DIGITAL DECORATION OF CERAMIC SLABS WITH HIGH COLOURFULNESS

A. Bresciani[1], C. Ricci[1], B. Spinelli[1], W. Medici[2]

[1] **SACMI, Imola BO, Italy**

[2] **INTESA, Casalgrande RE, Italy**

1. ABSTRACT

The digital printing of ceramic floor and wall tiles has represented the most important innovation in product aesthetics for about ten years. In recent times digital decoration has also spread to large porcelain stoneware ceramic slabs, with sizes up to 3 metres and more.

In spite of the great advantages introduced by the digital decoration technique in the ceramic field (production flexibility, uniformity of quality, high resolution printing, decoration without surface contact, etc.) the problem linked to reduced colour intensity of the resulting products has not been completely solved yet.

As a matter of fact, it is well-known that ceramic inks suffer from several restrictions with regard to their application by digital decoration, in particular the combination of high firing temperatures and the very high grinding degree of inorganic pigments. The consequence is a particularly restricted *colour gamut*, much lower than that of other competing products (laminates, plastics, fabrics, etc.).

To overcome this problem, a new digital inkjet decoration technique is being introduced herewith. It consists of a specially designed printing machine working with a new class of ceramic inks based on UV-curable vehicles, inorganic pigments and ceramic frit. The inks are applied onto ceramic slabs already fired at high temperature. The complete integration of the decoration with the ceramic substrate is achieved through a subsequent low-temperature third-firing process.

The new decoration process can be summarized as follows:

1) preparation of ceramic slab to be decorated, already fired at high temperature;

2) digital printing of the decoration, with high resolution and UV-curable inks;

3) temporary fixing of the decoration by UV curing;

4) re-firing at low temperature (ranging from 800 to 900 °C) in a third-firing kiln.

The polymerization of the UV-curable vehicle allows fixing the applied decoration on the non-absorbent surface of the ceramic slab, preventing coalescence of the drops and thus ensuring aesthetic results of the highest level. In addition, the third firing at low temperature preserves the colour capability of the inorganic pigments, allowing significant extension of the resulting *colour gamut*. The presence of ceramic frit in the ink ensures an effective bond between the decoration and the underlying ceramic surface, providing resistance to scratches and severe weather conditions.

As a result, the new process permits the aesthetic value of the ceramic slabs to be significantly increased, allowing the penetration of new markets and product fields. Actually it combines the inherent positive aspects of the ceramic material (durability, hygiene, stability) and aesthetic contents of the highest level. Furthermore, this technique also makes it possible to recover stock materials, at low cost, through a new decoration in order to make the products fit the evolution of market trends.

2. FOREWORD

Since its very first conception, ceramic ware was associated with colour and the infinite range of chromatic shades applicable by means of the most varied decoration techniques. The example reported in **Fig. 1** (glazed and decorated tiles dating back to the 5th century BC) is an astonishing proof of this, which still charms today. In the course of the centuries, ceramic production has improved the application techniques and materials in order to achieve even brighter and more lasting colours.

Fig. 1. *Persian Archers, Darius' Palace, Persepolis, 5th century BC*

Actually the decoration phase of ceramic tiles has always represented the distinguishing and typical element of the surface compared to other kinds of natural (wood, stone, marble, etc.) or man-made (fabrics, carpets, etc.) coverings.

The added value of decoration, also from the economic point of view, appears evident if we compare the results of Italian and Spanish ceramic companies, which are traditionally at the forefront for their products' design and aesthetic appearance, to those of other geographical areas.

For further confirmation, the last column of the table reported in **Fig. 2** indicates an average price per square metre of exported products, divided by Countries. It can clearly be observed (data of 2014) that Italy and Spain, totally (6.4 billion €), are above the value of China (5.5 billion €), which even exports almost twice the square metres (1,110 million vs. 653 million m^2).

