



Araştırma Makalesi - Research Article

# Development of Glaze Compositions to Increase the Durability of Decorative Paints Used in Glazed Porcelain

## Sırlı Porselenlerde Kullanılan Dekoratif Boyaların Dayanımını Arttırmak için Sır Bileşimlerinin Geliştirilmesi

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### ABSTRACT

Colorful paint works are carried out to highlight the visibility of ornamental and tableware products, such as cups and plates. As these products come into contact with detergents, food products or grime, erosion and abrasion occur in paint and patterns over time. In this study, transparent glaze compositions that can be applied on patterned products have been developed in order to minimize wear and damage to the paint on ornamental and tableware products such as porcelain cups and plates. It is aimed to have a compatibility with the glaze layer and the porcelain body, to have high transparency and brightness. Different glaze compositions have been implemented to porcelain wares containing precious metallic paints. Then the glazed products were conducted to final firing between 870°C-900°C. Colours values of porcelain wares were determined with L-a-b spectrophotometer colours measurement devices and  $\Delta E$  values was found to be lower than 0.50. Erosion and abrasion resistance were determined by staining test and washing test. According the results, the mass loss values are in the range of 2.7-3.4 mg (24h washing) and 7.9-8.3 mg (168 h washing). The morphology of the samples and the analysis of the phases formed during sintering were determined by X-ray diffraction (XRD) technique and scanning electron microscopy (SEM and EDX). Quartz-SiO<sub>2</sub> and Albite-Na (AlSi<sub>3</sub>O<sub>8</sub>) phases were observed in the structure of the glazes. The results showed that glaze compositions with high transparency and wear resistance can be obtained with only 30% frit content.

**Keywords-** Transparent Glaze, Porcelain Product, Metallic Decorative Paint, Durability, Frit

### ÖZ

Fincan ve tabak gibi süs ve sofraya ürünlerinde görseelliği ön plana çıkarmak için renkli boya çalışmaları yapılmaktadır. Bu ürünler bulaşık deterjanları, organik gıda ürünleri veya kir ile temas ettikçe boya ve desenlerde zamanla erzyon ve aşınma meydana gelmektedir. Bu çalışmada porselen fincan ve tabak gibi süs ve sofraya ürünlerinin üzerinde bulunan dekoratif boyaların zamanla meydana gelen aşınma ve hasarını en aza indirgeyebilmek için desenli porselen eşya üzerine uygulanabilen şeffaf sır bileşimleri geliştirilmiştir. Sır tabakasının porselen bünyeye uyumlu olması, yüksek transparanlıkta ve parlaklıkta olması amaçlanmıştır.

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Üzerinde değerli metalik boya bulunduran porselen ürünlere geliştirilen farklı sır kompozisyonları uygulanmıştır. Ardından 870°C-900°C sıcaklıkları arasında sırlanmış ürünler son pişirimleri yapılmıştır. Porselen ürünlerin L-a-b spektrofotometre renk ölçüm cihazı ile renk değerleri ölçülmüştür ve  $\Delta E$  değeri 0,5 bulunmuştur. Erezyon ve aşınma dayanımı lekelenme testi ve yıkama testi ile belirlenmiştir. Bu sonuçlara göre kütle kayıpları 2,7-3,4 mg (24sa yıkama) ve 7,9-8,3 mg (168sa yıkama) mertebelerinde bulunmuştur. Numunelerin morfolojileri ve sinterleme esnasında oluşan fazların analizleri X-ışınları kırınımı (XRD) tekniği ve taramalı elektron mikroskobu (SEM-EDX) ile belirlenmiştir. Kuvars-SiO<sub>2</sub> ve Albite-Na(AlSi<sub>3</sub>O<sub>8</sub>) fazları sır yapısında gözlenmiştir. Yapılan çalışmalar ile sadece %30 frit kullanılarak yüksek transparan özelliği ve yüksek hasar ve aşınma direncine sahip sır bileşimlerinin elde edilebileceği sunulmuştur.

**Anahtar Kelimeler-** Şeffaf Sır, Porselen Ürün, Metalik Dekoratif Boya, Dayanım Frit

## I. INTRODUCTION

Porcelain body is formed by firing a mixture consisting of 50% clay (generally kaolin (Al<sub>2</sub>(SiO<sub>5</sub>)(OH<sub>4</sub>)), 25% feldspar (melter) and 25% quartz (filling material).) One of the important steps in the porcelain production process is the glazing process. Glazes applied to the porcelain body are oxide mixtures that cover the body as a thin glassy layer by melting. The glazes bring technical, hygienic as well as aesthetic properties to porcelain body. In addition, visual perception is also important for tableware. In order to increase the visual perception, some applications, such as digital printing, decal printing, and painting are made to the products. However, as the operation time and external contact increase, wear and wiping begin are observed in paints [1,2].

