

Parlatılmış Porselen Karoların Leke Direncini ve Temizlenebilirliğini İyileştirmek için Dolgu Malzemesinin Sol-Jel Yöntemi ile Üretilmesi Part I: Kompozisyon ve Kimyasal Hazırlığı

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Özet

Bu çalışmanın temel amacı bünye yüzeyinde bulunan mikro-porları doldurarak parlatılmış porselen karoların leke dayanımını ve temizlenebilirliğini iyileştirmektir. Karo yüzeylerine püskürtülerek uygulanabilecek ve mekanik etki ile dolabilecek sol-jel dolgu malzemesinin tasarlanması ve hazırlanması işlemleri ile bu amaç takip edilmiştir. Özellikle porları tamamen doldurabilmek için dolgu malzemesi inorganik ve organik malzemelerin farklı oranlarda kullanılması ile hazırlanmıştır. Çözelti ile doldurulmuş porlar taramalı elektronmikroskopu ile analiz edilmiştir. Karo yüzeylerinin leke direnci ve temizlenebilirliği ISO-10545-14 standartına göre değerlendirilmiştir. Hazırlanan dolgu çözeltisinin boya, çay, kahve, şarap, yağ, derz dolgusu gibi kirletici partiküllerin sızmasını önlediği gösterilmiştir. Bu tür kirleticilerin bir temizlik maddesi ya da çözeltisi ile çıkabilmesine imkan tanımaktadır.

Anahtar kelimeler

Lekedirenci,
Porselenkaro; Dolgu;
Sol-gel

Production of Sealing Material by Sol-Gel Method to Enhance Stain Resistance and Cleanability of Polished Porcelain Stoneware Tiles Part I: Composition and Chemical Preparation

Abstract

Improvement stain resistance and cleanability of polished porcelain tiles by sealing the micro-pores on the surface of body was the main purpose of this study. This objective was pursued through the design and preparation of sol-gel sealer that was deposited on polished unglazed tiles by air-brushing and sealed by mechanical processing. In particular the sealer was prepared by mixing inorganic and organic materials in different amounts to fully fill the pores. The filled pores were characterized by scanning electron microscope. The stain resistance and the cleanability of the tile surface were measured by following the ISO-10545-14 standard. It has been shown that prepared sealing material prevents particles of contamination, paint, tea, coffee, wine, oil or tile cement from accumulating. It allows these contaminants to be simply removed with a respective cleaning agent or solution.

Key words

Stain resistance;
Porcelain tile; Sealer;
Sol-Gel

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1. Introduction

Porcelain stoneware tiles represent an advanced product developed in the sector of ceramic tiles. The particular mix of raw materials (a typical current composition contains 25-30 % of kaolin and ball clays, 50-60% of feldspar and 5-10% of quartz sand) and the high firing temperatures used, make it possible to obtain a dense ceramic, characterized by very high physical-mechanical characteristics (Menegazzo et al. 2002, Esposito and Tucci 2000). Porcelain stoneware tiles can be classified as glazed and unglazed porcelain tiles in general. Surfaces of the unglazed tiles are polished to enhance their

aesthetic and performance. To compete better with natural stone, during the past decade, polishing the working surface of porcelain stoneware tile has become a widespread industrial process. However, after this treatment the working surface of the tile is particularly sensitive to staining agents (Sanchez et al. 2006, Esposito et al. 2005, Esposito et al. 2002). There are several studies which focus on improvement of stain resistance via modifications in porcelain tile compositions. All these studies focus on enhancing densification and microstructure characteristics, in particular closed pore content, pore size, shape

and aspect ratio by using different raw materials or by changing the ratio of raw materials. (Esposito et al. 2005, Tucci et al. 2007, Junior et al. 2010, Suvaci and Tamsu 2010, Alwes et al. 2012). Controlling micro-structure characteristics during conventional fast cooking process is difficult. The best method is to develop a coating-filling material to close the defect when the defect is inevitable.

In order to design these new materials, nanomaterial and/or hybrid materials will be indispensable (Sanchez 2010). At present, these novel materials are hardly used in ceramic tile manufacturing processes. It is therefore necessary to develop a completely new methodology in order to suitably choose, handle, and incorporate these materials into the ceramic tile surface with a view to obtaining the desired properties.

