USE OF AGALMATOLITE ROCK IN THE FORMULATION OF ADDITIVES FOR THE SURFACE TREATMENT OF PORCELAIN STONEWARE TILE

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ABSTRACT

The majority of pores on the porcelain stoneware ceramic covering surface are defects introduced by stages of rectification and polishing. These surface pores are the main responsible factors for the introduction of staining agents, a problem that can compromise the aesthetic qualities of the product. This work proposes the use of agalmatolite rock to form additives applied on pieces with non-enamelled porcelain stoneware through a pulverization system, in a stage prior to firing. These additives seal open pores, facilitating the cleaning of the surfaces of the pieces. The following characterization techniques have been used in this work: X rays diffraction, differential thermal analysis, optical microscopy and scanning electron microscopy. Tests were conducted on covering surfaces according to ISO 10545-14 (NBR 13818/1997), and they have showed a significant increase in stain resistance in pieces where additives were used in relation to a current piece marketed by a Brazilian ceramic company. Through analysis of images obtained by microscopy techniques, it was possible to observe a reduction in open porosity and a fall in occurrence of pores with diameter larger than 15 µm in a piece where an additive was used, demonstrating the efficiency of the process used in this work.

1. INTRODUCTION

In recent years, the ceramic coverings industries have improved their products in a continuous process of technological development in order to add price to these products. Porcelain stoneware appeared as a consequence of this and it has gained a growing share of the national and world market due to properties such as low open porosity, high mechanical resistance to rupture and brightness. However, despite having characteristics that make it different from other kinds of ceramic coverings, porcelain stoneware is vulnerable to staining, which causes loss in aesthetic qualities of the product with use. As porosity in the surface of ceramic coverings is the main responsible factor for the entry of staining agents, and in order to produce pieces with lower porosity, the coverings industries try constantly to innovate the processing of ceramic pieces through the utilization of equipment and raw material which allow fabricating products with as few defects as possible. In this context, this work proposes the use of additives to enable reducing the surface porosity of coverings, in order to increase the stain resistance of pieces. These additives are formulated using agalmatolite rock, which stands out because it is a raw material with melting potential and low price.

2. POROSITY OF CERAMIC COVERINGS

The presence of pores in ceramic coverings is related to the manufacturing technology used in these. In polished coverings, surface porosity starts mainly during the polishing stage because defects are introduced in pieces, showing closed pores that were located inside the covering before. This happens because a thin coat of the product, between 0,5 and 1,0 mm, is removed resulting in a "new" surface with greater volume of pores[1]. Thus, despite achieving better aesthetic characteristics, polishing can compromise some technical characteristics of coverings, such as: stain resistance.

The phenomenon of staining is directly related to the existence of irregularities in the surface of a body, which facilitates the penetration of particles in the surface as well as making it more difficult to remove these. A greater or lesser susceptibility to the problem will be defined by the characteristics of these irregularities, which will be determined by size, shape and texture of the pores responsible for these, besides the amount per unit area. There is a relation between the size of pores and the occurrence of stains, which can reach a space of critical size where the phenomenon can be verified: from 15 to 60 μm[2,3]. Thus, a right way would be to eliminate totally the porosity present in the surface of covering; however, it must be considered that this is difficult to achieve. Thus, as a solution, it has been tried to produce pieces that present a lower number of small open and isolated pores. The stain resistance can also be related to the cleanability of a ceramic covering. Each kind of stain and each cleaning test are associated with class of cleanability, from 1 to 5[4]. If a class number increases, the ease of cleaning of the covering will also increase.

3. AGALMATOLITE

Agalmatolite is a metamorphic rock with rare occurrence that can present massive or lamellar form and a colour that varies from white to light green. It is formed essentially by two aluminium phyllosilicates – pyrophyllite and muscovite, associated with minerals such as sericite, tourmaline, quartz and feldspar[5]. Nowadays, the majority of the agalmatolite extracted in Brazil is commercialized to paint industries. The low price of commercialization to ceramic industry, accounting for about 10% of its total production,

does not reflect the excellent technical qualities and promising applications of agalmatolite in the ceramic coverings area.

