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Ceramic application of mica titania pearlescent pigments

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Abstract

Mica-based pearlescent pigments are widely applied in plastics, cosmetics, automobiles coatings among others, but they seem to be not explored by the ceramic industry. In this work, the potential of two commercial special effect pigments (with gold and silver lustre, respectively) in the decoration of ceramic tiles was appraised by testing them dispersed into several ceramic coatings fired in a wide range of temperatures (700–1150 °C). The pigments were characterized by XRD, FTIR, SEM, XRF and PSD, while their technological behavior was assessed by determining phase composition (XRD) and colorimetric parameters (DRS) of ceramic materials, including a Pearlescence Index. Results indicate that mica titania pigments are stable in glassy coatings up to 900 °C, any deterioration of their optical properties being due to anatase-to-rutile and muscovite-to-feldspar transformations occurring at higher temperatures or after long firing times. The pigment type with a gold shine is particularly suitable for third fire decoration of ceramic tiles, involving low temperatures and fast firing schedules, where it can replace expensive precious metals lustres. Moreover, a certain satin effect was appreciable in porcelain stoneware tiles, unexpectedly persistent after firing at 1200 °C.

Keywords: Mica titania pigment; Ceramic applications; Technological properties; Pearlescent pigment

1. Introduction

A pearlescent pigment is a kind of pigment showing a pearl-shine due to angle-dependent optical effects deriving from alternating transparent layers with different refractive indices ([1] and references therein). The most widely used pigments of this type consist of mica platelets coated with titanium dioxide (and sometimes other transition metal oxides) and their unique pearlescent effect occurs because the transparent mica particles allow a portion of the incident light to be transmitted. When this transmitted light meets further boundary surfaces, with different refractive indices, a portion of the light is reflected. The total reflected light is made up of portions that have travelled on different paths producing optical interference [1,2]. This lustre effect is also influenced by the mica particle size, so that the coarser is the platelet (e.g., >50 μm) the stronger is its shine; the opposite causes a satin appearance [1,3].

Titania-coated mica pigments are able to bear acid or alkali media and are thermally stable up to 800 °C. Furthermore, they are non-combustible and not self-igniting, do not conduct electricity and are innocuous to human health. For these reasons, mica-based pearlescent pigments can be used in nearly all thermoplastics, cosmetics, food packaging, children toys, paints, and automobiles coating [3]. These pigments can be also utilised for security purposes, since their angle-dependent optical effects cannot be easily counterfeited with copier machines or photographic techniques, so fostering their use on banknotes in many countries [4].

The peculiar characteristics of mica titania pigments, such as the illusion of optical depth or the eyecatching effect, are highly interesting also in ceramic decoration, as they cannot

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be reproduced otherwise with current ceramic pigments. In particular, the possibility to get a lustre effect, replacing precious metals, has been recently appraised in ceramic productions fired at low temperature [5] but no data are available in the literature. Previous studies concern just the utilization of mica residues as ceramic pigment [6] or component of glass–ceramics with iridescent surfaces [7].

As a matter of fact, the thermal stability of the titania-coated mica is a limiting factor for most ceramic applications, like for instance wall and floor tiles, for which sintering temperatures range from 1100 to 1250 °C. Anyway, there are niche products – such as the third fire decoration and other low temperature ceramics – where it could be possible to apply current pearlescent pigments into glassy coatings preserving their optical appearance.

Another problem in ceramic processing is mechanical stresses, which the titania-coated mica particles would undergo during glaze preparation and application. In fact, ceramic pigments are usually mixed together with the raw materials of the glaze then a suitable homogeneity of the slip is achieved by wet milling [5]. This operation can break the adhesion of the titania coating onto the mica particles, with consequent loss of the pearlescent effect. It should be modified by adding the pigment after wet grinding and sieving, homogenizing the slip by a mild stirring.

Nowadays, the ceramic industry is continuously looking for new materials that are able to impart some innovative aesthetic effects in decorated wares, especially wall and floor tiles or tableware. This work is aimed at assessing the possibility to apply titania-coated mica pearlescent pigments in ceramic tile decoration, involving different types of frits and porcelain stoneware bodies added with several pigment concentrations and fired in a wide range of temperatures. The technological behavior and thermal stability of pearlescent pigments have been assessed by evaluating colorimetric parameters, phase composition and surface microstructure.

