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Investigation of the Effect of Glaze Particle Size Distribution on Surface Properties of Floor Tile Glazes

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Abstract

Ceramic floor tiles are preferred in every area of life due to their technical properties such as chemical resistance, abrasion resistance, etc. In this study, the effect of glaze particle size on surface properties of glazed floor tiles was investigated, including the color perception, chemical resistance, resistance to surface abrasion and resistance to stains. To achieve this goal, glazes with in different particle sizes were prepared by ball milling within different milling times. Particle size distribution was determined by laser diffraction technique. The color perception was determined by L*-a*-b* values on a color scale that has blue, black, yellow, and brown inks. The chemical resistance, surface abrasion resistance, and stains were determined according to ISO 10545-13, ISO 10545-7 and ISO 10545-14, respectively. It was observed that the coarser glaze particle size resulted in decreased color perception while worsening the other surface properties as well. On the contrary, decreasing the glaze particle size resulted in more vibrant colors for blue, brown and yellow inks, while the color vibration of black ink deteriorated. According to the abrasion tests, finer glaze particle size gave the best abrasion resistance at different abrasion levels. It was observed that chemical resistance was deteriorated by decreasing the glaze particle size. There was no significant effect of glaze particle size on cleanability.

Sır Tane Boyutu Dağılımının Yer Karosu Sırlarının Yüzey Özellikleri Üzerine Etkisinin Araştırılması

Özet

Seramik yer karoları kimyasal dayanım, aşınma direnci vb. teknik özellikleri nedeniyle yaşamın her alanında tercih edilmektedir. Bu çalışmada sırlı yer karolarının renk algısı, kimyasal dayanım, yüzey aşınmasına karşı direnç ve lekelere karşı direnç, vb. yüzey özelliklerine sır tane boyut dağılımının etkisi araştırılmıştır. Bu amaca ulaşmak için, farklı tane boyutlarına sahip sırlar, farklı öğütme sürelerinde bilyalı değirmen ile hazırlanmıştır. Tane boyut dağılımı lazer kırınım tekniği ile belirlenmiştir. Renk algısı, mavi, siyah, sarı ve kahverengi mürekkepleri olan bir renk ölçeğinde L*-a*-b* değerleri ile belirlenmiştir. Kimyasal direnç, yüzey aşınma direnci ve lekeler sırasıyla ISO 10545-13, ISO 10545-7 ve ISO 10545-14'e göre belirlenmiştir. Daha kaba sır tane boyutunun renk algısının azalmasına neden olduğu, diğer yüzey özelliklerini de kötüleştirdiği gözlenmiştir. Öte yandan, sır tane boyutunun azalması mavi, kahverengi ve sarı mürekkepler için daha canlı renklerle sonuçlanırken, siyah mürekkebin renk canlılığı bozulmuştur. Aşınma testlerine göre, daha ince sır tane boyutu farklı aşınma seviyelerinde en iyi aşınma direncini vermiştir. Sır tane boyutu azaldığında kimyasal direncin azaldığı gözlenmiştir. Sır tane boyutunun temizlenebilirlik üzerinde önemli bir etkisi olmamıştır.

