THE EFFECT OF SURFACE-TREATED ANHYDROUS BORAX ADDITIONS ON HARD PORCELAIN PROPERTIES

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The utilisation of surface-treated anhydrous borax to facilitate densification of hard porcelain bodies, prepared by slip casting from suspensions containing mixtures of silicate-based raw materials, was investigated. After surface treatment with stearic acid, anhydrous borax powders were added to the initial mixture by partial substitution with potassium feldspars up to 3 wt. % to examine their potential effects on the finished product. By the addition of surface-treated borax to the suspensions, stabilised with different dispersants (Darvan 821A and Dolapix CE-64), hard porcelain bodies of high strength, which were fired at a lower temperature than the industrial firing temperature, were obtained. After studying the effects of the different amounts of surface-treated borax addition on the porcelain properties, it was found that the addition of borax causes distinct effects on the physico-mechanical properties of hard porcelain.

INTRODUCTION

Porcelains are highly vitrified ceramics that typically have a triple formulation made up of 50 % kaolinitic clay, 25 % flux and 25 % filler [1-4]. The clay acts as a binder for the other constituents in the green form, and provides plasticity to the body for shaping. The fluxes, e.g., feldspars, are used not only to reduce the firing temperature by reacting with the other components but also to achieve further densification by filling the pores within the microstructure. The filler is thermally stable at the firing temperatures of porcelains and minimises deformation. Low porosity values (< 0.5 %) and high glassy phase content (> 40 %) are typical characteristics of fired hard porcelains [4-6].

Porcelains have excellent technical, functional and aesthetic properties, such as relatively high strength, whiteness and as well as low water-absorption that provides impermeability to chemical substances and cleaning agents [7].

Technological innovations in the ceramic industry have been profoundly changing the manufacturing cycle and the requirements for raw materials. For keeping up the competitive capability, the porcelain industry needs innovations, which also require a revolution without compromising its quality. Adequate functional properties in high-end porcelain products have stimulated research into the use of new materials that are low-cost or lower the cost of production. The studies carried out in ceramic materials in the last 50 years can be distinguished into two lines: a) alternative raw materials; b) decrease the firing temperature [8].

There are some technical and economic difficulties associated with porcelain manufacturing due to the necessities for high-purity raw materials and the formation of a more glassy phase in the bodies to obtain the targeted porosity values in their microstructural design, compared to other traditional ceramics. These necessities have made the investigation of alternative raw materials inevitable, and there has been much research on new raw materials to be used in porcelain production [9]. In recent years, some primary and secondary raw materials, such as iron and steel slag [10], volcanic ash [11, 12], mine waste [13], rice straw ash [14], sugarcane bagasse ash [15], diopside [16], glass waste [17], wollastonite [18], colemanite [19, 20], and sandstone dust [21] have been used as alternative raw materials for porcelain production.

The firing process is a heat treatment process that gives sufficient strength to the formed ceramic green body in-service condition. The activation energy for the densification, e.g., of about 550 kJ·kg^{-1} in the sintering of silicate ceramics, is required during the firing process to increase the body temperature [7]. Hard porcelain products are often fired at about 1400 °C [22], which is a relatively higher temperature than that of other silicate ceramics, and, therefore, has a high specific energy consumption, e.g., 10 - 15 MJ·kg^{-1} in the firing conditions [7, 23, 24]. However, these values are 3-8 times higher in industrial firing conditions, because only a fraction of the energy is consumed for the reactions; the rest of it is lost as heat. The total cost share of energy is enormous in the production of ceramics; therefore, energy-saving efforts are of great importance both from the industrial and scientific point of view [7].

Fluxing agents play a fundamental role in the production process of vitreous ceramics since they significantly improve the microstructure in the end product by reducing porosity. Low porosity is achieved through the formation of more glassy phases during firing, which results from the progressive melting of the fusible minerals used within the body composition. Thus, fluxing agents, which are determinants in defining the product's firing temperature and are responsible for the pyroplastic deformation the ceramic body undergoes during firing, strongly affect the resulting microstructural characteristics of the porcelain [25]. Therefore, improvement in the mechanical properties and lowering of the firing temperature of porcelain products can be achieved by developing a proper glassy phase [26]. Furthermore, initiatives have focused on the use of alternative materials instead of the available fluxing agent in the industry, due to providing productivity with a considerable reduction in the energy cost. However, instability in the formed amorphous phase by the melting of fluxes on the firing state affects the technical properties of the industrially produced ceramics [27]. Besides, lower fusibility of alkali-containing fluxes such as feldspar due to the high-energy requirement for the crystal structure's destruction is another major challenge [28].