The glaze layer applied to porcelain should have in a composition that can develop at low temperatures. Because, subsequent to decoration process the products are fired at low temperatures. In order to obtain a low temperature glaze, frit should be present in recipes. However, frit causes an increase in cost [3]. Frit is obtained by precise weighing and mixing the raw powders according to the specified recipe and then melting and immediate cooling is performed to obtain a solid without any crystallization. It plays an important role in the development of low temperature grade glazes. As the frit ratio in the recipe increases, the firing temperature decreases. While an ordinary glaze composition includes the raw materials such as kaolin, quartz, feldspar, calcite, magnesite and dolomite in a certain amount, the frit is a key component in porcelain glazes, which can develop at relatively low temperatures. Boron and/or lead are the critical components of such low temperature frit. Lead can only be added to the glaze composition via frit. However, the utilization of lead in tableware is restricted by regulations due to its toxicity. Therefore, boron becomes a good alternative to lead for low temperature grade frit compositions. It is utilized in the form of borax or boric acid, which show cleaning and water-soluble properties. During firing stage of a porcelain whiteware, the frit melts at relatively lower temperatures. Since decomposition reactions had already been completed during fritization, a smooth surface without any gas defect can be obtained [4,5].

Since tableware products are used under a regular contact with metal knives, spoons and forks, high wear resistance against to mechanical scratching is required. The term “metal marking” is used to define damages of the tableware glazes by metallic cutlery [6]. These marks can also be accompanied by small cracks and scratches [7,8]. While metal marks are occurred by the deposition of metal particles due to the sliding/friction wear of metallic cutlery, scratches and cracks are the result of high pressure on the glaze by harder substances in metals. The surface roughness, hardness and the presence of crystalline phases are reported as the responsible parameters for metal markings [7-9]. Since these damages create sharp edges on the surface, the metallic particles form the cutlery built-up at these rough locations, which is observed as metal marks. In order to improve metal marking resistance, reduction of crystalline phases in final glaze layer by modifying of firing process and particle size reduction of quartz are essential [10]. Pee et al. tried to improve glaze hardness and to reduce surface roughness by adding low melting point frits (ZnO and B<sub>2</sub>O<sub>3</sub>) to a traditional celadon glaze [11]. They observed an increase in hardness and decrease in surface roughness as the frit content increased. According to the wear tests, metal marking resistance was improved significantly with increasing frit content, resulting from the reduction of friction coefficient. In another study Güngör and Altun investigated the effect of quartz particle size on metal marking resistance [10]. They found that the reduction in quartz particle size leads to a higher solubility of quartz in glassy matrix and therefore, lower quartz content in final glaze layer.

Apart from thermal and mechanical properties, aesthetic appearance is also important for glaze layers applied to tableware. In production of colored tablewares, a broad range of colors can be obtained by pigments added to the glaze compositions. However, to obtain a golden-view surface, only metallic paints are applied to the external surface of the glazes. Although these paints are very attractive in aesthetic point of view, they are

directly open to the external mechanical and thermal effects, and can easily be removed even after a short period of operation, and, therefore, result a significant reduction in aesthetic properties [12]. The studies are focused on the adhesion behavior of these metallic paints to the ceramic substrate and indicate that the bonding is strongly dependent on the diffusion level of gold through glass as a function of temperature [13, 14]. However, there is no any literature study on the improvement of the durability of gold metallic paints on tableware products to the best of our knowledge.

In this study, a protective glaze layer was applied to the gold-painted product to maximize the damage resistance of the paint on porcelain plates/cups and ornaments. The corresponding glaze layer is designed as compatible with the porcelain body and fully transparent to reflect the aesthetic view of underneath glaze. While this effect can only be achieved by applying a glaze layer composed entirely of low-temperature commercially, it was aimed to obtain the same effect by using mainly ceramic glaze raw materials to minimize the cost. Glazes with different compositions were prepared and utilized to porcelain tablets on which precious golden metallic paint was applied. The microstructural properties, crystallization and related transparent properties, color values, staining and washing tests of porcelain products were comparatively examined.