1. INTRODUCTION

Ceramic glaze comprises glass frit, raw materials such as kaolin, feldspar, nepheline, wollastonite etc., and filler pigments[1]. They may be bright, matt, opaque, satin, transparent or colored depending on surface texture, production type, component and fusibility[2]. A wide range of ceramic glazes are developed depending on firing temperature, the mixture of raw materials and the desired surface texture, as well as the properties of the final product[3]. Color perception, glossiness, roughness, stain resistance, scratching properties of the ceramic tile surfaces are provided by glaze application. In recent years, the demand for ceramic tiles was increased due to their superior surface properties, such as high resistance to abrasion, higher hardness and improved chemical resistance[4,5]. As a coating, the glaze, not only protect the tile surface against environmental effects but also provide smoothness, chemical and stain resistance, impermeability to liquids and gases[6,7,8]. Therefore, glazes are responsible for most of the final products' surface properties including acid or alkaline reactions, stains resistance, scratch resistance, etc. according to the TS EN 10545 Ceramic Tiles Standard[9]. Stains resistance of the glazed surface is measured with different staining agents according to the ISO 10545-14 standard. Staining agents are divided into three main groups (pastes, chemical/oxidizing action, forming a film) and their subgroups (green or red staining agent, iodine, olive oil etc.). After applying the staining agent, surface durability is observed for 24 h. In order to determine the stain resistance of the surface, cleaning procedure described in ISO 10545-14 standard is followed. Classification of the results are divided into five classes. Class 5 corresponds to the best stain resistance and ease of removing the stain, while Class 1 corresponds to the worst stain resistance and impossibility of removing the stain from the surface. Abrasion resistance of the surface is measured with different abrasion levels according to the ISO 10545-7 standard. The abrasion resistance of the glazed surface is determined by the rotation of abrasive load on the surface and the comparison of non-abraded surface. Classification of the results are divided into six PEI classes. PEI V corresponds to the best abrasion resistance, while PEI 0 corresponds to the worst abrasion resistance. Acid or alkaline reactions of the glazed surface is measured with three aqueous test solutions such as household chemicals (ammonium chloride solution, 100g/l), swimming pool salts (sodium hypochlorite solution, 20 mg/l), acids and alkalis (low concentration (L), high concentration (H)). After applying household chemicals, swimming pool salts and low concentration acids and alkalis, surface durability is observed for 24 h and high concentration acids and alkalis durability is observed for 96 h. Classification of the results for household chemicals and swimming pool salts divided into three class. Class A corresponds to best acid and alkalis resistance of the surface, while Class C corresponds to the worst acid and alkalis resistance of the surface. In terms of chemical durability, glazed surfaces have strong durability in the aqueous treatment except in strong acids and bases[10]. But the glaze layer consists of the amorphous phase, crystalline phases and closed porosities (e.g., bubbles). The closed porosities cause a decrease in the mechanical properties and decreased resistance to chemicals, scratching, stains, etc.[8,11]. The particle size and distribution of the raw glaze is one of the most important factors that influence all the tile surface properties among different glaze surface control methods. In addition, changes in the particle size distribution also affect the rheological behavior of the glaze slurry[12]. Rheological behavior plays a significant role in the successful application of the glaze and thus surface properties of ceramic tiles[13].

Several methods are used to improve the quality of the tile surface in the ceramic tile industry. One of them is to improve the smoothness of the glaze by reducing the particle size of the glaze and the viscosity of the molten glaze[14,15]. Bernardin A.[16] reported that decreasing the glaze particle size has resulted in the reduction of molten glaze viscosity, which caused uniformity in the glass layer and produced a glaze with a smooth surface. Bou E. et al.[17], was showed that the glossiness and surface roughness of the matt tile surface depends on the crystalline phases and the influence of glaze particle size on crystalline phase formations. Amoros J.L. et al.[18,19,20], investigated the sinter-crystallization kinetics of a SiO_2–Al_2O_3–CaO–MgO–SrO glass-ceramic glaze and the effect of particle size distribution on this mechanism. They reported that glaze sinterability was increased with decreasing glaze particle size.

The aim of this study is to investigate the effect of glaze particle size distribution on surface properties such as color perception, chemical resistance, surface abrasion, stain resistance of floor tile matt glazes and correlate this influence to formed crystal phases.

2. METHODS

A commercial matt frit (Akcoat, Turkey) (Table 1) and industrial grade raw materials (kaolin, feldspar, calcite, dolomite, nepheline, wollastonite etc.) were used to produce matt glazes. The composition of the glaze is given in Table 2.