Lately, some research has been performed to evaluate the feasibility of decreasing the firing temperature of porcelain by using additives. According to the relevant literature, there are various studies involving the employment of replacing potassium feldspar with soda-lime glass [29], glass waste [30], blast furnace slag [31, 32], bentonite [33], scrap-glass [34] and wollastonite [35]. The observed lower firing temperature over the feldspar porcelain makes it an economical alternative as well [26].

Boron oxide-bearing minerals can technologically be considered as important alternative raw materials since they have a glass-forming character and have been used in the ceramic industry to decrease the melting point, viscosity and thermal expansion of the glassy phase [9, 36]. Anhydrous borax ($Na_2B_4O_7$) is produced via fusion of borax deca- or pentahydrate at approximately 1000 °C [37]. The anhydrite form of borax is preferred to other hydrous forms in high-temperature applications since it does not cause any foaming problems arising from water dehydration [38].

In the ceramic industry, borates are considered as one of the most important network-former after silica. Our previous studies [19, 35] have shown that both additions of wollastonite (calcium silicate) and colema-nite (calcium borate) have a considerable effect of on the hard porcelain firing temperature. Therefore, the expectation is that by addition of sodium borate, as with calcium silicate and calcium borate, they will have a certain effect in the reduction of porcelain firing temperature and improvement in the mechanical properties, which has been a driving force in this work.

Industrial applications of some borates are limited due to utilisation difficulties in the aqueous systems. The main problem associated with using some borates as a constituent of aqueous systems lies its solubility behaviour that is influenced by the factors, such as temperature, environment, etc. Even if some borates, such as anhydrous borax, are dissolved in water more slowly than other hydrated forms, their direct usage is inconvenient. The solubility values of anhydrous-, penta- and decahydrate borax are given in the product datasheet to be 3.15, 4.63, and 6.15 wt. % at 25 °C, respectively [39].

The dissolution of borax in the suspension causes an alteration of the composition as well as deterioration of rheological properties. Besides its partial solubility, it can absorb water from the atmosphere during storage because of its inherent hygroscopic nature, and this leads to incorporation of the incorrect amounts into the composition [40]. To prevent above application failures, one must reveal a coating method to avoid water interacting with the boron oxide particle.

This study is aimed to pave the way for developing and utilising new borax powders, having low water-solubility and high hydration resistance. For this aim, anhydrous borax powders were treated with stearic acid by using a simple wet coating method to prevent their interaction with water. After identifying the conditions for the wet coating that provide the possibility to obtain anhydrous borax powders with improved properties, different amounts of borax powders were added to the hard porcelain composition to correlate its effect to the end product properties.

EXPERIMENTAL

Surface treatment of anhydrous borax

Anhydrous borax (ABX) powders of purity 99 % (Etibor–68) and a particle size of less than 500 μm was supplied by Eti Mine Enterprises (Turkey). Before the surface treatment, the ABX powders were ground for 2 h in a planetary ball mill to obtain particles smaller than 100 μm. Stearic acid (SA), encoded as Wilfarin SA-1865, was provided in the form of powder with a particle size < 10 μm. The dry-ground ABX powders were treated with SA to alter its hydrophilic surface properties in a reverse manner. The wet coating of the ABX powders with SA was performed with the following procedure:

The ABX powders were dried at 105 °C for 24 h, prior to treatment with the stearic acid, to remove the physically adsorbed water. Stearic acid was used at the mass fraction of 0.5, 1 and 2 % w/w to provide the highest coverage with the least amounts. Firstly, the coating solution was obtained by mixing the stearic acid with a large amount of water in an aqueous solution. For each experiment, the stearic acid powders were fed into 100 ml of water in a 250 ml beaker, held on the hot plate

of a magnetic stirrer at 80 °C, and mixing was performed at the rotation speed of 750 rpm to dissolve them. After the stearic acid was being dissolved in water, 10 grams of ABX powders were added into the solution to assure the completion of the stearic acid-ABX surface reaction and, accordingly, the mixture was vigorously stirred at 750 rpm for 30, 60 and 120 min periods.