## II. EXPERIMENTAL DETAILS

Industrial-grade kaolin, feldspar, dolomite, quartz and calcite obtained from a ceramic factory were used as raw materials in glaze recipes. Frit was added to these raw materials at different rates, in the range of 10-40%. The amount of frit in glaze compositions were tried to be kept minimum as long as full transparency was obtained. Chemical analyzes of raw materials are presented in Table 1. The grain sizes for Kaolin, K-Feldspar, N-Feldspar and Quartz are in the range of 45-50 µm, 25-30 µm, 35-40 µm and 30-35 µm, respectively. Glaze recipes were prepared at 6 different frit ratios, in the range of 10-40%. The composition of the glazes prepared within the scope of this study is given in Table 2. Feldspar, which is used as frit raw material in the glaze composition, is used to reduce the viscous liquid phase temperature and as a quartz filling material with high wear resistance and hardness [15]. Borax has been used to reduce viscosity and surface tension and provide resistance to scratches, cracks and surface staining before the glaze matures [16]. Frit is used to reduce the melting temperature of total glaze layer to avoid excessive crystallization [17].

**Table 1.** Chemical analysis of raw materials used in glaze recipe

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	CaO	MgO	Na <sub>2</sub> O	K <sub>2</sub> O	ZnO	Cr <sub>2</sub> O <sub>3</sub>	Zr <sub>2</sub> O <sub>3</sub>	SO <sub>3</sub>	KK
K feldspat 28 m	67.70	17.50	0.09	0.03	0.10		2.720	11.300					0.560
Quartz 45 m	99.050	0.480	0.030	0.060	0.020		0.020	0.050					0.290
Calsite	0.355	0.181	0.065	0.051	55.866	0.370	0.412						42.77
N- feldspar	67.812	20.405	0.046	0.001	1.466	0.051	10.075	0.010					0.110
Dolomite 63 m	0.725	0.429	0.098	0.029	39.363	13.776	0.415	0.035					45.13
Calcined kaolin	50.503	45.970	0.510	0.341	0.119	0.420	0.521	1.251				0.210	0.340
Kaolin	45.300	38.857	0.827	0.097	0.122	0.550	0.523	1.793		0.011	0.090	0.020	12.80
Frit	63.580	10.383	0.224	0.144	13.767	4.844	0.431	2.510	4.875		0.105		1.010

The raw materials specified in Table 2 were loaded into the jet mill (Refsan brand-Turkey) with alumina balls. The total weight of the mixture was set to 500 gr. Water was added to the mills at the rate of 40 % by weight of the mixture and mixed for 3 hours. The tablets with a diameter of 10 cm were first glaze fired at 1200-1300 °C, then pre-painted and, finally fired at 870 C° 100 minutes. The glaze compositions prepared on the fired tablets were applied by spraying 2.47 gr using a compressed air sprayer. The nozzle diameter of the spray gun (Refsan EFG brand-Turkey) was 1.2 mm and the spray distance was 20 cm. Then tablet's firing process was completed at 960 C° for 100 minutes.

**Table 2.** Compositions of prepared glazes

	10%	15%	20%	25%	30%	40%
<b>Na-feldspat</b>	23.08 gr					
<b>K-feldspat</b>	21.63 gr					
<b>Frit</b>	19.97 gr	20.88 gr	21.79 gr	22.70 gr	23.60 gr	25.42 gr
<b>Borax</b>	16.07 gr					
<b>Quartz</b>	18.09 gr	17.85 gr	16.8 gr	15.75 gr	14.07 gr	12.6 gr

The microstructural examination of the prepared glazed surfaces was performed by scanning electron microscope (SEM-Zeiss SUPRA 40VP-Germany). The surfaces of the samples were coated with Au-Pt alloy in order to obtained surface electrical conduction prior to SEM examination. Phase analyzes of the samples were

made by x-ray diffraction (XRD) method (Rigaku DMAX 2000 brand). By using Cu-K $\alpha$  radiation and X-rays at a wavelength of 1.54 Å, phase analyzes of glazes were performed at a scanning speed of 2°/min in the range of 2 $\Theta$ =10-90°. The raw material is characterized by Spectro IQ brand XRF device. The raw materials were mixed with Li<sub>2</sub>O<sub>4</sub>B<sub>7</sub> at a ratio of 1:10 and the samples were poured in glass form by melting over 1000 °C and placed in the XRF device.

Detergent strength test was performed on glazed porcelain samples. This test is a method used to determine resistance to alkaline liquid exposure at temperatures between 25 and 95 °C. The test was carried out by taking the chemical resistance tests in the literature as an example and considering the daily use of porcelain ware [18]. Detergent resistance tests were carried out by spraying the surfaces of the tablets glazed prepared at different frit ratios with dishwashing liquid and pressurized water at 95 °C. For comparison purposes, the unglazed tablet after decoration was also subjected to the test and is named as original in the table. It was aimed to measure the mass loss on the glazed surface as a result of the detergent exposure of the glaze. The samples were first exposed to detergent for 24 hours and then 168 hours, and then the mass losses were compared. The surface roughness of the samples was measured before and after the detergent tests. Within this test, it is aimed to examine the effect of pressurized water and detergent on the glaze surface. The samples were positioned on a parallel surface during measurement and the surface was scanned with a diamond-tipped drive unit. Measurements were made with Time TR200 Roughness Tester brand surface roughness measuring device. 5 measurements were taken from each sample and their arithmetic averages were taken and Ra values were used.

