unglazed porcelain tiles is dry colouring of the spray-dried powder used to make the body, which allows dry colouring to play a key aesthetic role in tile design. The dry colouring process basically consists of mixing the spray-dried powder with a pigment, so that the granules are covered by particles of the colorant. This process, which is conceptually simple, significantly modifies the microstructure of the green porcelain tile bodies, which are made up of a set of areas (spray-dried powder granules deformed during pressing) surrounded by a network of pigment particles.

Although this microstructural change is known to influence the green behaviour of the bodies, very few studies have addressed this subject [3]. This study has therefore examined the influence of some of the variables involved in the dry colouring process on the behaviour of these bodies during the different manufacturing process stages, as well as on the properties of the fired product. The variables considered were the type of spray-dried powder, powder particle size and moisture content, pigment type and content, pigment particle size, and fluidiser content.

Experimental

The materials used in the study were different spray-dried powders customarily used in the manufacture of porcelain tiles and calcined pigments of different nature. The particle size of one of these pigments (H1) was modified, as well as its fluidiser additive content. Tab. 1 details the characteristic diameters of the pigment particle size distributions (PSD), as well as their real density ($\rho_r$) and crystalline structure.

The work consisted of preparing dry-coloured spray-dried powders in which the spray-dried powder characteristics (type, particle size, and moisture content) as well as the pigment characteristics (nature, particle size, and fluidiser) were modified. A series of properties were determined of the green bodies (compaction diagrams and mechanical strength, RMS) made from the foregoing mixtures, and of the resulting fired pieces (bulk density, Dapc, linear shrinkage, LS, water absorption, WA, chromatic coordinates, and mechanical strength, RMc). In addition, observations were performed by optical microscopy and scanning electron microscopy (SEM), and the cohesiveness of some pigments was determined.

The methods used to prepare these mixtures, the forming and firing of the pieces, and the tests conducted are briefly described below.

Flowability

Pigment flowability was characterised using shear cells. The operation of these instruments, which are widely used to characterise powder flowability, is described in the references [4-6]. Shear cells measure, among other parameters, the cohesion (C) or shear strength of powder particle beds.

Preparation of the mixtures

The spray-dried powders and pigments were mixed by means of the device shown in Fig. 1. It consists of a cylinder with a series of radial deflectors into which the spray-dried powder and pigment are introduced. The cylinder is rotated in a frame for 120 seconds, so that the coating occurs when the powder enters into contact with the pigment, thanks to the radial walls that act as barriers, encouraging the mixing. This procedure provides a spray-dried powder similar to that obtained in industrial mixers.

Forming and Firing of the Test Pieces

Prism-shaped test pieces, 80 mm long, 20 mm wide, and about 7 mm thick were formed by uniaxial pressing at a moisture content of 5.5% (dry mass basis) and the pressure (P) needed to obtain a green porosity (e) of 26.0 ± 0.2 %, corresponding to the values customarily used in industrial practice. This required cal-

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**Table 1: Characteristics of the studied pigments**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Structure</th>
<th>$\rho_r$ (g/cm³)</th>
<th>$d_{10}$ (µm)</th>
<th>$d_{50}$ (µm)</th>
<th>$d_{90}$ (µm)</th>
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<td>0.7</td>
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<td>1.5</td>
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<td>6.6</td>
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<td>2.7</td>
<td>5.6</td>
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<tr>
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<td>Spinel</td>
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<td>4.5</td>
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</table>
calculating the real density of the mixtures and the corresponding compaction diagrams. When the test pieces had been dried in an oven at 110°C, some of these were fired in an electric laboratory kiln at different maximum temperatures with a residence time of 6 min. The heating rate was 25K/min and cooling was by forced convection. The bulk density of the green and fired pieces was determined by the dimensional method [7].

Mechanical Strength
Dry and fired mechanical strength were determined by the three-point bending test. The tests were conducted in a mechanical testing machine (Instron) at a constant strain rate of 1 mm/min. In the case of the dry test pieces, before performance of the tests, the pieces were placed in a vacuum desiccator until they reached ambient temperature, to keep their hydration to a minimum. Chromatic Coordinates
The chromatic coordinates (L*, a*, b*) were determined in a diffuse reflectance spectrophotometer using a D65 illuminant and standard observer at 10°.

Results and Discussion
Observation of the Pieces, Coloured Granules and Pigment Particles
In this section, cross-sections of the tiles obtained with the dry-coloured granules were observed by optical microscopy, while the granules and pigment particles were observed by SEM. Thus, in the former case it was sought to determine how the pigment particles were distributed in the piece and, in the latter, how the pigment particles were located on the spray-dried granule surface, and how the fluidiser was located on the pigment particles.