TOP EXPORTING COUNTRIES										
	COUNTRY	2011 (Sq.m Mill.)	2012 (Sq.m Mill.)	2013 (Sq.m Mill.)	2014 (Sq.m Mill.)	% on 2014 national production	% on 2014 world exports	% var 14/13	value 2014 (million €)	average export price (€/sq.m)
1.	CHINA	1,015	1,086	1,148	1,110	18.5%	41.4%	-3.3%	5,530	5.0
2.	SPAIN	263	296	318	339	82.7%	12.6%	6.6%	2,328	6.9
3.	ITALY	298	289	303	314	82.2%	11.7%	3.6%	4,109	13.1
4.	IRAN	65	93	114	109	26.6%	4.1%	-4.4%	364	3.3
5.	INDIA	30	33	51	92	11.1%	3.4%	80.4%	325	3.5
6.	TURKEY	87	92	88	85	27.0%	3.2%	-3.4%	450	5.3
7.	BRAZIL	60	59	63	69	7.6%	2.6%	9.5%	232	3.4
8.	MEXICO	59	63	64	62	27.0%	2.3%	-3.1%	296	4.7
9.	UAE	48	50	51	53	54.1%	2.0%	3.9%	n.a.	n.a.
10.	POLAND	36	42	48	42	31.3%	1.6%	-12.5%	200	5.2
	TOTAL	1,961	2,103	2,248	2,275	23.4%	84.8%	1.5%		
	WORLD TOTAL	2,346	2,520	2,655	2,683	21.6%	100.0%	1.1%		

***Fig. 2**. Results of the Top 10 Countries exporting ceramic tiles (year 2014) [1]*

One of the reasons for this competitive advantage is certainly represented by the higher skills of Italy and Spain in manufacturing products of higher aesthetic value. The other intrinsic characteristics of ceramic products (such as stability, resistance, healthiness, etc.) are substantially comparable.

3. DIGITAL PRINTING FOR CERAMIC TILES

The decoration must follow the technical development of modern production of ceramic tiles. **Fig. 3** shows the evolution in time of the decoration techniques in the industrial field and of the typical sizes produced.

During the 1980s, flat screen printing machines were used for reproducing, by mechanical devices, the manual work, using flat screens that were very similar to the ones for artistic purpose. The growth of sizes and printing speed, linked to the increase of plant productivity, allowed moving on, in the 1990s, to rotary screen printing machines, which permitted more efficient running of the lines.

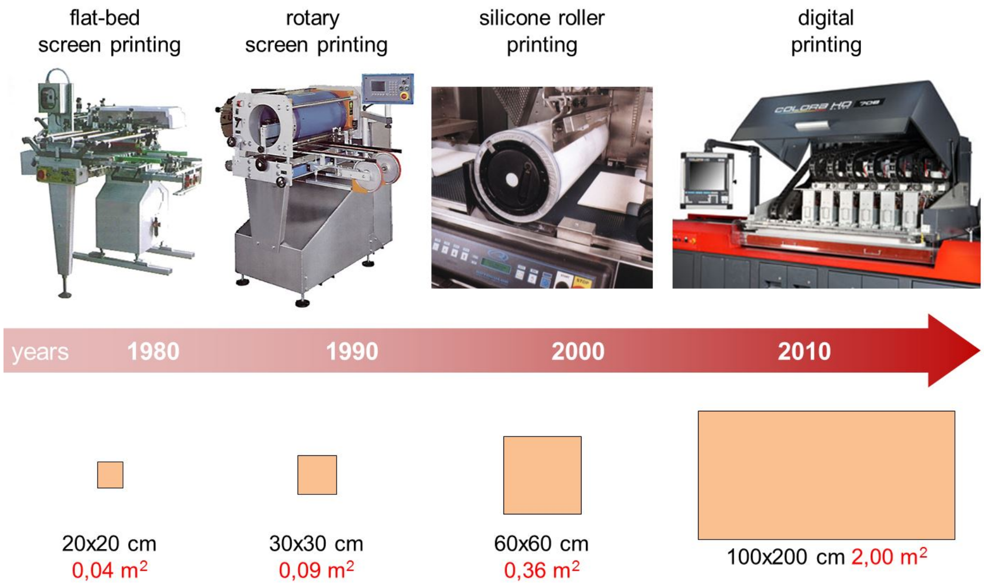

Fig. 3. *Evolution of the techniques for ceramic decoration*

A great change occurred halfway through the 1990s, with the introduction of rotary printing by silicone rollers, which gradually led to a huge increase in productivity and at the same time of decoration quality. Continuous decoration of tiles along the line was possible for the first time, with very high qualitative yield and without the need of frequent interventions for maintenance and/or setting.

Finally, after a long gestation that lasted about a decade, starting from 2010 the ceramic industry universally adopted digital decoration by means of single-pass inkjet printing machines. It involved without any doubt a great revolution in the ceramic field, whose effects are not complete yet, and which is expected to have repercussions also on other departments of the production process.

