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Effect of Quebracho Bark on the Properties of Opaque Glazes

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Abstract

In this work, the effect of quebracho bark (QB) on the physical and chemical properties of opaque glaze/glazes (OG) was investigated. Various ratios (0.25-10 weight percent) of quebracho bark were incorporated into the glazes to obtain experimental glaze recipes and melting temperatures of the glaze compositions were calculated through the fluxing factors of the oxides present in the glazes. Thereafter, the glaze compositions were fired at the calculated temperature value of 1100°C. Viscosity, thixotropy and pH tests were conducted on OG and OG+QB glaze suspensions. Standard coloring analyses, crazing resistance, impact resistance, resistance to acid and alkalis, water absorption, firing strength, and surface hardness tests were conducted. After establishing the Seger formulas, surface tensions of the glazes were calculated by making use of the molar surface tension factors of the oxides already present in the glaze compositions at the same sintering temperature of 1100°C. QB additions decreased the viscosity and standard thixotropy values of the OG and had no significant effect on the pH of the OG slurry. On the other hand, QB additions caused an increase in the whiteness (opacity) of the OG. No crazing and impact fractures were observed on the glaze surfaces. Furthermore, the glaze surfaces showed good resistance to acid and alkalis. On QB incorporation, water absorption decreased in all the experimental glazes. Firing strength and surface hardness increased with increasing QB content. According to the experimental results, 5 weight percent (wt. %) QB addition was found to be the optimum amount.

Keywords: Opaque glaze, quebracho, viscosity, additive, thixotropy, physical properties.

1. Introduction

Glazes are simply glass coatings on the surface of a ceramic body, either clear transparent or in various colours. They may also be glossy or matte, translucent or opaque, smooth or even textured. The effects are limitless depending on formulation, application and combinations [1]. If a glaze, when exposed to light, refracts light beams, it is called an OG [2,3]. The opaqueness of a glaze arises from the existence of tiny particles of substances which are insoluble in vitreous phase and have different refraction indexes, or from trapped air bubbles held in suspension within the glaze [2,3]. A surer way to achieve opacity is to add an opacifying agent or opacifier into a starting batch of either frit or glaze itself [4,5]. OG cover undesired substrate colours, overcome surface defects of a ceramic body, and also supply pleasant and satisfactory esthetical appearances, besides giving sufficient mechanical properties. The most commonly used opacifiers are zirconia ($ZrSiO_4$), ZnO, TiO_2 and SnO_2 which contribute to high manufacturing costs [4]. Among the many parts of plants that are used, bark products have always played exceptionally noteworthy roles. Traditionally bark products have been particularly prominent as sources of medicine [6]. Bark has also been used as a natural dye for textile industry [7], as a low cost adsorbent [8], and in leather industry [6]. In this work, the effect of QB, as an alternative material, on the physical and chemical properties of OG was investigated. The details of the study were presented in the following paragraphs.

2. Materials and Methods

2.1. Material and preparation of glazed tile samples

The OG and QB were provided by Ege Seramik Factory (Polat Holding Inc., Izmir, Turkey) and by Ünar Ltd. Company, respectively. The chemical analysis, the experimental compositions, and the calculated Seger formulation of the OG were respectively given in Tables 1, 2 and 3. The particle size of the OG was –45 µm and its specific gravity was 1.8 g/cm^3 (1800 L/g). The viscosity value of the OG (standard) at the factory was desired to be 24-25 s. QB was added to the standard OG at the weight ratios of 0.25, 0.5, 1.5, 2, 2.5, 3.5, 5, and 10 (wt. %) and mixed homogeneously with a magnetic stirrer (Chiltern) for an hour. The biscuit wall tiles previously cut in 5cm×5cm×0.5cm dimensions were dried in an oven (Heraus) for two hours at 150 °C and were cooled down to room temperature. Subsequently, the glaze mixture prepared was applied onto the surfaces of the tile samples by dipping method. After cleaning off the excessive glaze slip spread on the underneath and the sides of the tile samples, they were left to dry at room temperature for 24 hours and again dried in the same drying oven at 150 °C. Afterwards, they were heated to 1100 ºC in a muffle furnace (Rohde). The heating and cooling rate of the furnace (Protherm PAF120/12 model) was 15 ºC/min and the dwelling time was 2 hours.

