COMPOSITION OPTIMISATION OF PORCELAIN TILE BODIES DECORATED WITH SOLUBLE SALTS

A. Bresciani, A. Brusa, M. Federici*

Sacmi Imola - R&D Centre
Italy

INTRODUCTION

The work was undertaken with the following objectives:

1. Defining a methodology for verifying the suitability of different porcelain tile bodies for decoration with chromophore solutions.
2. Preliminary assessment of the effect of the different chemical, physical, mineralogical and optical properties distinguishing the bodies in terms of the aesthetic and technical characteristics of the finished product.
3. Analysis of the experimentation data to determine the existing correlations between the technological parameters of the bodies and their behaviour on applying chromophore solutions.

The determination of ideal forming, drying, decoration and firing conditions lay beyond the scope of the objectives mentioned; the conditions used, drawn from standard industrial practice, were held steady throughout the experiments.

The study was guided by at least three criteria:

- Attention to production reality: it was attempted to establish the simplest and most concrete possible study method that would reproduce normal production conditions.
- Awareness that developing a predictive model can entail a simplification for ceramic processes of the set of variables involved, and that such a model, though objective and based on experimentation, can therefore only have indicative value.

- The endeavour to carry out useful work for those involved in the subject, without putting forward a specific body formula, and leaving to one side the bonds that link each manufacturer to a raw materials supply, highlighting instead the determination of general process principles and mechanisms to guide body preparation and identify the most appropriate interventions for solving specific problems.

The study was organised in terms of the following stages:

1. *Definition of study context.*
2. *Experimental trials on a semi-industrial scale.*
3. *Analysis of experimental data.*
4. *General remarks.*

1. DEFINITION OF STUDY CONTEXT

Body behaviour was related to three basic characteristics:

1.1. PERMEABILITY TO CHROMOPHORE SOLUTIONS[1]

It is a fundamental property of the semi-finished products to be decorated, that stains (colouring solutions) should penetrate sufficiently into the mass to allow removing a few tenths of mm from the surface on polishing the finished products without impairing the decoration, which depends on:

- Mineralogical origin of the body (whose relationship to permeability is the aim of the experimental study), and particle-size fineness.

- Certain technological process variables (forming pressure, powder moisture content, temperature of the pieces to be decorated, etc.), which were held steady throughout the experiments.

- Characteristics of the liquid medium and diluted colouring salt (chemical origin of the chromophore ion and its complexing agent, density, medium viscosity and pH, etc.).

From an industrial point of view, it is important that absorption of the solution by the body should be:

- Sufficiently deep to allow removing a 0.6 ÷ 0.9 mm thick layer in polishing.

- Homogeneous, to avoid excessive chromatic variation and differences in decoration from arising, which would entail a proliferation of commercial shades.

Penetration depth is closely related to the body, whereas homogeneity depends on

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[1] *'Correlazione tra composizione chimico-mineralogica e colorabilità con sali cromofori in impasti di grès porcellanato'*. Tesi di licenza di G. Gioghi e M. Minganti. Istituto Statale d'arte per la Ceramica «G. Ballardini» Faenza - Curso di Perfeccionamiento en Tecnología Cerámica: "Ceramiche Speciali" - Año escolar 1996-97.

correct process management and corresponding in-plant and technological decision-taking, especially in the pressing, drying, decorating and storing-stabilising stages of the decorated tiles.

Since it is not possible to eliminate minor variations in the density of the green semi-finished body, which produce a minimum colour non-uniformity in the body's cross section, penetration depth is an important parameter in evaluating the suitability of a body for polishing without impairing the chromatic quality and integrity of the decorations (e.g. screen printing).

1.2. EFFECT OF WETTING ON MECHANICAL AND SURFACE PROPERTIES

The spraying of controlled amounts of water onto the dried bodies facilitates the absorption of successive solution applications, but might entail a greater or lesser fall in the mechanical properties and surface integrity of the half-finished products, which affects productivity in the decorating line.

1.3. DEVELOPMENT OF FIRING COLOUR (IN THE MATERIAL IN A NATURAL OR POLISHED STATE)

The chromatic yield of the finished product depends to a large extent on the reactions that give rise to the glassy matrix and new crystals in firing, and thus on the suitable combination between the body's chemical properties and those of the chromophore ion (e.g. cobalt aluminate crystallisation by reaction between free alumina and the dissolved cobalt applied in the solution).

Since the versatility of bodies on applying different salts is taken for granted in the objectives set in the experimentation, the most general possible condition has been sought, using ions without a specific chemical selective affinity towards any given body constituents in particular.

It was therefore considered convenient to start with a white base body, carrying out simple compositional variations in order to highlight the behaviour of each component.

