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True three-colour photoceramic

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This paper presents the true three-colour photoceramic, introduced by the authors since 1992, which allows wide new possibilities in the field of the ceramic decoration, for reproduction on ceramic (majolica, porcelain, earthenware, etc.) surfaces of images either photographic or painted images or even directly coming from computer-made image files. The correspondent technological process used to produce this kind of decoration involves new manufacturing procedures and the use of unusual devices. The physical principle involved in obtaining the formation of the image is based on the well-known physiological tristimulus effect, which is founded on a consolidated theory and practice utilised for classical photographic and TV reproduction. The novelty consists in having introduced this technique in the ceramic decoration field. To distinguish the technique described here from that already known as *polychromatic*, based on a careful and artistic hand-painting technique (but an artefact based on the operator's fantasy), we have called it: *true three-colour photoceramic process*® (the equivalent of the three-colour printing technique). Besides the due treatment of already known physical concepts, some technological problems are reported and discussed, which arose during the years of utilisation of this new technique. The behaviour "*in situ*" of true three-coloured photoceramics is also discussed here, in the light of many years of production and application. Physical and chemical aspects are considered, to further develop and improve this new technology of images reproduction.

1. Introduction

The activity for the introduction of a new technique began in 1990 as we were trying to develop a system of ceramic printing through an ink-jet printer [1]. In 1992 the authors changed radically their strategy and introduced a new technique for production of ceramic decors named *true three-colour photoceramic process*®. About this topic they issued a first publication in 1994 [2]. The aim was to supply photographic reproduction on porcelain ovals to be placed on family tombs in Italian cemeteries. The activity quickly involved fields also outside that of funerary inscriptions. Shortly before the publication of the cited paper [2], the firm assumed the company legal name of R.G.B to allow as much as possible a comfortable enlargement of the market of the involved enterprise. No technique to produce *true three-colour photoceramic* was available before 1992. After our first publication, some rival firms tried to realise a similar process, but without much success. As previously explained [2], the introduction of computer science in this field was the element that allowed the introduction of this new technique.

The physical principle of the *true three-colour photoceramic process*® is based on the physiological production of a colour sensation coming from the *tristimulus effect* of the eye, which is founded on a theory and practice already consolidated and utilised for classical printing and for photographic and TV reproduction. Until the introduction of this new technique the only method of production of coloured photoceramic was that based on the colour retouch technique, which allowed to obtain a polychromatic artefact through hand-painting with a brush, with deposition of one or more colours, softened if necessary, in defined areas on a black and white photoceramic, taking advantage of the existing grey scale to have a correct tone (photoceramic based on the grey scale has been available for a long time). At the end of the process the product was substantially a polychromatic reproduction. To produce these polychromatic photoceramics, even three (or more) colours were used in many cases; the obtained product, however, although polychromatic, never corresponds to a true *three-coloured reproduction* (this concept is deeply discussed later). Although a firing is involved, the obtained products did not generally show good environmental performances and the colours washed away during time. Since technicians in the specific field of ceramic decoration often use *n*-chromatic

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and n-coloured terms as synonyms (and giving rise ambiguities with the concept of polychrome), the authors introduced the prefix term "*true*" to indicate that in this case the perceived colour comes really from the tristimulus effect and not from direct perception of single colours covering specific areas such as in polychrome paintings. Some semantic confusion is generated in some people by the definition of three-chromatic reproduction, which in reality is a three-colour reproduction and not the particular use of polychrome reproduction with three colours, which would suggest that the prefix poly- should be substituted in turn by mono-, twice-, three-, four- and so on.

The serigraphy technique was (and still is) largely used in factories operating in the field of building ceramic material to produce artistically decorated tiles, which represents one of the most successful and profitable of the Italian industry. Also in this case the obtained product is a ceramic decorated in polychromy. To distinguish the new described *true three-colour photoceramic process*® here described from the already known polychromatic productions, based on hand-painting or serigraphy techniques, we have called it *true three-colour photoceramic* (the equivalent of three-colour printing technique on paper).

The Italian firm R.G.B. Ltd. has improved in time the technological process, with a production of about 400.000 true three-colour photoceramic reproductions on porcelain support, mainly funerary ones, to meet the wide demand in this sector in accordance with the Latin-Mediterranean (southern Europe) cult of the dead. After the first presentation of the process on 1992 [1] (necessarily concise and a bit cryptic), it is now time, after some years, to give more detailed information about this new ceramic technology and supply a quick introduction on its applications as well as on its performances and problems.

2. Colours perception

Studies on this matter were produced in the past and generated a specific science. It is possible to find a complete picture of this subject in many specialised books. Nevertheless some of the readers could need some ready information and therefore the authors decided to summarise some of important points here.

The problem of specifying object-colour perceptions, that is the perception of colours belonging to a non self-luminous body, has not yet been satisfactorily solved for the most general case, when an observer views a complicated scene composed of a large variety of objects and with different kinds of light illuminating them. The phenomenon of vision is in fact a mixing of psychophysical and psychological events [3].

The stimulus for colour perception is a pattern formed by radiant energy on the retina of the eye, which is sensitive in a small interval of wavelengths ranging between 380 mμ (UltraViolet threshold limit) and 770 mμ (InfraRed threshold limit). Various visual phenomena, such as simultaneous contrast, colour constancy, and colour memory, come into play and contribute significantly to the resultant colour perception of a complicated scene.

When human eyes view a scene, they constantly move across and around the scene, focusing now on one and now on another particular point or patch of light in the scene. In so doing, the chromatic sensitivity of the eyes changes rapidly and continuously and thus influences their colour perception. The fact that the eye constantly scans the scene, or shifts from one patch of light to another, is of great importance in perceiving colours. It is known that the physiological structure of the retina varies from *fovea* to periphery. It is consequently not surprising that to find that colour perception varies from one area to another of the retina. Even within the *fovea* there are significant differences, as revealed e.g. by the threshold sensitivity to light of different wavelengths. The fovea is highly sensible to red wavelengths (particularly in the orange band), whereas there is a sharp drop in sensitivity to blue wavelengths. This behaviour is exploited e.g. with far violet and fluorescent pigments, like those based on neodimium-phosphorum compounds which, added in trace to porcelain paste, confer to the obtained fine-ceramic products (pottery, sanitaryware, custom jewellery, home-wares and even dental enamels) shot effects on light surfaces. Colour matching with small fields subtending 20 minutes of arc or less shows that the fovea centre is substantially dichromatic [4], since all colours can be matched by a mixture of only two stimuli. This dichromatism (which is similar in its general characteristics to the colour defect known as trinatropia) is associated with the smallness of the visual field rather than the size of retinal area used to view it. The efficiency of the fovea centre is especially striking in view of its otherwise high acuity and discriminating power. Peripheral vision has consequently long been known to differ from fovea colour vision, since the fovea centre is devoid of blue receptors and therefore differs in this respect from other retinal areas. A stabilised retinal image is an image on the retina which remains always on the same set of retinal receptors. These receptors are cones and rods. The former are about 7 millions in all and are distributed over the whole retina, except in the spot area where the optic nerve joins. The latter, though very sensitive at the wavelength 510 mμ (green), do not yield colour perception but only produce sensation of achromatic or neutral colour perception, or grey scale. The continuous scan mentioned before determines a very small but significant shift of image focusing on the retina. Consequently the retinal receptors are continuously affected by a readjustment of colour and light intensity. The impression of colour is associated to the process of definition of the outline of the images brought at the same time by two different procedures of vision: the fovea and peripheral impressions. The formation of the image and the correspondent colours is then given by a complicated mechanism involving even the reconstruction of the image in the cerebral centres of vision. The difference between the colours perceived as belonging to the patches of light constituting a scene and those perceived as belonging to the particulars depicted by combination of those patches may be quite large. In fact, it can be demonstrated that an object reflecting light of any chromaticity whatsoever is perceived as grey if the object is placed in a properly designed scene [5, 6].