The effect of the glazes made after decoration on the decor color was tested with a Konica Minolta CM 2600d brand device by making color measurements. The color measurements of the glaze applied to the samples were made considering the L\* (Black-White value), a\* (Red-Green expansion) and b\* (Yellow-Blue expansion) values. According to these data, the  $\Delta E$  (Total Color Difference) value is the value that measures the color difference between the original surface and the glazed surface after decoration and is calculated according to the following equation [19];

$$\Delta E = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2} \quad (1)$$

### III. EXPERIMENTAL RESULTS

XRD measurements were made to determine the phase analyzes according to the varying frit ratio in the developed glaze composition as presented in Figure 1. Quartz-SiO<sub>2</sub> (JCPDS No. 01-070-3755) and Albit-Na(AlSi<sub>3</sub>O<sub>8</sub>) (JCPDS No. 01-089-6428) phases were observed in the content of the glazes. It is seen that as the frit ratio in the glaze composition increases, the crystallization of the glaze decreases. Since the frit lowers the melting point of the composition, the total amount of liquid phase at firing temperature increased. Therefore, the amount of undissolved crystals reduced. In this way, the structure remains amorphous without recrystallization under rapid cooling conditions and high transparency was obtained [20]. Consequently, a decrease in the peak number and intensity of the crystal phases is observed with the increase of the frit ratio (Fig.1).

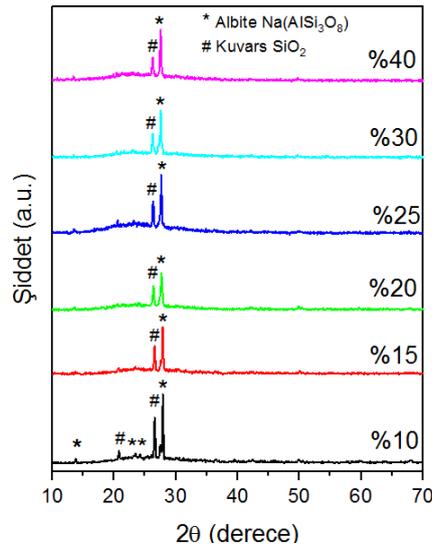


Figure 1. XRD patterns of glazes depending on varying frit ratio

For each frit ratio, the microstructures of the samples were examined by scanning electron microscopy and EDX analyzes were taken from different points. Figure 2 presents the SEM photographs of the surface of the glaze with 10% frit ratio and the EDX analysis taken from the general surface. The crystals formed on the

surface are clearly visible in the amorphous structure, proving the XRD results given in Fig.1. Since the crystalline regions were formed by the heavier elements (higher the atomic number), they were observed as brighter than the surrounding phases.

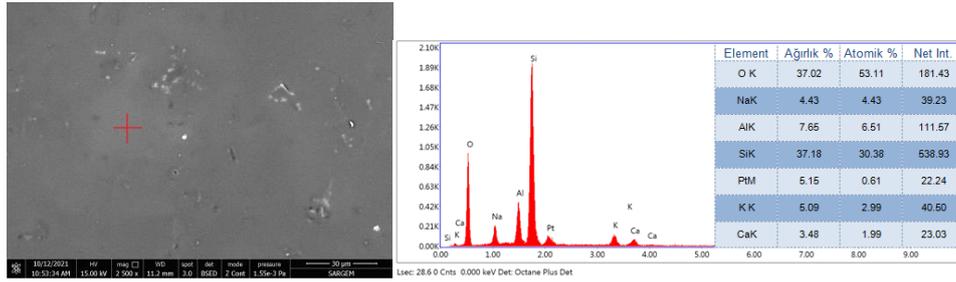


Figure 2. SEM photograph and EDX analysis of the surface prepared with a 10% frit ratio

In Figure 3, SEM photograph of the glazed surface with 15% frit ratio and EDX analyzes taken from different regions are given. The analysis made from crystals showed a slight difference from the matrix phase, which confirms the presence of quartz crystals. On the other hand, it was seen that the higher contrast phases contain high levels of Al and Na elements additionally [21,22]. Therefore, EDX analyzes confirmed that the phases in question are albite crystals. The EDX analysis taken over the matrix phase shows that the structure is an amorphous phase containing Si, Al, O elements as well as elements such as Na, Ca and K in the glaze composition. By combining the XRD (Fig.1) and EDX analysis, it is possible to conclude that the glaze structure was formed by amorphous phase containing Si, Al, O elements as well as elements such as Na, Ca and K in the glaze composition [23].