Fig. 2 presents a polished cross-section of a tile obtained from dry-coloured granules. It shows that the piece consists of a light-coloured matrix, corresponding to the cross-section of the spray-dried powder granules, in which some dark lines formed by the pigment particles may be observed. These lines come...
from the granule boundaries and joining surfaces. Depending on pigment content and characteristics (density, particle size etc.), the presence of regions rich in pigment will influence tile behaviour and properties, as set out further below.

Figs. 3, 4 depict industrially coloured granules with 1% H1 pigment. They show that there are numerous particles on the granule surface, the lighter-coloured ones corresponding to the pigment. These particles are distributed quite homogeneously across the entire granule surface; however, at larger contents, pigment agglomerations begin to be observed in preferential areas, for example, such as the characteristic void in spray-dried powder granules.

The dry colouring process used in the laboratory provided granules with an identical appearance to those of industrial granules, visually validating the colouring procedure described in section 2.

Fig. 4 presents the surface of the granule in greater detail, in which the pigment particles are observed to be practically deagglomerated, except for the harder aggregates originating from the calcination process. These results indicate that the industrial mixing process is quite effective.

Small quantities of fluidiser are customarily added to the pigments used to dry colour the spray-dried powder granules. These additives are mainly intended to decrease the cohesiveness between the pigment particles and, thus, increase their fluidability in order to improve pigment behaviour during proportioning, transport, and mixing with the spray-dried powder. Fig. 5 displays the appearance of Zr pigment crystals with fluidiser, using the secondary electron signal; the presence of certain lighter-coloured particles may be observed on the crystal surface, marked by circles, corresponding to the additive. This additive, in the percentage used in industrial practice, is unable fully to cover the pigment particle and accumulates mainly in the irregularities of the crystal surface and in inter-crystal voids. The fluidiser particles may thus be considered to act as spacers, positioning themselves between the pigment crystals, which favours crystal sliding and helps prevent crystall agglomeration.

**Cohesion Measurements**

Cohesion measurements were made of the industrial pigments, as well as of the H1 pigment, with different fluidiser contents (from zero to 4.0% mass). The variation of the cohesion of the different studied hematite beds with different fluidiser percentages has been plotted versus the applied pressure, in Fig. 6. It shows that, when pressure increases, the cohesion of all the studied beds increases. The effect of pressure decreases until it practically cancels out when the fluidiser percentage in the bed is raised. In addition, at the same applied pressure, cohesion decreases with fluidiser content.

The consolidation pressure or stress to which a powder is subjected during handling is not constant. Thus, the pressure that a powder undergoes during transport on a belt is not the same as the pressure undergone by a powder stored in a silo. The different levels of pressure to which a powder may be subjected during handling in the different industrial processing operations have been defined in Fig. 6.

In order to be able to compare the behaviour of different pigments and to quantify the effect of the fluidiser, since the pressure levels to which the pigments will be subjected during the proportioning and mixing operations are very low, it has been considered advisable to use the cohesion of these materials without normal stress, calculated as the ordinate
Process Engineering

Fig 10 left. Appearance of sample H1F observed by SEM.

Fig 11 right. Appearance of sample H1G observed by SEM.

Fig 12 left. Appearance of sample H1G observed by SEM.

Fig 13 right. SEM detail of a sample H1G agglomerate.

at the origin of the curves $C = f(\sigma)$ in Fig 6. These values, shown in Fig 7, indicate that for pigment H1 the increase in fluidiser content progressively decreases cohesiveness. This increase being more pronounced for the first fluidiser percentages (up to 1,5 %). Larger additive percentages do not significantly reduce cohesiveness, which indicates that suitable proportionning of the fluidiser will lie between 1 and 2 % for this pigment. This behaviour is consistent with industrial practice, where it has been verified that the absence of a fluidiser, in addition to adversely affecting the proportionning, makes it more difficult suitably to mix the pigment with the spray-dried powder granulate, giving rise to agglomerates.

The figure also presents the cohesiveness of the other tested pigment with 1,5 % fluidiser, showing that cohesion differs noticeably for the different studied pigments. This behaviour, which cannot be explained solely by considering average pigment particle size, needs further analysis since there are probably other parameters (particle size distribution, shape, fluidiser covering capacity, hygroscopicity, etc.), which also play an important role in this behaviour.