Serious studies on the perception of the colour were first carried out by the Association of American Railroads for railroad signalling. These studies led to the constitution of the International Commission on Illumination (*Commission Internationale de l'Eclairage*, CIE). A CIE diagram was drawn which shows chromaticity limits of lights used for railroad signalling [7, p. 305]. Chromaticity ranges for blue and purple signals overlap. Because of chromatic aberration of the eye [8] the blue signal usually appears as a red dot surrounded by an out-of-focus blue.

The problem of assessing the colour-rendering properties of a picture under different illumination conditions is of primary importance. The most artificial daylight sources do not compare very well with those of natural daylight of the same or similar colour.

Scenes and objects imaged on the retina of the eye determine by their chemical and physical properties the spectral distribution of energy in the retinal image. The objects imaged with the relation between chemical constitution of the substance (pigment or dye) and its ability to modify by absorption the incident-radiant energy have their own colour language.

As concerns the chromatic effects and aberrations that can occur with a determined selected set of basic colours, there are in the first place those involving the shapes of absorption bands, in particular when a strong dominant component is present. In particular, a bathochromic effect associated chiefly with a change in dominant wavelength is usually appreciated visually as a change in blue in the direction from yellow to orange, to red, to purple, to blue, to green, while a hypsochromic effect is also usually associated chiefly with a change in dominant wavelength and is usually appreciated visually as a hue change in the reverse direction.

3. Three-colour reproduction of images and the tristimulus effect

Without a good explanation it would seem that no difference exists between polychromatic and coloured reproduction. At first sight the periphrases "three-chromatic reproduction" and "three-colour reproduction" might be perceived to have the same meaning (but the reality of the conventional language of the sector is different). In fact, the term polychromatic in itself would semantically refer simply to a picture (image, writings, geometrical traces, spots, a mixture of all these things) produced with more than one colour. The term comes from polychrome (ancient Greek *polykromos* = endowed with many colours), which means the particular optical effect produced by a series of juxtaposed colours, mostly with decorative function. All artistic operas (paintings, frescos, decorated ceramic, etc.) produced since ancient times are in effect polychromatic pictures. Classical polychromatic pictures are characterised by the fact that each different colour fills specific areas in a continuous way (e.g. in a paint of a man the face is rose, the jacket is blue, the tie is yellow, the shoes are black, and so on). Variations of tonality and intensity are represented with gradation of the same colour or, sometimes, with superimposition of thin black lines, which could also represent e.g. folds, pleating, gathers or ripples. The borders between the areas at different colour are often marked with a black line, more or less thin to indicate more or less joining. All these contrivances correspond to as many conventional symbologies and have become standard and obvious during the centuries. The overall scenery is interpreted by the human brain, which automatically adopts the conventions and re-interprets them in an equivalent real scenery on the base of the psychology of every different subject. As concerns coloured reproductions, with the introduction of coloured photographic reproduction and of new printing technologies (XIX-XX centuries) a new way to issue images has been introduced, which appears direct and realistic. In this case, however, the chromatic appearance is obtained with a limited number of colours (produced through coloured substances), but the visual impression is that they are a variety of colours.

In this case the physical phenomenon involved is the above-mentioned *tristimulus effect* which acts at the level of human (and probably of most animals) retina. As the word itself suggests, the *tristimulus effect* is activated by three colours which are just those to which the retinal receptors are sensitive. Consequently all possible ways of reproduction must supply to eye vision an intimate combination of these three colours. This is the reason of the name *three-colour reproduction*. Between classic polychromatic picture and the three-coloured one there are many physical, physiological and psychological differences, which involve also the human capacity for perception (specific receptors for three specific colours in the retina, specific connections between these receptors and specific cells of the vision area of the brain) [4].

The *tristimulus effect* based technique of reproduction of images is widely used in a variety of human ways of communication (today part of the so-called multimedia interaction). The printing of coloured images on sheets of paper is today a routine technique (newspapers, periodicals, books, leaflets, geographic maps, decorated paper, and so on) carried out by the use of coloured inks (with pigments generally of organic chemical nature). The colour print is usually known as three-colour printing (only if the fundamental colours are used), or four-colour printing (if four colours are used, but in this case each colour must be calibrated to have the right complementary effect on all others). There is also a *corrected three-colour reproduction*, which also involves a neutral colour like grey, to produce a dark background in a grey scale. This allows warm or cold tones, darkening or lighting effects. Reproduction by this last method is adopted e.g. in TV imaging. The *true three-colour photoceramic* also adopts the *corrected three-colour* reproduction technique.

In printed reproduction on paper the intensity of colour is given by the amount of coloured ink deposited in the spot or, better, it is in close relationship with the amount of ink absorbed by the paper at the level of the spot. The technology of colour printing on paper approaches the described in this paper. It is therefore useful to examine the problem involved. A problem of chromatic saturation is possible when a threshold value of the amount of deposited ink is reached (no significant further absorption is involved after this value). Whatever the type of image reproduction, the spots of the basic colours must be of the same dimension and not exceed some microns of maximum dimension.

The final arrangement of the spots of all the colours involved must be correctly shifted to avoid masking the underlying points owing to the overhanging ones. The most frequent optical effect in case of such masking is called "*marbling*", occurring when the spots are not in rows but are displaced randomly. In this case a superposition of coloured spots with unpredictable effects (even chemical interaction among inks, with change of colour) becomes possible.

