STUDY OF THE EFFECT OF ADDITIVES ON THE FLOWABILITY OF CERAMIC POWDERS

Marcello Romagnoli, F.Bignami

Engineering Department of Materials and Environment,
University of Modena and Reggio Emilia, Modena. Italy
romagnoli.marcello@unimo.it

ABSTRACT

New techniques for tile decoration require the dispersion, via mixing, of pigment in dry state on the surface of spray-dried powder. To avoid non-homogeneities it is necessary to control the rheological properties of the pigment. Their flowability is correlated to the efficiency of mixing and its control can be done using chemical additives. A mixture design approach is an effective statistical method to study and optimise the effect of such substances. Fumed silica, Ca stearate and talc have shown a different effect on flowability and mixability of pigment. In particular, the first one has shown a good efficiency and it has permitted a sufficient dispersion. On the contrary, talc and Ca stearate demonstrated insufficient effectiveness. Mixture of additives have shown little or no interactions.

1. INTRODUCTION

Flowability is one of the most important properties of the powders when processes as blending, transfer, storage, feeding, compaction, fluidization and powder handling are involved in the industrial process. A better control during manufacturing optimizes the quality of the product.

Flow properties of powder must be studied in order to maintain product uniformity but also to avoid rigid situations, in which process breakdown may occur, with respect to imposed conditions. For these reasons, the need to understand the characteristic properties of powders and their behaviour in industrial processes has increased considerably during the past decade. However, in spite of this powder rheology has developed less, for example, than the rheology of liquids or suspensions.

In the last years, the interest in flowability of the powders in ceramic tile production has increased notably. The reason of such trend is due to the development of technologies for tile decoration before and after the pressing that use pigments in form of dry powders. Before the pressing, differently coloured spray-dried or micronized powders are mixed. In the first case, granites are obtained, as for example the commonly called "salt and pepper", or the macrogranites, produced by mixing spray-dried powders containing from 10 to 50% big grains (1÷8mm). Even tints are another typology, the simplest products from an aesthetical point of view[1]. They are obtained starting from uniformly coloured spray dried powders. These last ones are coloured by discontinuously adding concentrated "syrups" to the slip tanks, or by continuously batching and mixing the syrups themselves in the spray-drying[1]. More recently, attempts of colouring of spray-dried aggregates by dry mixing of pigments are carried out by tile and pigment producers. This technique needs an efficient dispersion of the pigment with the elimination of agglomerates.

After the pressing, dry glazing is another technique used to obtain high thickness of glaze and random distribution of pigments to reproduce natural stone. In all the cases, the results depend closely by the knowledge and the control of powder flowability that influences the storage, the transport, the mixing and, more in general, the handling of the materials[2].

Powders flowability depends on many different factors. Moisture, size distribution, particle morphology, pressure, temperature and time are some of the most important. The control of flow properties can be obtained, as in the case of the suspensions, also with the addition of specific additives for dry powders. These are usually very fine powders such as various types of silicates, stearates, phosphates, diatomaceous earth, starch, magnesium oxide, talcum, and fatty amines[3,4,5].

The mode of action of these conditioners in inhibiting agglomeration and improving flowability are various[6]:

(1) a solid barrier between the powder particles, reducing their attractive forces;

(2) lubricants of the solid surfaces, reducing the friction between the particles;

(3) neutralizers of electrostatic charges.

Powder flow characteristics are commonly investigated using measurements such as: the angle of repose and other handling angles; standardised flow rate as the flow through an orifice (FTO); apparent and 'tapped' densities and derived indices such as defined by Carr[7] or Hausner[8]. More fundamental and physical measurements are achievable using shear cells[9]. These cells are designed to condition powders under a known load and measuring forces needed to shear powder beds. On the other hand, this methodology is time and product consuming and the correct and reproducible preparation of samples is quite difficult to achieve and results can be very operator and know-how dependent[10]. Tap testing can be profitably used for routine checks or to establish conformity of different batches because empirical connections have been found between tap density values and shear cell determined flow functions[11].