The compositions, semi-finished and finished products have been characterised according to the following scheme:

A. BODY CHARACTERISATION.

a1. Chemical analysis in oxides

a2. Mineralogical analysis

a3. Clay ion exchange capacity (C.E.C. Cation Exchange Capacity)

a4. Organic carbon content

a5. Reject at 63 μm

a6. Reject at 45 μm

B. POWDER CHARACTERISATION.

b1. Moisture content

b2. Particle-size distribution on screen

C. PRESSING CHARACTERISATION (tiles size 320 x 320 x 9 mm).

c1. M.O.R. (modulus of rupture) on pressing

c2. Pressing expansion

D. DRYING CHARACTERISATION (drying to 0.5 % moisture content)

d1. M.O.R. (modulus of rupture) on drying

d2. Ratio (drying M.O.R. / pressing M.O.R.)

d3. Drying shrinkage

d4. Bulk density (mercury method).

E. CHARACTERISATION OF SEMI-FINISHED PRODUCTS ON APPLYING WATER AND CHROMOPHORE SOLUTIONS

e1. Salt solution application test on wetting the hot pieces (50÷55°C): solution penetration depth and surface drying time (airbrush application of 10 g of water - 120 seconds - application of colouring solution by double disk booth - measurement of drying time). Solutions used: containing chrome and iron.

e2. Wetting trial with assessment of reduction in mechanical strength (airbrush application of 30 g water - 120 seconds - measurement of M.O.R).

F. CHARACTERISATION OF FIRING COLOUR (rough and polished surface).

f1. Colorimetric indices (L,a,b) of the coloured and non-coloured, natural and polished, fired body.

L = whiteness index

a = +a red; -a green

b = +b yellow; -b blue

NOTE. The comparison was performed between materials with the same degree of vitrification.

2. SEMI-INDUSTRIAL SCALE EXPERIMENTAL TRIALS

A. BODY CHARACTERISATION

Nine bodies were formulated and prepared, of which two were opacified with zirconium silicate and alumina; the chemical, mineralogical, and particle-size characteristics are detailed in the following table:

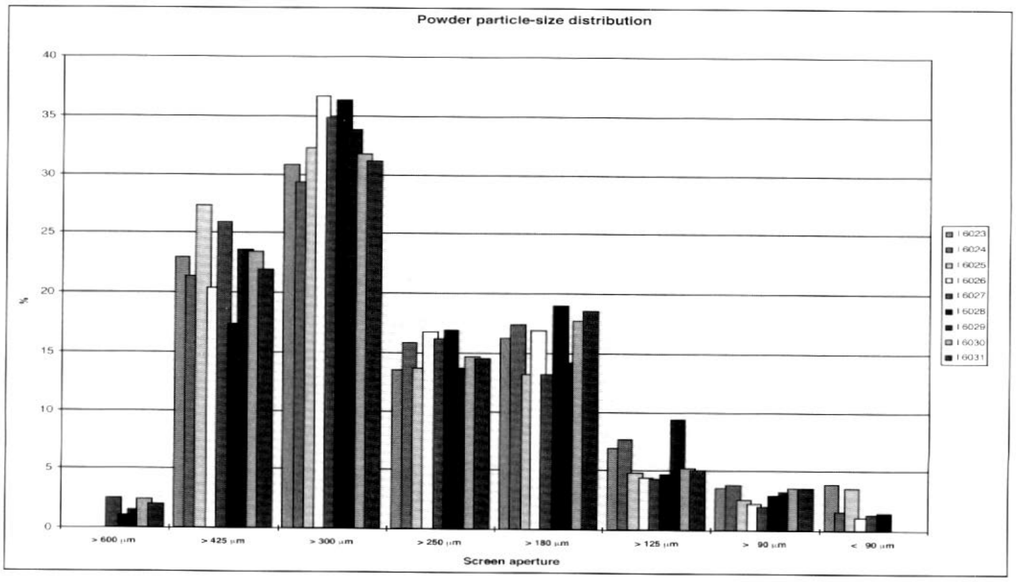
Body code	**I 6023**	**I 6024**	**I 6025**	**I 6026**	**I 6027**	**I 6028**	**I 6029**	**I 6030**	**I 6031**
Composition %									
ILL-KAOL. PLAST. CLAY	30	21	14	25	25	25	30	28	28
KAOL.-MONT. PLASTIC CLAY		10							
KAOLIN	15	13	27	17.5	17.5	17.5	18	15	12
SODIUM FELDSPAR	45	45	45	43	43	43	21	43	47
POTASSIUM FELDSPAR		1.5	2.5	0.5	0.5	0.5	20		
QUARTZOSE SAND	10	9.5	11.5	14	14	14	11	8	7
$ZrSiO_4$								6	
CALCINED Al_2O_3									6
Green body mineralogy %									
KAOLINITE	+++	=	↑	=	=	=	↑	=	↓
ILLITE	++	↓	↓	=	=	=	=	=	=
MONTMORILLONITE		+							
ALBITE	++++	=	=	=	=	=	↓	=	=
ORTHOSE	+	=	=	=	=	=	↑	=	=
QUARTZ	++	=	=	↑	↑	↑	=	↓	↓
OTHERS	+	=	=	=	=	=	=	↑	↑
Chemical analysis % green body									
SiO_2	69,2	68,2	67,5	69,8	69,8	69,8	67,7	66,7	65,0
Al_2O_3	19,7	20,4	21,2	19,3	19,3	19,3	20,2	18,9	24,4
TiO_2	0,5	0,4	0,3	0,4	0,4	0,4	0,5	0,5	0,5
Fe_2O_3	0,5	0,5	0,4	0,5	0,5	0,5	0,5	0,5	0,5
CaO	0,4	0,4	0,4	0,4	0,4	0,4	0,2	0,4	0,4
MgO	0,3	0,3	0,2	0,3	0,3	0,3	0,3	0,3	0,3
K_2O	1,2	1,2	1,4	1,2	1,2	1,2	4,1	1,1	1,0
Na_2O	4,3	4,3	4,3	4,1	4,1	4,1	2,3	4,1	4,5
ZrO_2	0	0	0	0	0	0	0	3,7	0
P.F.	3,9	4,3	4,3	4,0	4,0	4,0	4,2	3,8	3,4
Organic carbon, ppm	180	186	84	150	150	150	180	168	168
Part.-size parameters of the body									
Reject at 63 µm	0,7	0,8	0,4	1,8	0,7	0,1	0,8	0,4	0,5
Reject at 45 µm	4,5	4,7	2,6	8,8	3,7	1,1	3,0	2,5	2,9