A correct shift is obtained when the points are arranged in a way that allows a continuous periodic reproduction of an elemental planar symmetric geometric figure with a n-fold rotational axis. From structural crystallography it is well known that geometrical figures which allow a planar bi-dimensional (2D) periodic continuum have $n = 3$, 4 or 6 (triangle, square or hexagon). If all the flanked points are well displaced to form a heterochromatic motive, the obtained reproduction is very good (good print) and the overall displacement of the points is said to be well *registered*. In this case the spots of all colours will be displaced flanked with formation of a heterochromatic motive called "*chromatic rose*". A correct rose displacement is shown in Fig. 1; the four spots at different colour are geometrically arranged on the corners of a rhombus (however, other kinds of reciprocal displacement can be adopted). Whatever the type of image reproduction (three- or four-colour printing) the spots of the basic colours must be of the same size and not exceed some microns of maximum size.

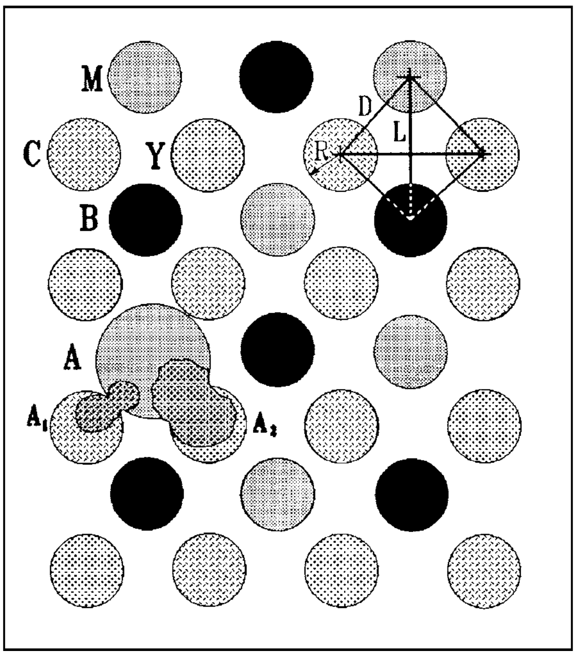


Figure 1 Final arrangement of the coloured spots in the four-colour printing. C = cyan, M = magenta, Y = yellow, B = neutral colour (grey scale). R = radius of the spots, D = inter-spots distance, L = diagonal of the formed rhombus. A is an example of possible chemical interaction in which A_1 is a spot partially reacted, A_2 is a case of inter-diffusion with practical disappearing of the yellow spot.

From the above description it should be clear that there is a wide difference between a polychromatic reproduction by the use of three colours for polychromy and a three-colour reproduction for tristimulus effect.

4. Formulation of the colours in tristimulus effect

Instrumental measurements on colours are based on weighted linear equations that correspond to the combination of three pure monochromatic wavelengths of the selected primary basic colours. Generally the adopted basic colours are: Red, Green and Blue, which form the so called RGB system of reference. The wavelengths of these three basic colours are: $\lambda_{RED} = 700.0$ nm; $\lambda_{YELLOW} = 546.1$ nm; $\lambda_{BLUE} = 435.8$ nm. Other terns of pure monochromatic colours can be adopted as well; the only pre-condition is that every colour of the chosen tern must be completely independent from the other two in the chromic perceiving formation by the tristimulus effect [9]. Such independence is also defined as orthogonal colours (term acquired from analytical geometry). The colours of every tern must be able to reproduce all possible visible colours by the tristimulus effect to be defined as orthogonal among them. However, perception of a specific monochromatic colour in an intimate mixture of colours also depends on the relative energy of reflectance. Therefore two different situations can arise: *metameric colours*, which correspond to lights of identical tristimulus values but different spectral energy distribution, and *isomeric colours* which instead correspond to lights of identical spectral energy distributions (and consequently equal tristimulus values). Methods for evaluating these situations were devised in past [7].

The visual responses can however be non-linearly related to the tristimulus values based on the fundamental primaries of colour vision [10]. Ceramic pigments are constituted of substances that do not give a monochromatic spectral line (that is, at a specified wavelength), but supply a spectral curve that generally covering the whole visible range. They consequently give rise, in general, to metameric colours. The conditions to obtain metameric colours were developed in past [11]. Metameric colour impression behaves independently of the adaptive state of the eye. The eye stimuli obtained with the combination of different metameric colours of the same three basic colours could not be the same: to obtain the same stimulus it is necessary that the obtained spectral overlaps are the same. If the selected basic set of colours is based on metameric colours, instead of a set of linear equations, it should operate with a set of integral-differential equation based on differential intervals of wavelength ($\Delta\lambda$), in which also the associated weight is a function of the wavelength λ.

Three corrected orthogonal colours were adopted for true three-colours photoceramic productions, which are exactly complementary to the classical RGB system of reference; they correspond to: magenta, yellow and cyan. Each of these colours does not come from a specific wavelength of its own but (ideally) from a continuous spectrum of all visible wavelengths (which produce the sensation of white), from which the specific RGB wavelengths have been cut off one at a time by suitable filters to obtain these complementary colours. This choice is due to the highest stability of the possible pigments, to the narrower interval of wavelength of their perception and to the fact that they represent exactly the negative of the primary RGB colours. On the other hand, for similar reasons these colours have been adopted for a long time now in the field of colour photography.

5. Applied technology

Ceramic pigments, which were generally discovered accidentally, are not produced for their utilisation as basic colours for three-colour printings, but to bring a specific true colour into the mono- or poly-chromatic decoration of ceramic tiles. Till now no firms producing ceramic pigments would think of devising a method to manufacture pigments specifically dedicated to the introduced true three-colour reproduction process. The present world market available would be very narrow, whereas the production costs are certainly still too high to supply standard lots with very narrow margins of physical variations, although produced in different times.

It is therefore better to utilise directly the ceramic pigments already offered by the market, selecting those which do not undergo any significative variation of chemical composition at the production time and/or any chemical modification with the firing temperature. In fact, it is possible to make up for the problems arising with the utilisation of commercial pigments by calibrating the attributable variables of the computer program which supervises the absolute amounts and the combination ratios of every colour assigned to each point of an image. The calibration is necessary because each lot of acquired pigment of a specific colour (defined by a code and correspondent to a standard atlas of colours; the Italian ceramic field generally adopts a Minsell-like system or *pantone*) shows a spectrum that is similar but not equal to other lots of the same pigment. The resulting colour is the same for an intimate composition of coloured compounds which corrects deviations, but in association with other colours the resulting perception can change a bit.

The main problem was how to find the correct proportions of the four constituents required to produce a colour match able to fit all the possible wanted colours with the utilisation of a basic set of ceramic pigments. It is a problem involving the colorant power: the less the quantity of ink or pigment needed to reach such effect the greater this power.

