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DRYGLACER

PROJECT COORDINATOR : **EMILCERAMICA S.p.A. (I)**
Prof. Carlo I?ALMONARI

PARTNERS :			
	PP	EMILCERAMICA	(I)
	1?	TORRECID	(E)
	SC	CENTRO CERAMICO	m
	Sc	ITC-AICE	(E)

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ADVANCED DRY GLAZES AND DRY GLAZING TECHNOLOGIES FOR FLOOR AND WALL TILES

G.RONZONI, G.BOGGIA — **EMILCERAMICA S.p.A.**
Via Ghiarola Nuova, 29 -
41042 Fiorano, Modena (I)

F.SANMIGUEL — **TORRECID S.A.**
Carretera Castellon - Partida Torreta
12110 Alcora, Castellon (E)

C.PALMONARI, G.TIMELLINI — **CENTRO CERAMICO** - BOLOGNA
Via Martelli, 26 - 40138 Bologna (I)

J.L.AMOROS — **Instituto** de **Tecnologia Céramica ITC-AICE**
Campus Universitario del Riu Sec -
12006 Castellon (E)

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CONTENT:

Abstract

The aim of the research project was to develop new glazes and new dry glazing Technologies for single fired and double fired floor and wall tiles, with specified surface characteristics (in terms of aspect of the surface itself, compactness of the glaze layer, mechanical and chemical resistance) .

The research activities have included: (i) a laboratory scale experimentation, to develop the new dry glazes and study their application characteristics, (ii) a design phase for new glaze application processes and equipments, suitable to give *glazed surfaces with the specified characteristics, and (iii) pilot line experimentations in order* to *optimise the new glazing process, as well as to veri fy the achievement of the scheduled objectives. Environmental impact and possible environmental benefits of the new technologies have also been considered.*
The new processes and products developed have been finally qualified. The cost/benefit ratio has been studied for all the products/processes developed, in order to obtain useful indications for the future exploitation and industriali-sation activities.

1. Introduction

This research project has dealt with the glazing operations of ceramic floor and wall tiles. The conventional technologies present various technical, productive , operative limitations, due to which the glazing- phase accounts at presents for some of the main obstacles to the achievement of a fully reliable and automated ceramic process, in a full quality perspective.

The objectives of this project were the following:
•to develop glazes and dry glazing-processes to be used to produce even tint, smooth and gloss or matt glazed surfaces, as well as compact glaze layers, when fired in the conventional firing cycles for ceramic tiles;
•to develop glazes and dry glazing process where the use of water (as well as water wasting) is effectively minimised.

The attention has been focused on two types of mechanical dry glaze applications:

i) glaze application in the dust pressing phase (in Italian, *smaltopressatura*) , and

ii) dry glaze application in form of powder distributed on the dried or fired tile surface.

2. Materials and methods

2.1 Materials

20 different glazes, identified and specified as a function of i) product type; ii) surface type; iii) type of application; iv} type of powder glaze have been initially considered and experienced at laboratory level:

Product	*Surface*	*Application*	*Powder*	*Sample N°*
Single fired BI tiles	Gloss	Dust Pressing	S	1
			G	2
		Spreading	G	3
			MF	4
	Matt	Dust Pressing	S	5
			G	6
		Spreading	G	7
			MF	8
Single fired BIII tiles (Monoporosa)	Gloss	Dust Pressing	S	9
			G	10
		Spreading	G	11
			MF	12
	Matt	Dust Pressing	S	13
			G	14
		Spreading	G	15
			MF	16
Double fired BIII tiles	Gloss	Spreading	G	17
			MF	18
	Matt	Spreading	G	19
			MF	20

Legenda for Powder Type:
S = **Spray dried powder**
G = **Granulate (granulated powders** with **adhesives]**
MF = **Milled** "flowable" frits/glasses

2.2 - Technical approach

Each product/process developed has passed four steps, as specified in the following:

Step 1: Laboratory experimentation, directed towards determining, on a laboratory scale, the conditions which permit the achievement of dry glazed surfaces with the specified characteristics (in terms of composition of the glazes, powder morphology and particle size distribution, powder flowability, adhesion conditions between glaze and body, firing behaviour of the glazes) .

