ANALYSIS OF SOME FACTORS RELATED TO THE DEGRADATION OF GLAZED CERAMIC TILES THROUGH ABRASION

C. Feliú, M.J. Ibañez, A. Moreno, J.V. Carceller
Institute of Ceramic Technology, University of Valencia
Research Association of Ceramic Industries (A.I.C.E.). Castellón.

1. INTRODUCTION

Ceramic paving and tiling require a combination of technical and aesthetic properties, these are provided by the support and/or glaze. The search for quality in ceramic products has been directed for the most part at the study of these properties, with a view to their suitability of use.

One of the most important properties of ceramic paving is its resistance to abrasion, this is decisive in many cases when defining use. Abrasion can be defined as the undesired changed of the tile surface due to loss of mass, provoked by mechanical forces (rubbing, impact,...).

Numerous methods for determining resistance to abrasion for tiles are described in the bibliography (Table I).

2. DETERMINATION OF RESISTANCE TO ABRASION

The PEI method, described in the european standard, EN-154 "Ceramic tiles. Determination of resistance to abrasion. Glazed tiles", was chosen as the method for determination of resistance to abrasion.

This method was chosen by CEN as it simulates the wear on he glazed surface during actual use better than other methods.

TABLE 1 - ABRASION METHODS

METHOD	FUNDAMENTALS
GLAZED TILES	
PEI (EN, ASTM)	CORUNDUM AND STEEL BALL BEARINGS DAMP SYSTEM EVALUATION BY LOSS OF ASPECT
LOSS OF WEIGHT AT 6000 REVS (EN)	CORUNDUM AND STEEL BALL BEARINGS DAMP SYSTEM EVALUATION TROUGH LOSS OF WEIGHT

METHOD	FUNDAMENTALS
GLAZED TILES	
MCC (EN)	PORCELAIN & SILICON CARBIDE CYLINDER BEARINGS DRY SYSTEM EVALUATION BY LOSS OF ASPECT
SANDBLASTING 6000 REVS (EN)	SANDBLASTING DAMP SYSTEM EVALUATION BY LOSS OF ASPECT
ROBINSON (ASTM, UPEC)	WHEEL BEARINGS UNDER LOAD DRY SYSTEM EVALUATION BY LOSS OF ASPECT
UNGLAZED TILES	
CAP (EN)	STEEL AND CORUNDUM WHEEL BEARINGS UNDER LOAD DRY SYSTEM EVALUATION BY LOSS OF VOLUME
AMSLER (DIN, NEN, NBN)	ABRASIVE STEEL DISC BEARING UNDER LOAD DRY OR DAMP SYSTEM EVALUATION BY LOSS OF WEIGHT
TABER (ASTM)	ABRASIVE WHEEL BEARINGS DRY SYSTEM EVALUATION BY LOSS OF WEIGHT
UPEC	STEEL WHEEL BEARINGS UNDER LOAD DRY SYSTEM EVALUATION BY LOSS OF ASPECT

Figure 1- Abrasioned glaze in actual conditions of use.

Figure 2- Abrasioned glaze resulting from PEI method.

Figures 1 and 2 show electronic microscope photographs of ceramic paving abrasioned during use (transit of people), and samples of the same paving abrasioned by PEI. As can be seen, the appearance of both abrasioned specimens is similar, which confirms that the PEI method simulates quite well the wear that is produced during the actual use of glazed ceramic paving.

The PEI method consists of submitting the glazed surface of tiles to the action of an abrasive load composed of steel bearings, corundum, and distilled water, in a standardised abrasometer. The levels of abrasion specified in the above test are 150, 300, 450, 600, 750, 900, 1200 and 1500 revolutions.

The clean, abrasioned samples are examined with the human eye, under 300 lux light, from a distance of 2m and a height of 1.65m. The lowest abrasion level at which there is appreciable change in the surface's appearance determines the PEI class of the tested piece, in accordance with the data given in Table II.

TABLE II

Damp system abrasion test (PEI method)	
Abrasion level Visible defect at (revs)	Class
150	I
300, 450 or 600	II
750, 900, 1200 or 1500	III
> 1500	IV

It is, however, obvious that the resistance to abrasion measured according to the PEI method involves the visual estimation of a series of changes in physical properties, in contrast to other methods that base the measurement of this characteristic on loss of weight or on the depth of the mark left by the abrasion.