2. Materials and methods

Two commercial pearlescent pigments were taken into consideration, Merck Iriodin® 300 ''Gold Pearl'' and Merck Iriodin® 100 ''Silver Pearl'', hereafter called ''Gold'' and ''Silver'', respectively. They were characterized by the physical and chemical viewpoints by XRF spectrometry (S4-Explorer, Bruker do Brasil), thermogravimetric analysis (10 °C/min up to 1000 °C, TA Instruments), specific surface area by nitrogen adsorption (BET, ASAP 2000, Micromeritics), particle size distribution by photosedimentation (0.3–100 μm, Sedigraph 5100, Micromeritics), and infrared spectroscopy with DTGS detector (400–2500 cm^{-1}, MB 102, Bomem). Morphological aspects were observed by scanning electron microscopy (SEM S440, Leica) and optical microscopy in reflected light (SZX9, Olympus). Phase composition was analyzed by X-ray diffraction (5–80° 2θ, Co Kα radiation, D5000, Siemens). Colorimetric parameters were measured by optical spectroscopy (400–700 nm, MSXP 4000S, Hunterlab) using several illuminants (A, C, D_{65}, F and TL84) and observer 10°, expressing the results in CIE $L^*a^*b^*$ coordinates.

Four commercial frits for ceramic tiles and a porcelain stoneware body were used in technological testing, consisting in the pigment addition (from 5% to 40% wt.) to a slip followed by mild stirring, shaping, drying and firing. In the case of frits, glazing was accomplished by sprinkling over a ceramic substrate, fast firing in an electric kiln (60 min cold-to-cold) at maximum temperatures ranging from 700 to 1150 °C depending on the frit properties. In the case of porcelain stoneware, the slip was dried (100 °C overnight) and powders mildly deagglomerated in a porcelain mortar, humidified (7% water) and hand pelletized, then uniaxially pressed (50 mm diameter, 40 MPa); these disks were sintered in an electric kiln at 1200 °C (60 min cold-to-cold).

Table 1
Main chemical and physical features of glassy coatings and porcelain stoneware body used in technological testing

Component property	Unit	Glassy coating				Porcelain stoneware	
		F1	F2	F3	F4	Body	Liquid phase
B_2O_3	wt. %	11.7	8.9	11.8	19.8	<0.1	<0.1
MgO		<0.1	1.1	0.2	0.3	0.5	1.0
CaO		0.5	7.9	2.9	2.5	0.7	1.1
ZnO		1.0	5.0	2.5	6.0	<0.1	<0.1
BaO		<0.1	1.4	2.8	9.2	<0.1	<0.1
PbO		5.5	2.7	0.2	0.8	<0.1	<0.1
$\sum$ alkalis		7.2	6.1	5.3	8.2	5.9	10.6
Maturing temperature (softening) T_1	°C	930	940	910	720	1210	–
Temperature of half sphere T_2		1265	1180	1240	820	–	–
Temperature of ''melting'' T_3		1290	1230	1280	855	–	–
Viscosity at T_1	kPa s	4.90	4.93	5.41	2.99	–	4.40
Surface tension at T_1	mN m^{-1}	293	326	324	292	–	330
Refractive index	1	1.503	1.539	1.505	1.549	–	1.490

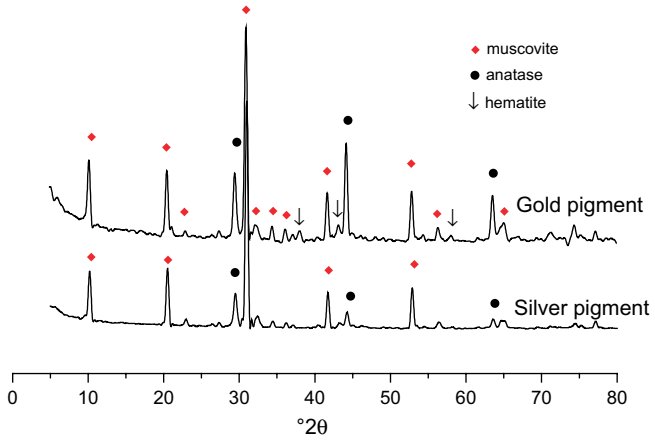

Fig. 1. X-ray diffraction patterns of the Gold and Silver pigments.