Step 2: **Planning and design of the pilot production line**. This step has been devoted to develop the machinery, the lay-out and the tentative operative parameters for the pilot line experimentation. These experimentations were scheduled, of course, only for those products for which the previous step had given successful, or at least promising, results.

Step 3: **Pilot line experimentation** included the installation and the experimentation of the pilot production lines.

Step 4: **Environmental considerations** was aimed to the study of the environmental problems related to the new process developed.

It is worth emphasising the "iterative" nature of such a technical approach, with each technical choice/option to be subjected to a feed-back optimisation process, on the–basis of the progress results achieved.

In this framework, among the 20 starting glazes the most promising products have been identified, on the basis of the results of the early lab experiments. These are five glazes, as specified in Table I, on which the attention has been focused, to cover the whole development path, from Step 1 to Step 4.

Samples of these **glazes** have been produced and progressively optimised by Torrecid, and submitted to Emilceramica for the glaze application experiments.

This report if focused -just on the glazes listed in Table I.

Table I - Glazes on which the experimentation and development activities have been focused.

Glaze			*Corresponding Glazed Tile*				
Mark	Form	Colour	Use	Techn.	Glaze Appl.	Surface	EN Class
1S/5	**Spray-dried powder**	**white**	**Floor**	**single firing**	**dust press.**	**Gloss**	**BI BIIa**
1S/7	**Spray-dried powder**	**blue**	**Floor**	**single firing**	**dust press.**	**Gloss**	**BI BIIa**
4MF1 4MF1+18MF	**Milled frit**	**white**	**Floor**	**single firing**	**drop**	**Gloss**	**BI BIIa**
5S/8	**Spray-dried powder**	**white**	**Floor**	**single firing**	**dust press.**	**Matt**	**BI BIIa**
18MF	**Milled frit**	**white**	**Wall**	**double firing**	**drop**	**Gloss**	**BIII**

2.3 - Methods

All the glazes, and in particular those prepared for the pilot line experiments, have been characterised as regards:

- the chemical analysis
- the dilatometric analysis
- the thermal expansion coefficients for specific temperature ranges;
- heating stage.

All the glazed tiles produced, and in particular those manufactured in the pilot line experiments, have been characterised, according to the existing standards [1, 2] as regards:

- Water Absorption (EN 99)
- Mobs Hardness (EN 101)
- Vickers Hardness
- Abrasion Resistance (ISO 10545-7)
- Chemical Resistance (EN 122)
- Crazing Resistance (EN 105)
- Glaze porosity (total porosity and pore size distribution – light optical observations of the polished cross section and image analysis)

The processes developed and experienced for both glaze production and glaze application have been characterised and assessed as regards:

- the most significant processing and operative parameters, including production yield, of the pilot line experiments carried out;
- water balance
- environmental impact
- production costs.

3. Results and discussion

A selection of the results achieved is presented and discussed in the following sections. This selection does not include confidential results. However, it is suitable to highlight and document the "performance" of such results, in an exploitation perspective. Moreover, this selection has been made with the purpose of documenting to what extent the project objectives have been achieved.

3.1 - The glaze production processes

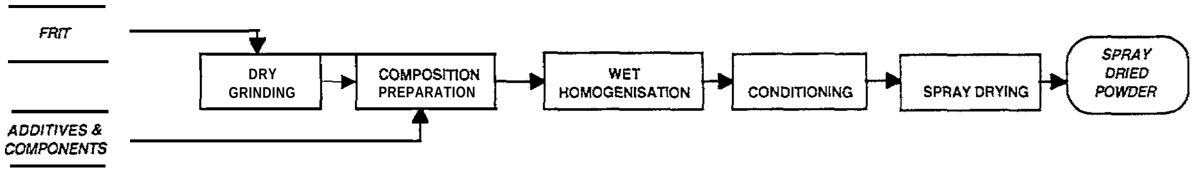
Three different glaze production processes (**DRYGLACER**, **WET PREPARATION** and **DRY GRINDING &** SIZE CLASSIFICATION) have been developed and experienced by Torrecid. The flow sheets of these processes are reported in Figures 1, 2 and **3**, respectively.