Sol-gel technique can be used to prepare these materials. Sol-gel process is a wet chemical method creating nanocrystalline or nanoscaled amorphous materials (Brinker and Scherer 1990, Hench and West 1990). With this well-established synthetical technique inorganic materials (glassy or ceramic) and inorganicorganic (hybrid) polymers or nanocomposites can be processed to form (nano)particles, coatings, fibers, or bulk materials (Schottner, 2001).

The objective of this study is to develop organic-inorganic solution by using sol-gel method, which can close the pores on the surface of polished porcelain tiles and other surface defects. It was aimed to increase the stain resistance and cleanability of the polished porcelain tiles with the developed solution.

2. Materials and Methods

Because the solution composition is to be prepared to close the defects on the surface of the polished porcelain tiles, surface micro-structure has been inspected first. The surface microstructure was examined by scanning electron microscopy (SUPRA-Zeiss-50). Then, solution compositions suitable for the identified surface micro-structure have been developed.

2.1. Composition Design

It was designed to use four different components in the solution in order for the prepared filling solution to close the surface defects and easily fill the pores and other defects. The first of them is the binder, which will bridge the filling material and tile structure and enable their binding with each other. Methyltriethoxysilane (MTEOS) (Ger, Aldrich) has been used as the binder. The second is filling material. Filling material is the organic or inorganic particles that will fill the inside of the pores. The third one is the functional agent that will prevent the stain keeping and help to clean the stain easily. Octyltriethoxysilane (Dynasylan® OCTEO, Degussa) and Hexadecyltrimethoxysilane (HDTMS, Dynasylan® 9116) have been used as the functional agent. The fourth one is the solvent that will enable filling material to flow into the pores by providing a viscosity to the coating. Solution compositions that are prepared by paying attention to the four components are seen in Table 1.

Table 1. Designed composition

	1 (g)		2(g)		3(g)		4(g)	
MTEOS	10-15	20-25	MTEOS	10-15	20-25			
HDTMS	20-30	20-25	OCTEO	17-26	15-18			
Organic filler	20-25	18-20	Organic filler	15-20	16-20			
Solvent	50-60	40-50	Solvent	50-55	45-50			
n_{MTEOS}/n_{HDTMS}	1	2	n_{MTEOS}/n_{OCTEO}	1	2			

2.2. Preparation of Solution and Application

Binder (MTEOS), functional agent (OCTEO or HDTMS) organic filler and solvent mixture was stirred for 30 minutes at ambient temperature. Then, required amount of water-acid mixture was drop wise added into the solution within 10 minutes. The reaction was allowed to continue for 30 minutes and then homogenous solution was obtained.

Solutions were applied onto the tiles, which was heated at (80 °C) on the drying-oven, by means of dropper and solution scoured with the help of a soft cloth by scattering.

After the application, tiles have been kept for a week in order for the solvent to move away completely and the solution reaction to complete. At the end of the week, test of the tiles were done.

2.2. Test Procedure

There is an existing standard regarding the determination of the resistance to stains: ISO 10545-14 "Ceramic Tiles"-Part 14: Determination of Resistance to Satins" (1997). The test method consists of maintaining various staining agents (green staining paste-chromium oxide particles in light oil, olive oil, and iodine solution) in contact with the working surface of the tile for an established time, then cleaning with various agents and finally a visual inspection to detect any changes.

The stain resistance and the cleanability of the tile working surface were appraised following the ISO-10545-14 standard. Stain tests were done for the stain makers (tea, coffee, red wine, methylene blue solutions, potassium permanganate and black joint filler) apart from the standard staining agents. Stained conditions of tile surfaces are seen in Figure 1.

Liquid stains were applied onto the tile with dropper and iodine solution was closed with watch glass. Black joint filler was applied with spatula then the stains were kept on the tiles for 24 hours. Tile surfaces were cleaned then.