2.2. Methods of physical and chemical tests

Viscosity, thixotropy and pH tests were conducted on OG and OG+QB glaze suspensions. Furthermore, the physical tests such as variation in colouring parameters, impact and crazing resistance, resistance to acids and alkalis, water absorption, firing strength, and surface hardness were carried out on OG and OG+QB glazed tiles.

Table 1. Chemical analysis of OG (wt. %).

	CaO	MgO	Na_2O	K_2O	ZnO	Al_2O_3	SiO_2	ZrO_2
%	8.37	2.38	8.05	4.65	11.25	7.01	50.1	8.19

Table 2. Experimental OG compositions.

Composition (%)	Denotation
100 OG	0 QB
99.75 OG+0,25 QB	0.25 QB
99.5 OG+0.5QB	0.5 QB
99 OG+1 QB	1 QB
98.5 OG+1.5 QB	1.5 QB
98 OG+2 QB	2 QB
97.5 OG+2.5 QB	2.5 QB
96.5 OG+3.5 QB	3.5 QB
95 OG+5 QB	5 QB
90 OG+10 QB	10 QB

Table 3. Seger formulation of OG.

0.270 CaO	0.130 Al_2O_3	1.606 SiO_2
0.115 MgO		0.135 ZrO_2
0.250 Na_2O		
0.10 K_2O		
0.270 ZnO		

2.2.1. Viscosity and thixotropy tests

Viscosity and thixotropy were determined by using DIN 53211 Flow Cup with 4 mm nozzle according to the related standard [9].

2.2.2. pH values

All the glaze suspensions were subjected to pH tests using a pH-meter (pH 7110 benchtop meter).

2.2.3. Colour variation

The colorimetric analyses of the whole samples were carried out at Ege Seramik Inc. using Erichsen Spectromaster 565-D according to TS EN ISO 10545-16 [10]. The results were given as trichromatic chromaticity coordinates. Whiteness or opacity is given with ”L” values, variation between green and red colours with “a” values, and finally variation between blue and yellow colours with “b” values [11-12].

2.2.4. Crazing resistance

Crazing resistance of OG and all QB glazes were determined according to TS EN ISO 10545-11 [13].

2.2.5. Impact resistance

Impact resistance test was applied to all the samples according to TS EN ISO 10545-5 [14].

2.2.6. Resistance to acid and alkalis

The resistance to acid and alkalis were determined according to TS EN ISO 10545-13 [15].

2.2.7. Water absorption

The water absorption of OG and QB tiles were determined according to TS EN ISO 10545-3 [16].

2.2.8. Fired strength

This test was applied to all the glazed tiles according to TS EN ISO 10545-4 [17].

2.2.9. Surface hardness

All the glazed bodies were subjected to surface hardness test according to TS EN 101 [18].

3. Results and Discussion

3.1. Viscosity tests

Figure 1 shows the variation in flow time (viscosity) with QB concentration. The flow time initially decreased with increasing QB content from 10.9 down to 10.1 approximately between 0.25 and 2.5 wt. % QB. Afterwards, the flow time increased progressively with increasing QB content about up to 11.2 s at 10 wt. % QB. When the viscosity of the standard OG (24-25 s) was taken into consideration, one can say that QB addition had a strong decreasing effect on viscosity. In other words, decreasing viscosity can be translated as an increase in fluidity of the OG slurry containing QB.