Another property involved in giving problems in this specific application is the covering power, which is the capability of a coloured ink or pigment to mask completely by coating a coloured surface (even black) on which it is deposited. However, the colorant power is a concept a bit different from that of covering power. As concerns photoceramic matter, taking into account that ceramic pigments can interact chemically when in contact among them, the spot dimension and the gap between two spots must be strictly obeyed to avoid the situation of the A case of Fig. 1. Differently from coloured press on paper, in photoceramic reproduction a spot is not absorbed but englobed by the background glaze. For the te-chnique adopted, a spot can assume circular shapes, from a thin planar layer to a semi-sphere. Because ceramic pigments are highly mat, the material under the surface of a spot participates at a very small extent in the reflection phenomena. This determines a problem of "*saturation*" of the reachable intensity of coloration, which normally precedes the basic problem consisting in the reaching of the physical-optical sensation of saturation. The quantity of light reflected by a spot is therefore not proportional to the volume of the spot, but simply to the cross-section area viewed by the eyes of an observer. In this case it is necessary to play with the amount of area that is really covered by the pigment. Therefore the spot must be always circular, but it must change its diameter in direct proportion to the wanted intensity of colour of the spot, until a threshold maximum diameter is reached, which corresponds to the saturation threshold. On the other hand the maximum diameter of the spot allowed is conditioned by the spot dimension above mentioned. To be able to do this the operator needs very fine and controlled powders, which are generally obtained by the adoption of special sieves equally grained.

Also in this case a bad registration can obviously give rise to the same occurrence with the consequence of obtaining an awful masquerade instead of a good reproduction. What is important in this case is to respect the positional symmetry of the centres of all the spots. On the other hand, a bad registration can lead also to direct contact among the spots; it is well known that changes in the chemical structure of a pigment can produce a hyperchromic effect that corresponds to increasing the strength of a dye or to increasing the tinting strength, effects. These effects are well known for most dyestuffs.

The reproduction of every series of points of the same basic colour is obtained by different methods. There is an old technique of photographic reproduction based on the preparation of different transparent polymeric sheets; each of these sheets is reporting the spots distribution of one colour alone (Fig. 2). A suitable, well-registered overlapping of these sheets gives rise to a reproduction called *overlay-printing*.

6. The process of pigment deposition

The problems and physical solutions encountered in the setting-up of pigment deposition were similar (but not equal) to those of the colour photostatic technique. In this presented new photoceramic technique the coloured pigment is deposited on the surface of a suitable (even standard) polymeric sheet for photographic decalcomania (some gelatine-like types of commercially available sheets for traditional photoceramic reproduction can be utilised). The surface of the sheet is preventively modified physically and chemically in order to impress suitable dielectric and

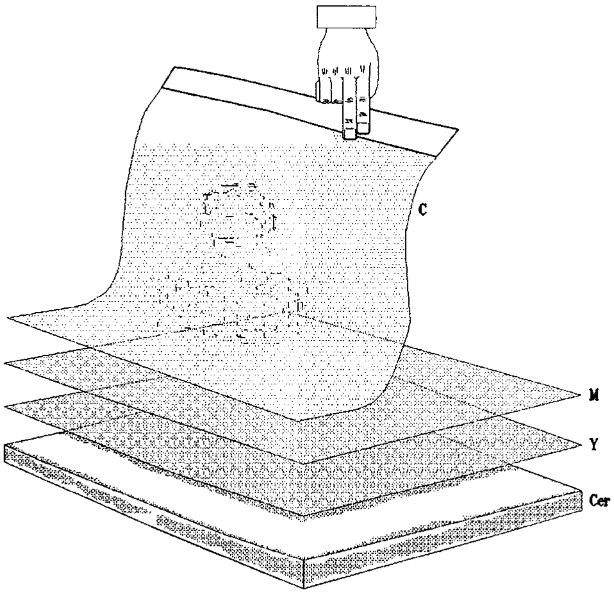


Figure 2 Schematic example of overlay-printing procedure. C = cyan layer, M = magenta layer, Y = yellow layer and Cer = substrate (also ceramic) already covered with the background glaze.

electro-optical properties (patent requested). The surface is activated by a photoplotter to produce *active* spots, with technical treatments which are exactly similar to those of photostatic reproduction with toner. Active spots can be produced by both electrostatic induction and the photo-polymerisation process (it depends on the above-mentioned kind of chemical treatment). Every active spot corresponds to a point of formation of the image and must correspond to a photographic positive. The deposition of every pigment powder has to be processed. At the very beginning it was performed by hand, simply by carefully shading the pigment on a suitable photoceramic sheet. Now it is carried out by an aspersion device, consisting of a special camera in which the activated sheet is placed and across which the powder is introduced by a careful ventilation with controlled slow flow of air. The powder is attracted by the active points and it adheres there more firmly than elsewhere. Therefore the powder of pigment remains deposited in the positions in which the image has to form more firmly than elsewhere. The amount of powder attracted and adhered is obviously proportional to the intensity of activation of the spot. The degree of activation of a spot is obviously proportional to the original intensity of radiation of the specific wavelengths bands separated by filters coming from that point of the source image, while it is proportional to the luminance for the points of contrast (points with black powder), which must grant a greys scale. Consequently, the greater the activation of a point the greater the quantity of powder that will be trapped by it. The excess of powder is automatically removed through the same soft ventilation exercised by the properly devised system above described and consequently only the powder attracted by the active spots remains. This system allows the salvage of the pigment through a pneumatic filtering of the outflow. Every sheet must be overlapped and carefully registered on the previous ones on the surface on which the image must be reproduced. The surface must be already covered by a background transparent glass enamel on which the spots must adhere and just slightly sink after suitable firing at 700–800°C (the temperature depends on the softening point of the adopted glass).

Differently from grey scale reproduction, where only one sheet is needed, the *corrected three-colour technology* of image reproduction needs four independent sheets. Three sheet must contain in turn the complementary colours (cyan, yellow, magenta) of the image coming from the primary filters (red, green, blue); the fourth sheet must contain the contrast (*luminance*), obtained with deposition of different amounts of black pigment. In the photographic field, filtering is obtained by reproducing the image through a specific coloured filter, and the grey scale is not necessary. In the case of this technology the filtering is automatically obtained through computer processing by means of suitable programs of image processing.

Here follow some examples of disposition of the coloured spots, registered on photografic paper, but reproduced in white and black in this paper (Figs 3b–h). The reader can distinguish the background (generally the lighter colour) and the spots displaced regularly, as mentioned above. These photograms were detected through an optical stereographic microscope on the surface of a photoceramic reporting the image of a young woman (refer to Fig. 3a).