In the ceramic industry, agalmatolite can be used as a melting raw material in the formulation of porcelain and porcelain stoneware, because, besides presenting a vitrification temperature (1240 ºC) in the same line of temperature as the firing of these products (1200 – 1250 ºC), it has a considerable content of alkalis (alkaline oxides such as K_2O and Na_2O) present in its composition, which varies from 4 to 11%[6]. Agalmatolite also stands out for having a white firing colour and being a cheap raw material, presenting a much lower price than nepheline for example (a mineral that has been used by ceramic industry in the formulation of additives): about one third of price per ton of nepheline.

4. EXPERIMENTAL PROCEDURES

4.1. CHARACTERIZATION TECHNIQUES

The techniques used for the characterization of agalmatolite rock and the additive were: XRF, XRD and DTA. A chemical analysis of agalmatolite rock was done through the X-ray fluorescence technique (XRF), in a Netzsch instrument, 409c model. Knowledge of the chemical analysis of the rock was fundamental so that, with the percentage of constituents, it was possible to calculate the formulation of the additive prepared with accuracy. The X-ray diffractometry technique was used in this work in order to identify the mineralogical stages of agalmatolite rock and also to verify the possible phase changes when the rock is subjected to high temperatures. For the realization of this technique we used X-ray diffraction, Xpert model, with copper radiation Ka ($\lambda = 1{,}5418$ A), with power of 40 KV and 30 mA. One of the prepared additives was characterized through a differential thermal analysis (DTA), in a Setsys instrument, 1750 model, in order to verify its fusion temperature and the decomposition temperature of its constituents.

4.2. ADDITIVES

Through the knowledge of the chemical composition of agalmatolite rock (Table 4), it could be observed that the three oxides present in the largest quantity were respectively SiO_2, Al_2O_3 and K_2O. Therefore, the SiO_2 - Al_2O_3 - K_2O system was used to formulate specific additives, trying to obtain compositions of different points, located in the most interesting phase diagram region. The region for choosing the points was selected in such a way that these points were between the isotherms of 1000 and 1200 ºC, which allows fusion of the additives at temperatures lower than the maximum firing temperature of porcelain stoneware, which is about 1220 ºC. Table 1 shows the compositional percentages of the chosen points, represented by "P".

OXIDE COMPONENT	PERCENTAGE IN MASS (%)				
	P1	P2	P3	P4	P5
SiO_2	55,0	55,0	52,0	60,0	64,0
Al_2O_3	10,0	12,0	8,0	8,0	7,0
K_2O	35,0	33,0	40,0	32,0	29,0

Table 1. Compositions, in oxides, of chosen points in a certain region of the phase diagram of the SiO_2 - Al_2O_3 - K_2O system.

In order to obtain the points indicated in Table 1, three raw materials were used, responsible for supplying the necessary quantities of SiO_2, Al_2O_3 and K_2O demanded by the system: quartz, agalmatolite and potassium nitrate. Potassium nitrate (KNO_3) was added in the raw materials mix because it effectively helps in the content of potassium oxide (K_2O), as a decomposition reaction of KNO_3 occurs at temperatures about 400 ^oC, promoting a production of K_2O during the sintering stage. The formulations of additives prepared and represented by "H" were determined by percentages in mass of each raw material used, as can be observed in Table 2.

CHOSEN POINTS IN DIAGRAM	ADDITIVE FORMULATED	PERCENTAGE IN MASS (%)		
		Agalmatolite	Quartz	Potassium nitrate
P1	**H1**	22,8	25,8	51,4
P2	**H2**	28,9	23,1	48,0
P3	**H3**	18,2	25,0	56,8
P4	**H4**	19,4	32,6	48,0
P5	**H5**	17,4	37,9	44,7

Table 2. Formulation of additives, choosing points in the phase diagram and percentages in mass of raw material.