Digital printing allows great advantages in comparison with previous techniques:

- **production flexibility**: due to the absence of any intermediate printing means (rollers, screens, etc.), it is possible to vary the decoration at will, theoretical allowing tiles to be printed all different one from the other;
- **printing quality**: the possibility of jetting drops of very small size (minimum volume up to 6 pl, corresponding to printed dots of 45 µm diameter) and great resolution (up to 400 dpi, that is a pitch of 63 µm between two adjacent dots), achieving almost photographic quality, which was unconceivable by traditional techniques;
- **productivity**: the top-performing machines allow printing at maximum resolution up to 48 m/min, with a printing width, which can be theoretically increased at will, up to 1.600 mm in practice, and without any limit in the advance direction;

- **non-contact printing**: another feature is that the printing heads do not touch the ceramic product, thus printing both smooth and structured surfaces indifferently, with the same quality and without mechanical stress on the tile, which can be therefore very large and/or thin;

- **reliability**: thanks to the absence of contact and moving parts and to the total electronic control, the reliability and the yield of modern digital printing machines for ceramic products are close to 100%;

- **performance stability**: based on a few inks of standard colours, digital printing permits perfect reproduction of patterns also later in time, with shade constancy and high uniformity of the decoration.

- **optimization of consumptions**: only the necessary quantity of ink is applied, without any dispersion or waste.

Owing the abovementioned reasons, ceramic digital printing has gradually emerged as the standard decoration system in the production of ceramic tiles and slabs and it is nowadays used in the majority of cases where the decoration is applied.

However, in spite of the great advantages listed above, there is an aspect not completely solved yet, linked to the reduced chromatic intensity of the products obtained in this way.

As a matter of fact, the restrictions the ceramic inks are subjected to, for their digital application, are well-known; in particular, the combination of high firing temperatures (up to 1.220°C) and very high grinding degree of colouring inorganic pigments (under 1 µm).

Actually, the high firing temperatures accelerate the collapse of the colouring pigments, in particular in the case of chromophore crystal-based pigments (e.g. spinel, olivine, and sphene), leading to partial or total loss of colouring effect. Strong grinding accelerates the collapse and makes chemical attack easier, due to the higher specific surface of the resulting fine pigments.

The consequence is a decidedly restricted spectrum of reproducible colours (also called *gamut*) in comparison with the dyes prepared for traditional printing techniques (such as screen printing pastes).

Fig. 4 shows an indicative comparison between the gamut achievable with a set of digital inks, for porcelain and wall tile ceramic substrates, and the gamut of a series of "historical" ceramic products decorated by the traditional system in the past years (at SACMI Ceramic Laboratory). The measurement technique used is based on the L*a*b* coordinates according to the standard CIELAB 1976 [2].

The diagram of **Fig. 4** shows colour coordinates a* b*, reducing the comparison to a bi-dimensional plane. As a matter of fact, coordinate L* represents the sample brightness and is not responsible for the "colour", on first approximation. A more correct comparison, from the mathematical point of view, should be based on the evaluation of colour spaces volume in the reference system L*a*b*, but this is clearly more tedious and would not help during this analysis.

Therefore, we can homogeneously compare different samples by verifying their position on the a*b* plane; the "stronger" the colour is the more the represented point is far from the origin, that is it is more saturated. Actually, the following scalar is defined as colour saturation or chrominance C*:

$$C^* = \sqrt{a^{*2} + b^{*2}} \quad (1)$$

the higher the C* value is, the higher the colour intensity is.