Although the PEI method simulates well the mechanical wear that the piece undergoes during use the fact that loss of facing is determined visually constitutes a problem. Thus, it must be considered that one of the real causes of deterioration of the glazed surface is the retention of dirt caused by the change in texture. In PEI evaluation, the nature of the agents used in the abrasive process and the subsequent cleaning of the samples with diluted hydrochloric acid make it unlikely that the pores opened by abrasive action will be full of dirt. This means that visible deterioration caused by the test will be lessened due to cleaning.

3. FACTORS THAT INFLUENCE THE LOSS OF ASPECT OF A GLAZED SURFACE

The visual estimation of loss of aspect on which the PEI method is based must be related, in an undetermined manner, to the resistance to abrasion and to other factors such as loss of shine, change of colour, change of texture, etc.... Of all these factors resistance to abrasion, measured as loss of mass, is the one that can best be related to the physical properties of the glaze, to its microstructure and to its component properties (glaze matrix hardness, hardness of additives, moduli of elasticity of both, matrix-additive bond, etc...).

There are two ways to increase the resistance to loss of aspect of glazed surfaces, that are well known by manufacturers of ceramic paving. These are:

- the use of suitably designed models to disguise loss of shine, change in colour and increase in retained dirt which arise with actual abrasion of the piece.

- increase the resistance to abrasion of the ceramic glaze and decrease its porosity, by altering its composition and process variables.

3.1 Influence of visual aspect

Manufacturers of ceramic tiles know only too well that glazes with very similar technical characteristics (resistance to abrasion and porosity) behave radically different from each other during use.

From the analysis of the results obtained from making an exhaustive examination of a large number of ceramic tiles abrasioned during use, a series of factors that considerably influence the loss of aspect of the glazed surface have been determined. These factors are the following:

- the colour of the base glaze
- the number and level of dispersion of the different colours in the piece

- the shine of the glazed surface

a) Influence of the colour of the base glaze

Abrasion substantially increases the microrugosity of the glazed surface, in such a way that the tone that the human eye sees is whiter than that which the glaze exhibited before abrasion.

Because of this, light colours disguise change in tonality, produced by abrasion, better than dark colours. Consequently, glazes that contain light colours, all other factors being equal, generally have a higher class of PEI. However, it is noted that light usually behave less well during use than other colours, since abrasion is associated with retention of dirt on the glazed surface.

b) Influence of the number and degree of dispersion of colours in the piece.

The visual effect of various colours in one piece can diminish the loss of aspect due to abrasion, however, the capacity for concealment is related to the degree of dispersion of the colours. Colours exclusively localized in different areas of the piece will act as plain colours, and granite type applications with various colours, uniformly distributed, will conceal the loss of aspect.

c) Influence of shine of the glazed piece.

In spite of the fact that a loss of aspect in the glazed surface due to loss of shine is not recognised by the PEI visual evaluation method, this loss is detected when examining installed tiles abrasioned during use. As a result, this factor must be borne in mind when designing the glazed surface.

It has been observed that loss of shine is produced in the first stages of abrasion, this depends considerably on the development of the technical characteristics of the glaze (hardness, initial shine, etc....). Obviously, glazes that were not originally very brilliant will exhibit loss of shine caused by abrasion to a lesser extent.

Besides these three factors, other factors, that may have, on certain occasions, a decisive importance for the product's behaviour during use, must be kept in mind, such as:

- glaze texture
- glaze thickness
- penetration of certain applications (blasting, serigraphs, etc....).

It should be mentioned that the influence of the previously enumerated factors in the loss of aspect of a piece is complicated, making it difficult to establish relationships between PEI and these factors.

It must also be remembered that actual visual perception of the deterioration of a material in use is dependent, on many occasions, on the location in which it is installed, and on lighting conditions.

3.2 Influence of resistance to abrasion and the porosity of the glaze.

The influence that the microstructure of the glaze (percentage and size of pores, vitreous phase, crystalline phases, etc....) and the properties of its components exert on the resistance to abrasion is very complicated, and sufficient experimental data is not available to be able to determine this influence. However, all other factors being constant, it seems very likely that when the hardness of the vitreous matrix and additives increases, the resistance to abrasion increases.