B. POWDER CHARACTERISATION

Body code	**I 6023**	**I 6024**	**I 6025**	**I 6026**	**I 6027**	**I 6028**	**I 6029**	**I 6030**	**I 6031**
MOISTURE CONTENTD	5.70	5.70	5.40	5.45	5.65	5.65	5.40	5.40	5.70

The table shows that the powders were prepared at the most uniform possible moisture content values, around 5.5%.

Powder particle-size distribution was also quite consistent:



C. PRESSING CHARACTERISATION

Body code	**I 6023**	**I 6024**	**I 6025**	**I 6026**	**I 6027**	**I 6028**	**I 6029**	**I 6030**	**I 6031**
SP PRESSING PRESS, kg/cm^2	400	400	400	400	400	400	400	400	400
GREEN M.O.R., kg/cm^2	8.1	8.9	6.8	7.4	7.8	7.0	7.4	7.6	6.7
PRESSING EXPANSION, %	0.75	0.65	0.75	0.65	0.70	0.70	0.70	0.70	0.75

D-E. DRYING AND SEMI-FINISHED PRODUCT CHARACTERISATION ON APPLYING WATER AND CHROMPHORE SOLUTIONS

Body code	**I 6023**	**I 6024**	**I 6025**	**I 6026**	**I 6027**	**I 6028**	**I 6029**	**I 6030**	**I 6031**
Dry characteristics									
RESIDUAL MOISTURE %	0.65	0.85	0.15	0.70	0.65	0.65	0.75	0.70	0.65
DRY M.O.R. kg/cm^2	25.4	32.7	16.0	22.5	21.0	21.0	21.3	26.5	21.4
DRY/GREEN M.O.R. RATIO	3.1	3.7	2.4	3.0	2.7	3.0	2.9	3.5	3.2
DRYING SHRINKAGE %	0.03	0.09	0.00	0.03	0.06	0.00	0.00	0.06	0.00
BULK DENSITY BY MERC. g/cc	1.913	1.947	1.861	1.924	1.921	1.891	1.864	1.939	1.867
BULK DENSITY BY MERC. H_2O=0%,g/cc	1.901	1.930	1.858	1.911	1.909	1.879	1.850	1.925	1.855
Wetting trial, 30 g water airbrushed onto dry, hot pieces (50˝558 C)									
M.O.R. 120" after applic., kg/cm^2	16.2	21.4	12.1	16.0	14.2	14.5	14.4	17.8	13.4
Double disk application trial with diluted chromophore solutions, 20g on wet surface									
DRYING TIME (s)	70	180	35	80	65	55	55	75	60

F. CHARACTERISATION OF FIRING AND FIRED COLOUR (natural or polished surface)

Each body was fired in a roller kiln at a peak vitrification temperature, determined in previous tests at different temperatures with identical samples to the ones used in the experimentation.

The coloured specimens were fired 24 h after applying the salts.

The penetration depth of the stain solution was determined by microscopy, as the average of several points in the tile cross section.

Body code	**I 6023**	**I 6024**	**I 6025**	**I 6026**	**I 6027**	**I 6028**	**I 6029**	**I 6030**	**I 6031**
Fired characteristics									
FIRING TEMPERATURE, 8 C	1210	1210	1210	1210	1210	1210	1200	1210	1210
FIRING CYCLE, min	58	58	58	58	58	58	58	58	58
FIRING SHRINKAGE %	7.4	7.0	8.7	6.8	7.2	7.8	8.1	7.7	8.0
WATER ABSORPTION, %	0.01	0.01	0.00	0.03	0.01	0.00	0.01	0.00	0.01
M.O.R., kg/cm^2	430	440	430	490	470	470	440	440	440
Double disk application trial with diluted chromophore solutions, 20 g on wet surface									
AVG. PENETR. DEPTH. (mm)	1.97	1.63	2.03	1.63	1.66	1.63	1.88	1.72	1.90

The colorimetric parameters of the various fired bodies in a natural and polished state were found by averaging several measurements run at the specimen surfaces, both non-coloured and coloured by the chrome salt solution, using a D65/2° light source with specular light.