Fired samples were characterized by X-ray diffraction (10–80° 2θ, Cu Kα radiation, Geigerflex, Rigaku) and diffuse reflectance spectroscopy (400–700 nm, MSXP 4000S, Hunterlab) under D_{65} and A illuminants for visual angles of 2° and 10°. Color is expressed in the CIE $L^*a^*b^*$ parameters: L^* = white(100), black(0); a^* = red(+), green(−); b^* = yellow(+), blue(−). Moreover, in order to quantify the optical effects of mica titania pigments, two indices were calculated: the Pearlescence Index (PI) and the Metamerism Index (MI). The former is an attempt to measure the angle-dependent effects causing the pearlescent shine [3,8] involving two different visual angles (2° and 10°) for the same illuminant (D_{65}); it is expressed as:

$$\mathrm{PI} = \sqrt{(\Delta L^*_{10} - \Delta L^*_2)^2 + (\Delta a^*_{10} - \Delta a^*_2)^2 + (\Delta b^*_{10} - \Delta b^*_2)^2} \qquad (1)$$

The latter takes into account the variable coloration under different illuminants (here sun light D_{65} and incandescence bulb A) for the same observer (10°) that is known as metamerism; it is expressed as:

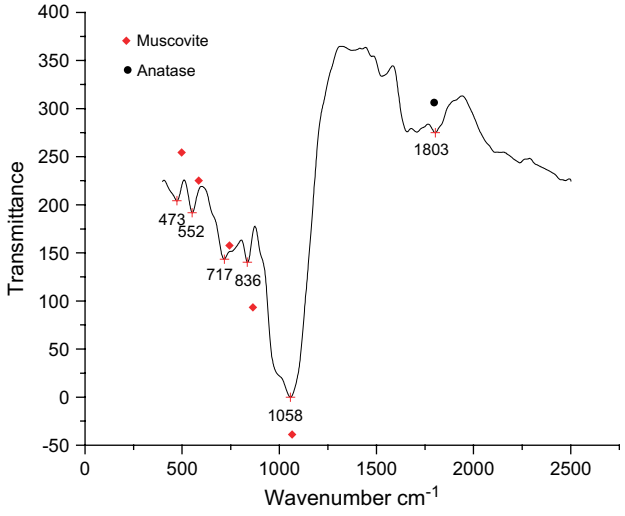

Fig. 2. FTIR pattern of the Gold pigment.

Table 2
Chemical composition, specific surface area and particle size distribution of mica titania pearlescent pigments; n.d. = not determined

Component property	Unit	Gold pigment	Silver pigment
SiO_2	wt. %	28	n.d.
TiO_2		38	n.d.
Al_2O_3		22	n.d.
Fe_2O_3		5.3	n.d.
Na_2O		1.3	n.d.
K_2O		6.1	n.d.
Specific surface area	$m^2\,g^{-1}$	3.3	12.4
Median particle size	μm	6.2	5.2
Particles 1/20 μm	wt. %	96.7	96.0

$$\mathrm{MI} = \sqrt{(\Delta L^*_{65} - \Delta L^*_A)^2 + (\Delta a^*_{65} - \Delta a^*_A)^2 + (\Delta b^*_{65} - \Delta b^*_A)^2} \qquad (2)$$

The chemical composition of frits and porcelain stoneware body, determined by inductively coupled plasma emission spectrophotometry (ICP-OES, Liberty 200, Varian), is presented in Table 1, together with the main technological features (i.e., maturing temperature and melting point by hot-stage microscopy) and physical parameters (i.e., viscosity, surface tension, refractive index calculated after the chemical composition) useful to understand the ceramic behavior.

3. Results and discussion

3.1. Properties of pigments

Both Gold and Silver pigments are constituted by muscovite (mica polytype $2M_1$) and titanium dioxide in the crystalline form of anatase [9] as revealed by X-ray diffraction (Fig. 1) and FTIR spectroscopy (Fig. 2). The Gold sample also contains hematite as a coating additive providing the golden shade of the pigment. Therefore, the chemical composition is characterized by large amounts of TiO_2, SiO_2, Al_2O_3, K_2O and Fe_2O_3 (Table 2).

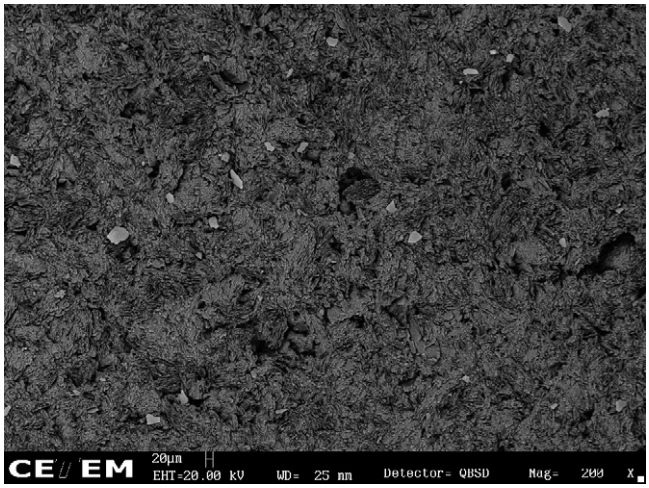

Fig. 3. SEM micrograph of the Gold pigment.