Suspensions were prepared with additives in porcelain jars, weighing the solids (raw material) on analytic scales in the proportions shown in Table 2, in a way that they totalled a mass of 500g for each formulation, and in a next stage adding 300 ml of water. 350g of big balls and 150 g of small balls of alumina were put in the jars with additive suspensions. The grinding was done after this, using a Servitech Gira Moinho Piriquito, for a set time of 40 min, obtaining a reject on a 44 μm mesh below 1% for all the suspensions. The density and the drainability of each additive suspension were determined using a pycnometer (V= 100 cm^3) and a Ford cup (601 – F8) respectively.

4.3. SURFACE TREATMENT

The pieces of porcelain stoneware which received surface treatment were supplied by a Brazilian ceramic covering company. The pieces of this covering had a 40 X 40 cm format and were recently pressed (green). The following experimental procedures were done in the company, using for this, the company's materials and equipments. The additive suspensions were applied on the porcelain stoneware pieces, as illustrated in Figure 1, using a pulverization system known as application cabin, or airbrush applications, which has an air compressor, a hose and a gun.

Figure 1. Application of additive suspensions on porcelain stoneware pieces.

This pulverization system allows the suspension to leave the gun and reach the surface of the covering as little water drops, containing additive particles. The little water drops of the suspensions enter in the piece by capillarity, acting as a vehicle for the transport of the particles, taking them inside the open pores. The mass of additive suspension applied on each piece was

fixed at 40 g and determined by weighing the piece on a scale, before and after the application. With the gun joined to the compressor, the exit pressure of the suspension was 2 kgf/m^2.

After the application of the suspension, the pieces were dried in an oven at temperature of 110 ºC, during 30 min. The main purpose of drying was to allow most of the water contained in the additive suspension to evaporate, thus forming a coat of additive particles in the surface of the covering. The pieces were fired in an industrial roller kiln of 102 m length. The time of the firing cycle used was 50 min., reaching a maximum temperature of 1220 ºC for 5 min. During the firing of the piece, the additive coat melts, giving rise to a liquid phase that, by capillarity, covers the volume of the open pores. Then, these pores are filled by melted additive, promoting a fall in the points of interconnection. Thus, as the piece cools, the liquid phase solidifies and promotes a greater densification of the ceramic covering surface. Next, the surface of the covering was polished using an industrial polishing machine of the Ancora type, having 32 polishing heads. Though polishing removes a thin surface coat of the pieces, revealing the pores which were closed before, when the described treatment is done, most of the pores which were open are filled and sealed by the solidified additive, which reduces the number of open pores in the "new" surface of covering, as it shown in Figure 2.

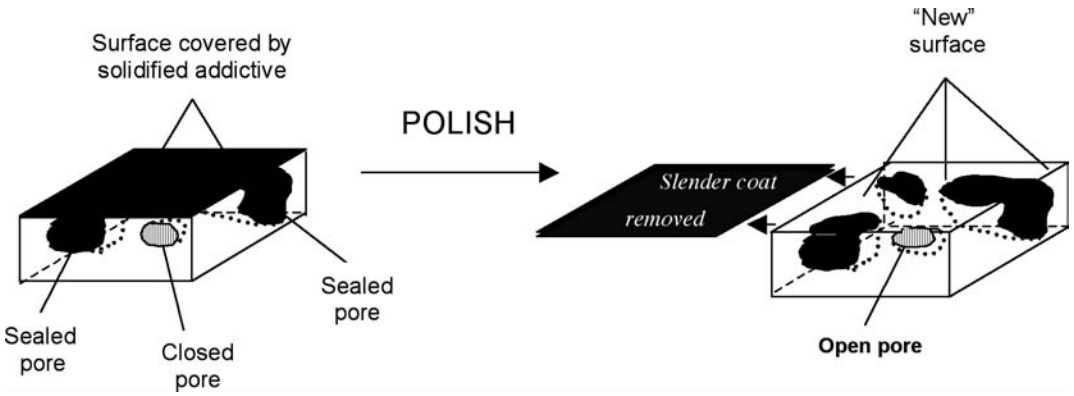


Figure 2. Surface appearance of the ceramic piece before and after polishing.