BODY	CODE	WHITE NON-POLISHED BODIES				NON-POLISHED BODIES COLOURED WITH Cr SOLUTION				POLISHED WHITE BODIES				POLISHED BODIES COLOURED WITH Cr SOLUTION			
		L*	a*	b*	DE	L*	a*	b*	DE	L*	a*	b*	DE	L*	a*	b*	DE
I 6023	STD	78.2	0.3	10.3	0.0	44.6	-3.7	11.6	33.9	78.6	0.3	10.1	0.5	57.0	-1.4	17.3	22.4
I 6024	Montmorillonite >	77.9	0.3	10.3	0.4	44.0	-3.8	10.8	34.4	78.3	0.3	10.2	0.1	55.2	-1.0	16.5	23.9
I 6025	Kaolin >	79.9	0.3	8.9	2.2	44.6	-6.3	10.8	34.3	80.3	0.6	9.1	2.5	55.8	-3.3	15.8	23.3
I 6026	Quartz > coarse mill.	79.7	0.2	9.4	1.7	45.2	-4.6	12.5	33.5	80.1	0.2	9.4	2.1	59.4	-1.5	17.2	20.1
I 6027	Quartz >	79.2	0.2	9.5	1.3	44.7	-4.4	12.2	33.9	79.7	0.3	9.6	1.6	58.0	-1.3	17.1	21.4
I 6028	Quartz > fine mill.	78.8	0.3	9.6	0.9	43.7	-4.7	11.3	34.9	79.0	0.3	9.6	1.1	57.2	-1.4	16.9	22.1
I 6029	Potassium feldspar >	77.3	1.0	9.9	1.3	46.3	-3.7	12.6	32.2	78.0	1.0	9.7	1.0	59.1	-1.1	17.3	20.3
I 6030	Zirconium white	85.2	-0.3	7.7	7.4	48.3	-4.1	14.6	30.6	85.1	-0.2	8.0	7.3	65.9	-1.3	17.1	14.1
I 6031	Alumina white	82.8	-0.1	7.8	5.2	47.9	-4.0	12.9	30.7	83.0	-0.1	7.9	5.4	64.8	-0.8	15.4	14.4

3. ANALYSIS OF EXPERIMENTAL RESULTS

3.1. Permeability to stain solutions

Measured parameters:

Penetration depth of the chrome stain solution in a cross section of the fired specimen (mm).

The value found was the average of several measurements run on the magnified (30x) image of the cross section with an optical microscope.

Parameters considered:

The characteristics that most affected absorption are set out below.

Discussion of results

1) Average penetration depth was 1.78 mm, sufficient to allow polishing; colour uniformity was not assured when polishing was very deep.

2) Reference body (I 6023, Standard) exhibited high permeability, decidedly above the average value and is an example of a correctly formulated body.

3) With regard to the reference body and all the average values, body I 6024 enriched with montmorillonitic clay exhibited modest permeability (1.63 mm.). This result is related to the great plasticity of this type of clay, which encourages densification in pressing (confirmed by the very high dry bulk density values and dry-to-green M.O.R. ratio), lowering porosity, while having the same mineralogical characteristics as montmorillonite, i.e., tendency to absorb interlaminar water causing swelling and obstructing the capillaries where the stain solution was to penetrate.

4) Regarding the reference body and all the average values, body I 6025, enriched with kaolin, exhibited a decidedly high permeability (2.03 mm). This was in principle related to the fact that kaolin can impede reciprocal particle movement, owing to scarce surface interaction with water, therefore limiting compaction in pressing, which produces reduced values for bulk density in the semi-finished products.

5) Although absorption was quite fast, as the very short drying times indicate, the bodies enriched with quartzose sand (I 6026-8) nevertheless exhibited quite a low penetration depth, regardless of the mill reject. This suggests a chemical type of interaction between the solute and the quartz, whose mechanisms need to be verified and explained.
From a physical point of view it can be observed that when quartz particle-size was coarse (short milling), the clay matrix exhibited few breaks and capillarity was limited, so that the mass was not very permeable; however, with long milling the fineness of the clay particles, which favours the formation of a mass containing capillaries with small cross sections, is balanced out by the existence of a homogeneously dispersed particle network, which encourages clay matrix discontinuity. These effects tend to reciprocally balance each other out when the degree of milling is changed.