The amount of staining was determined by visual inspection after each cleaning step:

1. mild washing with warm water,
2. washing with warm water plus a neutral detergent,
3. vigorous brushing with a rotary equipment plus an alkaline detergent (Dondi et al. (2005).

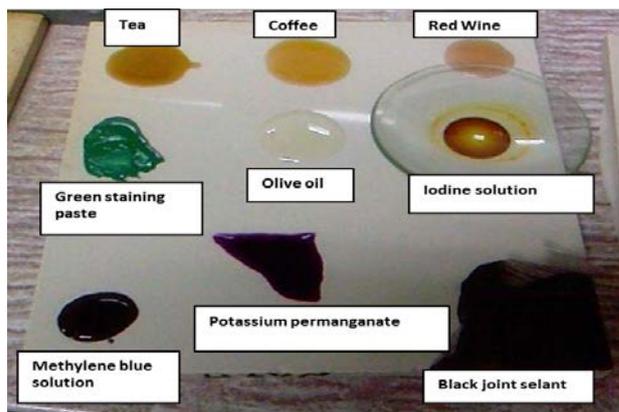


Figure 1. Staining agents applied on the tile surfaces.

The microstructure of sealed polished porcelain stoneware tile surfaces was examined by scanning electron microscopy (SUPRA-Zeiss-50). In addition, as a function of the prepared solutions, microstructure and stain resistance variations of porcelain stoneware tile were compared and discussed.

3. Results and Discussion

Micro-structure of the porcelain tile surfaces that are polished in Vitra polishing line is seen in Figure 2. The surface can both have many pores under $5\mu\text{m}$ and include bigger pores (about $20\text{-}30\mu\text{m}$).

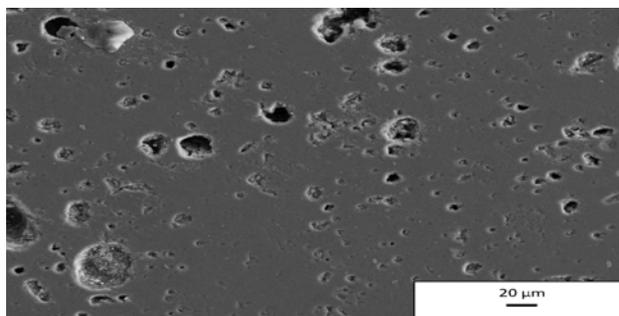


Figure 2. SEM micrographs of the standard porcelain stoneware tile after polishing.

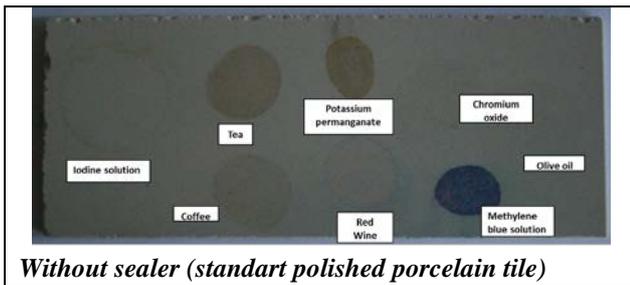
Stain tests were done after the solution number 1,2,3 and 4, which were mentioned in Table 1, were applied on the polished porcelain tile. Staining agents that are applied to the tiles are seen in Figure 3. In order to see how much the developed filling solution increased the stain resistance, stain is applied onto the standard polished porcelain tile surface, on which no protective filling solution is applied. Stains that stay after the hot water test on the coated and uncoated surfaces is seen in Figure 4.



Figure 3. Staining agents that are applied to the tiles, which are coated with solutions number 1, 2, 3, 4

After the test on surfaces that were filled with solutions number 1,2,3 and 4, methylene blue, potassium permanganate, tea and iodine stains stayed. Other stains were easily cleaned with just water. Solutions, where HDTMS was used, were seen to scatter well on the surface and to fill the pores in a better way. Especially solution number 4 whose $n_{\text{binder}}/n_{\text{functional agent rate}}$ was increased twice with regard to solution number 3 was seen to enable the surfaces to be cleaned faster and easier. It is predicted that the performance of this recipe, where only organic filling materials are used, will increase if inorganic filling materials are included. Organic filling material was decreased %50 and inorganic material was added and it was denoted as 4S.