Table 3
Colorimetric parameters (CIE $L^*a^*b^*$) of pearlescent pigments under different illuminants (10° visual angle)

Illuminant		Gold pigment	Silver pigment
A – incandescent	L^*	83.33	93.03
lamplight (~2850 K)	a^*	10.94	0.80
	b^*	38.86	2.56
C – light	L^*	80.13	92.52
from overcast sky (~6770 K)	a^*	5.10	0.05
	b^*	36.97	2.56
D_{65} – artificial	L^*	80.10	92.68
daylight (~6500 K)	a^*	6.07	0.15
	b^*	36.56	2.47
F – light	L^*	82.33	92.84
from a cool	a^*	3.76	0.10
fluorescent source	b^*	41.61	2.93
TL84 – light	L^*	81.78	92.88
from a fluorescent source	a^*	6.22	0.22
	b^*	41.45	2.82

The particle size distribution is almost entirely concentrated in the 1–20 μm range, with a median size as low as 5–6 μm, which corresponds to specific surface areas from 3 to 12 $m^2 g^{-1}$ (Table 2). These features are confirmed by morphological observation under SEM (Fig. 3).

The colorimetric parameters are summarized in Table 3. The Gold pigment is characterized by a strong yellow hue ($37 < b^* < 42$) with a certain red component ($4 < a^* < 10$) that contributes to the golden appearance; its colorimetric data change significantly upon the illuminant, denoting a noteworthy metameric effect. The Silver pigment exhibits rather constant colorimetric values under different illuminants, implying a negligible metamerism, with a very high brightness ($L^* \sim 93$) and a yellow cast ($b^* \sim 3$).

The thermogravimetric analyses show an almost negligible weight loss up to 1200 °C, indicating that these pigments, when calcined alone, are stable even at rather high temperatures (Fig. 4).

3.2. Behavior in ceramic applications

Pearlescent pigments were tested in varying concentrations in different ceramic matrices (frits for glassy coatings and body for porcelain stoneware tiles) that underwent diverse firing conditions.

Glassy coatings – obtained by adding increasing amounts of titania-coated mica to a ceramic frit for low temperature applications – exhibit a rapid increase in Pearlescence Index and yellow color up to 15% pigment (Fig. 5). For higher concentrations, colorimetric parameters are quite steady around mean values of 3.2 PI, 37.5 b^* and 6.2 MI, that correspond to a highly pearlescent surface with a strong golden lustre effect. As far as the Silver pigment is concerned, the colorimetric parameters are completely different, with a very low Pearlescence Index (PI ~ 0.5) as well as low values of yellow ($4 < b^* < 6$) and metamerism ($1 < \mathrm{MI} < 2$).

Similar aesthetic results were achieved also with the other ceramic frits representing on the whole a wide range of chemical compositions, hence requiring different firing conditions. In general, the desired lustre effect is acceptably maintained even after quite high temperatures, often close to 1000 °C.

In particular, the glassy coatings added with the Gold pigment are characterized by analogous trends in function of firing temperature (Fig. 6). In fact, between 950 and 1150 °C (for frits F1 and F2) or between 700 and 800 °C (for frit F4):

- the PI is more or less fastly decreasing;
- the yellow coloration and metamerism index exhibit a quick drop (b^*) or a limited decrease (MI) followed by a counteracting tendency at higher temperatures.

In contrast, the glassy coating F3 shows values of PI, b^* and MI increasing up to 900 °C, demonstrating that the Gold pigment is fully stable up to such a maturing temperature.