Two main innovative aspects are worth of mention at this point:

- the new process **DRYGLACER** is characterised by a cycle time appreciably shorter, compared to that of the conventional processes for the production of spray dried glazes. In fact, the total time to spray drier is reduced to 8 h, against 17.5 h required by the conventional process. This is a very interesting result. This process, however, cannot be applied to the production of glazes of complex composition. Examples of such glazes are 1S/7 and 5S/8, for which the wet preparation process is, at present, without acceptable alternatives;

- the **DRY GRINDING & SIZE CLASSIFICATION** as well represents a new development (as such, not commercially available) . The main advantages are the following: i) it is based on a dry grinding process, and therefore do not require water; ii) it is suitably efficient, in terms of grain size reduction: any required grain size can be achieved, according to the product demand; iii) it is highly flexible: it can be used to prepare every type of milled glazes, both for direct application by spreading/drop, and for the preparation of granules by either granulation or spray drying.

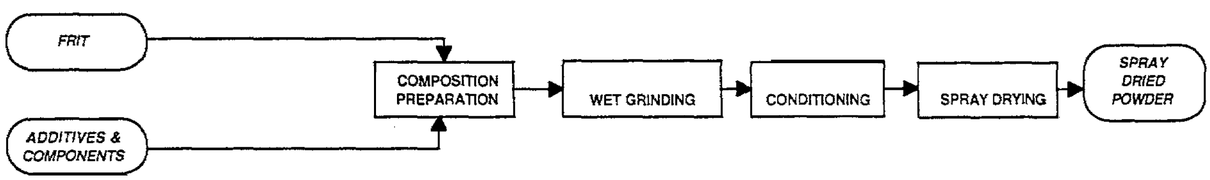
Glaze:	1s/5
Process	DRYGLACER



Time required (ref.: 5000 kg of frit)		2h 30 min	30 min		2 h		3 h	Total time to spray drier 8 h

Figure 1 - The DRYGLACER Process

Glaze	1S/7; 5S/8
Process:	WET PREPARATION



Time required (ref.: 5000 kg of frit)		30 min		14 h		3 h	Total time to spray drier 17.5 h

Figure 2 - The WET PREPARATION Process

Glaze:	4MF/1; 18MF
Process:	DRY GRINDING & SIZE CLASSIFICATION

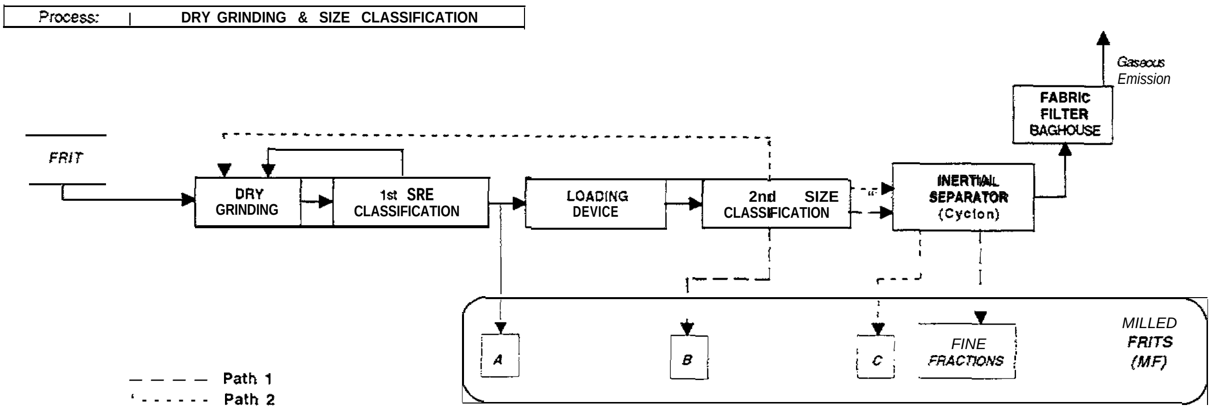


Figure 3 - The DRY GRINDING & SIZE CLASSIFICATION Process

3.2 - The glaze application experiments

The flow sheets of the pilot lines installed and operated by Emilceramica to manufacture the new dry glazed tiles are reported in Figures 4, 5 and **6.** Figure **4** refers to the single fired products glazed by dust pressing, Figure 5 to the single fired product glazed by spreading/drop, and Figure **6** to the double fired product, glazed once again by spreading/drop.