**Influence of Pigment Content**

The tests were conducted using the STD spray-dried powder and H1 pigment in percentages from 0 to 4,0 %, which cover the usual pigment range used in industry. Fig 8 shows the pressing pressure needed to keep the porosity of the green pieces steady as a function of pigment content, which was calculated from the corresponding compaction diagrams. It may be observed that as pigment quantity increases, the pressing pressure needs to be raised, the relation being of the exponential type. The increase in pressure is not important for the pigment percentages used in industry (for 2 % pigment, the pressure increase is just 10 kg/cm²); however, when the pigment percentage is raised to 4 %, the increase in pressure begins to become notable: for the studied pigment this was 40 kg/cm².

These results are consistent with the findings obtained elsewhere, where the increase in pressing pressure was related to the deficient packing displayed by the pigment particles which, as already indicated, are concentrated in certain regions of the piece (corresponding to the granule boundaries). In this case, for pigment percentages below 2,0 %, the increase in pressure was practically zero, because the pigment particles were individualised on the surface of the granules. This kept a highly porous pigment particle shell or layer from forming between the granules after pressing. In contrast, when the pigment quantity was 4,0 %, there were a great number of pigment particles on the granule surface, which led to the formation of a highly porous pigment particle shell or layer after pressing. The presence of these pigment-rich areas makes it necessary to increase the pressing pressure in order to improve overall tile compactness and thus compensate the high porosity of the pigment areas.

The influence of pigment content on tile dry mechanical strength is also
shown in Fig 8. It may be observed that the increase in pigment content produces a gradual decrease in mechanical strength, this tendency being more pronounced for pigment contents below 2.0%. Larger pigment contents do not lead to further reduction of mechanical strength. Since green tiles formed from spray-dried powders fracture preferentially along the inter-granule junctures [8] and the pigment is concentrated in these same areas, it may be concluded that the presence of the pigment has two effects: weakening of the inter-granule bonding forces and increased natural flaw size, which explains the observed decrease in mechanical strength [3].

With regard to the fusibility of the composition, no changes were detected in the maximum densification temperature (T_m) for this pigment, as Tab. 2 shows. The table also includes the mechanical strength values of the fired pieces (RMc), which show that there is a small loss of mechanical strength (12%) at a pigment percentage of 4.0%. The reason for this decrease could be related to the existence of pigment-rich areas, which sinter differently from the rest of the piece, and act as crack-initiating flaws. However, at the pigment quantities (< 2.0%) used in industrial practice, no significant changes should be observed in this property.

Finally, Fig. 9 shows the evolution of the chromatic coordinates with H1 pigment content. The most important feature of this figure is the colour saturation observed at 2.0% pigment content.

Influence of Spray-dried Powder Characteristics

In this section the influence of spray-dried powder type of composition, particle size, and moisture content were studied. It was observed that the use of spray-dried powders from different manufacturers did not appreciably influence the change in the behaviour and properties of the pieces made using this decorating technique, although some differences were detected during the drying stage (such as the appearance of small cracks), which stemmed from the characteristics of the spray-dried powder used and not from the dry colouring process.

The results corresponding to the influence of spray-dried powder particle size are presented in Tab. 3, which details the values obtained for the STD spray-dried powder with 1% H1 pigment (STD), and for this same sample prepared from the particle size fraction larger than 200μm (STD > 200) and smaller than 500μm (STD < 500). The results indicate that there are no appreciable differences between the tested samples, owing to the low percentage of granules smaller than 200μm and larger than 500μm customarily found in this type of spray-dried powder (below 15%).

Optical microscopy showed that as spray-dried powder moisture content rose, the powder's capacity to cover itself with pigment particles also increased. Thus, when the spray-dried powder contained no moisture, the pigment was concentrated almost exclusively in the granule void, whereas at larger moisture content the pigment particles were distributed more uniformly across the granule surface. However, it should be noted that, at the usual spray-dried powder moisture contents (between 4 and 7%), no appreciable differences were observed in the way the pigment distribute itself across the granules, thus leading to no significant differences in colour when spray-dried powder moisture content is modified.

Influence of Pigment Characteristics

The pigment characteristics studied in this section were particle size, type of pigment and fluidiser content.

Influence of pigment particle size

This study phase was conducted with the STD spray-dried powder
and H1 pigment in percentages of 1.0 and 2.0 %, modifying pigment particle size (H1F and H1G) as indicated in section 2. Tab. 1 gives the characteristic PSD diameters of these samples.