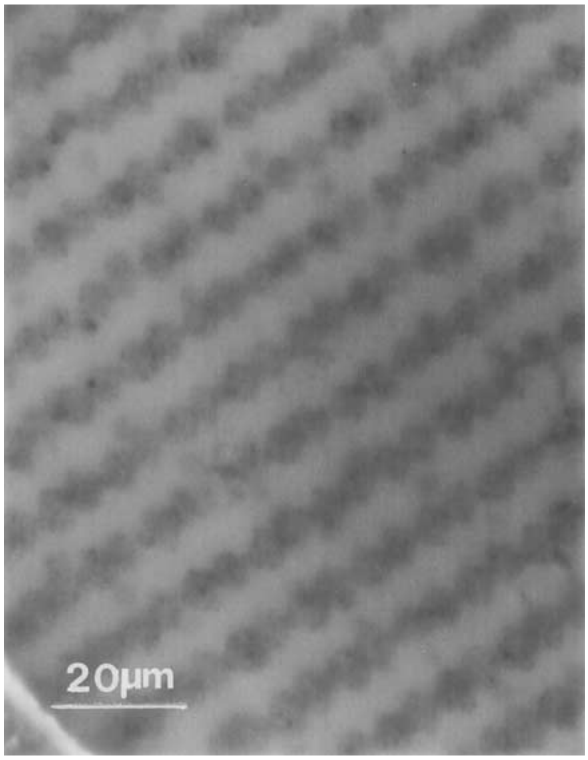
7. Technical problems connected to the ceramic pigments

Much of the work involved consisted in a screening of innumerable ceramic glazes and of pigments classified as *black, cyan, magenta, yellow* and *green*. Many commercial products of different firms were tested to evaluate their suitability as materials for true three-colour photoceramic. Most of the examined materials were for covering of porcelain supports. It has to be remembered [1] that this choice was bound to the initial target of this technique, intended to correspond to the cultural traditions of commemoration of the dead in the cemeteries of Mediterranean countries (like e.g. Italy and Spain), whose tombs carry typically ovoid porcelain photography featuring the dead. It is however obvious that this photoceramic technique can be applied as well on tiles of other ceramic typologies (e.g. grés, earthenware, *Tuscany cottoforte*, etc.), as on the other hand has already been done, and that the possible attainable products can be commercially oriented to other social destinations (e.g. tiles decorated even with photos of present or ancient works of art), which also has been already done.

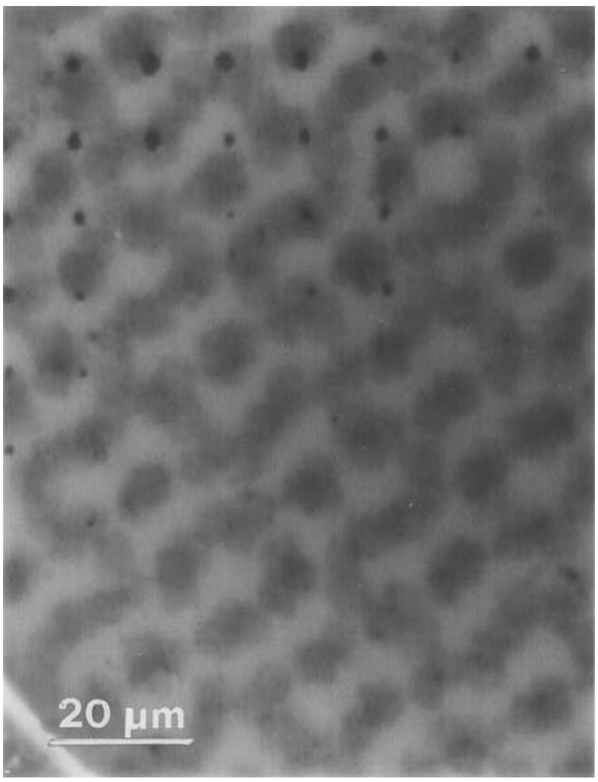
The crucial problem is the performance of the glaze(s) to be utilised, which must answer in particular the following requirements:

- compatibility with the supporting material (in terms of firm adhesion and equivalence of thermal expansion coefficient);
- high degree of solidity (resistance, toughness, durability over time);
- high wettability on pigment micro-grains with no sign of their dissolution, not even partial.

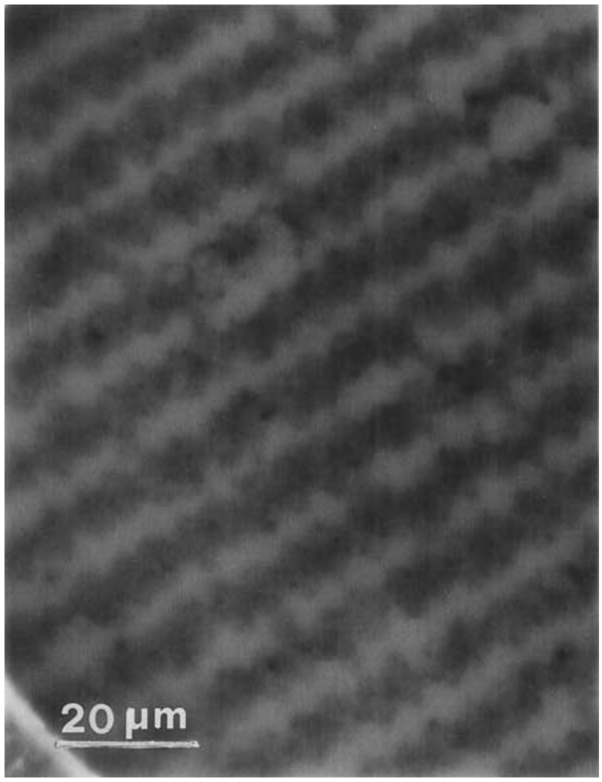
(a)



(b)