4.4. STAIN RESISTANCE TEST

After they had been polished, the porcelain stoneware pieces were subjected to the stain resistance test, according to the procedures determined by the ISO 10545 -14 standard (NBR 13818/1997). This test was also done on a polished commercial piece (Bianco) of porcelain stoneware that did not receive surface treatment, so that it was possible to confront the results obtained in both cases. The reagents applied in the surface of pieces of porcelain stoneware, called "staining agents", are classified by presenting: penetrating action (methylene blue, methylene red and chromium green), oxidant action (iodine) and capacity for film formation (olive oil). Other products such as coffee and red soil were included in the list of staining agents used in this work. The staining agents that stain the coverings were applied as drops, in such a way that they scattered in a circular plane area, remaining in contact with the surface of the covering during 24 hours. The covering was subjected successively to the following systematic cleaning procedures: surface cleaning with warm water, manual cleaning with dishwashing liquid, red crystal paste (abrasive) and alkaline detergent. After

each cleaning process, the pieces were subjected to a visual examination and if the stains were not removed, the next cleaning procedure was used in the same sequence. According to the ease of stain removal and the cleaning test used, the pieces were organized in cleanability classes, as can be seen in Table 3.

CLEANABILITY CLASSES	KINDS OF STAINING / CLEANING TESTS	CLEANING EASE
1	Stain non removed	Cleanability smaller ⇩ Cleanability bigger
2	Stain removed with alkaline detergent	
3	Stain removed with red crystal paste (abrasive)	
4	Stain removed with dishwashing liquid	
5	Stain removed with warm water	

Table 3. Cleanability classes, kinds of staining and cleaning test

4.5. CHARACTERIZATION OF THE FINISHED PRODUCT

In order to associate the results obtained of the stain resistance test with the efficiency of the surface treatment used in the polished ceramic pieces, a characterization was performed of the pieces of treated coverings and also of a piece of a non treated covering (commercial product), through optical microscope techniques (OM), using a Leica optical microscope, DM 4000M model and an scanning electron microscope (SEM), using a Philips microscope, XL 30 model with tungsten filament. The analyzed pieces of covering were chosen according to the results obtained in the stain resistance test.

In the sequence, analysis was performed of some digital images obtained by SEM, in order to quantify the open porosity present in the surface of the coverings with treated and non treated surfaces with the additive, which allows a comparison between both cases. The analysis of the digital images was done by using Imago 2.2 software, which calculates the percentage of pores present per total areas of the images and provides a size distribution of these pores.

5. RESULTS AND DISCUSSION

The chemical analysis of agalmatolite rock, obtained by XRF, is shown in Table 4.

OXIDES	SiO_2	Al_2O_3	K_2O	Fe_2O_3	TiO_2	CaO	MnO	LOI
Percentage in mass (%)	58,84	30,24	5,72	0,32	0,30	0,02	0,01	4,70

Table 4. Composition in oxides of agalmatolite rock.

It is possible to observe through the chemical analysis of agalmatolite rock that its composition presents favourable characteristics for forming ceramic materials. The analyzed agalmatolite consists of about 89% in mass of SiO_2 and Al_2O_3; the former represents about 59% of rock total mass. Another important characteristic is the content of alkalis present in the rock: about 6% of K_2O, what provides it with the properties of a melting material.

Diffractograms were obtained of the natural agalmatolite rock (thus called because it was not subjected to any thermal treatment) and of the sintered rock at a temperature

of 1200º C. These diffractograms were compared as shown in Figure 3. In relation to the mineralogical characteristics of natural rock, it was observed that it consisted of three crystalline phases: quartz (SiO_2 – JCPDS 5-490), pyrophyllite ($Al_2Si_4O_{10}(OH)_2$ – JCPDS 25-22) and illite ((K,H_3O) $Al_2Si_3AlO_{10}(OH)_2$ – JCPDS 26-0911).