The main parameter on which attention has been focused to summarise the general behaviour or performance of the pilot line experiments is the "1st choice yield" resulted.

3.2.1 - *Spray dried glazes for dust pressing glazing*

For all of the three products under examination, the first choice yield was low, compared to a conventional production line . This means that each process needs further optimisation activity (e.g. in a possible industrialisation phase) . It is worth noting that, while for **5S/8** no tile without defects could be produced, for the other products top quality levels ranging from **37** % (for 1S/5) to **45 %** (for 1S/7) have been achieved.

3.2.2 - *Milled frits for application by spreading/drop*

For the single fired product (4MF1+18MF), a 47.7 % 1st choice yield has been achieved in the pilot line experiments . Rejects are as high as 10%.
For the double fired product (18MF) a 30 % 1st choice yield has been achieved. Rejects are at a 4 % level.
Also in these cases, the results achieved, which document the need of further optimisation to be carried out in the industrialisation phase, should be considered as unsatisfactory for any industrial production line. However, in the light of the effective development of the project, and considering the early stage of the development activity, the results achieved are worth of interest, and promising as well.

In summary, for the production yield point of view, the pilot line experiments were not successful, but nevertheless promising, with respect to future industrialisation activities.

Glaze	[S/5; 1S/7; 5S/8
cycle	Single Firing
Glaze application:	DUST PRESSING

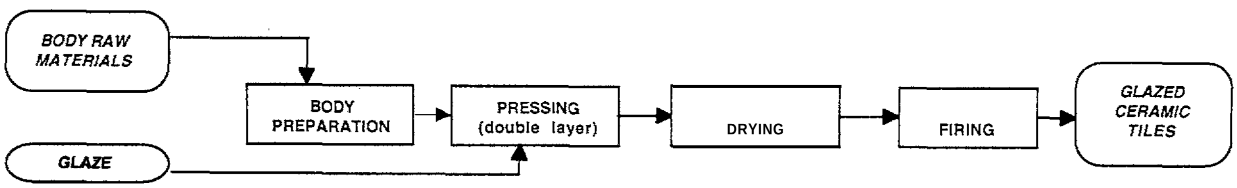


Figure 4-Single firing cycle with glazing by DUST PRESSING

Glaze:	4MF/1+18MF (70/30)
Cycle:	Single Firing
Glaze application:	SPREADING/DROP

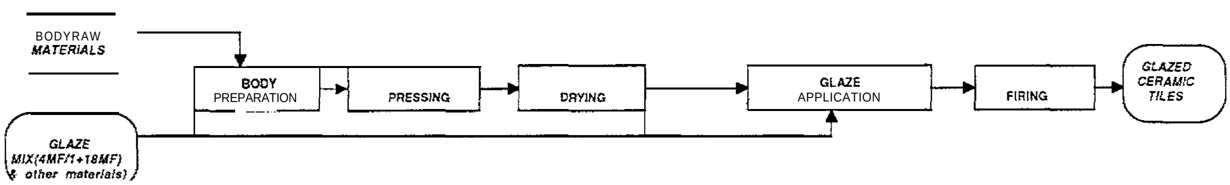


Figure 5-Single firing cycle with glazing by SPREADING/DROP

Glaze:	18MF
Cycle:	Double Firing
Glaze application:	SPREADING/DROP

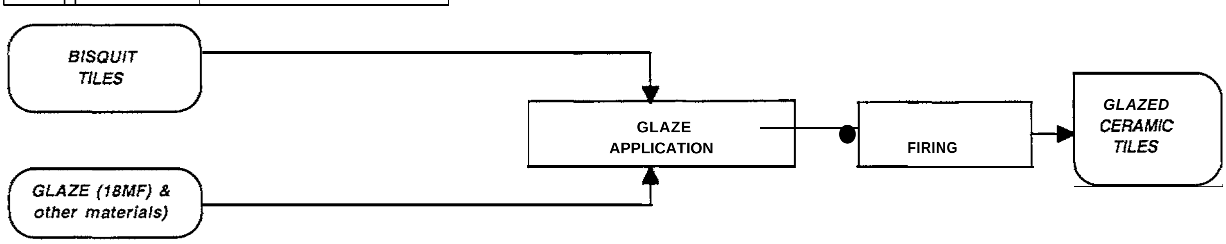


Figure 6-Double firing cycle with glazing by SPREADING/DROP

3.3 - **Water balance**

The reduction of water consumption and wasting was one of the main expected advantages of the new processes to be developed in the framework of the project.

3.3.1 - *Spray dried glazes for dust pressing glazing*

These products do not" require any water for the glaze application process.
As regards the glaze preparation process, the product 1S/5, prepared by the DRYGLACER process, is characterised by lower water requirements and consumption (0.55÷0.95 L/kg, against 0.94÷1.35 L/kg for 1S/7 and 5S/8).