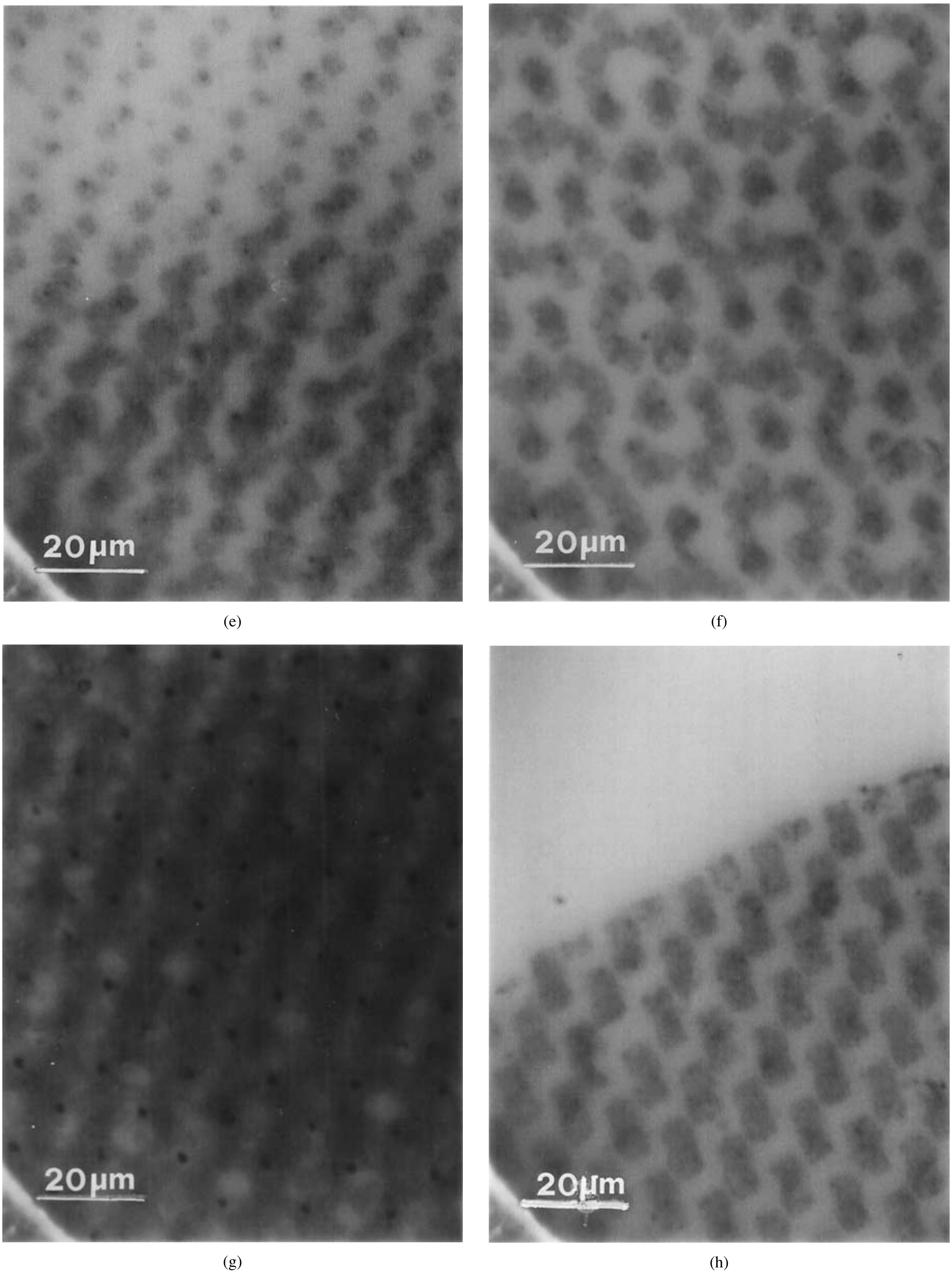


(c)



(d)

Figure 3 (a) Reproduction of a true three-colour photoceramic on a family tombstone oval porcelain of a (still living) young woman. This image was taken for this paper directly from the oval prototype (made on 1995) through a plotter (trimmed for the best shot). Being the oval not flat, but cambered (thicker at the centre, thinner at the boundary), the obtained image does not correspond at all to the quality of the original, for resolution, focusing and diffraction effects of the colours. This image serves however only as a reference to have an idea from where the optical microscope was focused to take the magnified images of the spot arrangements in chromatic roses of Figs 3b–h. (b) Chromatic rose of skin (spot 1) detected by an optical stereoscopic microscope on the mentioned photoceramic in the side of the chin. (c) Chromatic rose of the white blouse with a shaded part (spot 2) detected by an optical stereoscopic microscope on the mentioned photoceramic. (d) Chromatic rose of the white teeth (spot 3) detected by an optical stereoscopic microscope on the mentioned photoceramic. (e) Chromatic rose of the lighted blond hairs (spot 4) detected by an optical stereoscopic microscope on the mentioned photoceramic. (f) Chromatic rose of the grey background part (spot 5) detected by an optical stereoscopic microscope on the mentioned photoceramic. (g) Chromatic rose of the magenta sweater (spot 6) detected by an optical stereoscopic microscope on the mentioned photoceramic. (h) Chromatic rose of the old rose background part (spot 7) detected by an optical stereoscopic microscope on the mentioned photoceramic *(Continued)*.



(e) (f) (g) (h)

Figure 3 (Continued).

Therefore, to have a final product corresponding to these needs, the set-up of this technique was extremely hard and severe. Because it was considered absurd to think of a direct production of specific glazes, given the commercial inconsistency of the quantity to be supplied, even for a worldwide production, a prolonged activity of selection of both pigments and enamels was carried out on products which on the market are available from producers of pigments for tiles.

The encountered problems are:

1. variability in the chemical composition of different lots of glazes, which exceed the maximum tolerance allowed;

2. chromatic variability of different lots of pigment;

3. imperfect chromatic orthogonal colouring character of the selected basic pigments;

4. rising effect of the image referred to the interfacial plane of the ceramic support;

5. saturation effect due to the maximum amount of pigment which can be lodged in each active spot.

As concerns point 1. (variation in the chemical composition of glazes), it has to be remembered that the observed maximum compositional variations are inside the standard intervals allowed by the norms that regulate the production of decorated or artistic ceramics (in particular tiles decorated by serigraphy lines series); the interval allowed by true coloured photoceramic has shown, however, to be narrower, being the optical effects more influent on the visual perception when used to activate the tristimulus effect. Therefore a careful selection of the produced lots became necessary, which was carried out by a test of fitness (in practice by producing a standard photoceramic and evaluating the overall performance).

The problems involved in the point 2. (chromatic variability) are due to two obvious factors: compositional and/or of preparative methodology. Also in this case the observed chromatic variations are within the standard intervals allowed by legal regulations prescribed for the production of decorated or artistic ceramics (in particular tiles decorated by serigraphy lines series), but they became problematic in true three-colour photoceramic visual rendering, because of the greater sensitivity of the biophysical phenomenon involved (visual perception).