The prepared solutions were filtered through filter paper with a pore size of 4 - 12 microns and the remaining solution was transferred to a 250 ml conical flask. The remaining powders on the filter paper were air-dried for 24 h and then oven-dried at 50 °C for approximately 48 h until a constant weighing was attained. After the coating process, the amount of anhydrous borax that was dissolved during the wet coating process was measured to be 0.2 ± 0.05 wt. %, and this mass loss was assumed to be negligible. The separated powders, from the filter paper, were kept in order to be used for further measurements and characterisations.

Characterisation of the surface-treated anhydrous borax powders

Determination of the coating yield

The ABX powders are water-soluble materials and also have a high tendency towards hydration. Therefore, this investigation was conducted to study the feasibility of the stearic acid coating, as a means of preventing the interaction of the borax powders with water. The effect of the surface treatment on the water-interaction of borax powders was firstly evaluated by determining the coating yield of the stearic acid on the ABX powders.

The coating yield evaluation test, as described in our previous work [41], involves subjecting surface-treated powders, which are incorporated into the water, to magnetic stirring at 750 rpm for 1 h. The water-insoluble parts of the powders were collected using a filter paper and subsequently dried at 50 °C until a constant weight was reached. The amounts of the maximum soluble powders (m_0), the water-insoluble parts of the surface-treated (m_1) and untreated ABX powders (m_2) were measured for each processing period, and then the coating yield (%) was calculated according to Equation 1. All solubility tests were performed three times and the values of m_0, m_1, and m_2 used in Equation 1 were the calculated averages of these measurements.

$$\text{Coating yield (\%)} = [(m_1 - m_2) / m_0] \times 100 \qquad (1)$$

Evaluation of the stearic acid coating durability

In addition to the coating yield, we attempted to get an idea about the durability of the stearic acid coating on the ABX surfaces by subjecting them to the repeated washing process. The obtained weight loss values after each washing process, as the solubility indicator, were compared to determine the durability of the coating material in water.

For this experiment, 10 g (m_0) of surface-treated ABX powder was dispersed in 100 ml of water in a beaker, followed by mixing at 750 rpm at room temperature for 1 h on a magnetic stirrer. Following the stirring process, the solution was filtered through a filter paper, and the remaining powders on the filter paper were allowed to dry at 50 °C until a constant weight was achieved. After the first (1st) washing process, the weight of powders, which were scraped out of the filter paper and dried to a constant value, was noted as m_1. Under the same conditions, the undissolved powders that were obtained after the first washing process were subjected to repeated washing, and the values of m_2 and m_3 were determined after the second (2nd) and third (3rd) washing processes, respectively.

The measurement was repeated three times for each sample after every washing process. After the triple washing processes, the % solubility values of the surface-treated ABX powders, based on their weight loss, were determined separately according to Equation 2, and the coating durability was comparatively evaluated.

$$\text{Weight Loss (\%)} = (m_0 - m_{1,2,3}) / m_0 \times 100 \qquad (2)$$

Wettability measurements

The wettability tests were performed to evaluate the effect of the SA coating on mitigating the water interaction of the ABX. The sessile drop method (KSV Attension ThetaLite TL 101), which involves depositing a small drop of pure water on disc-shaped samples, was used for determining the wettability of the powders at 25 °C, in terms of the contact angle. The measurements were performed three times for each sample, and the average values were obtained.

Preparing the porcelain suspension

The suspensions were prepared by using local raw materials such as kaolin, quartz and potassium feldspar, all of which was supplied from the porcelain manufacturers in Turkey. The chemical analyses and some physical properties of the raw materials, used in the preparation of the suspensions, are presented in Table 1 and Table 2, respectively.

The recipe was prepared based on a combination of traditional hard porcelain where kaolin, potassium feldspar and quartz were mixed at proportions of 50 wt. %, 25 wt. %, and 25 wt. %, respectively. The surface-treated anhydrous borax, having both the lowest water-solubility and highest wettability, was used as another fluxing agent besides feldspar, which has relatively high-energy requirements for crystal network destruction.