This work has the target to study the efficiency of the additives on the flowability of pigments used in the production of tiles. In particular, their effect on the flowability will be measured by Hausner Ratio methodology and the results will be compared with those obtained mixing pigments with spray-dried powders. The methodological approach used will be the mixture-design. Differently from the most used approach "try and error", the statistical method of mixture-design, a part the Design Of Experiments (DOE), can be used to study the influences of two or more additives. It is a structured and organized method for determining the relationship between the components and the output of the process. A correct experimental planning permits to get more information with a lower effort and reduces the subjectivity of the results increasing their technical and scientific values. It generates a map of the response over a specified region of formulation. By means of mixture design it is possible to discover the critical variables, to define mathematical models and, by them, to optimise the product and the industrial process[12,13].

2. EXPERIMENTAL

Two different industrial pigments used in the production of gres were tested: a Fe-Cr black hematite pigment; a Ti-Sb-Cr yellow pigment. The industrial grade additives used were: Ca stearate; hydrophobic fumed silica with a SSA of 130m^2/g; talc. The blends were obtained mixing the three substances according to an augmented simplex-lattice design (figure 1)[12]. The run order for experiments was randomised to counteract any time-related effects. The mixtures were prepared put in a polyethylene bottle, pigment and additive(s) and mixing in a laboratory mixer for 30 minutes as shown in Table 1.

SAMPLE Nr.	Silica (wt.%)	Ca Stearate (wt.%)	Talc (wt.%)	HR Black pigment	HR Yellow pigment
1	1,00	0,00	0,00	1,74	2,02
2	0,00	1,00	0,00	1,98	2,28
3	0,00	0,00	1,00	2,08	2,49
4	0,50	0,50	0,00	1,93	2,19
5	0,50	0,00	0,50	1,95	2,07
6	0,00	0,50	0,50	2,12	2,38
7	0,67	0,17	0,17	1,86	2,10
8	0,17	0,67	0,17	2,06	2,35
9	0,17	0,17	0,67	2,08	2,21
10	0,42	0,42	0,17	1,97	2,22
11	0,42	0,17	0,42	1,96	2,20
12	0,17	0,42	0,42	2,09	2,30
13	0,33	0,33	0,33	2,00	2,23
Black pigment as received				2,15	-
Yellow pigment as received				-	2,32

Table 1. Composition of the mixtures and HR for black and yellow industrial pigment.

The flowability was determined using the Hausner Ratio (ASTM standard D4164). It is defined as the tapped bulk density divided by the aerated bulk density (equation 1). A low Hausner Ratio means that the sample has a high flowability and vice versa[4,5].

Ecuation 1

where:

ρ_f = Tapped bulk density;
ρ_i = Aerated bulk density;
V_i = Initial volume;
V_f = Final volume.

After tapping, the mixture of pigments and additives were added to spray-dried for gres, at the constant percentage of 2 wt%, with the same methods used above. The blends were pressed to obtain tiles with a laboratory uniaxial press at 49Mpa (~500 kg/cm^2). Five samples were prepared for each formulation. The tiles (discs of about 40mm diameter and 8 mm thickness) were dried overnight at 110°C and fired in the same time in an industrial cycle for gres at 1215°C and 50 minutes for the whole cycle.

The degree of dispersion of the pigment was determined by image analysis using the open source software: ImageJ ver.1.32J by Wayner Rasband, National Institutes of Health, USA, http://rsb.info.nih.gov/ij/. The areas of concentrated pigment more of **0,01 mm^2** were considered.

3. RESULTS AND DISCUSSION

Due to strong interactions possible among the components, the potential for use of modern experimental design and data analysis is large in the development or optimisation of new formulations or dispersants. In this study, the dispersant blended consisted of three different additives. The relative composition of the three substances in the dispersants can be visualised in a mixture-triangle. Each position inside this triangle corresponds to a mixture of the three surfactants x_1, x_2 and x_3. At the vertex, the dispersant coincide with the 100% of one additive. The position in the middle of the triangle corresponds to a dispersant consisting of equal amounts of the three surfactants; in the middle of each edge equal amount of the two additives at the corner. Finally, three compositions have a predominant surfactant while the other two are equal but minority. The compositions are presented in figure 1.