The reason indicated in the point 3. (imperfect chromatic orthogonal colouring character of the base components) implies an inability to cover all the chromatic spectrum. In fact, ceramic pigments do not reflect a specific monochromatic line (or very thin band around it) or vice versa the correspondent ideal (metameric) pure complementary one (as it would theoretically be in the case of the adopted tern of colours here used), but they normally reflect a wide spectrum of radiation with many maximum peaks and minimum depressions distributed all along the whole interval of the different visible wavelengths, which forms a metameric perception of a colour. Unfortunately, use of the selected pigments (which on the other hand behave very well on most of the spectrum) resulted in a failure in particular of the reproduction of fiery red. Also the thinness of the pigment powders can influence the colour: in some cases, below a certain threshold size of the grains of the powder, a change of colour was observed. This could depend either on a too wide chemical interference between powder and glaze or on an interfering scattering process which occurs when the size of the grains approximates the wavelength of the reflected light. The problem of the imperfect chromatic orthogonal colouring character of the base components was temporarily resolved in the last years by resorting to a fourth pigment, whose chromatic spectrum is able to compensate the chromatic deviation coming from the other three utilised pigments (which allowed to operate in a *corrected four-colour technique* of reproduction). This contrivance, however, increases the costs of production and needs further set-up, because, at the present, it is necessary to select carefully the fourth pigment every time and perform many different reproductions of the wanted image by trials-and-errors method, till the achievement of the best result.

Point 4. involves a problem (rising effect of the image) which is part of the first point. It comes from a too marked maximum angle of refraction (together with a too thick layer) of the utilised background glaze on which the micro-spots of pigment are deposited.

Point 5. concerns the maximum quantity of powder that can be caused to adhere on an active spot of the sheet. This obviously depends on: (1) the dimension of the spot, (2) electrostatic polarisability of the material constituting the sheet, (3) complementary electrostatic polarisability of the pigment grains, (4) the degree of porosity of the aggregate of deposited pigment. This last point emphasises the types of specific performances required for both sheet and pigment.

8. The nature of glazes and pigments

The nature of the enamel that covers the substrate must be selected in conformity to the nature of the support, but taking into account the nature of the pigments utilised. It must be perfectly compatible with the substrate material (similar thermal expansion coefficient and good wettability during application). Its temperature of application should range around 700–1050°C, depending on the type of interactivity with the support material. Opaque crystalline, low borax, no barium, lead-silicate enamels are good as first coverings of the substrate. On white porcelain even transparent crystalline is good as well. However, to avoid a problem of apparent suspension of the image from the background, the adopted glaze must reach a sufficient softening state at the temperature of firing to allow a sufficient sinking of the micro-clots of coloured powders coming from the activated, and well registered, sheets put on the surface of the enamelled substrate. These coloured micro-clots must sink just below the surface of the enamel in such a way as to be completely covered by it. This serves also to defend from external injuries the coloured spots which cannot escape from the surface in time. Therefore the softening properties of the enamel must be such to be able to englobe the deposited clots of pigment, by their partial or total sinking, at temperatures ranging from 700 to 900°C, with a complete wetting and without any dissolution. The temperature of softening will be as low as that of application on the support. On the other hand the enamel thickness must be as thin as possible to avoid effects of either back-reflection from the ceramic substrate (especially if this is specular such as a porcelain) or total refraction of the enamel (particularly if it is lead-rich). If a protective covering is considered, a further low temperature transparent glaze can be adopted which melts between 700 to 900°C. Its presence introduces an enamel/glaze interface which can produce some optical illusion (movement of the image with the visual angle, multiple reflections of the image, etc.). Normally these illusions are undesired, but sometimes are wanted. The selection of a suitable enamel is not easy; the combination between an enamel and a proper glaze is still less easy, even when the optical illusions are to be introduced intentionally.

9. The coloured pigments

As concerns the pigments, their production is widely empirical. Those examined by chemical analysis and by X-ray diffraction have shown extremely variable compositions, as listed for some of them in Table I. The compositional families of detected crystalline phases belong frequently to: garnets, zircons, perowskites, spinels. Among yellow pigments there are also the antimoniates (but these are less useful because are easily dissolved by many enamels, although their chromatic spectrum would be the optimal for the yellow). Many pigments are instead amorphous (hard glass at high temperature of melting). On the other hand, not all producers supply information on the technical modality of production (including composition). Colours are generally obtained by inclusion of transition elements into the crystalline lattice of the main composition: first row of the Mendeliev's periodic table (V to Cu), Cd, Lantanides (Pr, Nd, Eu, Gd). The experience suggests that the colours containing Cu, V, P, Pb, Sn, Cd, and sometimes Co are to be considered with care, becausae they generally contains one or more compounds which are too soluble in the enamels and diffuse too much in the neighbourhood of the deposited micro-clots.

The amount of these chromophoric elements is extremely variable: they can constitute the fundamental composition or can be present in traces, even below the threshold of analytical sensitivity. To give an idea of the variability of composition, an example is reported in Table I that concerns some of the examined pigments (identification though X-ray diffractometer). A series of oxides, such as ZnO, La_2O_3, Al_2O_3, Y_2O_3, ZrO_2, SnO_2, PbO, Ta_2O_5, SiO_2, Nd_2O_3, etc., together with possible phosphoric compounds, may be added either to the composition during the chemical synthesis or during the milling, to obtain special effects (matt, iridescence, translucency, fluorescence, etc.).

However, for the target of this technology are important some particular physical properties of the pigments. Their more important properties are: quite complete insolubility in the adopted enamel, complete wettability in the same enamel, high electrostatic polarizability (to be deposited on the photoceramic sheets).

An important parameter to be carefully considered in the choice of a colouring agent is the colorant power. This is the capability of a coloured pigment to impart a colour (more or less intense) to a white pigment with which it is intimately mixed. Such power increases (but only until a threshold limit) with the increase of the fineness of the pigment. There is therefore an effect on glaze colour by the particle size of pigments. One such effect comes from the tendency of the pigment to dissolve in a molten glaze is a function of the pigment surface area per unit volume, which in turn is inversely proportional to the particle size [12].

TABLE I Identified components by X-ray diffractometry of some pigments

Colour	Producer	Content	Recognised main components	JCPDS card association
Black	P1	Spinels	$CoCr_2O_4$	35-1321/22-1084
			$CoMnCrO_4$	26-474
			$NiCr_2O_4$	23-1271/23-1272
			$NiFe_2O_4$	10-325
			$FeCr_2O_4$	34-140
			Others$^{(1)}$	
Red	P1	Malayerite	$CaSnSiO_5$	25-176
		Cassiterite	SnO_2	21-1250
		Grossularia	$Ca_3Al_2(SiO_4)_3$ (traces)	39-368/33-260
			Others$^{(2)}$	
Yellow	P2	Antimoniate	$Pb_2SnSbO_{6.5}$	39-928
Yellow	P1	Antimoniates	$Pb_2SnSbO_{6.5}$	39-928
			$PbSb_2O_6$ (traces)	34-912
			$Pb_2Sb_2O_7$ (traces)	39-834
Blue	P1		$CoAl_2O_4$	10-458
			$ZnAl_2O_4$	05-669
			Others$^{(3)}$	
Blue	P2	Amorphous	—	—
Magenta	P2	Amorphous	—	—

$^{(1)}$(Ni,Fe)(Fe_2O_4), $(Mn,Cr,Fe)_2O_3$; $^{(2)}$$Ca_3Cr_2(SiO_4)_3$ (Uvarovite); $^{(3)}$$Ca_2SiO_4$, $CaSiO_3$, $CaCo(PO_4)_2$, $CaCo_2Si_4O_{10}$.