Stained condition and condition after cleaning with water of the 4S solution applied tiles and standard polished porcelain tiles, to which no solution is applied, are given in Figure 5.



Without sealer (standart polished porcelain tile)

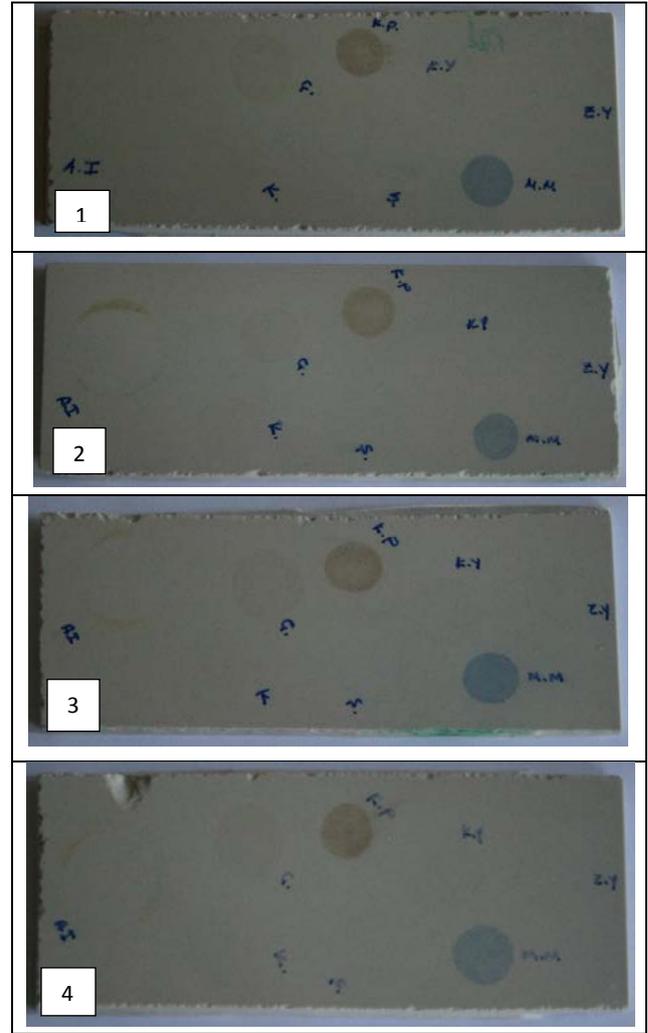


Figure 4. Comparative images of surfaces to which no solution is applied with the surfaces to which filling solution number 1,2,3 and 4 are applied.

Tea, coffee, red wine and black joint sealant stains which are not in the standards but are seen in daily life are cleaned when they are washed with hot water. Methylene blue and potassium permanganate stains left small stain after detergent use.