Figures 10 to 13 present the appearance of the particles in the pigment samples observed by SEM, which clearly show that whereas sample H1F is exclusively made up of individualised pigment crystals (the primary crystal has even been broken up), in the H1 samples and particularly in the H1G sample, the presence of pigment crystal aggregates and agglomerates that have formed during the calcination process. The difference between the aggregates/agglomerates of these two last samples lies in their quantity, size, and porosity. Thus, whereas sample H1 (Fig. 11) displays some quite compact, small-sized aggregates, in sample H1G (Figs. 12, 13), in addition to the aggregates, quite large agglomerates with more open structures are observed. The fact that sample H1 contains aggregates might be because these have greater hardness (understood as mechanical strength), which were, therefore, more difficult to disaggregate into their constituent crystals during the milling process.

The modification of H1 pigment PSD did not significantly influence the behaviour during pressing of the coloured spray-dried powder, since the pressing pressures for these compositions were 450 kg/cm² when the pigment percentage was 1.0 %, and 460 kg/cm² at 2.0 % pigment.

With regard to the dry mechanical strength of the pieces, this property is plotted against the average size of the pigment used for the compositions that contained 1.0 % and 2.0 % pigment in Fig. 14. It shows that, independently of the pigment percentage used, when pigment particle size rises, tile mechanical strength also increases. This indicates that the use of pigments with a larger particle size offsets to some extent the loss of mechanical strength related to the dry colouring process, values being reached close to that for the STD spray-dried powder with the pigment having the largest particle size.

In order to determine why tile mechanical strength decreases when pigment particle size decreases, the rupture cross-section was observed by SEM. Fig. 15 and 17 show the appearance of the pieces with 2.0 % pigment. It may be observed that the rupture cross-section consists of two areas: one with a darker colour, corresponding to the fractured spray-dried powder granules, and another with a lighter colour, corresponding to the surface of the non-fractured granules, which is where the pigment particles are found. It is in this latter area that the most important differences are noted. Thus, when pigment particle size is very small (H1F), the small pigment crystals are observed to cover practically the entire granule surface. That makes contact between neighbour granules difficult, thus reducing their junctures and, hence, decreasing tile mechanical strength. For the intermediate-sized particles (H1, Fig. 16), the presence of some pigment crystal aggregates allows greater contact between neighbouring granules, since the pigment is unable to cover the granule surface so efficiently, which leads to an increase in mechanical strength. Finally, the great quantity of large-sized agglomerates in the pigment with the largest particle size (H1G, Fig. 13) leaves a large area of the granule surface uncovered, thus increasing the contact surface between the granules and, hence, tile mechanical strength.

These results suggest that one of the lines of action for decreasing as far as possible the loss of dry mechanical strength could involve increasing pigment particle size. However, it is known that an increase in particle size can adversely affect colour intensity of development in the fired tile, because it decreases the interaction between the rays of light and the pigment particles [9]. With a view to quantifying the influence of pigment particle size on pigment yield, pieces were fired at the maximum densification temperature and their chromatic coordinates were then determined. These results are presented in Fig. 18, which shows that the reduction of pigment particle size provides the pieces with a smaller value for the L* coordinate and larger values for the a* coordinate. The b* coordinate is steadier, though it increases slightly in the composition with the smallest-sized pigment. The results explain why this pigment needs to be subjected to vigorous milling in air jet mills and indicate that an increased degree of milling favourably affects colour development. However, the increase in the a* and b* coordinates for the pigment with the smallest particle size suggests that, for this size, the pigment is beginning to dissolve, with the ensuing incorporation of iron into the liquid phase.

These results could open up the possibility of increasing the intensity of porcelain tile body colours without excessively decreasing dry tile mechanical strength by incorporating larger percentages of pigments with a larger particle size.

Influence of the type of pigment

The use of pigments of different nature slightly influences pressing behaviour, making it necessary to modify the applied pressure if tile porosity is to be held. Table 4 indicates the increase in applied pressure for each composition with respect to the non-pigmented spray-dried powder (STD). It may be observed that this effect is very small when the pigment quantity used is
1.0% and slightly greater when 2.0% colorant is introduced. Larger pigment percentages have a significant effect on tile porosity. The use of colorants with the dry colouring technique reduces tile mechanical strength, as Fig. 19 shows, in which dry mechanical strength is plotted versus pigment content in tiles with constant porosity for different tested colorants. Pigment type is observed to have an essential influence on mechanical strength, it being possible to classify the pigments into two groups based on the reduction in mechanical strength that they cause with 2.0% pigment content. Thus, there is a first group comprising the pigments Zr and Es, which produce loss of mechanical strength below 10%, and a second group comprising pigments H1, Ru, H2N, and Ct with losses of about 20%. For the pigment percentages used in industrial practice (about 1%), the decrease in mechanical strength is below 1.5% in all cases, which ensures that the tiles will perform well mechanically.