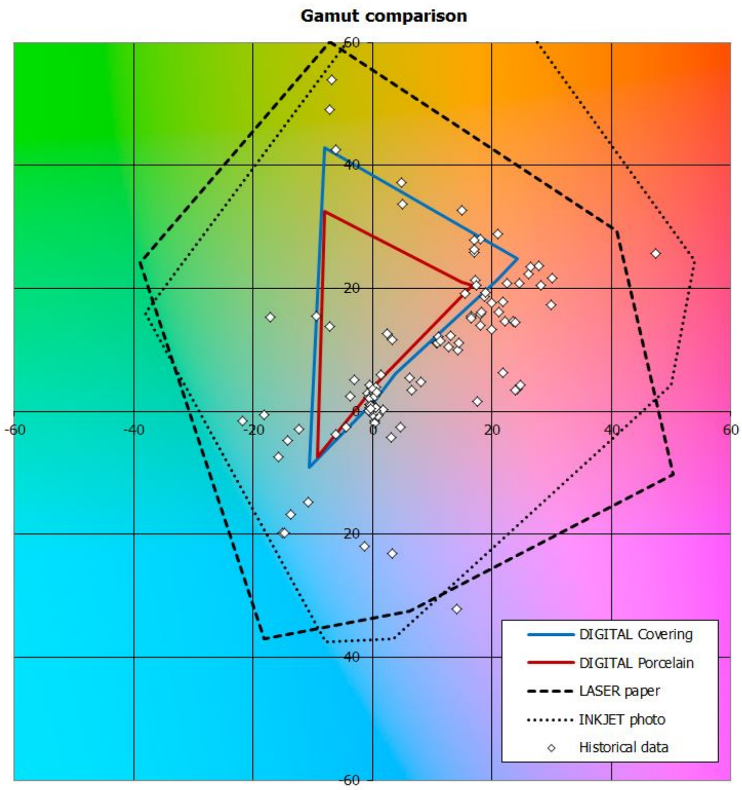

Fig. 4. *Gamut comparison of different printing systems*

By examining **Fig. 4** it is evident that the gamut of digital printing for porcelain tiles (red curve) is more restricted than the one relating to wall tiles. This difference (sets of digital inks being equal) mostly lies in the higher firing temperature for porcelain tiles (1.220 °C) than for wall tiles (1.080 - 1.120 °C). The curves are longer vertically (yellow-blue, b* axis) and narrower horizontally (green-red, a* axis); in contrast, the most suitable shape of a "balanced" gamut is substantially circular, such as for example the one of laser printing on paper (broken curve) or photographic inkjet (dotted curve).

The comparison with "historical" products realised by traditional techniques (white spots) shows that a lot of colours available in the past are no longer available for digital decoration. Saturation levels of reds (a*>20, b*>20), of deep yellows (b*>30) and of blues/greens (b*<-10) are not achieved on products printed by digital systems.

As a result, the lack of this chromaticity penalizes the expressive opportunities and therefore makes the products "duller" and less pleasant, in particular if compared to other floor and wall products (laminated, fabrics, etc.).

4. DECORATION WITH UV-CURABLE CERAMIC INKS

In order to solve the problem of colour weakness caused by over-grinding the pigments, the only way to preserve all the previously described benefits of digital decoration is decreasing the max temperature of the thermal treatment to reduce the attack of chromophore crystals.

Therefore, a new technical approach has been developed, where the digital decoration is applied on **fired ceramic products**, with the necessary structural stability, resuming some techniques similar to third-firing ones.

The inks to be used for this new kind of digital decoration must show some particular characteristics:

- good adhesion to already glazed and vitrified slab surface, by adding special UV-curable vehicles;
- use of pigments suitable for medium temperatures, with stronger colour development;
- use of ceramic frit, mixed with the ink, with the aim of enhancing colour and brightness of the decorated surface.

A typical formulation of UV-curable ceramic ink is as follows:

pigment	10 ÷ 40 %
ceramic frit	20 ÷ 40 %
organic vehicle	20 ÷ 40 %
UV photo-initiators	1 ÷ 3 %

The **new decoration process** can be summed-up as follows:

1) preparation of ceramic slab to be decorated, already fired at high temperature;
2) digital printing of the decoration, with high resolution and UV-curable inks;
3) temporary fixing of the decoration by UV curing;
4) re-firing at low temperature (ranging from 800 to 900 °C) in a third-firing kiln.

Definitely, the presence of UV-curable vehicle permits a sudden fixing of the jetted drops on the vitrified ceramic surface, avoiding the coalescence and therefore ensuring aesthetic results of a very high level.

Fig. 5 shows a comparison by optical microscope of a portion of the decorated tiles, with areas printed at 50% covering rate: on the left without UV treatment and on the right with UV treatment. In the case of non-treated area the drops tend to melt up and form aggregates of about 1 mm, causing a dramatic loss of printing resolution (from original 360 dpi to less than 50 – 100 dpi).

Effectively the UV treatment "freezes" the liquid drops, which are likely to be already fixed to the substrate.