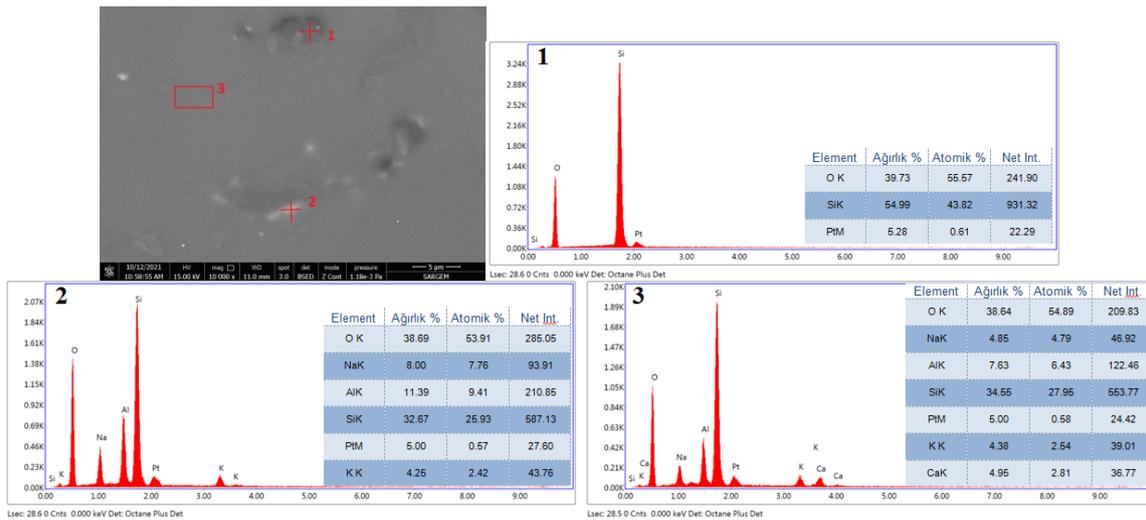
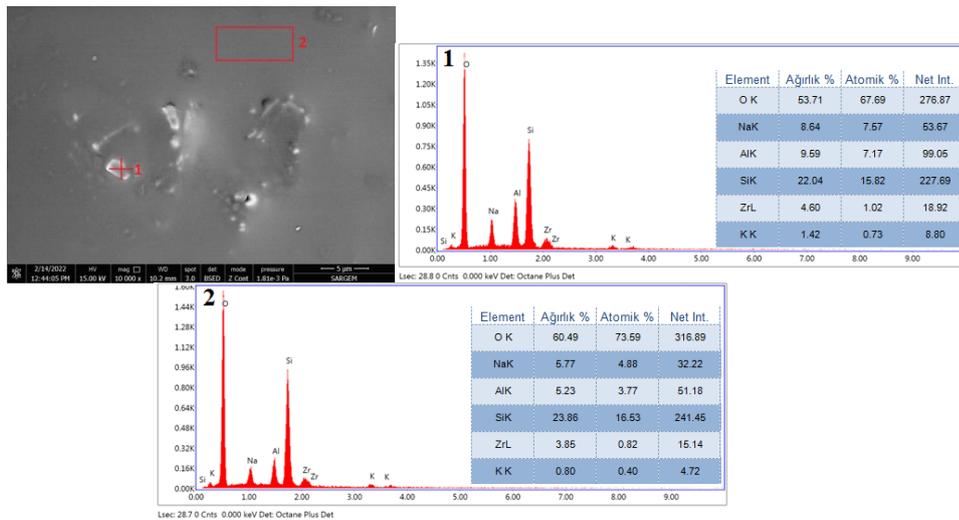
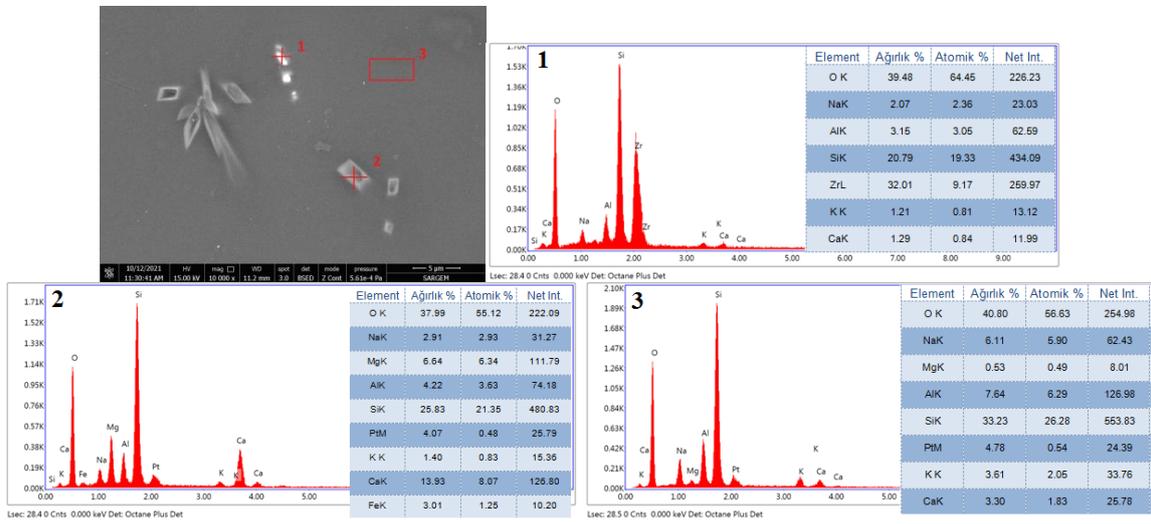
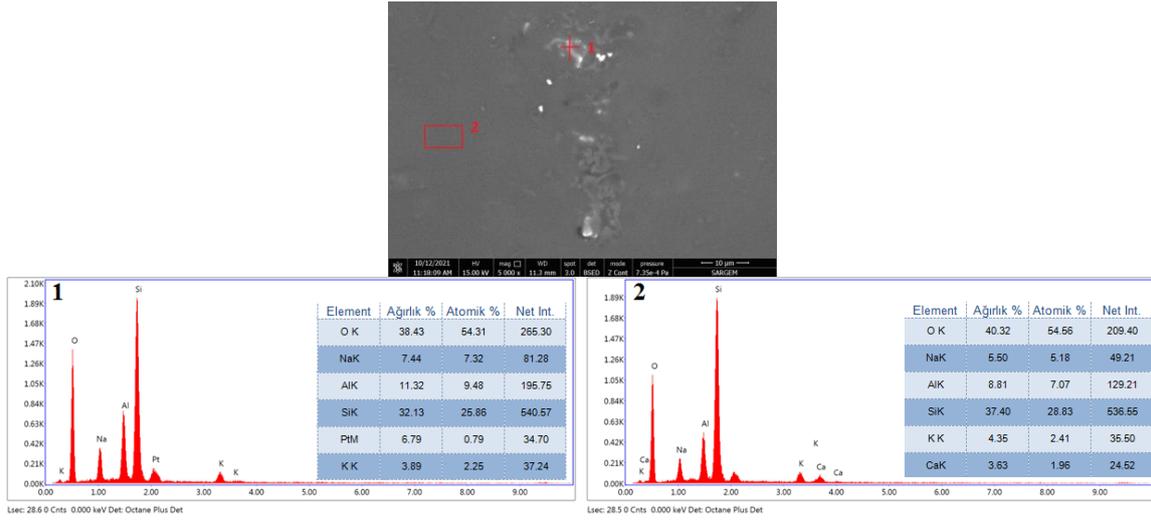