The loss of the lustre effect at high temperature, connected with the rapid decrease in pearlescent shine and yellow color, is explained by the decomposition of the titania–mica

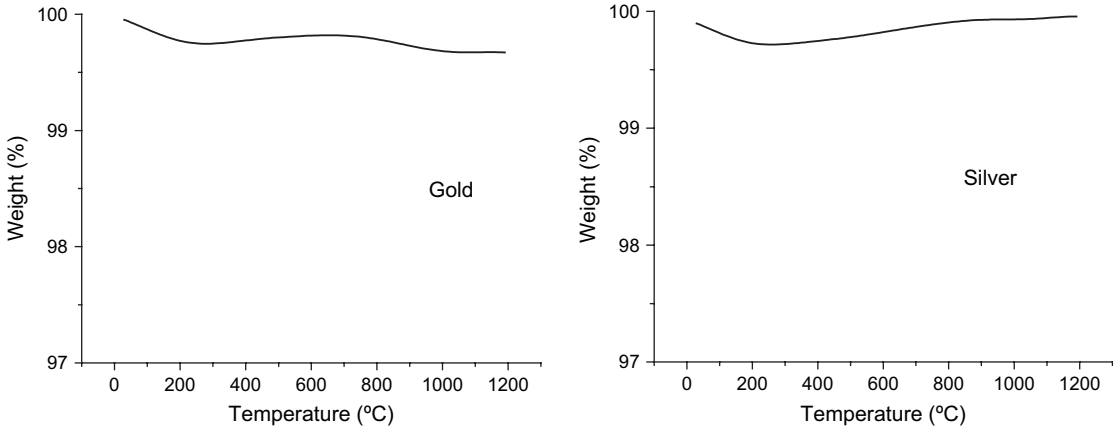

Fig. 4. Thermogravimetric analyses of the pearlescent pigments.

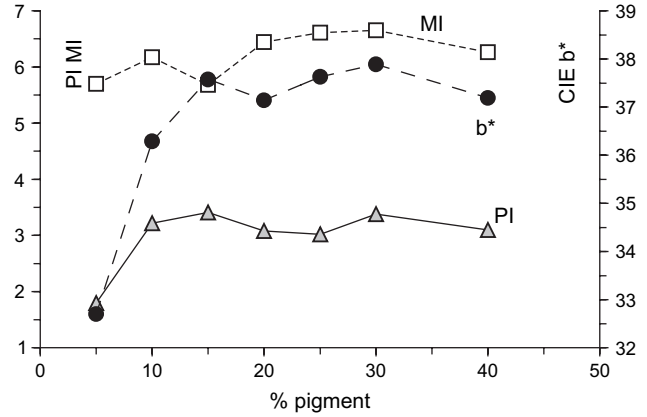

Fig. 5. Colorimetric parameters (Pearlescence Index, PI; Metamerism Index, MI; CIE Lab *b**) of the glassy coating obtained by adding increasing amounts of Gold pigment to the frit F3 and firing at 800 °C.

composite. This reaction has a slow rate, as in fast firing conditions both muscovite and anatase are preserved even after treatments at maximum temperatures around 1000 °C (Fig. 7). Higher temperatures and/or slow firing cycles promote both the anatase-to-rutile and muscovite-to-potassic feldspar transformations, according to the following reaction:

$$KAl_2Si_3AlO_{10}(OH)_2 \rightarrow KAlSi_3O_8 + Al_2O_3 + H_2O \qquad (3)$$

as clearly detected in slow-fired samples (Fig. 7).

These reaction products tend to opacify the glassy coating, by greatly increasing the light scattering occurring at the particle–glass border, so changing the color and interfering with the angle-dependent effects of the pearlescent pigment. The

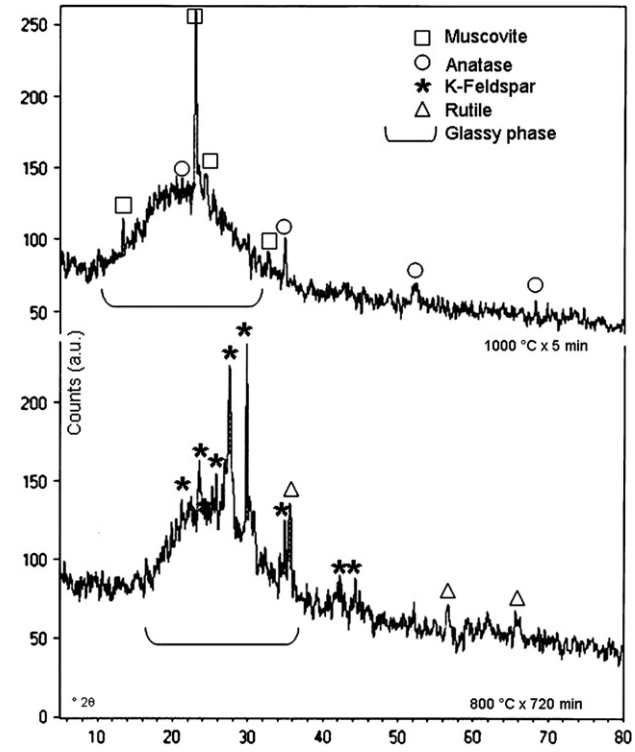

Fig. 7. X-ray diffraction pattern of the glassy coatings obtained by mixing 5 wt. % pearlescent pigment and frit F2 fast (up) and slow fired (down).