The achievement of the project objectives can be considered as fully satisfactory for 1S/5, due to the remarkable reduction of water needs, with respect to conventional technologies for both glaze preparation and glaze application. For the other two glazes, prepared by the wet process, the achievement of the objective is considered acceptable, due to the fact that, for these products as well, no water is required for the application phase.

3.3.2 - *Milled frits for application by spreading/drop*

For these glazes (4MF1, 18MF and their mixes) no water consumption is associated to the glaze Preparation process.
The application of 4MF1+18MF in a single fired floor product requires 1.29 L/m2. This value is quite lower, compared to the reference levels associated to the "glaze preparation and application phase" in the existing sectorial 'stu-dies [3] (7÷15 L/m2 for conventional technologies, 3 L/m2 for high washing efficiency techniques) . Emilceramica has compared this glazing line with one of its glazing lines producing a rather similar product, using conventional wet glazing technologies, and has found that the water consumption, strictly associated only to the glaze application phase, is reduced by 23 %.
The application of 18MF in a double fired wall product requires 0.95 L/m2. Once again, this value is quite lower, compared to the reference sectorial levels [3] . Emilceramica has compared this glazing line with one of its glazing lines producing a rather similar product, using conventional wet glazing technologies, and has found that the water consumption, strictly associated only to the glaze application phase, is reduced by 12 %.
In summary, considering the whole q-laze cycle - from glaze production to glaze application --the achievement of the project objective related to water balance should be considered as satisfactory.

3.4 - **Technical specifications of the glazed tiles developed**

Table II reports the results of the characterisations carried out o-n the five products under examination (products which have reached the pilot line experiment phase; it is worth mentioning that these results reflect the progressive optimisation process carried out by Emilceramica, based on the feed-back of several intermediate experiments) .

Table II - Technical specifications of the products developed. Summary Table .

Characteristic	Ref.	1S/5	1S/7	5S/8	4MF1 + 18MF	18MF
Water Absorption (%)	EN 99	2.8	3.5	5.6	3.4	
Mohs Hardness	EN 101	3	3	5	5	4
Abrasion Resistance (PEI Class)	ISO 105'45-7	V	II	V	V	V
Methilene blue (Resistance Class)	EN 122	2	1	3	1	1
K-permanganate {Resistance Class)	EN 122	3	2	3	2	1
HCl (Resistance Class)	EN 122	AA	AA	AA	A	AA
KOH (Resistance Class)	EN 122	AA	Ah	AA	AA	AA
Crazing Resistance	EN 105	yes	yes	yes	yes	yes
Pores area (%)		4.7	5.3	23.2	4.4	0.5
Pore average diameter (μm)		10.1	9.'7	12.6	21.2	11.7