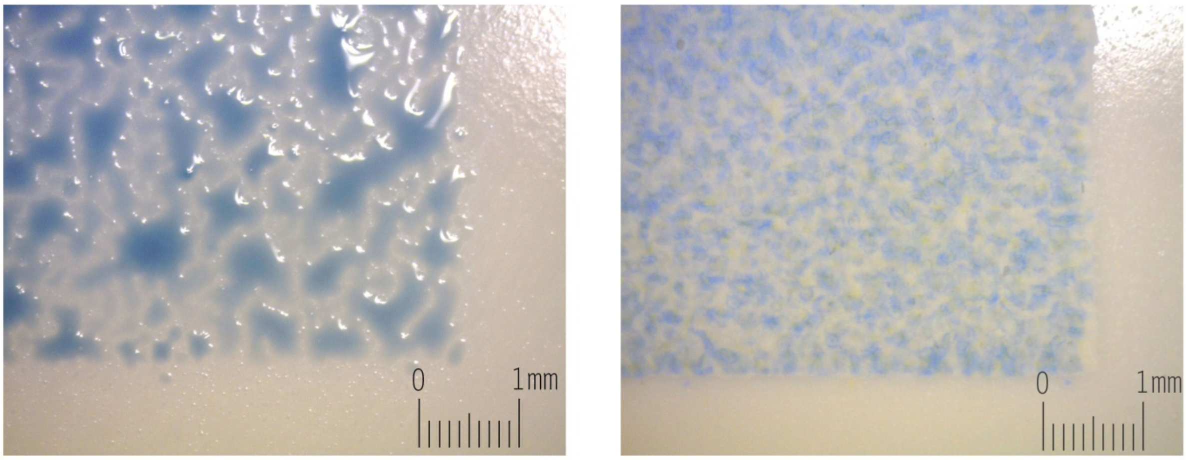

***Fig. 5**. Enlargement by optical microscope after printing: without UV (left) and with UV (right)*

Re-firing at low temperature keeps most of the chromatic power of ceramic pigments and permits widening considerably the thus achievable gamut. **Fig. 6** below shows a re-firing curve optimised for large porcelain slabs, applied during experimental tests; max. temperature is 850°C and the cycle is 60 minutes.

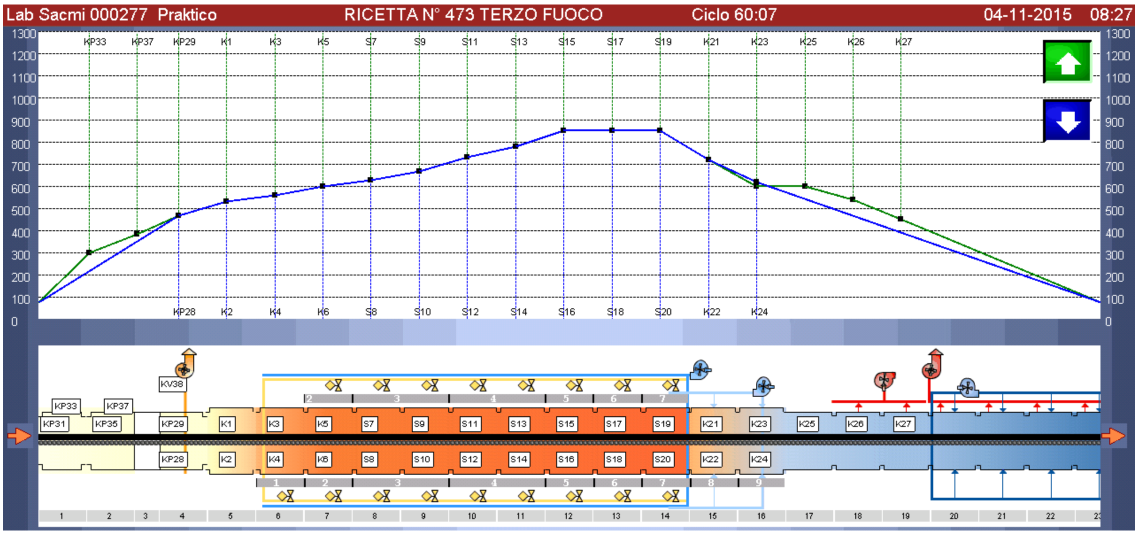

***Fig. 6**. Re-firing curve for porcelain tiles*

The presence of ceramic frit in the ink is necessary for ensuring an efficient binding action between the decoration and the ceramic surface underneath and provides resistance to scratches and severe weather conditions.

From the operating point of view, an example of the **innovative line** with UV-curable decoration is reported in **Fig. 7**. This decorating line could be placed at the end of the industrial ceramic process. The semi-finished ceramic slabs, coming from an intermediate storage, are fed on a conveying line toward the digital printing machine.