increasing yellow shade at high temperature is probably related to a convergency of factors:

– the formation of rutile after anatase implies a shift into the visible range of the absorbance band, due to the Ti^{4+}–O^{2-}

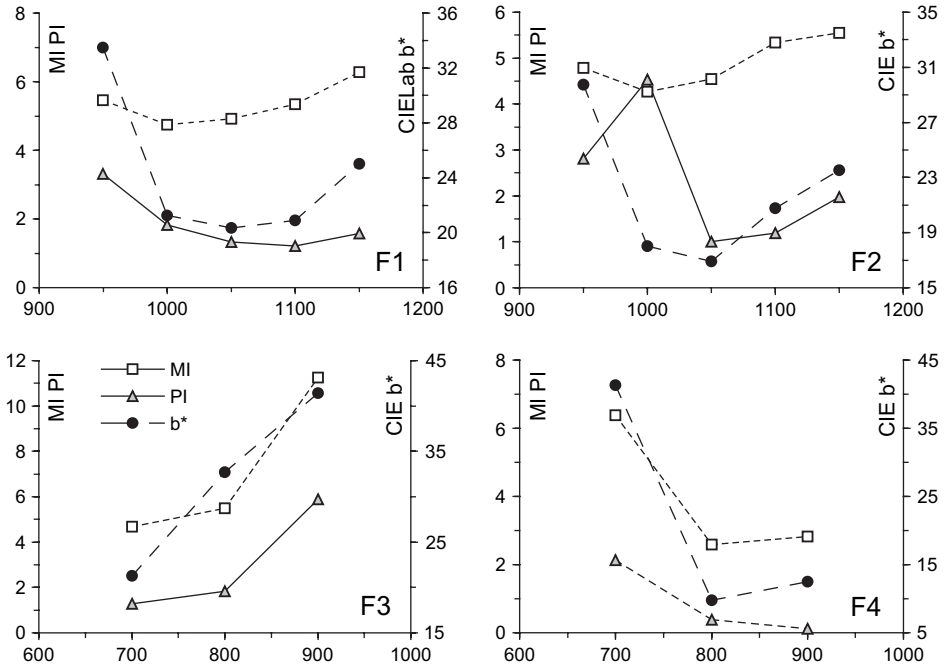

Fig. 6. Colorimetric parameters (Pearlescence Index, PI; Metamerism Index, MI; CIE Lab *b**) of the glassy coating obtained by adding the Gold pigment to four frits and firing at different temperatures (°C).

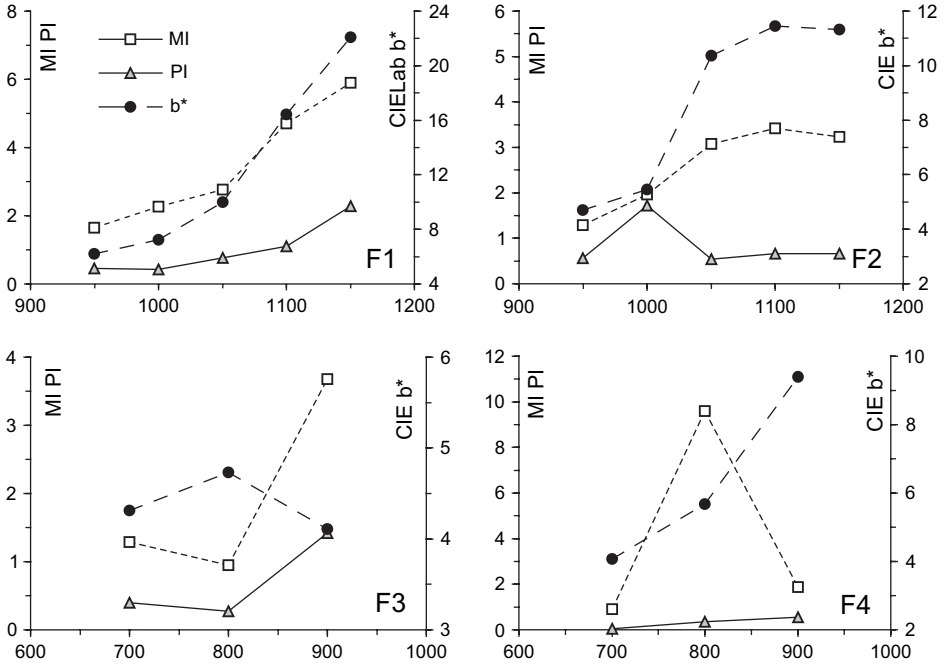

Fig. 8. Colorimetric parameters (Pearlescence Index, PI; Metamerism Index, MI; CIE Lab b^*) of the glassy coating obtained by adding the Silver pigment to four frits and firing at different temperatures (°C).