6) With regard to the two white bodies (I 6030-1), the body containing alumina white (I 6031) exhibited a more marked permeability, which was not due to its different specific weight (approx. 4 g/cc for alumina and 4.5÷4.6 g/cc for zirconium silicate) and thus to the differing volume taken up the particles, but to the fact that to hold a certain chemical equilibrium in the clay, the increase in alumina has been compensated by reducing the kaolinite content in favour of complementary non-clayey minerals (albite).

7) The organic carbon proportion in the different clay bodies fluctuated within a very narrow range; this was because of the selected raw materials used, a use already consolidated in Europe. It is therefore difficult to gauge the importance of this parameter with regard to permeability, but there is no doubt that in clays with a high proportion of organic matter (relatively widespread in other geographic areas), the hydrophobic behaviour of such organic matter can hamper absorption of water solutions.

BODY	CODE	Penetr. mm	Drying sec.	Illite %	% Montm.	Kaol. %	Quartz %	Albite %	K-Feld %	Oters %	Org. C	% Rej. 63μm	% Rej. 45μm	D ap. g/cc	MOR$_E$/ MOR$_V$
I 6023	Standard	1.97	70	9	0	26	20	38	5	2	180	0.7	4.5	1.901	3.1
I 6024	Montmorillonite >	1.63	180	7	2	26	20	38	5	2	186	0.8	4.7	1.930	3.7
I 6025	Kaolinite >	2.03	35	6	0	29	20	38	5	2	84	0.4	2.6	1.858	2.4
I 6026	Quartz > coarse mill.	1.63	80	8	0	26	23	37	4	2	150	1.8	8.8	1.911	3.0
I 6027	Quartz >	1.66	65	8	0	26	23	37	4	2	150	0.7	3.7	1.909	2.7
I 6028	Quartz > fine mill.	1.63	55	8	0	26	23	37	4	2	150	0.1	1.1	1.879	3.0
I 6029	Potassium feldspar >	1.88	55	9	0	29	20	18	23	1	180	0.8	3.0	1.850	2.9
I 6030	Zirconium white	1.72	75	9	0	25	17	37	4	8	168	0.4	2.5	1.925	3.5
I 6031	Alumina white	1.90	60	8	0	23	17	40	4	8	168	0.5	2.9	1.855	3.2
	Average	**1.78**	**75**	**8.0**	**0.2**	**26.2**	**20.3**	**35.6**	**6.4**	**3.2**	**157**	**0.69**	**3.76**	**1.891**	**3.1**
	Max.	2.03	180	9	2	29	23	40	23	8	186	1.8	8.8	1.930	3.7
	Min.	1.63	35	6	0	23	17	18	4	1	84	0.1	1.1	1.850	2.4
	STD dev.	0.03	1725	1.0	0.4	3.4	6	44	39	7	952	0.23	4.77	0.001	0.2

3.2. WETTING EFFECTS

Measured parameters:

- Modulus of rupture of the green semi-finished products (size 320x320x9 mm, approx. weight 1700 g) surface wetting at 50÷55°C by airbrush application of 30 g water, measured 120 s after application.

- Examination of eventual deterioration in surface quality as a result of wetting. None of the inspected bodies showed any significant surface degradation after wetting.

Parameters considered:

The parameters that play a part in impairing mechanical properties after wetting are detailed in the following table:

BODY	CODE	Wet MOR_B	MOR_B/ MOR_E	illite %	Montm. %	Kaol %	Quartz %	Albite %	K-Feld. %	Others %	Org. c ppm	% Rej. 63µm	% Rej. 45µm	D. ap. g/cc
I 6023	Standard	16.2	0.64	9	0	26	20	38	5	2	180	0.7	4.5	1.901
I 6024	Montmorillonite >	21.4	0.65	7	2	26	20	38	5	2	186	0.8	4.7	1.930
I 6025	Kaolinite >	12.1	0.76	6	0	29	20	38	5	2	84	0.4	2.6	1.858
I 6026	Quartz > coarse mill.	16.0	0.71	8	0	26	23	37	4	2	150	1.8	8.8	1.911
I 6027	Quartz >	14.2	0.68	8	0	26	23	37	4	2	150	0.7	3.7	1.909
I 6028	Quartz > fine mill.	14.5	0.69	8	0	26	23	37	4	2	150	0.1	1.1	1.879
I 6029	Potassium feldspar >	14.4	0.68	9	0	29	20	18	23	1	180	0.8	3.0	1.850
I 6030	Zirconium white	17.8	0.67	9	0	25	17	37	4	8	168	0.4	2.5	1.925
I 6031	Alumina white	13.4	0.63	8	0	23	17	40	4	8	168	0.5	2.9	1.855
	Average	**15.6**	**0.68**	**8.0**	**0.2**	**26.2**	**20.3**	**35.6**	**6.4**	**3.2**	**157**	**0.69**	**3.76**	**1.891**
	Max.	21.4	0.76	9	2	29	23	40	23	8	186	1.8	8.8	1.930
	Min.	12.1	0.63	6	0	23	17	18	4	1	84	0.1	1.1	1.850
	STD dev.	7.59	0.00	1.0	0.4	3.4	6	44	39	7	952	0.23	4.77	0.001

Discussion of results

1) Nearly all the bodies lost about 30% of their mechanical strength after wetting.