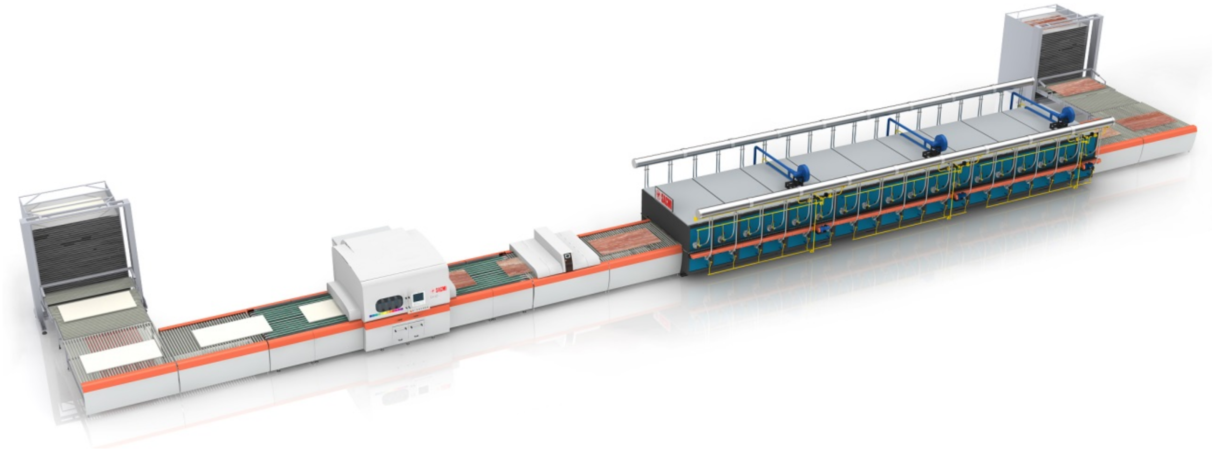

***Fig. 7**. Layout of the innovative line with UV digital decoration*

The printing machine, equipped with piezo inkjet heads, can be a plotter or a single-pass printer in accordance with the expected productivity of the line and the size to be processed. The printing machine is equipped with LED UV lamps, which carry out decoration "pinning" just after printing; a UV kiln equipped with high power mercury lamps is placed downstream for complete polymerization of the UV resins.

Therefore, the decorated product is conveyed to a re-firing thermal machine, usually a single-layer roller kiln, which provides for definitive fixing of the decoration and its full integration into the glaze surface.

The adoption of a thermal process for fixing the decoration in the glass matrix of the ceramic surface must be highly preferred to other "cold" printing processes (such as the application of transparent coating paints, varnishes of different nature, etc.). Actually this allows excellent chemical and physical integration and consequently good performance with regard to resistance to abrasion and sunlight.

The energy costs of re-firing can be easily estimated. With relation to a thermal cycle as reported in **Fig. 6**at 850°C max. temperature, on an already fired product, a specific consumption not higher than 1200 kJ/kg can be assumed. Considering that 1 m^2 ceramic product with standard thickness weighs about 23 kg, and assuming an energy cost of 0,36 €/Nm^3 for natural gas [3] (corresponding to 34,5 MJ/Nm^3 thermal energy), we obtain the following re-firing cost C_{fire}:

$$C_{fire} = \frac{23\,\frac{kg}{m^2}\cdot 1200\,\frac{kJ}{kg}}{34500\,\frac{kJ}{Nm^3}}\cdot 0{,}36\,\frac{€}{Nm^3} = 0{,}80\,\frac{Nm^3}{m^2}\cdot 0{,}36\,\frac{€}{Nm^3} = 0{,}29\,\frac{€}{m^2} \qquad (2)$$

This cost is clearly acceptable, considering the expected aesthetic and logistic advantages.

5. EXPERIMENTAL ACTIVITY

In order to validate the process described above, a series of printing tests with different types of inks and substrates have been carried out in order to evaluate the chromatic yield, comparing the results also with the state of the art of ceramic digital decoration.

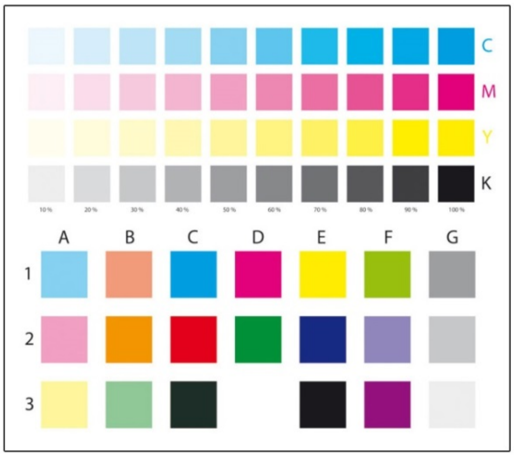

Fig. 8. *Reference image*

Fig. 8 reports the reference image printed during each test, at 360 dpi resolution.