As remarked previously, the presence of pigment particles hinders the contacts between neighboring granules, this effect being more pronounced as the quantity of pigment particles increases. Pigment particle content depends mainly on the percentage of added pigment, pigment real density and PSD. With a view to having a simple, easily calculable parameter ($S^*$) related to pigment particle quantity, the following equation has been used:

$$S^* = X_p \cdot \frac{S}{\rho_h}$$

where $X_p$ is the pigment quantity (mass-%) and $S$ the specific surface area of the sample per unit volume, assuming the particles to be spherical. The value of $S$ is readily obtained from the PSD, and some PSD instruments even provide it directly.

Fig. 20 shows the dry mechanical strength of the pieces for each tested pigment. There is a certain scatter in the results, probably due to the non-sphericity of the pigment particles, although a clear trend can be observed. Thus, as the value of $S^*$ increases (larger number of pigment particles), the mechanical strength of the pieces decreases for the two tested pigment contents. These results underscore the importance of
pigment particle quantity on mechanical strength, and the usefulness of parameter $S^*$ for establishing the influence of a given pigment on tile dry mechanical strength. In regard to firing behavior (Table 5), small changes were detected in the maximum densification temperatures ($T_{max}$) for the compositions with 2.0% pigment, though neither the linear shrinkage (LS) nor the bulk density (Dapc) of these pieces varied between the different colored compositions: this allows the conclusion that the tested types of pigment have no appreciable influence on these properties. However, small variations in fired mechanical strength (RMc) were observed, which were always below 10% except in the composition with the C1 pigment, in which this reduction was close to 20%. The greater number of pigment particles in this composition (the real density of the C1 pigment is lower than that of the remainder) could be the reason for this difference.

Influence of fluidiser content
This section studied the influence that the fluidiser content had on the pressing behavior and mechanical properties of the pieces. The study was conducted using the H1 pigment and STD spray-dried powder.

It was observed that the presence of the additive used (colloidal silica) in the tested percentages (from 0 to 4.0% mass-% with respect to the pigment) did not influence the pressing pressure needed to obtain the required porosity in the compositions with 1.0% and 2.0% pigment. An increase of 10 kg/cm² was only observed in the composition with the largest fluidiser content. In regard to dry mechanical strength, the evolution of dry mechanical strength with fluidiser content for both tested pigment percentages is presented in Fig. 21. It shows that mechanical strength does not vary significantly when the fluidiser addition is raised, though a small reduction in this property is observed with the first fluidiser additions.

Conclusions
This study has examined the influence of spray-dried powder and pigment characteristics on the behavior and properties of dry-coloured porcelain tiles. The most important conclusions are as follows:

- **Spray-dried powder characteristics have no appreciable influence on the properties of the dry-coloured tiles in the variation ranges customarily observed in industry**
- **Determination of the cohesion of a given pigment allows appropriate proportioning of the fluidiser to be established. However, when the cohesion values of different pigments were compared, these values could not be correlated with pigment characteristics, probably because there are other parameters (PSD, particle shape, electrostatic forces, hygroscopicity, etc.) that also play an important role in this behavior.**
- **The presence of pigment at the spray-dried powder granule boundaries only modifies the porosity of the green tiles at large pigment contents. At the pigment percentages typically used in industrial practice (below 2.0%), no important differences were observed.**
- **Dry mechanical strength decreases in the tiles when the dry colouring technique is used. This is because the pigment particles position themselves at the granule boundaries, weakening the inter-granule bonds and reducing the mechanical strength.**
- **For a given pigment, the loss of mechanical strength decreases as pigment particle size increases, which must be related to the increased inter-granule contact area.**
- **The pigment characteristics that have the greatest influence on tile properties are their particle size and real density. The crystalline structure of the pigment and fluidiser content have no appreciable effect on the tiles.**
- **A parameter ($S^*$) has been defined related to the quantity of pigment particles that are introduced into the composition. This parameter allows the loss of dry mechanical strength to be appropriately related to pigment characteristics.**
- **The dry colouring technique does not significantly modify the fusibility of the composition, or the properties of the fired pieces.**

**Literature**


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<tr>
<th>Property</th>
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<th>H1</th>
<th>H2N</th>
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