Similarly, when the porosity of the glaze is reduced, the abrasioned glazed surface will react better to retention of dirt.

3.2.1 Hardness

The analysis of results obtained from experiments on different ceramic tile models and their corresponding hardnesses (Vickers hardness) has shown that there is no relationship between these characteristics. This is probably due to the fact that other factors which considerably influence the glaze's resistance to abrasion were not maintained constant. However, when the hardness of one ceramic glaze was exclusively varied, it was noticed that the resistance to abrasion was directly proportional to the hardness of the vitreous phase. (Table III).

TABLE III

GLAZE COMPOSITION AT 6000 REV(MG)	VICKERS HARDNESS NO.	LOSS OF WEIGHT
Pb-Si-Na	470	345
Zn-Pb-Alkalines-Earth Alkalis-Al-Si-B	585	270
B-Na-Ca-Si	640	245
Al-Si-B-Alkalines-Earth Alkalis	646	245

On the other hand, the difference between the hardness of a material and its resistance at surface level should be clearly distinguished.

Hardness is defined as the resistance of a material to penetration by another material. This property is clearly inherent to the material and depends only on its nature, therefore it is a physical property. To study this property the Vickers Hardness Test is used; this consists of the indentation of an inverted diamond pyramid of standardised dimensions into the glaze for a certain period of time, under a predetermined load; the extent of indentation is subsequently measured.

However, the "hardness" of ceramic tile glazes is traditionally measured by Mohs' resistance to surface scrathing method, this method was adopted by the CEN as european standard EN 101 "Ceramic Tiles. Determination of hardness at surface level according to Mohs". The test involves tracing 4 lines on the tile surface using each one of the minerals of the Mohs scale. The hardness of the glaze is that of the mineral with the lowest hardness which has produced a line.

This resistance method was developed by Mohs for homogeneous materials and in these cases the resistance to scratching may possibly be equivalent to hardness. However, the glazed surface of ceramic tiles is composed of a mixture of materials and various types of additives with different granularities; also, in the majority of cases, the texture of the tile is far from being smooth and uniform.

Mohs' hardness test for ceramic tiles, like the PEI method, is clearly influenced by the visual aspect of the glaze (colour, shine, texture, etc...). The glaze of model 17, according to the test carried out using the method described in standard EN 101, has a hardness of 9 Mohs. The lines produced with minerals of a lower hardness were not visible to the human eye, and besides, the rough texture of the glaze made it difficult to scratch the surface. However figure 3 shows the line produced on the same glaze using quartz (Mohs' hardness 7). It is clear that the glaze visually behaves like a material of a hardness number 9, but that the glaze does not have a hardness of 9.

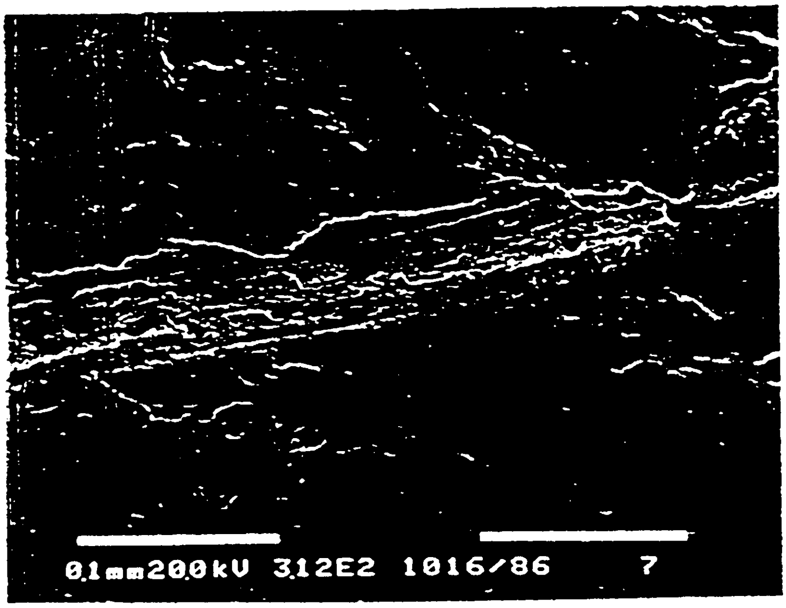


Fig. 3 Line produced on glaze 17 by quartz.