Figure 1. Augmented simplex-lattice design[11].

The results obtained as average of five measures, are shown in table 1. In the last two rows, the values of the industrial pigments "as received" are reported. In figure 2 the 3D plot for yellow pigment and in figure 3 the 3D plot for black pigment are presented.

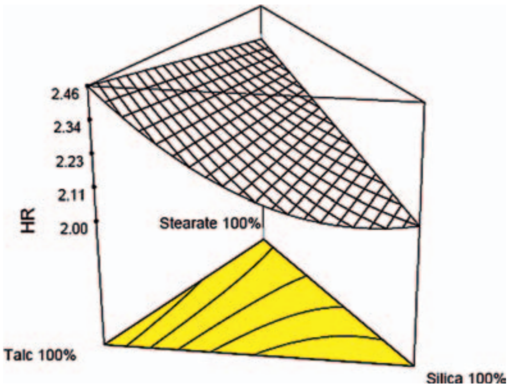

Figure 2. 3D response surface for yellow pigment

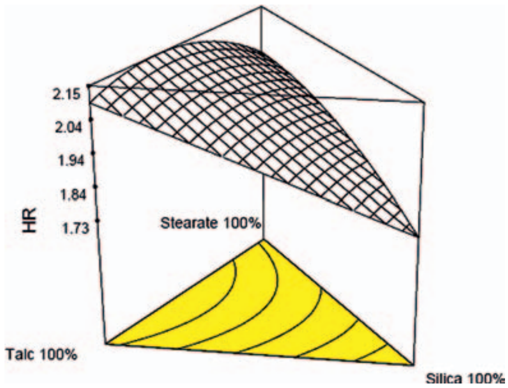

Figure 3. 3D response surface for black pigment

In the case of yellow pigment, talc shows the worse fluidising action among the three additives. The mixture with this substance has the highest value of H.R. Stearate allows obtaining a slightly lower value. However, considering the associated error of the measure, quantifiable in ± 3,5% for stearate and ± 7,3% for talc, the two H.R. values can be considered statistically different with a 95% of confidence level. The fumed silica allows getting the lowest H.R.. The equation 2 represents the mathematical model for the system. Little synergic interaction is present between talc/silica of which the importance is very limited, as evidenced by the low negative value of the coefficient. It determines a little negative curvature of the surface in the 3D plot in figure 2,

Ecuation 2

Ecuation 3

where:

S = wt.% of fumed silica;

St = wt.% of Ca stearate;

T = wt.% Talc.

Black "as received" pigment has a flowability better than yellow one and this advantage remains also in the mixture with the additives. However, talc shows the worse fluidising action among the three additives and stearate has statistically a bit lower value. The fumed silica proves itself the most efficient additive. The equation 3 represents the mathematical model for the system. The coefficient for fumed silica is the lowest. Little competitive interactions are present between silica/stearate and stearate/talc. In the 3D plot of figure 3 such interactions determine a positive curvature of the surface.

In figure 4, two samples for each pigment obtained using mixtures of pigment and additives with different H.R. are presented. The sample (a) is the most homogeneous among the tiles obtained using yellow. The mixture is the nr.1 that presents the lowest values of H.R. The sample (b) is the nr.3 that has the higher HR and shows some non-homogeneities.

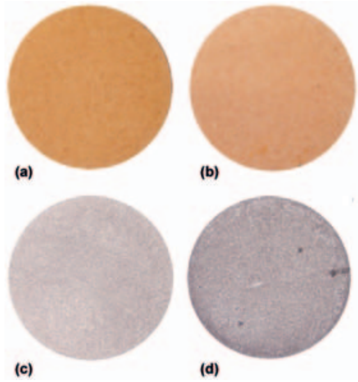

Figure 4. Yellow samples: (a) formulation nr.1; (b) formulation nr.3.
Black samples: (c) formulation nr.1; (d) formulation nr.6.