TABLE II Identified mean atomic composition (Oxides wt%) of the indicated pigments

Colour	P_2O_5	SiO_2	SnO_2	B_2O_3	Al_2O_3	Cr_2O_3	Fe_2O_3	Sb_2O_3	Mn_3O_4	PbO	MgO	CaO	NiO	CoO	Na_2O	K_2O
Black	—	0.22	—	—	—	28.72	27.68	—	10.26	—	—	0.12	9.46	23.28	—	—
Red	—	27.82	38.22	10.89	0.90	0.38	—	—	—	—	0.27	15.95	—	—	4.88	0.67
Yellow	—	—	18.53	—	—	—	—	27.44	—	54.02	—	—	—	—	—	—
Blue	17.19	20.84	—	—	—	—	—	—	—	—	0.10	13.96	—	47.87	—	—

10. Computer aid

As previously described [2], a Quantel Co. Ltd. image computer, with suitable dedicated hardware and usual software for painting and images treatment, is used. Obviously, further proper software was written containing the computing procedures expressly dedicated to this activity.

A first problem of the software is that it must take into account that ceramic pigments could chemically interact when in contact among them. The spot dimension and the gap between two spots must be strictly obeyed to avoid the situation of case A of Fig. 1. It must be remembered that differently from coloured pressing on paper, in photoceramic reproduction a spot is not absorbed but englobed by the background glaze. In the adopted technique a spot can assume circular shapes, starting from a thin planar layer until becoming a semisphere. Because ceramic pigments are highly mat, the material under the surface of a spot participates to a very small extent in the reflection phenomena. As previously told, the quantity of light reflected by a spot is therefore not proportional to the volume of the spot, but simply to the cross-section area viewed by the eyes of an observer. In this case it is necessary to play with the amount of area that is actually covered by the pigment. Therefore the spot must be always circular, but it must change its diameter in direct proportion to the wanted intensity of colour of the spot until reaching a threshold maximum diameter, which corresponds to the saturation threshold. To have the possibility to do this, the operator needs very fine and controlled powders. The selection of the fine powders is generally obtained by the adoption of special, equally grained sieves, but all other remaining procedures concerning visual effects are the task of software routines. Metameric non linear equations and their visual responses are in practice too complicate to be inserted in the software. The structure itself of the possible equations could change depending on the particular selections of available pigments. It is instead more practical to adjust experimentally the linear coefficients by introduction of correlation coefficients for every tern of available pigments. Unfortunately this procedure must be repeated every time a new lot of pigment is used, even if the pigment is produced by the same manufacturing house and with the same commercial code. In fact, ceramic pigments, generally discovered accidentally, are not produced for their utilisation as basic colours for tri-chromic printings, but to impart a specific true colour to the mono- or polychromatic decoration of ceramic tiles.

11. The solidity of the obtained true three-coloured photoceramics

The solidity of a colouring pigment is its resistance to different agents which could alter or solve it. There are many different types of resistance to possible agents like to:

- photons action (natural light or ultraviolet radiation);
- inclement weather;
- chemical substances (acids, alkalis, solvents, etc.);
- atmospheric pollution (e.g. sulfide or sulfidryl gases, oxidants, reducing agents, motor exhausts, etc.).

A deceitful agent is fog, particularly in shore-line zones (for the further content of sea salts), because it englobes active micro-particles (in particular biological ones, such as spores, moss and fungous bacteria) and solves all possible corrosive gaseous chemicals (SO_x, NO_x, HCl, all thinkable species of organic acids).

12. Results and perspectives

From the introduction of this new technique (1992), about three hundred thousand photographic reproductions by true three-coloured photoceramic were made for cemetery destination. Shapes and dimensions were the most different. Generally the support was a porcelain oval, but also rectangular grés-like bricks were used as supports. These products were placed in all Italian localities with all possible climates (mountain, marine, continental, Mediterranean, etc.), were subjected to sudden thermal changes and exposed to all kinds of inclement weather. No product has shown failure due to intrinsic reasons; only few samples have broken uniquely for accidental factors due to carelessness of the operators (masons, cemetery custodians, owners of the tombs, etc.).

The market of this new technique of reproduction on ceramic is not limited to the world of the dead alone, but also to artistic reproduction for decorative purposes. This opens a wider range of markets. For example, the firm RGB Ltd. has reproduced on commission two giant photoceramic panels with reproduction of an image of Walt Disney (4.80 m × 2.40 m) for the naval fleet of Walt Disney America Inc. (whose first transatlantic liner was launched from an Italian dock on June 1998).

Another big work-project involved the realisation of a swimming-pool with reproduction of a genuine master on ceramic tiles (dimension 10 m × 1.20 m).

There are many initiatives going on, involving commissions by public and private institutions (offices, dining rooms, halls, building fronts, floors, etc.).

The presented technique of image reproduction is very well suitable for the serial reproduction of images. Similarly to the ceramic decalcomania for ceramic reproductions, it is possible to produce transfers on polymeric supports already ready to be applied on ceramic surfaces. In fact, it is possible to perform four separate reproduction on continuous suitable independent polymeric tapes of the decomposition into the three fundamental colours and of the greys of the wanted image. It is possible to superimpose these tapes, already well registered through a suitable device with automatic control, obtaining a multi-layered tape. This multi-layered tape can be notched or pre-cut to separate easily each single transfer with the image reproduced at the moment of the utilisation. So treated it can be coiled around a spool to be used afterwards when required by the ceramic production. If the multi-layered tape is enriched with a further basic layer that contains already the powder of a suitable low-melting glaze, these transfers can be utilised for serial reproductions on whatever surfaces, not necessarily flat, of ceramic nature (including enamelled metallic objects, ultra-thin ceramics, etc.). The field of commercial fashionable application becomes so very wide, concerning object with whatever destination of use (therefore not necessarily limited to memorial porcelains or tiles for decorative lining walls of buildings).

This process so developed can be utilised even on ultra-thin tiles produced by tape-casting (without use of press) with a consequent unlimited possibility of reproduction of images and colours.

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