The method for determining resistance to scratching, defined in standard 101, studies the complete behaviour of the surface when scratched, but does not determine the value of a physical property.

As proof of the above, the following tests were carried on various glazes:

- Mohs' hardness test as described in standard EN 101.

- Mohs' hardness test and visualization of scratches produced by minerals by rubbing the glazed surface with a graphite pencil of low hardness, and subsequently cleaning with dry cotton. The graphite penetrates the scratches, making them visible.

- Vicker's hardness test using a LECO M-400 microdurometer, with 500g load and a 15sec application time.

100 indentations were produced on each glaze, these were randomly distributed over the surface. The results obtained are shown in Table IV.

In the table, it is seen that the Vickers Hardness Number for the glaze is not related to its hardness determined according to standard procedure. So when an attempt is made to see the scratch marks more clearly, by rubbing a graphite pencil on the glazed surface, the determined values for hardness are generally lower than those obtained according to standard procedure.

TABLE IV

MODEL	HARDNESS		
	MOHS' HARDNESS TEST		VICKER'S HARDNESS TEST
	EN-101	MODIFIED	AVERAGE
1	5 - 4	4 - 3	620
7	5	3 - 4	598
8	4	3	562
9	5 - 4	4	650
10	6	6	631
11	5 - 4	3	624
13	5 - 4	4 - 5	556
14	5 - 4	4	575
17	9	6	640
18	5	4	646
20	5	4 - 5	552
21	6 - 5	4	537

Figures 4 and 5 demonstrate how, for homogeneous surfaces (model 1), the distribution of Vickers Hardness in the glaze approximates a normal curve, while for heterogeneous surfaces (model 16) there are various distributions pertaining to each zone of the glaze surface.