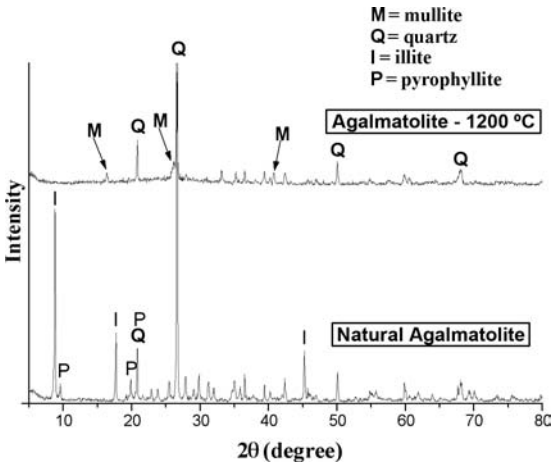


Figure 3. Diffractograms of samples of natural agalmatolite and sintered agalmatolite at a temperature of 1200 ºC.

The agalmatolite sintered at 1200 ºC presents the crystalline phases: quartz and mullite. As porcelain stoneware also presents quartz and mullite as the only crystalline phases in its microstructure[7], it can be said that the surface of the covering is mineralogically very similar to the additive coat that was formulated using agalmatolite rock.

The DTA curves obtained by the analysis of H5 additive are presented in Figure 4.

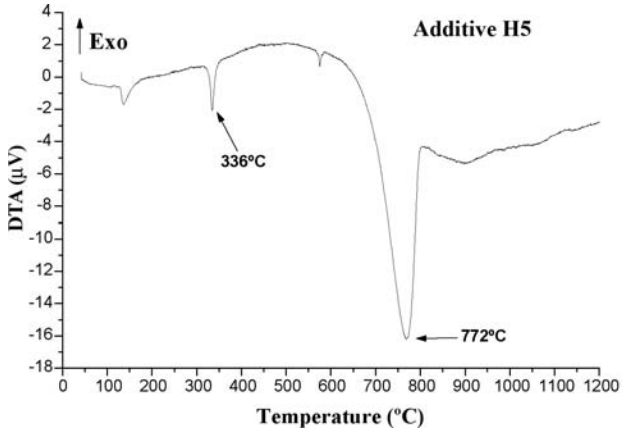


Figure 4. Differential thermal analysis of H5 additive.

Two increased endothermic peaks were observed, with different temperatures. The first peak occurs at the temperature of 336 ºC, as a consequence of the decomposition of KNO_3 present in the additive. Between 650 ºC and 800 ºC the second peak was observed, which was related to the fusion of the additive because of its intensity. Thus, the thermal analysis indicated that the particles of H5 additive melt at a temperature of 772 ºC, which allows the formation of a liquid phase that is able to penetrate the open pores of the surfaces of coverings by capillarity.

The values obtained in the determination of suspension density and drainability are presented in Table 5.

Additive suspension	H1	H2	H3	H4	H5
Density (g/ cm^3)	1,59	1,61	1,59	1,60	1,60
Drainability (seconds)	3,2	3,3	3,2	3,3	3,3

Table 5. Values of density and drainability of additive suspensions.

Thus, according to the average density values, about 1,60 g/cm^3, it can be said that the prepared suspensions presented a relation (in mass) of 60% water and 40% solids (regarding the raw materials used).

The stain resistance test was performed on polished pieces of porcelain stoneware treated superficially with the formulated additives (Table 2) and a piece referenced STD in this work, which is commercialized nowadays by a Brazilian ceramic covering company, which did not have any surface treatment. In order to facilitate the discussion of the results, the treated pieces received the same code as the respective additive applied to them, in other words: H1, H2, H3, H4 and H5. The results obtained are given in Table 6.