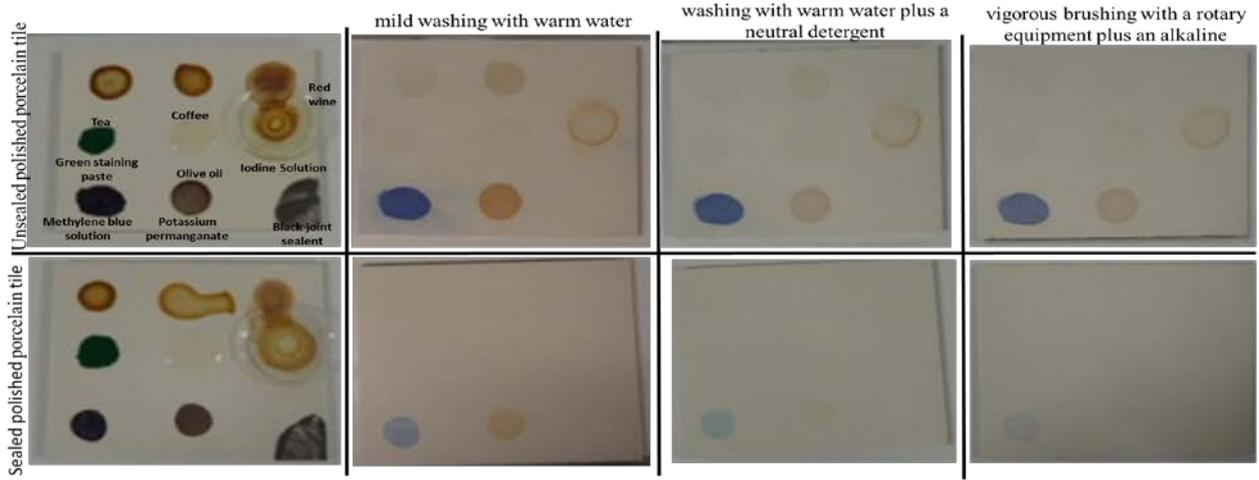


Figure 5. Stain resistance of unsealed and sealed tiles

All the staining agents that are mentioned in the standards (green staining paste, olive oil, iodine solution) are cleaned easily from the tile surface to which 4S filling solution is applied when it is washed with water. While green staining paste and olive oil is cleaned with just water, iodine solution is cleaned after detergent use. Polished porcelain tiles that is coated with 4S filling solution provides the ISO 10545-14 standards.

When 4S solution applied tile surface (Figure 6) and cross-section (Figure 7) are examined, it is seen that the solution filled all of the pores and defective areas completely.

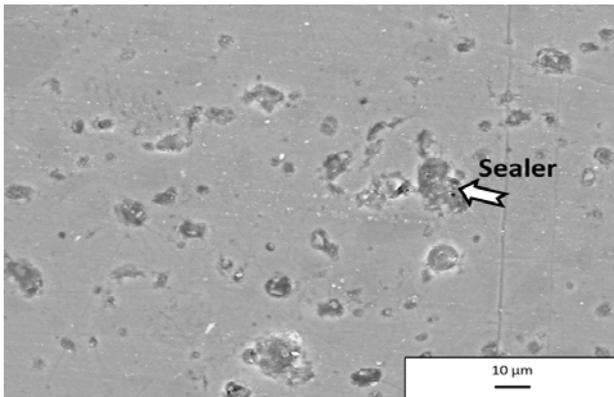


Figure 6. SEM micrograph of the 4S filling solution applied polished porcelain tile surface

When looked at the cross-section (Figure 7), it is seen that filling solution can get into the pores and is bound to the porcelain tile structure.

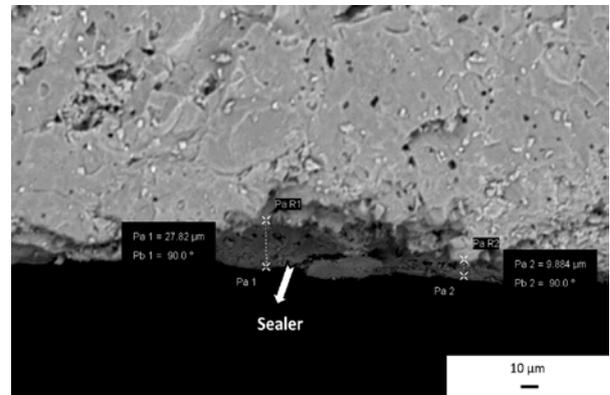


Figure 7. SEM cross-section micrograph of the 4S filling solution applied polished porcelain tile surface

4. Conclusions

Filling solution that is prepared for polished porcelain tile surfaces have been able to fill the pores and therefore, enabled the polished porcelain tiles to have the stain resistance that is expected by ISO 10545-14 standard.

It has been identified that the type and amount of hydrophobic functional agent, which is used to provide the desired stain resistance and to make the solution fill the pores completely, and the amount and type of the filling material are quite important. It is identified that using organic and inorganic materials together as filling material increases the stain resistance of the solution.

It is seen that the pressure that is created by rubbing facilitates the material to fill in the pores and rubbing process enables the pores to fill with less material than pulverization process. There is a risk for the pores of not being filled completely

during pulverization process and residual solution stays on the surface. It is also seen that rubbing creates polishing effect and does not change the luminosity.

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