Table 1. Oxidic composition of the frit

Oxide	SiO_2	Al_2O_3	CaO	MgO	ZnO	K_2O	Na_2O	BaO
(in wt.%)	47-52	17-20	8-11	0-2	10-12	4-6	0-2	4-6

Table 2. Oxidic composition of the glaze

Oxide	SiO_2	Al_2O_3	CaO	MgO	ZnO	K_2O	Na_2O	BaO
(in wt.%)	50-52	16-18	11-13	0.5-1.5	3-5	1-3	1-3	1-3

Glaze compositions were ball milled with alumina balls for 10, 20, 30, 40 minutes and applied to the green porcelain bodies by a 0,6 mm applicator. The glazed porcelain bodies were dried at 110 °C for 30 minutes and then fired at 1200 °C for 55 minutes in an industrial fast-firing regime. Particle size distribution was determined by laser diffraction technique (Malvern, Mastersizer 3000). Color perception of the surface was evaluated by a spectrophotometer (Conica Minolta, CM 600d). XRD analysis was employed to evaluate crystallization (D8 Eco, Bruker). The thermal behaviour of the samples was analyzed by a heating microscope (Misura, HSML-ODT 1400-30). The characteristic temperatures of the samples were obtained from an automatic software (Misura 3.32) analysis which were evaluated from calculations using geometric parameters based on the shape of the sample (height, width, contact angle). Resistance to chemicals was measured in high concentration acids, bases and low concentration acids, bases according to ISO 10545-13 standard. Resistance to stains was measured according to an ISO 10545-14. Abrasion resistance of surfaces was tested according to ISO 10545-7 with an abrasimeter (Gabrielli Italy).

3. RESULTS AND DISCUSSION

The mean particle sizes of the samples are given as a function of milling time in Figure 1. It was observed that the mean particle size decreased dramatically from 11.20 µm to 7.26 µm in milling time from 10 minutes to 20 minutes. Between 20 minutes and 40 minutes, the mean particle size decreased slightly from 7.26 µm to 5.51 µm. Therefore, 20 minutes of milling time is determined as optimum time in terms of milling efficiency for the given matt glaze composition.

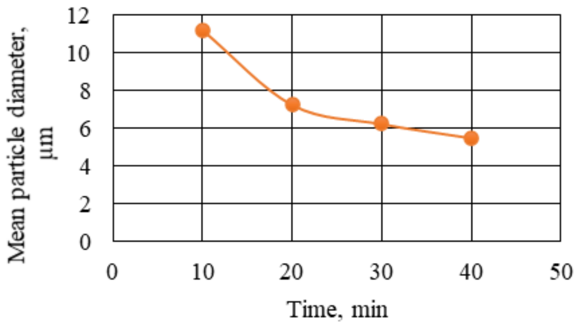

Figure 1. Glaze mean particle size as a function of milling time

Figure 2 represents the crystalline phases that occurred after sintering the glazes through the different milling times. Anorthite and free quartz peaks are observed in all samples. The intensity of the free quartz peak (26°) decreased when the milling time reached 40 minutes. On the other hand, the peak intensity of the anorthite (27.5°) phase increased with increasing milling time, which indicates that the crystallization is increased with decreased particle size for the same sintering regime and glaze composition