metal–ligand charge transfer, that absorbing the violet wavelengths causes a yellow drift [10];
- the diffusion of iron oxide into the glassy phase, in the case of the hematite-coated Gold pigment, resulting in a more efficient absorption of the blue light by the Fe^{3+} ions, leaving an orange-yellow coloration [10].

The colorimetric parameters of the glassy coatings containing the Silver pigment exhibit a different evolution with temperature, in respect of the results achieved with the Golden pigment (Fig. 8):

- the PI is moderately increasing (e.g., from ~0.5 to 1–2);
- both b^* and MI present a strong growth (e.g., from ~5 to even 23 b^*).

These tendencies are to a large extent attributable to the above-mentioned phase transformations: particularly the conspicuous increase in the yellow coloration is likely to be due to the abundant rutile formation, therefore indicating the decomposition of the mica titania pigment.

The behavior of the titania-coated mica pigments in the porcelain stoneware body is somehow surprising: even if the pearlescent appearance was lost, as easily predictable by the high firing temperature (1200 °C), an appreciable satin effect appeared, also associated with a color change, consisting mainly in a significant increase of yellow (e.g., from $b^* \sim 12$ of the undoped body to $b^* = 17$–20 of the body added with the Gold pigment). The color variation is another time connected with both the anatase-to-rutile transformation and the dissolution of iron in the glassy phase, that in porcelain stoneware bodies is usually as high as 50–70% [11]. The satin effect may be due to the persistence of extremely fine-grained mica particles [1,3].

3.3. Pigment stability versus chemical composition of ceramics

The differing thermal stability exhibited by titania-coated mica pigments in borosilicate glasses might be explained by the variable amounts of chemically aggressive oxides, such as B_2O_3, CaO, ZnO, BaO, PbO or alkalis, present in the vitreous phase (Table 1). An attempt to relate pigment stability with chemical environment was carried out by extracting the principal components through a multivariate statistical (factorial) analysis [12]. For this purpose, both the Pearlescence Index (PI); and the yellow parameter b^* were taken as indicators of the pigment stability. In order to compare the different colorimetric values obtained with various glassy coatings, a normalisation was performed taking the value of the pigment as a reference:

$$\mathrm{PI}_{\mathrm{norm}} = \mathrm{PI}_{\mathrm{glass}}/\mathrm{PI}_{\mathrm{pigment}} \quad (4)$$

$$b^*_{\mathrm{norm}} = b^*_{\mathrm{glass}}/b^*_{\mathrm{pigment}} \quad (5)$$

Highly stable pigments have normalised values close to unity, while values approaching zero indicate a progressively lower stability. These normalised parameters show a strong mutual correlation (Fig. 9A) demonstrating that the deterioration of the optical performance is a phenomenon involving at the same time loss of pearlescence and color change.

The results of the principal components analysis exhibit different relationships of pigment stability with temperature and chemical composition. The inverse correlation of $\mathrm{PI}_{\mathrm{norm}}$