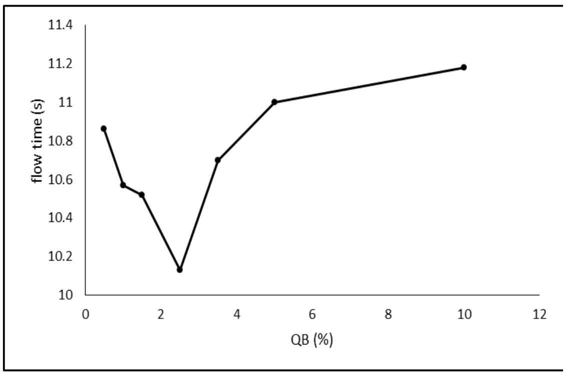

Figure 1. Variation in flow time (viscosity) with respect to QB content.

3.2. Thixotropy tests

Figure 2 indicates the variation of thixotropy values of the glaze suspensions with increasing QB content. The thixotropy values of experimental OG decreased approximately from 13.8 % at 0.25 wt. % QB down to a minimum of 11 % at 5 wt. % QB content. Afterwards, the thixotropy values slightly increased about to 11.5 % at 10 wt. % QB content. Thus, it was clearly seen that QB had a great effect on thixotropy as in the case of viscosity. QB additions decreased the standard thixotropy value of 27-28 % down to 11 % at 5 wt. % QB addition, which corresponded to 61 % decrease in thixotropy. In other words, decreasing thixotropy values can be interpreted in such a way that QB additions help the standard OG to keep its fluidity after a certain period of time.

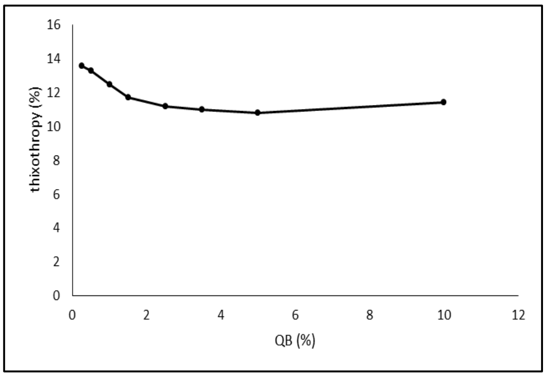

Figure 2. Variation in thixotropy with respect to QB content.

Viscosity of glaze slurries is an important factor in their performance. The higher the viscosity, the thicker the application of glaze on ceramic ware [19]. However, a least amount of glaze should be deposited over the entire piece in order to use glaze slurry economically. An opaque glaze will require a thicker coating of glaze to provide a consistent colour and finish over the whole piece [20]. On the other hand, a thixotropic glaze slurry that stiffens quickly when left undisturbed can be very disturbing leading to need of a lot of agitation during storage. In the present study, QB additions decreased the viscosity and thixotropy values of standard OG acting as an effective deflocculant without compromising from the quality and properties of standard OG as it was exhibited from the standard test results which were given in the following sections below.

3.3. pH tests

Figure 3 depicts the variation of pH values with increasing concentration of QB. The pH values varied between 7 and 8. When the pH value of standard OG, which is between 7.2 and 8.2, was taken into account, it was seen that QB had no significant effect on the pH of OG slurry (Figure 3).

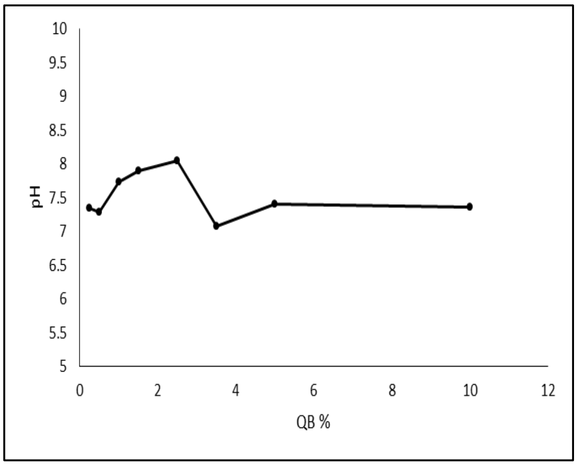

Figure 3. Variation in pH with respect to QB content.