Figure 3. SEM photograph and EDX analysis of the glazed surface with 15% frit ratio

Figure 4 shows the SEM and EDX analyzes of the sample prepared with 20% frit glaze. In the SEM images of the glazed surfaces prepared with 10%, 15% and 20% frit ratios, it was seen that there are SiO<sub>2</sub> phases in different sizes and varying proportions, which are dispersed in the structure at regular intervals [24]. Figure 5 indicates the SEM and EDX analyzes of the sample prepared with a 25% frit glaze. It has been determined that starting from 25% frit ratio, in addition to quartz formation on the surfaces, small amounts of crystals in acicular structure with very high length/width ratios are formed. The absence of peaks belonging to these crystals in the XRD graphs given in Figure 1, confirms that their amounts are quite limited, and shows that they didn't have any considerable effect on the transparency. The acicular structure of these phases and the fact that the glaze reflects the general composition indicates the formation of wollastonite crystals in the structure [25]. Figure 6 shows the SEM and EDX analyzes of the sample prepared with a glaze containing 30% frit. Crystal structures are seen brightly in the amorphous structure that appears light gray. According to the EDX result, dispersed SiO<sub>2</sub> phases are observed in the amorphous structure [26]. Figure 7 presents SEM image and EDX results of the sample prepared with glaze containing 40% frit. Similar to other samples, quartz crystals dispersed in an amorphous structure were detected in this SEM image.