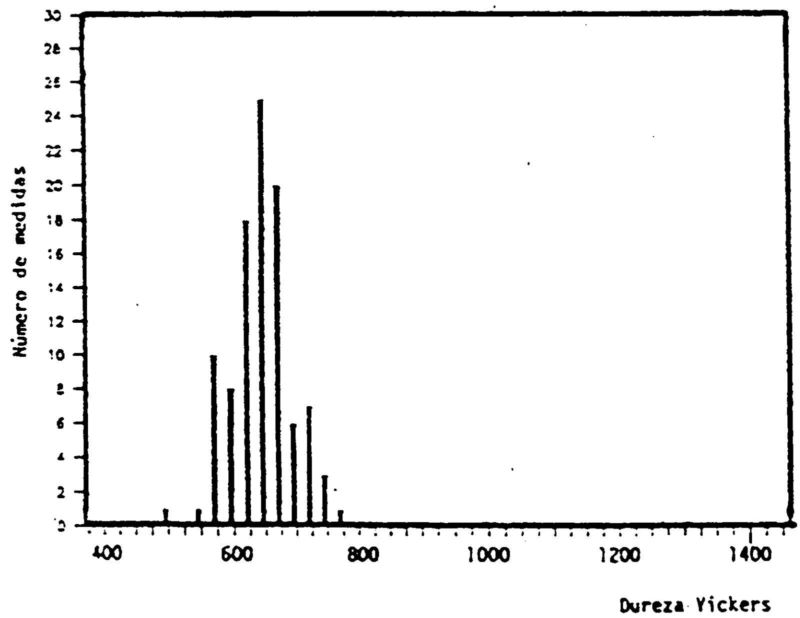


Fig. 4 Distribution of hardness in glaze 1

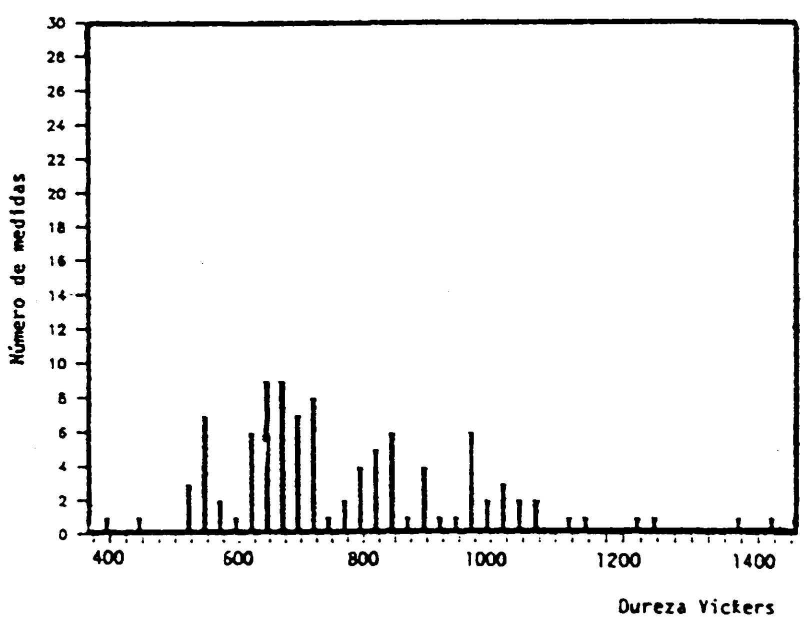


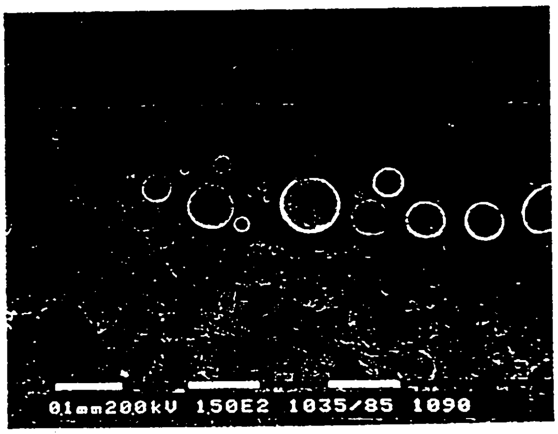
Fig. 5 Distribution of hardness in glaze 17.

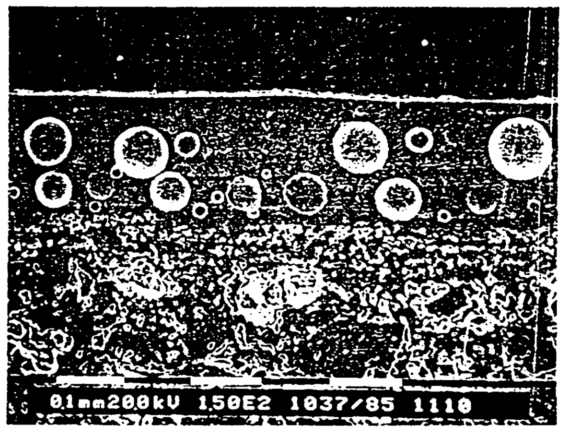
To summarise, it is only possible for the Vickers Number of the glaze to be equivalent to its resistance to scratching when the glaze is homogeneous. It may be expected that the loss of shine, that occurs in the initial stages of abrasion is related to the glaze's resistance to scratching. However, as mentioned above, this characteristic does not determine the loss of aspect of the glaze in more advanced stages of abrasion.

3.2.2 Porosity

As mentioned above, the majority of ceramic glazes have a porosity that is related to the composition of the glaze and to production process variables.

This porosity, initially closed, progressively opens up as abrasion increases, this implies an additional loss of aspect due to retention of dirt.





Figs. 6 & 7 - Transverse section of two different glazes, as observed through an electronic microscope.

As can be seen from figures 6 and 7, the size of the pores in the glaze and their distance from the surface is as important as the total porosity of the glaze. The closer the closed pore is to the surface of the glaze (generally the case for larger sized pores) the easier it will become an open pore, susceptible to the retention of dirt.

In order to remind ourselves of the effect that retained dirt has on the loss of aspect in ceramic glazes, a method has been developed that allows pieces abrasioned using the PEI method to be dirtied, in a reproducible way.