3.4. Colour variation

Table 4 gives the variation in the colour of the glazed tiles containing various ratios of QB. There was no significant variation in the colouring parameters of the experimental glazes. However, the "L" values of the standard OG was much lower than those of the experimental glazes, which demonstrated that QB additions clearly increased the opaqueness (whiteness) of the standard OG (Table 4, Figure 4).

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Table 4. Variation of colour with respect to QB content.

Sample	L	a	b
Standard OG	86.58	0.23	13.68
QB 0,25	95.17	2.17	4.94
QB 0,5	95.68	1.83	3.95
QB 1	95.76	1.99	3.76
QB 1,5	95.62	1.96	3.65
QB 2	95.6	1.96	3.65
QB 2,5	95.31	1.83	4.44
QB 3,5	95.14	1.69	3.94
QB 5	94.18	1.91	4.38
QB 10	94.88	1.38	3.86

Figure 4. Glazed tiles subjected to colorimetric analyses.

3.5. Crazing and impact resistance

The results of crazing and impact resistance tests of the experimental OG revealed that no crazing was detected on the glazed surfaces of the tiles (Figure 5). The impact tests were also conducted after the crazing resistance test on the same glazed tiles. None of the glazed surfaces was fractured after the impact tests (Figure 5).

Figure 5. Glazed tiles subjected to crazing and impact resistance.

3.6. Resistance to acid and alkalis

The resistance to acids and alkalis of the experimental OG can be seen in Figure 6. Firstly, resistance to alkalis was tested and no sign of abrasion on the glaze surface and no deterioration in the glaze colour were detected. Afterwards, resistance to acids test was carried out and again the glazed surfaces were smooth and no deterioration in colour was observed (Figure 6).

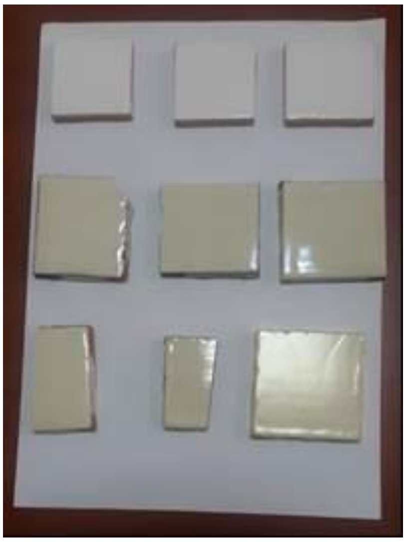

Figure 6. Glazed tiles subjected to resistance to acids and alkalis tests.

3.7. Water absorption

The water absorption values clearly decreased with increasing QB content (Figure 7) and reached to a minimum at 10 wt. % QB content. When the maximum water absorption value of standard OG (18% maximum) in the factory was compared with those of the experimental OG compositions, it was seen that QB clearly decreased the water absorption values throughout the experimental compositions.

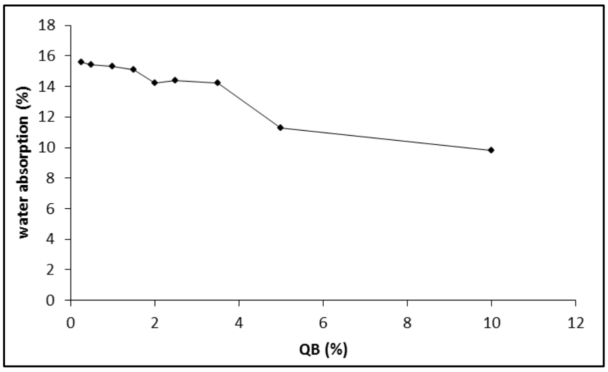

Figure 7. Variation in water absorption with respect to QB content.

3.8. Firing strength

Figure 8 shows the variation of firing strength with QB concentration. Firing strength increased with an increase in QB content. Especially, at 5 and 10 wt. % QB contents, the firing strength values were respectively around 80 and 105 N/mm^2 (Pa) reaching a maximum value at 10 wt. % QB. When the factory value of 40 Pa is taken into account, the firing strength increased by 100 % and over.