2) In the case of body I 6024, the effect of the toughness of a 2% montmorillonite proportion present amongst the components, produced very high strength values for the semi-finished products.

3.3. DEVELOPMENT OF COLOUR IN FIRING

Measured parameters:

- Colorimetric indices L, a, b of the fired specimens and their change compared to the reference, corresponding to non-polished standard composition I 6023.
- Colorimetric indices L, a, b of the fired and polished specimens (average polishing depth 0.6 mm) and their change compared to the reference, corresponding to non-polished standard composition I 6023.

Parameters considered:

The following table details the colorimetric indices of the fired, non-polished bodies, non-coloured and coloured with the chrome salt, together with their chemical compositions (ΔE represents the change compared to reference body I 6023, ΔE' represents the change relative to the non-coloured body being studied):

		NON-POLISHED BODIES																	
		WHITE BODIES				CHROME COLOURED BODIES													
BODY	**CODE**	**L***	**a***	**b***	**DE**	**L***	**a***	**b***	**DE**	**DE'**	**SiO_2**	**Al_2O_3**	**TiO_2**	**Fe_2O_3**	**CaO**	**MgO**	**K_2O**	**Na_2O**	**ZrO_2**
I 6023	STD	78.2	0.3	10.3	0.0	44.6	-3.7	11.6	33.9	33.9	69.2	19.7	0.5	0.5	0.4	0.3	1.2	4.3	
I 6024	Montmorillonite >	77.9	0.3	10.3	0.4	44.0	-3.8	10.8	34.4	34.1	68.2	20.4	0.4	0.5	0.4	0.3	1.2	4.3	
I 6025	Kaolin >	79.9	0.3	8.9	2.2	44.6	-6.3	10.8	34.3	36.0	67.5	21.2	0.3	0.4	0.4	0.2	1.4	4.3	
I 6026	Quartz > coarse mill.	79.7	0.2	9.4	1.7	45.2	-4.6	12.5	33.5	35.0	69.8	19.3	0.4	0.5	0.4	0.3	1.2	4.1	
I 6027	Quartz >	79.2	0.2	9.5	1.3	44.7	-4.4	12.2	33.9	34.9	69.8	19.3	0.4	0.5	0.4	0.3	1.2	4.1	
I 6028	Quartz > fine mill.	78.8	0.3	9.6	0.9	43.7	-4.7	11.3	34.9	35.5	69.8	19.3	0.4	0.5	0.4	0.3	1.2	4.1	
I 6029	Potassium feldspar >	77.3	1.0	9.9	1.3	46.3	-3.7	12.6	32.2	31.5	67.7	20.2	0.5	0.5	0.2	0.3	4.1	2.3	
I 6030	Zirconium white	85.2	-0.3	7.7	7.4	48.3	-4.1	14.6	30.6	37.7	66.7	18.9	0.5	0.5	0.4	0.3	1.1	4.1	3.7
I 6031	Alumina white	82.8	-0.1	7.8	5.2	47.9	-4.0	12.9	30.7	35.5	65.0	24.4	0.5	0.5	0.4	0.3	1.0	4.5	

Discussion of results

1) All the bodies were white, as the L index values indicate.

2 As is well known, the whitening effect of micronised zirconium silicate is, at the same addition to the composition (6 % dry weight), superior to that of alumina (zirconium white exhibits L = 85.2 versus L = 82.8 of alumina white).

3) As observed in the variations of ΔE' compared to the non-coloured value, which were very high for the bodies with a high kaolin content, whitened with zirconium silicate and alumina, the colouring effect was heightened by the white bodies. Similarly, a reduction can be observed of the colouring effect with the substitution of sodium feldspar by potassium feldspar (ΔE'=33.9 for the standard body, ΔE'=31.5 for the body containing potassium feldspar).

4) Comparing the a* and b* indices in the different coloured bodies, it can be observed that the green colour of the body with a high kaolin proportion was particularly noticeable (see value a*), while zirconium rather tended to yellow (see value b*).

The following table sets out the colorimetric indices of the polished fired bodies versus those of the non-polished bodies (ΔE" represents the variation relative to the polished non-coloured body being studied):