STAINING AGENTS	STD	H1	H2	H3	H4	H5
Red soil	1	1	1	1	1	1
Methylene blue	1	1	1	1	1	1
Methylene red	1	1	1	2	2	2
Coffee	1	1	1	1	2	2
Olive oil	2	3	2	5	2	5
Iodine	1	5	2	3	5	3
Chromium green	5	5	5	5	5	5

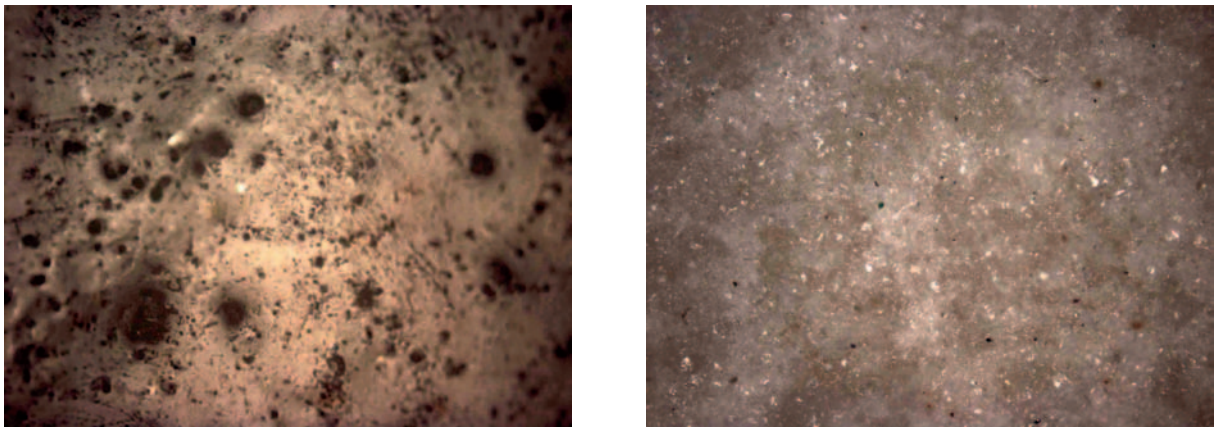
Table 6. Cleanability classes (from 1 to 5) attributed to porcelain stoneware pieces which were analyzed, according to the types of staining agents.

It was observed that the STD piece (which is nowadays commercialized as being a reference of resistance to the staining agents) was the one that presented less stain resistance, because five from seven staining agents applied were not removed after all the cleaning tests, and thus remained in the surface of the covering (class 1). Among the pieces treated superficially, it can be noted that the H5 piece (treated with H5 additive) was the one that presented the greatest stain resistance, thus obtaining higher numbers in the cleanability classes, which indicates that the stains produced in the test were more easily removed than in the other cases. In any event, it was possible to organize the treated pieces in a rising order of cleaning ease: H2<H1<H3<H4<H5.

As all the pieces that received the surface treatment underwent exactly the same procedures: application of additive, sintering, polishing and staining test, it can be said that the variable responsible by the different results obtained in the stain resistance test depends on the composition of the additives formulation. According to the compositional percentages relating to the chosen points in the ternary diagram (Table 1), and based on the results of cleaning ease (Table 6), it was observed that if the

content of Al_2O_3 was reduced, an increase in the stain resistance of the pieces occurred. One of the roles of Al_2O_3 is to increase the viscosity of the liquid phases present during the firing stage[8]. Thus, the reduction in the Al_2O_3 content in the additive composition can reduce the viscosity of the liquid stage obtained by fusion during the firing of porcelain stoneware, which provides greater facility of penetration in the surface pores of the piece, filling them with more efficiency.