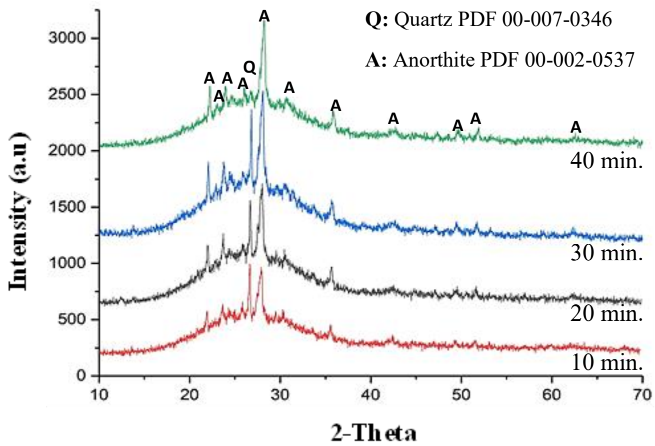

Figure 2. XRD patterns of glazes at different milling time

The effect of the glaze particle size on the thermal behavior of glazes is shown in Table 3. It can be seen clearly that the glaze sinterability is increased with decreasing mean particle size from 11.2 µm to 7.26 µm. This is attributed to the increased surface energy of the particles.[19] Decreasing the mean particle size further has only a limited effect on the characteristic temperatures of the samples, i.e., the sintering and softening point decreased only 6 °C and 8 °C respectively between 7.26 µm and 5.51 µm, while the softening point remained similar. It can be seen from Figure 3 that the sample with coarser particle size started to shrink at higher temperature than the other samples.

Table 3. Thermal behavior of glaze with different milling time

Mean Particle Size (d_{50}) (µm)	Sintering Point (°C)	Softening Point (°C)	Half-sphere Point (°C)	Melting Point (°C)
11.20	1152	1160	1206	1230
7.26	1134	1150	1194	1220
6.23	1134	1144	1194	1216
5.51	1128	1142	1194	1224

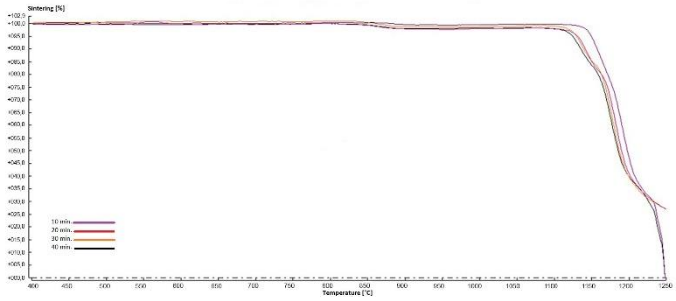

Figure 3. Thermal behavior curve of glazes with different the milling times

Table 4 shows the influence of glaze particle size on color perception of the tile surfaces. It was observed that coarser glaze particle size resulted in decreased color perception of the tile surface. The color of brown due to increasing a* value, blue due to increasing a* and b* values and yellow due to increasing whiteness (L) value resulted in more vibrant color when the particle size decreased. On the contrary, the color vibration of black ink decreased with decreased glaze particle size. The whiteness (L) is not affected by the glaze particle size and remained stable among different glaze particle sizes for each color.

The results of the surface abrasion tests are given in Table 5. It was observed that finer particle size resulted in the best abrasion resistance at different abrasion levels. This is attributed to the increased anorthite crystallization as well as hardness with decreased glaze particle size (See Fig. 2)[21, 22]. The abrasion resistance is increased from PEI III to PEI IV by decreasing the particle size from 7.26 µm to 6.23 µm. It was interesting to show that even 1 µm was enough to change the abrasion resistance class of the ceramic tile. This indicates that a threshold exists for the glaze particle size which can influence the abrasion resistance drastically if it is reached.

Table 4. Results of color perception measurement according to CIE lab space

		Mean Particle Size (d_{50}) (μm)			
Color	**CIE Lab. Space**	**11.20**	**7.26**	**6.23**	**5.51**
Blue	L	46.49	46.26	46.36	45.64
	a*	7.91	8.31	8.34	9.07
	b*	-29.29	-30.07	-30.03	-31.04
Brown	L	50.1	49.93	48.88	49.93
	a*	15.99	16.33	16.07	17.35
	b*	22.15	22.28	20.83	21.12
Yellow	L	68.67	70.31	69.65	69.77
	a*	9.54	8.84	9.47	9.42
	b*	29.55	28.76	28.52	26.89
Black	L	33.56	33.45	34.26	33.49
	a*	-0.26	-0.23	-0.19	-0.01
	b*	0.11	-0.04	-0.58	-0.53