The results achieved can be evaluated with reference to the standard requirements reported in [1] and [2] .
As far as the *products glazed by dust pressing (1S/5, **1s/7** and 5S/8)* are concerned, the overall picture can be considered as unsatisfactory. Only 1S/7 is acceptable, since all the surface characteristics are in compliance with the standards [1, 2] (despite the rather low levels of Mobs hardness and abrasion resistance, to be associated, however, to the gloss surface and to the rather dark colour, respectively) . Moreover, with lS/T a rather low porosity of the glaze layer could be reached.
For the white products, on the contrary, low levels of stain resistance have been achieved.

As regards the *single fired floor tiles glazed by spreading/drop (glaze 4MF1 + 18MF)*, the technical specification, reported in Table II, documents the compliance with the standard requirements for all the surface characteristics. Further improvements are expected in a successive possible industrialisation phase. In any

case, the achievement of the project objectives under consideration can be considered as satisfactory: the position of this new product, compared to the convectional products, is good.

Finally, as regards the *double fired wall tiles (glaze 18MF), glazed by spreading/drop*, all the surface characteristics result at the highest level, according to the respective standard classifications. Also Mobs hardness (4) can be considered as a rather high level, for a wall tile with a gloss surface. An almost fully compact glaze layer has been obtained. Therefore the achievement of the project objectives under consideration can be considered as satisfactory, and particularly interesting and promising.

3.5 **Cost/benefit analysis**

A detailed cost analysis has been carried out for all the five products under consideration. The cost have been determined and analysed, making reference to both the manufacturing phase, and to the main cost items (materials, manpower, energy, etc.). A comparison has therefore been made possible among the new developed products and the conventional ones (i.e. products of the same type/class, glazed by wet methods) . Moreover, some considerations on the cost/benefit ratio have been made for each product.

As far as the *products glazed by dust pressing (1S/5, 1S/7 and 5S/81* are concerned, the cost of the new products developed is quite higher, compared to that of the corresponding conventional products. There is, of course, a remarkable impact associated to the cost of the glaze, that is strongly influenced by the development costs. Anyway, despite the cost reduction which can be envisaged, assuming that this glaze is produced at large industrial scale, a circumstance must be considered: that the dust pressing glazing technology is "intrinsically" associated to the application of quite high amounts of glaze per unit surface, compared to the conventional or alternative glazing technologies. Therefore, the cost of a dust pressing glazed product is expected to be always higher than for any glazed tile. As discussed above, this cost increase is not counterbalanced and justified by **a** comparably strong increase in quality and performance.
In summary, from the cost/benefit ratio point of view, the products/processes under consideration are unsatisfactory.

As regards the *single fired floor tiles (glaze 4MF1 + 18MF)*, and *the double fired wall tiles (glaze 18MF), both glazed by spreading/drew*, the production costs of the new products/processes developed are of the same order of the corresponding conventional products/processes. Of course, it should be considered that this relation is valid, once the production yield problems encountered in the pilot line experiments will have been solved. Taking into account this limit, but considering also the technical and environmental benefits associated to the new products, as discussed above, the new products/processes developed can be considered as acceptable from the cost/benefit ratio point of view.

3.6 Scientific results

As reported in section 2.2, the technical approach adopted was based on a preliminary formulation of glazes and preliminary application experiments, starting from the actual knowledges and experiences of the industrial partners, followed by a development phase through iterative experiments and a feed-back optimisation process, until (hopefully) the expected results.

During these experiments several problems have been encountered: more precisely, several deviations from the expected results (for example, defects on the glazed surface, or bad behaviour of the glaze in the application stage, etc.) .

These problems have been faced with a systematic approach, based on a clear identification of the origin of the defect, and successively on the identification of the more convenient way to prevent its occurrence.

Both these phases - the phase of "diagnosis" and the phase of "therapy" - involved some basic scientific and/or technical aspects which were not suitably known or understood. Therefore, it was decided to dedicate time and resources to a systematic study and experimentation of these aspects.