This method involves pouring a few drops of a mixture of mineral oil and powdered active carbon, 85:15 by weight, onto the abrasioned sample. Active carbon is used, as the dirt that is normally trapped in ceramic tiles is black in colour.

Using a brush with a constant rotational movement and which exerts a uniform pressure, the mixture penetrates into the open pores of the abrasioned glaze. Afterwards any residual mixture is removed with soap and water, using a similar brush to the one above.

Once this process is completed, the samples are classified according to the conditions specified in standard EN 154.

To study the effect of the porosity of the glaze on its loss of aspect, an evaluation was carried out of the number and size of pores opened through abrasion at 1500 revolutions, for various ceramic tiles sold commercially. To perform the experiment on black glazes, their pores were filled with a mixture of mineral oil and anatase.

Table V gives details of the distribution of open pores in abrasioned and non-abrasioned areas, and the surface area that the pores occupy, for all the glazes tested. It can be seen that the majority of glazes tested showed an appreciable level of open porosity after being abrasioned, the volume and size of the pores varying from one glaze to another.

TABLE V

Model	Number of pores per cm^2 in non-abrasioned area.				Number of pores per cm^2 in abrasioned area				Area occupied by pores in abrasioned area ($mm^2/cm^2 * 10^{-3}$)			
	> 100	100 - 60	60 - 40	< 40	> 100	100 - 60	60 - 40	< 40	> 100	100 - 60	60 - 40	< 40
1	0	0	0	0	0	0	0	0	0	0	0	0
13	0	0	0	0	0	0	0	0	0	0	0	0
7	0	0	0	1	0	0	2	12	0	0	4	4
10	0	0	0	0	0	0	2	12	0	0	4	4
2	0	0	0	1	0	0	1	69	0	0	2	22
9	0	0	0	10	0	0	3	212	0	0	6	67
14	0	0	0	300	0	0	10	643	0	0	21	202
3	0	0	0	15	0	0	10	674	0	0	21	212
20	0	0	0	400	0	0	2	940	0	0	4	295
21	0	0	0	1000	0	0	14	3264	0	0	30	1025
11	0	0	0	0	0	1	48	744	0	5	102	234
18	0	0	0	0	0	3	15	44	0	15	32	14
4	0	0	0	10	0	8	69	542	0	45	146	170
6	0	0	22	10	0	3	63	310	0	15	134	97
8	0	1	3	35	0	6	119	982	0	30	253	308
5	0	0	0	5	1	0	6	119	13	0	13	37
19	0	0	0	5	2	8	17	66	26	40	36	21
15	0	1	15	0	3	8	118	31	40	40	250	10
23	0	0	30	60	2	28	106	390	26	60	225	122
22	1	6	2	0	3	37	45	2	40	186	96	1
12	0	0	0	20	1	37	215	295	13	186	456	93
17	2	20	40	2	7	41	149	55	93	206	316	17
16	10	0	0	0	44	71	128	0	584	356	272	0

In table VI standard PEI values, modified PEI values for dirtied abrasioned surfaces, total area occupied by pores in the non-abrasioned area and the area abrasioned at 1500 revolutions are given for each one of the glazes studied. It emerges from the study that:

- The modified values of PEI are substantially different to the corresponding standard PEI values. In effect, the visual aspect of glazes 6 and 15, which are dark coloured, improve when dirtied, since the whitening that the abrasion test produces is reduced. On the other hand, in light coloured glazes the same treatment exaggerates loss of aspect. It should be mentioned that the behaviour of the glazes in the test with modified PEI values, is similar to that observed in real conditions of use.