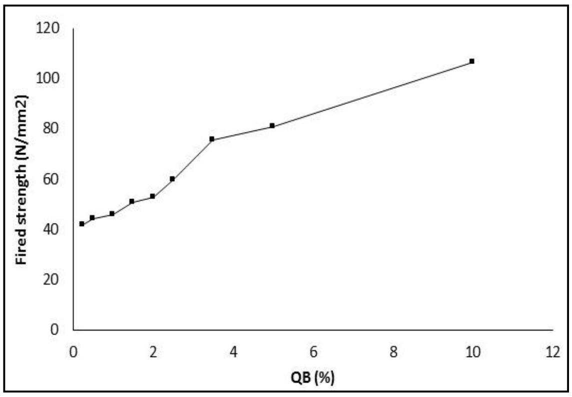

Figure 8. Variation in firing strength with respect to QB content.

3.9. Surface hardness

The surface hardness of the experimental OG compositions increased with increasing QB content (Figure 9). On the other hand, the surface hardness of the standard OG varies between 5.5 and 7 as reported by the factory. Thus, it is seen that the surface hardness values of the experimental OG were coherent with the standard values as seen from Figure 9.

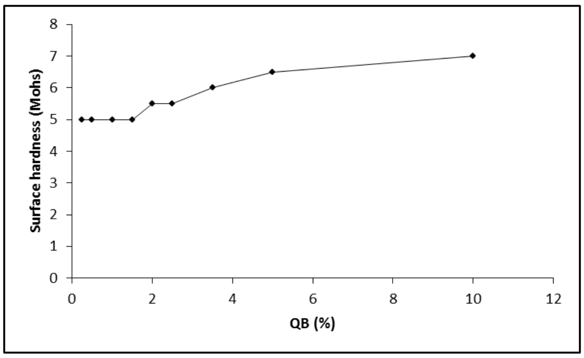

Figure 9. Variation in surface hardness with respect to QB content.

In the light of the discussion above and the experimental tests carried out in the present work, 5 wt. % QB addition to the standard OG was found to be the optimum level. In this case, the viscosity will be around 11 s (the second highest) (Figure 1) and thixotropy 10.9 % (the lowest one) (Figure 2) among those of the rest of the experimental OG while the pH value will be around 7.25 being in conformity with that of standard OG. In other words decrease in viscosity and thixotropy will be respectively 56 and 61 %, which is desirable for OG slurry. At 5 % QB addition, L value of the OG will be increased by around 10 % (Table 4, Figure 4), which will definitely contribute to the opaqueness (whiteness) of the standard OG without compromising on the quality of the OG as far as the crazing resistance, impact resistance, and resistance to acid and alkalis are concerned (Figures 5 and 6). On the other hand, the water absorption value will be around 11 % which means a 39 % decrease in water absorption. Furthermore, at 5 wt. % QB content, the firing strength will be 80 N/mm^2 (Pa), which leads to about 100 % increase in the firing strength which is desirable for this property. Similarly, the surface hardness will be around 6.25 which is in conformity with that of the standard OG.

4. Conclusions

The conclusions of this study were drawn as follows:

- QB additions had a strong decreasing effect on the viscosity of the OG,
- QB additions decreased the standard thixotropy value of the OG,
- QB had no significant effect on the pH of the OG slurry,
- QB additions clearly increased the opaqueness (whiteness) of the OG,
- No crazing was detected on the glazed surfaces of the tiles due to QB additions,
- None of the glazed surfaces was fractured after the impact tests due to QB additions,
- The glaze surfaces demonstrated good resistance to acid and alkalis in spite of QB additions,
- QB incorporation clearly decreased water absorption throughout the experimental compositions,
- Firing strength increased with an increase in QB content,
- Surface hardness increased with increasing QB content,
-5 wt. % QB addition was found to be the optimum amount.

The results gathered demonstrated that QB was a good deflocculant and definitely increased strength, hardness and opacity of the glazes without compromising on the other qualities and properties of the standard OG.

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