		NON-POLISHED BODIES				POLISHED BODIES					CHROME COLOURED BODIES				
BODY	**CODE**	**L***	**a***	**b***	**DE**	**L***	**a***	**b***	**DE**	**DE'**	**L***	**a***	**b***	**DE**	**DE"**
I 6023	STD	78.2	0.3	10.3	0.0	78.6	0.3	10.1	0.5	0.5	57.0	-1.4	17.3	22.4	22.9
I 6024	Montmorillonite >	77.9	0.3	10.3	0.4	78.3	0.3	10.2	0.1	0.4	55.2	-1.0	16.5	23.9	24.0
I 6025	Kaolin >	79.9	0.3	8.9	2.2	80.3	0.6	9.1	2.5	0.5	55.8	-3.3	15.8	23.3	25.7
I 6026	Quartz > coarse mill.	79.7	0.2	9.4	1.7	80.1	0.2	9.4	2.1	0.4	59.4	-1.5	17.2	20.1	22.1
I 6027	Quartz >	79.2	0.2	9.5	1.3	79.7	0.3	9.6	1.6	0.5	58.0	-1.3	17.1	21.4	23.0
I 6028	Quartz > fine mill.	78.8	0.3	9.6	0.9	79.0	0.3	9.6	1.1	0.3	57.2	-1.4	16.9	22.1	23.1
I 6029	Potassium feldspar >	77.3	1.0	9.9	1.3	78.0	1.0	9.7	1.0	0.7	59.1	-1.1	17.3	20.3	20.4
I 6030	Zirconium white	85.2	-0.3	7.7	7.4	85.1	-0.2	8.0	7.3	0.3	65.9	-1.3	17.1	14.1	21.2
I 6031	Alumina white	82.8	-0.1	7.8	5.2	83.0	-0.1	7.9	5.4	0.2	64.8	-0.8	15.4	14.4	19.7

The polishing can be observed to produce a slight rise in the L index.

Besides comparing the values of ΔE", the table shows that the body with a high kaolin content kept its enhancement of the chromophore effect, while the bodies whitened with zirconium and alumina lost much in this sense with regard to the other polished bodies.

4. GENERAL REMARKS

Summarising it can be stated that:

1. Reference body (I 6023) was shown on the whole to be the most balanced composition with regard to both mechanical characteristics and permeability. Thus:

- Under industrial forming conditions (400 kgf/cm^2), it was decidedly tough both in its green (8.1 kgf/cm^2) and dry (25.4 kgf/cm^2) state, as well as after wetting (16.2 kgf/cm^2), therefore keeping possible rupture and tensing of the semi-finished products during decoration, conveying and storing prior to firing down to a minimum.

- Permeability was very satisfactory (average penetration 1.97 mm), very close to that of the body with a high kaolin content (2.03 mm);

- The same was found for surface drying time (70 s), which was more than acceptable.

- At the industrial milling rejects set (0.7% at 63μm; 4.5% at 45 μm) the degree of vitrification at a peak firing temperature of 1210°C was in line with standard values for the highest quality (M.O.R. 430 kgf/cm^2, water absorption 0.01%), ensuring good mechanical properties and surface hygiene.

- Although the degree of whiteness was lower than that of the bodies with a high kaolin and quartz content, the value of the L index was close to the average value for the non-opacified bodies, just as the body colouring property (as shown by the ΔE values of the coloured bodies compared to those of the non-coloured ones, whether at natural or polished surfaces). The bodies with high kaolin (I 6025) and quartz (I 6026-8) proportions, although exhibiting better chromatic properties presented other limitations: body I 6025 was not very tough in the green state, while bodies I 6026-8 exhibited a lower than average penetration depth, which could become a problem especially in the case of screen-printing runs on surfaces that are to be polished.

2. Of the two opacified bodies, the zirconium white-containing body (I 6030) appeared to exhibit more interesting behaviour compared to that of the alumina-containing formulation (I 6031). Thus:

- It was much whiter, as the values for the L index at the natural surface (85.2 for I 6030, 82.8 for I 6031) as well as at the polished surface (85.1 for I 6030, 83.0 for I 6031) show, while also colouring more easily (ΔE' = 37.7 versus 35.5 at the rough surface, ΔE'' = 21.2 versus 19.7 at the polished surface).

- It exhibited more than satisfactory mechanical strength in the green body (7.6 kgf/cm^2), in the dry state (26.5 kgf/cm^2), and after wetting (17.8 kgf/cm^2), by far exceeding that of body I 6031 (respectively 6.7, 21.4, 13.4 kgf/cm^2 in the green, dry and wetted state).

- Drying time was short (75 s), though higher than that of body I 6031 (60 s).

- At mill rejects resembling industrial values (0.4% at 63μm; 2.5% at 45 μm) the degree of vitrification at a peak firing temperature of 1210°C was in line with standard values found for the highest quality (M.O.R. 440 kgf/cm^2, insignificant water absorption), assuring good mechanical properties and surface hygiene.

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[1] *'Correlazione tra composizione chimico-mineralogica e colorabilità con sali cromofori in impasti di grès porcellanato'*. Tesi di licenza di G. Gioghi e M. Minganti. Istituto Statale d'arte per la Ceramica «G. Ballardini» Faenza - Curso di Perfeccionamiento en Tecnología Cerámica: "Ceramiche Speciali" - Año escolar 1996-97.

- The only disadvantage to body I 6030, compared to I 6031, was it lower penetration depth (1.72 mm versus 1.90 mm), which much be considered case by case together with other factors.