Sample (c) is prepared with the black pigment and the additives of formulation nr.1 while the (d) is with the nr.6. The difference of homogeneity is evident. Agglomerates of pigment in the sample, prepared using the mixture with the worst flowability, are clearly visible.

The degree of dispersion of the pigments in the fired tile was determined also by image analysis. The average percentage of area with concentrated pigment (APACP) was calculated for each sample. Only areas higher than about 0,01mm^2 were considered. Elevated values of APACP mean an insufficient homogenisation. The results are presented in figure 5 for yellow and figure 6 for black where the HR versus APACP is plotted. By the graphs, a direct correlation between these two parameters appears. To lower flowability of the pigment corresponds a worse dispersion. The samples obtained with the blend pigment/additives with the lower flowability show a poorer inclination to the dispersion of the pigment on the surface of spray-dried powders. This is due to the formation of aggregates. The explanation is that the same forces that determine the cohesion as: excessive humidity; irregular shape of the particles and roughness; electrostatics on the surface; reduce the flowability. For this reason the measure of flowability can give some indications about the mixability between the pigment and the spray-dried.

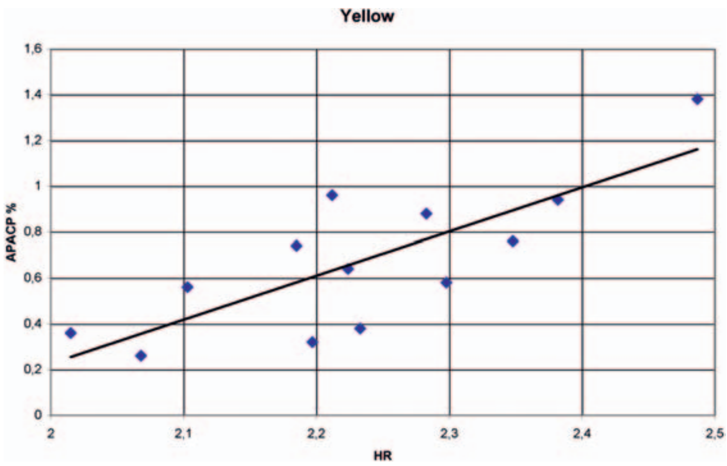

Figure 5. Average percentage of area with concentrated pigment (APACP) vs. H.R. for yellow pigment

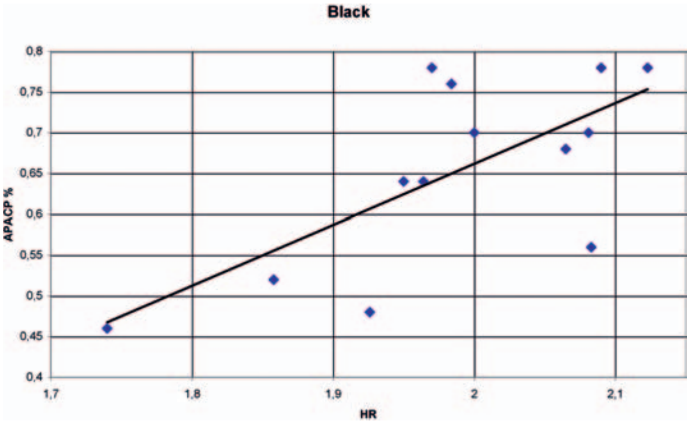

Figure 6. Average percentage of area with concentrated pigment (APACP) vs. H.R. for black pigment

4. CONCLUSION

The determination of flowability by measuring the Hausner Ratio is a useful parameter to determine and optimise the mixing behaviour of pigment and spray-dried powder for gres. A clear relationship between these two parameters was pointed out: pigments with a higher value of H.R. show an inadequate dispersion on the surface of gres aggregates. A correct dispersion can be obtained using additives. In this work, the fumed silica with has shown a good efficiency and it has permitted a sufficient dispersion. On the contrary, talc and Ca stearate proved not enough effectiveness. Mixtures of additives have shown little or no interactions.

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