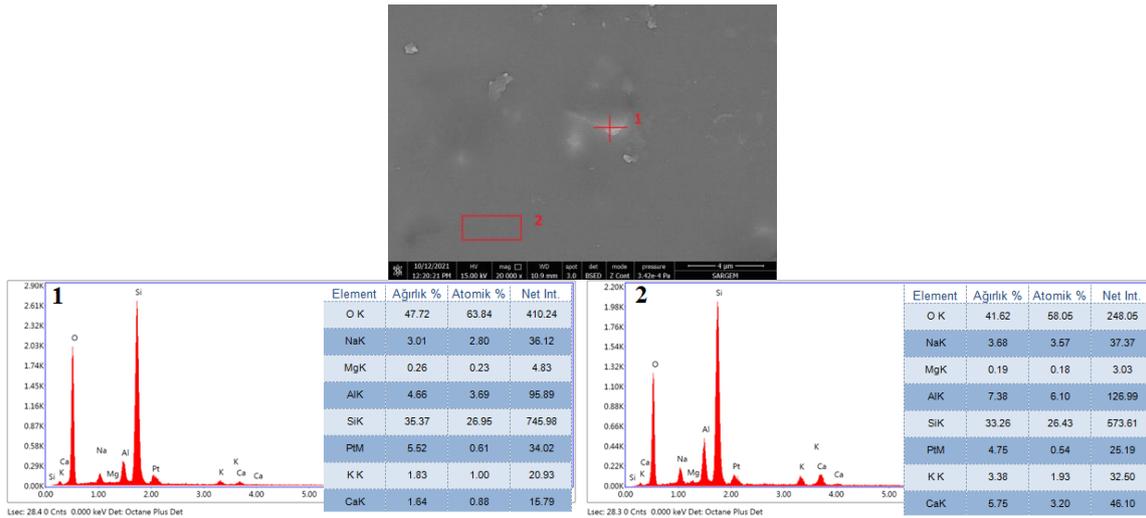


Figure 7. SEM photograph and EDX analysis of the surface prepared with a 40% frit

Table 3 shows weight changes of the samples before and after the detergent tests. Weight change in all samples after washing indicates the amount of wear of the glaze from the surface [27]. There was no a significant difference in the other samples with protective glaze compared to the original sample that was not glazed after decoration. Because even the effect of washing with detergent and pressurized water is not enough to cause damage to a high-strength protective layer like glaze, no significant change has been observed. With the

Table 3. Detergent resistance test mass loss results

Sample	24 Hour			168 Hour		
	First Weigh	Second Weigh	Mass Loss (mg)	First Weigh	Second Weigh	Mass Loss (mg)
%10%	135,7101	135,7072	2,9 mg	135,7072	135,6989	8,3 mg
%15%	135,7658	135,7624	3,4 mg	135,7624	135,7546	7,8 mg
%20%	141,3385	141,3353	3,2 mg	141,3353	141,3271	8,2 mg
%25%	141,4446	141,4419	2,7 mg	141,4419	141,4339	8 mg
%30%	137,9386	137,9358	2,8 mg	137,9358	137,9277	8,1 mg
Original Sample	135,6061	135,6034	2,7 mg	135,6034	135,5955	7,9 mg

increase of the frit ratio, closer values to the original sample were obtained. The mass loss at the rate of 30% frit was measured as very close to the mass loss value in the original sample and the protective glaze layer showed durability in the washing test.

In addition, the surface roughness values of the samples were measured before and after the detergent resistance test. The effect of the detergent used, the water at high temperature and pressure, and the change in surface roughness were investigated. Figure 8 shows the surface roughness values for each sample before and after the detergent test. As in the weight loss results, there was no a significant difference in the roughness values before and after washing in the original sample without glazing after decoration and the other samples with protective glaze. This indicates that there was no wear, deterioration and roughness on the sample surface after washing with detergent [28].

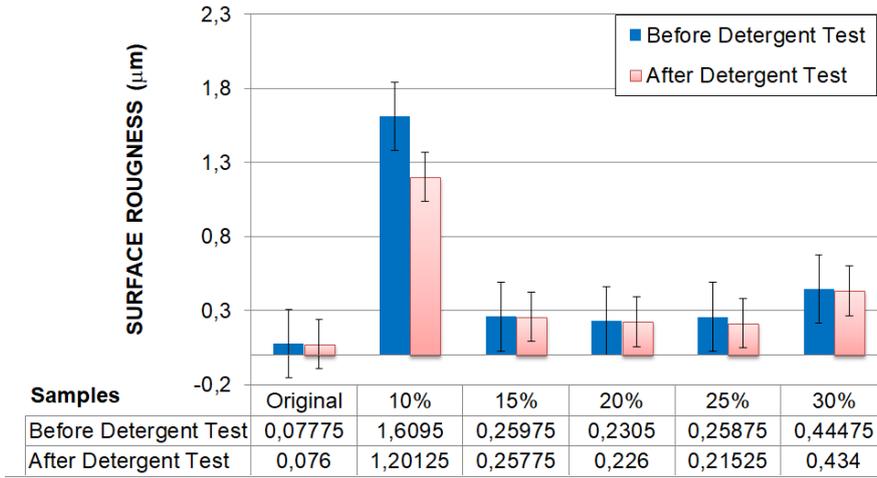


Figure 8. Surface roughness values for each sample before and after the detergent test