TABLE VI

Model	Description	PEI EN-154	PEI Modi-fied	Total Area Occupied by Pores (in mm2/cm2*10+3)	
				Abrasioned Area	Non-abrasioned Area
1.	White base. Brilliant. Smooth	> 1500	> 1500	0	0
2.	White base. Matt. Smooth	> 1500	> 1500	24	1
3.	White base. Brilliant. Smooth Blasted grey.	1500	450	233	5
4.	White base. Brilliant. Smooth Powdered grey	> 1500	300	361	3
5.	White base, Brilliant. White serigraph. Matt. Relief	> 1500	> 1500	64	1
6.	Black base. Brilliant. Grey serigraph. Matt. Relief	600	> 1500	246	50
7.	Light beige base. Brilliant. Beige serigraph. Matt. Relief	> 1500	600	8	1
8.	Grey base. Brilliant. Grey & white serigraph. Brilliant	>1500	450	621	22
9.	White base. Matt . Grey and white serigraph. Relief	> 1500	> 1500	73	3
10.	Green and brown grain. Waxed.	> 1500	1500	8	0
11.	Beige base. Brilliant. Smooth. Beige & brown serigraph. Brilliant	> 1500	1500	336	0
12.	Grey base. Brilliant.	> 1500	450	748	6
13.	Black base. Brilliant. Relief White, garnet and green serigraph.	> 1500	> 1500	0	0
14.	White base. Matt White and grey serigraph. Matt.	> 1500	1500	223	94
15.	Brown base. Matt Blasted brown. Rustic.	450	1200	340	37
16.	Beige base. Matt Blasted brown. Rustic.	> 1500	750	1212	132
17.	Beige base. Matt Grain of assorted dark colours	> 1500	1500	630	211
18.	White base. Matt Fine brown grain	> 1500	1500	61	0
19.	White and brown grain. Brilliant. Imitation granite	> 1500	1500	123	1
20.	White grain. Brilliant. Grey, brown & beige serigraph.	> 1500	> 1500	299	125
21	White base. Brilliant . Relief Grey, black and brown serigraph.	> 1500	> 1500	323	47
22.	White, grey and black grain. Brilliant, Imitation granite.	> 1500	> 1500	323	47
23.	Beige base. Fine black, red, white and grey grain. Brilliant.	1500	600	433	83

- Generally, as the open porosity of the glaze increases the loss of aspect increases, according to the modified test. However a definitive relation between porosity and loss of aspect cannot be established since there are various factors (texture and design of surface), that tend to conceal, as happened in the test using standard PEI values, the effect of dirt.

When glazes 4 and 22 are compared, it can be observed that, although their porosity is very similar, the modified PEI values are substantially different. This is due to glaze 22 having a decorative grain effect that disguises the effects of retained dirt, while glaze 4 has a light, single colour surface, for the most part.

Besides porosity, the micro rugosity of the abrasioned glazed surface also retains dirt. Consequently, glazed surfaces with no appreciable open porosity can exhibit significant loss of aspect if the surface is quite rough (models 3 and 7).

The preferential localization of porosity in applications (serigraphs, blastings, grains, etc...) means that, in models with a light colour base and a dark application, the visible deterioration, through retention of dirt, is not as great as would be expected, given the size and number of pores present (models 3, 19 and 14).

In cases where the original glazed surface (model 17) has a considerable amount of open porosity, although the number of open pores does increase, there is no substantial loss of aspect.

On the other hand the loss of aspect of a glazed surface, during use, has been seen to be more noticeable when the size of the open pores is big (over 60 micras), since these pores can be detected by a simple look. Pores of smaller dimensions lead to a uniform darkening when they get dirty, which makes the deterioration caused by abrasion less perceptible.

4. Summary and Conclusions

Some of the factors that determine the loss of aspect of ceramic tiles through abrasion have been shown. It has been seen that the PEI method adequately reproduces the effect of abrasion on glazed surfaces. However, the evaluation of loss of aspect that abrasion causes is significantly lacking.

The retention of dirt on the abrasioned glazed surface was seen to be one of the causes that considerably worsens the visual aspect of paving, once it is installed. To examine this effect a reproducible experimental procedure was developed based on the PEI method.

The results obtained show that the modified PEI method is much more restrictive than the standard EN-154 PEI method. The open porosity of the abrasioned glazed surface was seen to considerably influence the modified PEI value.

5. BIBLIOGRAPHY

(1) Enrique, J.E.; Negre, F.; Ferrandis, M.J.; Técnica Cerámica, 158, 505-510, 1987.

(2) Van der Klugt, L.J.A.R.; Interbrick, 1 [5], 12-16, 1989.

(3) Pagano, M.; Interceram, 28 [3], 306-307, 1979.

(4) UNE 67-154-85 Asociación Española de Normalización y Certificación (AENOR).

(6) UNE 67-101-85 AENOR.