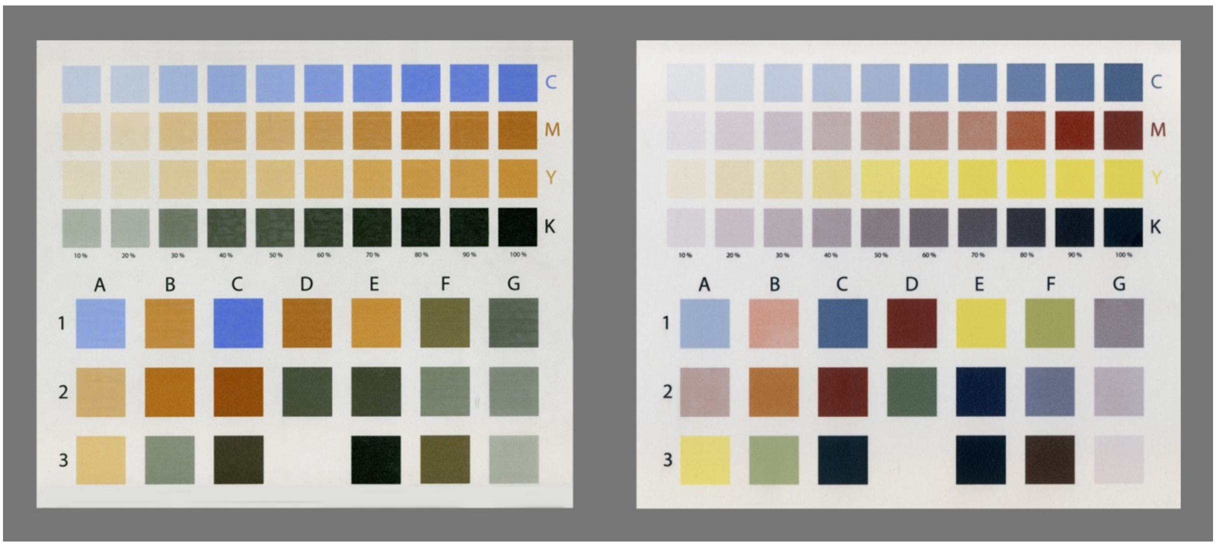

Fig. 9. *Comparison of porcelain tiles (matt glaze)*

Fig. 9 shows a comparison between standard inks (on the left) and UV-curable inks on matt glazed porcelain tiles; the higher chromatic accuracy of UV-curable inks is evident, in particular in the range of yellows and intermediate colours such as pink, orange and green.

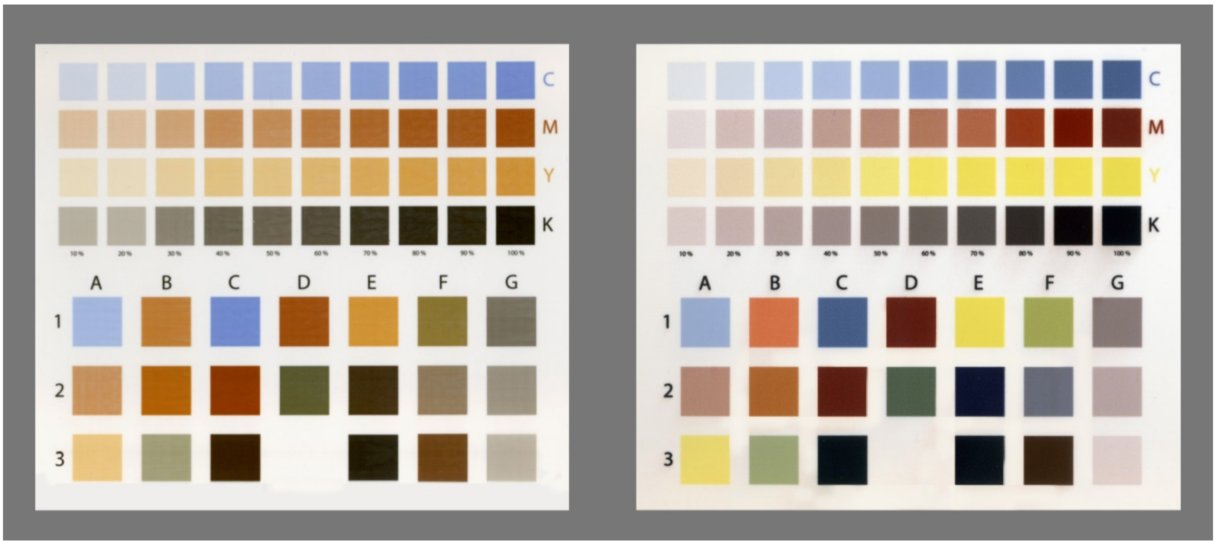

Fig. 10. Comparison of porcelain tiles (glossy glaze)

Fig. 10 shows a comparison between standard inks (on the left) and UV-curable inks on glossy glazed porcelain tiles; also in this case, the higher accuracy of UV-curable inks is evident, and as a result of the higher brightness of the glossy background glaze the colour saturation is even higher.