Thus, three extra body formulations were designed by the addition of the surface-treated anhydrous borax up to 3 wt. %. The designed formulations were encoded

as P_0, P_1, P_2, and P_3 where, 'P' stands for porcelain while '0, 1, 2, and 3' stand for wt. % surface-treated anhydrous borax. The composition of the designed formulations is given in Table 3. The suspensions of P_0, P_1, P_2, and P_3 with a water content of 35 wt. % were prepared and then favourable dispersant amounts, determined as a result of rheological studies on the standard composition, were added to achieve a good dispersion of the ceramic particles in the aqueous solution.

The rheological behaviour of the suspensions has been known to play a crucial role in slip casting processing, and in turn, on the microstructure and properties of the final products. A well-dispersed slurry can be obtained by choosing a suitable dispersant and its critical quantity [19]. Therefore, rheological measurements were carried out to optimise the stabilisation conditions of the suspensions with different concentrations of dispersants by using a rotational stress-controlled rheometer (Anton Paar – MCR 102 model). The measurements were performed at a constant temperature (25 °C) using a plate and plate configuration (PP/50; 50mm diameter of the plate).

Table 1. The chemical analyses of the raw materials present in the porcelain recipe.

Oxides	Kaolin	Quartz	Potassium feldspar	Anhydrous borax
SiO_2	47.30	97.50	66.6	–
Al_2O_3	36.30	1.21	17.2	–
Na_2O	0.05	0.02	3.11	30.27
Fe_2O_3	0.85	0.05	0.23	–
TiO_2	0.05	0.05	–	–
CaO	0.10	0.02	0.50	–
MgO	0.38	0.48	0.06	–
K_2O	2.29	0.03	11.5	–
B_2O_3	–	–	–	68
Others*	0.21	0.12	0.21	–
LOI	12.21	0.28	0.59	–

* *(P_2O_5; SO_3; Cr_2O_3; SrO; ZrO_2)*

Table 2. Some properties of the raw materials present in the porcelain recipe.

Raw materials	Particle size (micron)			Specific surface area ($m^2 \cdot g^{-1}$)
	$d_{0.9}$	$d_{0.5}$	$d_{0.1}$	
Kaolin	22.76	5.57	1.12	11.80
Quartz	44.47	15.83	3.97	0.59
Potassium feldspar	80.11	28.92	4.46	0.96
Anhydrous borax	100.70	41.10	6.80	1.00

Table 3. The designed formulations for the hard porcelain.

Compositions (wt. %)	P_0	P_1	P_2	P_3
Kaolin	50	50	50	50
Quartz	25	25	25	25
Potassium feldspar	25	24	23	22
Modified-ABX*	0	1	2	3

* *ABX treated with 2 wt. % SA for 60 min*

Sweep measurements were conducted in the shear rates ranging from 1 to 1000 s^{-1}. Two types of commercially available dispersants, Darvan 821A (R.T. Vanderbilt, USA) and Dolapix CE-64 (Zschimmer & Schwarz, Germany), with five different amounts in the range from 0.2 to 1 wt. % were used for suspension stabilisation. To prepare the suspensions, the water, the dispersants, and the raw materials were mixed for 15 min at a speed of 750 rpm using a magnetic stirrer. During the homogenisation process, the water content was adjusted to 35 wt. %. The suspensions of P_0, P_1, P_2, and P_3 with the appropriate dispersant amount, determined by the rheological measurement on the base composition, were prepared.

After determination of the stabilisation conditions of the base suspension, the slurries of the P_0, P_1, P_2, and P_3 formulations, with a fixed 65 wt. % solid loading, were prepared by mixing the constituents at 750 rpm for 15 min on a magnetic stirrer. The as-prepared aqueous slurries were poured into a plaster mould with dimensions of approximately $10 \times 2 \times 1$ cm. The slip cast bodies were first air-dried at room temperature for 24 h, followed by oven drying at 105 °C for 2 h. The dried samples were heated to 1200 °C at a ramp speed of 10 °C·min^{-1} in an air atmosphere, and after soaking at this temperature for 1 h, the samples were allowed to cool to room temperature. Although the hard porcelain products are fired industrially at a relatively high temperature in the range of 1380 - 1450 °C, the temperature employed in this study is as low as 1200 °C due to the addition of borax that reduces the formation temperature of the glassy phase.