The L\*a\*b values of the surfaces glazed according to different frit ratio and not glazed after decoration, and the  $\Delta E$  values calculated using the formula are presented in Table 4. The graph showing the change in  $\Delta E$  calculated according to these values is given in Figure 9.  $\Delta E$  values were lower than 0.50 in all glazes. The light test results of the glazes represent the change in the level of difference that is acceptable, invisible to the eye [19].

Table 4. L\*a\*b values of samples

Sample	L	a	b	$\Delta E$
Original	84,4	-3,6	+0,17	0
%10	84,3	-3,5	+0,1	0,157
%15	84,1	-3,6	+0,2	0,301
%20	84,2	-3,3	+0,2	0,361
%25	84,2	-3,5	+0,1	0,314
%30	84,1	-3,5	+0,1	0,323

After the glazed bodies were exposed to foods such as tomato paste, olive oil and vinegar, they were washed in the dishwasher and the remaining stains on their surfaces were visually inspected. Figure 9 shows a photograph of the tablets where the staining test was performed. The staining test results are presented in Table 5. After the food particles are left on the glazed body, it is kept for 2 hours and then 24 hours. No staining was observed in the washed samples after 2 hours. After waiting for 24 hours, no staining was observed in the washed samples. This test shows that the surface roughness and gloss properties of the glazes are produced in such a way that they do not allow stains on their surfaces. The degree of cleaning of glaze surfaces consisting of different crystal phases embedded in an amorphous phase mostly depends on the surface roughness and the chemical composition of the phases on the surface [29].



Figure 9. Samples subjected to the staining test

Table 5 Stainin test results

Sample	Tomato paste stain		Olive oil tain		Vinegar stain	
	2 h	24 h	2 h	24h	2 h	24 h
Original	Out	Out	Out	Out	Out	Out
10%	Out	Out	Out	Out	Out	Out
15%	Out	Out	Out	Out	Out	Out
20%	Out	Out	Out	Out	Out	Out
25%	Out	Out	Out	Out	Out	Out
30%	Out	Out	Out	Out	Out	Out

#### IV. CONCLUSIONS

Colored paint applications are made in order to increase the visual perception in tableware and ornamental products such as plates and glasses. As these products come into contact with dirt, detergent or food products, wear and erosion occur in patterns and paints after a certain period of time. In this study, transparent glaze compositions that can be applied on patterned products have been developed in order to minimize the damage and wear on the paints on porcelain tableware and ornaments. It was aimed that the glaze layer has high transparency, brightness and harmony with the porcelain body. Within the scope of this article, glaze compositions were prepared in frit ratios of 10%, 15%, 20%, 25%, 30% and 40%. The different glaze compositions developed have been applied to porcelain products containing precious metallic paints. Then, the glazed products were subjected to final firing between 870°C-900°C. Some important results obtained within the scope of this study are;

- In glaze compositions from 10% to 30% after firing, it has been observed that 10% of the opacity of the glazed surface and its compatibility with the body are less than 30%.
- Quartz-SiO<sub>2</sub> and Albite-Na(AlSi<sub>3</sub>O<sub>8</sub>) phases were observed in the structure of the glazes and it is seen that the crystallization of the glaze decreases as the frit ratio in the composition of the glaze increases. It shows that with decreasing crystallization, the structure becomes more amorphous with increasing frit ratio. This resulted in high transparency.
- SEM and EDX analyzes confirm the crystal regions in the amorphous phase and the XRD analyzes of the varieties of crystals. No cracks were observed on the surface of the glazes examined by SEM.
- The surface roughness improved as the frit ratio in the glaze increased.
- As a result of detergent resistance tests, in glaze compositions that are highly compatible with the body, mass losses are very small, that is, it has been observed that there is no wear.
- In the staining test results, all the stains came out after washing and this shows that the surface properties are suitable.
- As a result of color measurements,  $\Delta E$  values are lower than 0.50 and represent the change in an acceptable, invisible level of difference under these quality conditions.
- Obtained results showed that glaze compositions with high transparency and wear resistance can be obtained with only 30% frit content.

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