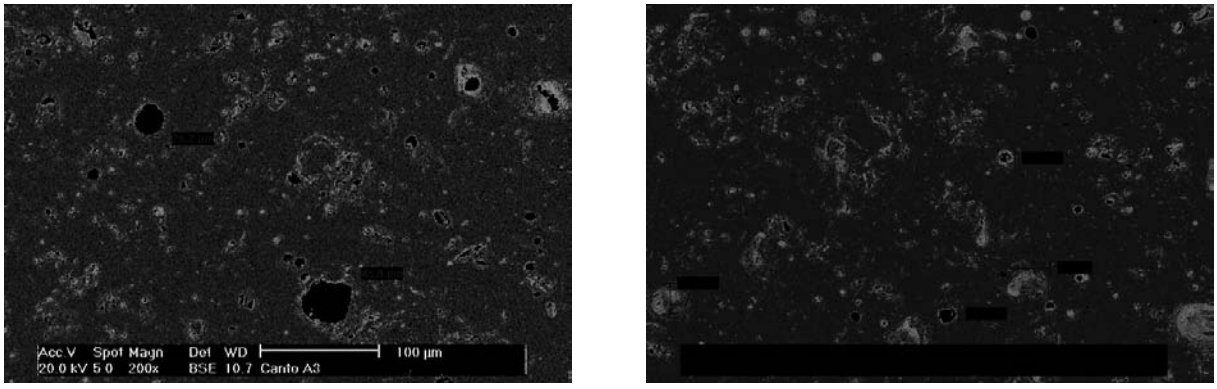
According to the results obtained with the tests, the pieces STD and H5 were chosen, which presented respectively, the worst and best performance in the stain resistance test, for analysis by microscopic techniques. This test was also conducted with pieces that had not been polished, in order to observe the appearance of the thin coat of melting additive in the surface of the covering. Figure 5 shows images related to this, obtained by OM.



(a) *(b)*

*Figure 5. **Micrographs obtained in OM of body tests without polishing of the STD piece (a) and H5 (b) with a magnification of 100x.***

The micrographs revealed open pores with different sizes in the STD (a) surface of covering, while in an image of the H5 (b) piece it is possible to notice the absence of open pores in the surface of the covering due to the thin coat of additive. In the images of the body tests on the polished coverings (Figure 6), it could be observed that in the STD body test (a), there are many open pores with diameters bigger than 20 μm, while in the H5 body test (b), fewer open pores were observed compared to (a).



(a) *(b)*

*Figure 6. **Micrographs obtained in SEM of body tests of STD (a) and H5 (b) pieces, using a magnification of 200x.***

In Figure 6 (b), it can also be noted that the open pores have diameters smaller than 17 μm. Together with this fact, the existence of some "cavities" filled by the additive, which possibly are closed pores present inside the piece before polishing, justifies the increase of H5 stain resistance. In order to quantify the reduction of open porosity in the H5 piece (treated with the additive) in relation to the STD piece (without treatment), the images obtained by SEM of the polished body test were analysed, using Imago software. Averaging the percentages of pores present in the body tests corresponding to the coverings not treated and treated with the additive, values were respectively obtained of 4,11% and 3,12%. Therefore, it may be stated that the H5 piece, superficially treated with the additive, presented 24% porosity less than STD piece which did not receive any treatment. Besides having quantified the porosity, the software provided information about the distribution of the pore diameters, identified from the analyzed images. In the body tests corresponding to the non-treated piece (STD), values were obtained of about 30,5%, while in the body test of the H5 piece the value was 25,2%. Therefore, the H5 piece resists staining better because besides presenting a reduced porosity, as already seen before, it also has a lower percentage of pores with diameters bigger than 15 μm.

6. CONCLUSIONS

The percentage in mass of Al_2O_3 in the developed additives is directly related to the stain resistance of the analyzed pieces. The best results of the tests are regarding pieces that had additives with a lower percentage of Al_2O_3 in their formulation. All the treated pieces presented a greater stain resistance than the commercial non treated piece (STD). Therefore, it may be stated that the methodology developed in this work is efficient, because it is relatively simple and has a low price, which allow its reproduction on an industrial scale.

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