The following is a list of the more significant studies carried out in the framework of the project.

- Effects *of the addition of different binders and plasticizers to the glaze slip on the characteristics of dust pressing glazes and their pressing behaviour*
- *Occurrence of surface defects for incomplete covering of the surface.* Influence *of the applied weight, grain size and viscosity of the melt of the Milled Frit*
- *Spray drying of glazes* for dust pressing glazing. *Influence of the physical parameters (number and type of nozzles, pressure and drying temperature)*
- *Spray drying of glazes for dust pressing glazing. Influence of the theological parameters of the slip*
- *Glazes for dust pressing.* Influence *of moisture content, clay fraction content and grain* size distribution *on the pressing behaviour*

- *Milled frits for application by spreading/drop. Study on the possibility of improving morphology and flowability*

- *Single fired tiles produced by dust pressing glazing. Effects of grain size distribution, pressing pressure and firing temperature on the porosity of the glaze layer*

- *Single fired tiles produced by dust pressing glazing. Effects of the* gaseous emissions *from the body during firing on the porosity of the glaze layer*

- *Single fired tiles produced by dust pressing glazing. Effects of the firing cycle on the occurrence of defects*

- *Single fired tiles produced by dust pressing glazing. Identification,* analysis *and prevention of the defects associated* to *the pressing phase*

The results of these studies have had a remarkable impact on the behaviour of the project and on the technical development of the activities: most of the problems encountered have been identified and solved through these studies. Moreover, these studies have brought about a significant progress in the knowledges, awareness and know-how of the partners, and should therefore be regarded as a basic output from the project.

4. Conclusions

Five glazes to be dry applied on single fired and double fired floor and wall tiles have been developed. Three glazes were in the form of spray died powders, to be applied by dust pressing glazing; two glazes were in the form of milled frits, to be applied by spreading/drop,

Both the respective production and application processes have been designed, developed and realised at pilot scale.

Pilot line experiments have been carried out. The glazed tile manufactured have been characterised, as regards the surface chemical and mechanical properties. The manufacturing processes have been characterised as regards (i) the production yield, (ii) the environmental impact, with particular regard to the water consumption; (iii} the production costs. Considerations on the cost/benefit ratio of the new products and processes developed have been made, on the basis of the results above.

It has been found that, while the glazes for dust pressing are still affected by serious problems, as regards the surface properties of the tiles, and are characterised by high costs, the glazes for spreading/drop have good surface characteristics (in particular, beside a full compliance with the standard requirements, a very compact structure, compared to the conventional glazes for wet application) , and costs which make these products very promising, from the cost/benefit ratio point of view.

For all the products, water consumption associated to the whole glaze cycle (from glaze preparation to glaze application) resulted appreciably reduced, in comparison with the conventional glazes and glaze production and application processes. No other environmental problem has been identified. Therefore, dry glazing has been shown as characterised, as a whole, by a lower environmental impact, compared to conventional wet glazing.

From a general point of view, the partners do consider positively the behaviour of the project and the results achieved, despite the fact that some specific objectives have not been achieved.

In any case, it is worth pointing out that, according to the contract programme (as well as to the Brite Euram Programme pre-competitive "philosophy") , the products developed are not ready to be put on the market, since their aesthetic aspect is too poor (even tint tiles are not commercially suitable, in a time where the market requires mainly decorated tiles, and decorations are often applied also on unglazed tiles, like porcelain stoneware, typically never decorated in the past).

For this reason, the results achieved - and which will be exploited - are associated mainly to the **know-how -** in glaze production and glaze application - subtended to the products and processes developed.

In this respect, the importance of the technical and scientific results achieved, as listed in section 3.6, is worth of further emphasis: these outputs represent, in particular for the industrial partners of this project, and subsequently for the whole European ceramic industry as well, important and concrete results, suitable for a "competitive" exploitation, and effective in view of the reinforcement of the competitiveness of the European ceramic tile industry.

5 References

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[2] CER.Labs - *Ceramic Tiles. The International Standards* - Ed. Int. CER.Labs, Bologna (1995}

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