Table 5. Results of the resistance to surface abrasion according to ISO 10545-7

Mean Particle Size (d_{50}) (μm)	Class
5.51	PEI IV
6.23	PEI IV
7.26	PEI III
11.20	PEI III

The chemical resistance of the glazes is given in Table 6. The results indicated that the chemical resistance of the tile surface deteriorated as the mean particle size decreased. The glaze with a mean particle size of 5.51 μm is the most affected by high concentration acid. The results showed that the same threshold of glaze particle size for abrasion resistance is also applicable to the chemical resistance since the class of chemical resistance for swimming pool salts and household chemicals improved from Class B to Class A for particle size of 6.23 μm and 7.26 μm respectively.

Table 6. Results of the resistance to chemicals according to ISO 10545-13

Mean Particle Size (d_{50}) (μm)	Swimming Pool Salts	Household Chemicals	Acids and Alkalis	
11.20	A	A	LA	HA
7.26	A	A	LA	HA
6.23	B	B	LB	HB
5.51	B	B	LB	HC

It was observed that the glaze particle size has no significant effect on the surface cleanability of the tiles (Table 7). All of the samples have Class 5 cleanability for iodine, chrome green, oil and tea.

Table 7. Results of the resistance to stains according to ISO 10545-14

Mean Particle Size (d_{50}) (μm)	Iodine	Chrome Green	Oil	Tea
11.20	Class 5	Class 5	Class 5	Class 5
7.26	Class 5	Class 5	Class 5	Class 5
6.23	Class 5	Class 5	Class 5	Class 5
5.51	Class 5	Class 5	Class 5	Class 5

4. CONCLUSIONS

In this study, glazes with different particle sizes were prepared by ball milling within different milling times. The effect of glaze particle size on surface properties of glazes tiles was investigated. The chemical resistance, surface abrasion resistance, and stains were determined according to ISO 10545-13, ISO 10545-7 and ISO 10545-14 standards respectively. It was observed that the color intensity of brown ink is increased due to the increase in a* value from 15.99 to 17.35. The color intensity of blue ink is increased due to increase in a* value from 7.91 to 9.07 and b* value from -29.29 to -31.04. The color intensity of yellow ink is increased due to increase in whiteness (L) value from 68.67 to 69.77. On the contrary, the coarser particle size resulted in decreased color perception. The color vibration of black ink deteriorated by decreasing (L) value from 33.56 to 33.49, a* value from -0.26 to -0.01 and b* value from 0.11 to -0.53. XRD analysis showed that the main crystalline phases are anorthite and SiO_2 (free quartz) for all samples. The peak intensity of the anorthite phase increased with the decreasing glaze particle size from 11.20 μm to 5.51 μm, while the intensity of the free quartz peak decreased for the finest glaze particle size of 5.51 μm. According to the heating microscope analysis, the coarser particle size resulted in an increased sintering point from 1128°C to 1152°C for the particle size of 11.20 μm and 5.51 μm respectively. The abrasion tests showed that the finer glaze particle size yields the best abrasion resistance at different abrasion levels. It was observed that the chemical resistance degraded by decreasing the glaze particle size from 11.20 μm to 5.51 μm, whereas the surface cleanability did not change with the glaze particle size. Although the best abrasion resistance was achieved with 30 minutes milling time, chemical resistance of this sample was worse than 20 minutes milling time. Overall, it was observed that 20 minutes milling time gave best results according to ISO standards.

- The decreasing particle size resulted in more vibrant colors for blue, brown, and yellow inks, while the color vibration of black ink deteriorated.
- According to the abrasion tests, finer glaze particle size gave the best abrasion resistance at different abrasion levels.
- It was observed that chemical resistance was deteriorated by decreasing the glaze particle size.
- There was no significant effect of glaze particle size on cleanability.
- Overall, it was observed that 20 minutes milling time gave best results according to ISO standards.

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