NOTES

[1] With regard to the mechanisms that govern the absorption of solutions and deposition of chromophore ions inside the mass, the following elementary processes can generally be identified:

- Mass transport from the surface inwards into the mass by capillary action.
- Surface absorption and eventual interlaminar absorption of water molecules by the clay constituents till surface saturation and/or saturation of the voids between the clay plates, with greater or lesser swelling of the plastic matrix, resulting in restriction of the cross section of the capillary tubes and increased resistance to liquid transport.
- Possible interaction of an electrostatic and/or chemical type of the solute's cationic or anionic part with unsaturated bonds present at the crystal grain boundary.
- Precipitation of chromophore metal salts by oversaturation of the solution as a result of the evaporation of the aqueous solvent.
- Undesired precipitation of scarcely soluble salts and metal hydrogens that have formed as a result of exchange reactions from solutes in specific pH conditions (e.g. precipitation of iron hydroxides in a basic environment, if moderately so).

LIQUID MASS TRANSPORT

With regard to capillary action[2], the Poiseuille equation can again be considered, which describes laminar flow of a fluid in a granular bed as a result of a pressure gradient:

$$\Delta H = \frac{K_2 \cdot \mu \cdot v_f \cdot \rho_t^2 \cdot S^2 \cdot (1-F)^2 \cdot d}{\rho \cdot g \cdot F^3}$$

where: ΔH = pressure gradient (cm liquid column)

K_2 = Kozény constant (5 for spherical particles)

μ = dynamic viscosity of the liquid (poise)

r = density of the liquid (g/cm^3)

v_f = flow rate (cm/s)

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[2]. PERRY'S CHEMICAL ENGINEERS' HANDBOOK (IVTH EDITION). PERRY, CHILTON, KIRKPATRICK. 1963, McGraw-Hill. (15-39÷40).

ρ_t = true density of the solid particles (g/cm^3)

S = particle specific surface area (cm^2/g)

g = acceleration by gravity = 980 cm/s^2

F = porosity of the medium (dimensionless)

d = granular bed depth (cm)

taking into account the absorption potential due to capillary forces:

$$P = \frac{X \cdot \sigma}{r \cdot \rho \cdot g}$$

where: P = absorption potential (cm liquid column)

X = packing factor (= 12.9 for rhombohedral packing ; = 4.8 for cubic packing)

σ = liquid surface tension (dyne/cm)

r = solid particle mean radius at whose interstices lie the capillaries (cm)

ρ = liquid density (g/cm^3)

g = acceleration by gravity = 980 cm/s^2

allows deriving a valid equation under steady-state conditions:

$$v_f = k \cdot \frac{P_s - P_d - d}{d} \cdot \frac{\rho \cdot g \cdot r^2}{\mu}$$

where: k = proportionality factor that depends on packing and particle shape:

P_s, P_d = absorption potential at the surface and at depth d.

It can therefore be observed that:

- v_f increases with the square of r: particles with finer size fractions obstruct permeability
- v_f decreases with μ: more viscous liquids slow down the process
- v_f increases with P_s - P_d: the larger the difference between absorption potential at the surface ($P = (X\ \sigma)\ /\ (r\ \rho\ g)$) and inside the body, the more the process is facilitated. This condition often arises, if it is considered that the densification produced by pressing the powder is greater at the surface than inside the compact, owing to an energy fraction that disperses by friction inside the mass

(Xs > Xd), and that the powder with the finest size fraction tends to be dragged to the surface by the air exiting the material during compaction ($r_s < r_d$).

SURFACE ADSORPTION AND INTERLAMINAR ABSORPTION

The surface adsorption and interlaminar absorption mechanisms by the clay minerals are well-known from the literature and treatment of the subject lies outside the scope of this study. However, it deserves to be noted that:

- Adsorption is facilitated by surface reactivity, and therefore by its ionic activity and defect concentration, more striking in the case of silicates with a high degree of silicon and aluminium ion substitution in the crystal lattice (illite type structures), and by the material's specific surface area, hence as a result of its particle-size fineness.

- Interlaminar absorption is a peculiarity of clay minerals with a T-O-T (tetrahedral-octahedral-tetrahedral) structure, and is also favoured in this case by a high degree of silicon and aluminium ion substitution in the lattice (e.g. montmorillonite).

SOLUTE INTERACTIONS WITH COMPLEMENTARY MINERALS

Under certain conditions interactions of an electrostatic and/or chemical type cannot be excluded by the cationic or anionic part of the solute with unsaturated bonds or particularly reactive groups (-OH, -O- Na+ , etc.) present at the grain boundary in silica crystals. In particular, it has been shown that in common glasses, in which there is no ordered silica lattice, there may be up to 4.6 silane group ≡Si-OH per nm^2, as well as non-associated ones (according to pH) or with the hydrogen atom replaced by a metal cation, which constitute linking sites for other ions present in the environment[3].

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[3]. *'La superficie del vetro: basi scientifiche per la ricerca industriale'*. PASCAL CHARTIER. Rivista della Staz. Sper. del Vetro n. 4 - 1997.