Fig. 11 illustrates, similarly to **Fig. 4**, the distribution of the gamut on the plane a*b* CIELAB space. The use of UV-curable ceramic inks considerably extends the reproducible colour space, thus including a great part of the "historical" colours of traditional decoration, obtained from screen printing pastes, which were lost due to standard digital printing.

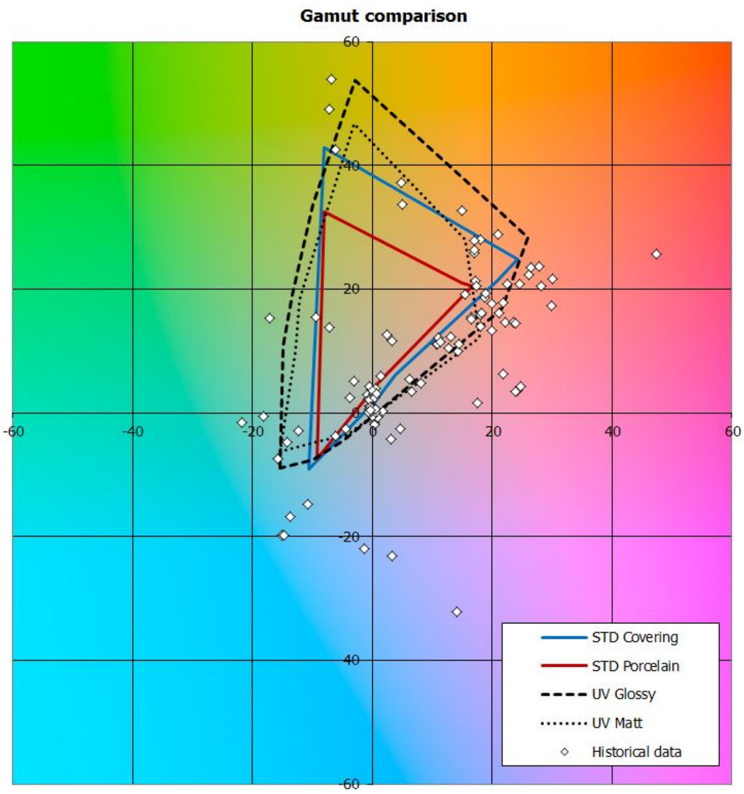

***Fig. 11**. Gamut comparison between standard and UV ceramic inks*

6. CONCLUSIONS

An innovative process for the digital decoration of fired ceramic slabs by the application of special UV-curable ceramic inks has been introduced. The decoration is performed at ambient temperature through a special digital machine, on semi-finished slabs from an intermediate storage. After the application of decoration, a thermal re-firing cycle allows definitively fixing the colours on slab surface to ensure their inalterability in time and resistance to abrasion and atmospheric agents.

The new process permits increasing considerably the aesthetic value of ceramic slabs and allows the penetration into new markets and product fields, combining the intrinsic positive aspects of ceramic material (durability, healthiness, stability) with aesthetic and chromatic content of a very high level.

This operating method can provide a reduction of finished product stock since it makes it possible to produce and store slabs of large size and neutral (white) background, which are subsequently decorated and cut to the desired final sizes according to market demand. Therefore, the opportunity of flexible and "just in time" production becomes concrete, with competitive costs, and an important reduction in finished product stock.

Furthermore, this technique also makes it possible to recover unsold stock materials, at low additional cost, by means of a new decoration that makes the products fit the evolution of the market trend.

REFERENCES

[1] ACIMAC Survey dept., "World Production and consumption of ceramic tiles", 3rd edition 2015

[2] International Standard ISO 11664-4:2008(E) - CIE Colorimetry - Part 4: 1976 L*a*b* Colour Space

[3] EUROSTAT, Gas prices for industrial consumers - European Union, last update 29/10/15 http://ec.europa.eu/eurostat/web/products-datasets/-/nrg_pc_203