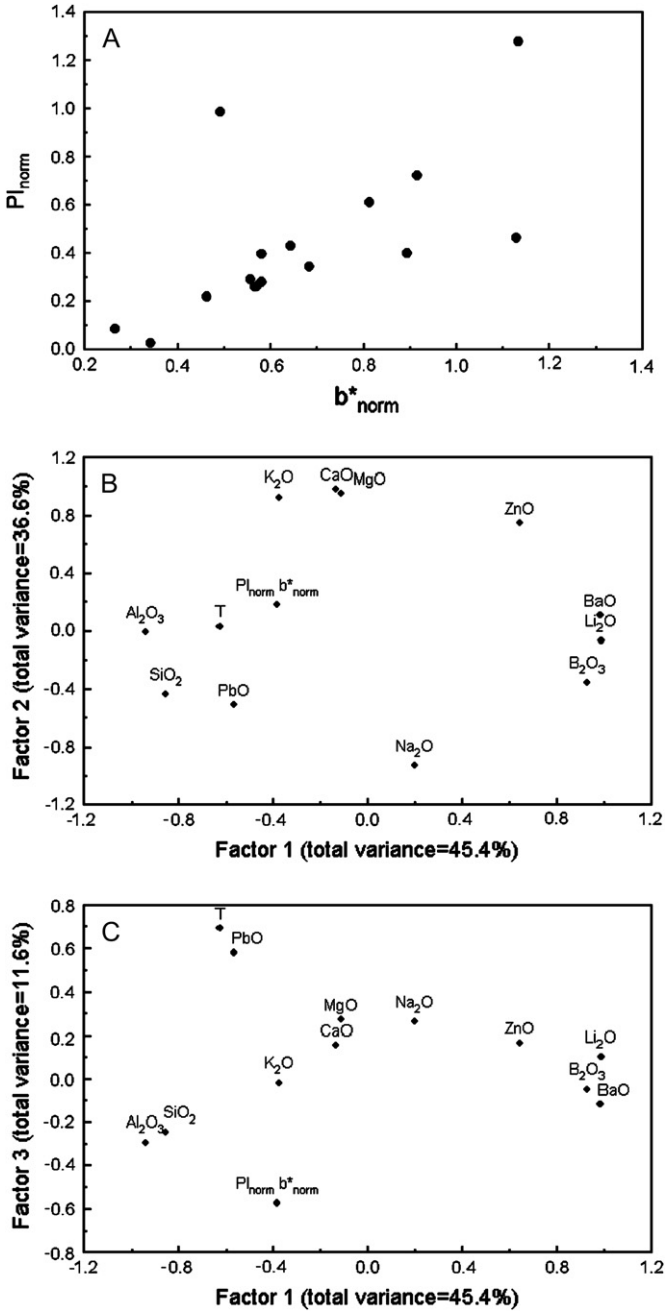

Fig. 9. Technological performance of the Gold pearlescent pigment in ceramic coatings: (A) correlation between the changes in yellow color (b^*_{norm}) and Pearlescence Index (PI_{norm}), (B) principal components analysis of contrasting factors 1 and 2, and (C) factors 1 and 3.

and b^*_{norm} with B_2O_3, BaO, Li_2O, ZnO (Fig. 9B) or T and PbO (Fig. 9C) confirms the detrimental effect of increasing temperature on the muscovite and anatase stabilities as well as the strong aggressiveness of boron, barium, lead, lithium and zinc oxides on the titania coating of mica. Somewhat uncertain is the location of sodium, potassium, calcium and magnesium in the graphs, suggesting a less pronounced role of alkaline and alkaline-earth oxides in the chemical attack of pearlescent pigments. Silica and alumina seem to have a scarce influence during firing of special effect pigments.

4. Conclusions

Two different mica titania commercial products (with gold and silver appearance, respectively) were tested in a wide range of ceramic matrices, varying in chemical composition and firing temperature. Results proved that special effect pigments can be actually used in low temperature ceramic applications. Although the literature indicates that these pigments are stable only till 800 °C, their metallic like lustre and pearlescent effect persist in glassy coatings even after firing close to 1000 °C for fast cycles.

However, the pigment based on anatase- and hematite-coated mica (gold lustre) behaves more suitably in the ceramic process than the one displaying a silver shine. Pearlescent effect and yellow color increase with concentration of the Gold pigment up to 15 wt. % added to a low temperature ceramic coating; further additions do not change significantly the colorimetric parameters.

Deterioration of the optical performance, involving loss of pearlescent effect and color change, is related to both anatase-to-rutile and muscovite-to-potassic feldspar transformations. These reactions tend to yellow and opacify the ceramic coating, interfering with the angle-dependent effect of titania-coated mica. Moreover, attention must be paid in avoiding strong mechanical stresses, such as those developed during grinding, that may damage the titania–mica assemblage; therefore, pearlescent pigments should undergo just a mild stirring in the glaze slip.

Conversely to what expected, the titania-coated mica develops an appreciable satin effect in a porcelain stoneware body, besides its high firing temperature (1200 °C). If this behavior might be exploitable, the already wide range of uses of special effect pigments should be furtherly broadened.

Pearlescent pigments, particularly those coated with titania and iron oxide exhibiting a golden lustre, are suitable for decoration of ceramic tiles at the third fire stage, which requires low temperatures and very short firing cycles. In this niche application, they can replace the very expensive lustres based on precious metals.

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