Evaluation of the physical properties of the fired bodies depending on the surface-treated ABX addition was carried out by measuring some characteristics (linear shrinkage, bulk density, apparent porosity, water absorption). The linear shrinkage was calculated as the difference between the initial and final lengths divided by the initial length and expressed as a percentage. The water absorption, bulk density, and apparent porosity of the samples were determined via the standard test method as described in ASTM C373-88. Finally, the bending strength (σ_f) of the fired bodies having dimensions of $90 \times 18 \times 9.5$ mm was measured using a Shimadzu AG–IS 100 kN in an electronic universal tester on three test pieces by a three-point loading test with a span of 50 mm and at a cross-head speed of 0.5 mm·min^{-1}. A minimum of three measurements for each piece over the entire test categories was taken, and all the measured test values were averaged for each test.

RESULTS

Coating yield of the stearic acid on the anhydrous borax

To determine the insolubility percentage, for the evaluation of the coating yield, the raw and surface-treated ABX powders were analysed via a water solubility

test. The raw ABX not subjected to treatment with SA was partially soluble in water (28.2 %), and its water-insoluble amount was 71.8 %. When the surface of the ABX was coated with SA, as seen in Table 4, the amounts of insoluble powder for all the samples were more than 78 %. These results suggest that the hydrophobic organic molecules (SA) were partially bonded to the ABX surface. The highest amount of insoluble powder of 95.4 %

Table 4. The water-insoluble powder amounts of the ABX as a function of the processing period.

Processing period (min.)	Amount of SA (wt. %)		
	0.5	1	2
30	86.5 ± 0.01	86.1 ± 0.05	86.3 ± 0.05
60	87.8 ± 0.02	88.4 ± 0.03	95.4 ± 0.01
120	89.1 ± 0.01	88.6 ± 0.01	89.0 ± 0.03

Table 5. The coating yield values of SA on the ABX as a function of the processing period.

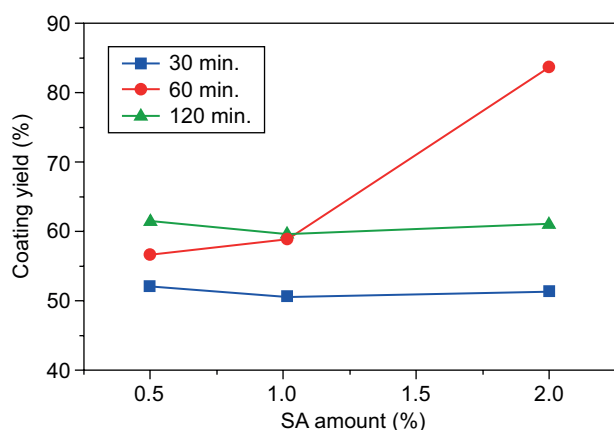| Processing period (min.)	Amount of SA (wt. %)		
	0.5	1	2
30	52.1	50.7	51.4
60	56.7	58.9	83.7
120	61.4	59.6	61.0

Figure 1. The effect of the processing parameters on the coating yield of the SA.

was obtained for the ABX coated with 2 wt. % SA for 60 min.

The coating yield values calculated using Equation 1, are presented in Table 5 and Figure 1.

The coating yield, as represented in Table 5, varies between 50.7 % and 83.7 %, and the maximum yield was achieved for the sample coated with 2 wt. % SA for 60 min. In the coating processes performed with 0.5 and 1 wt. % SA, the coating yield increased by the increased processing period. With a further increase in the amount of SA (2 wt. %), the coating yield increased up to the processing period of 60 min, but then decreased for the remainder of the experiment (for 120 min). It has been envisaged that the reduction in the coating yield, which was observed for the ABX sample treated with 2 wt. % SA for 120 min, may be due to the weakening of the resistance of the coating film that was kept under the continuous stirring conditions at a constant temperature (80 °C) for a long time.

Notably, in comparison with the results of our previously presented dry coating of anhydrous borax [41], it was understood that when the stearic acid is coated on the anhydrous borax surfaces by the wet method, a higher coating yield but lower wetting angle values were obtained. This result has proven that the coating quality is highly dependent on both the type of the modifier and preferred coating technique.

Coating durability of the stearic acid on the anhydrous borax

The coating durability of the surface-treated and untreated ABX powders was discussed in terms of the variations in the solubility values obtained after the triple washing tests. The averages of the solubility values measured in the three times repeated experiments were used as the experimental results for comparison. The experimental error was less than 1 % for all the solubility measurements. The weight loss values of the untreated ABX powders, as the solubility indicator, were measured as approximately 40, 75 and 95 wt. % after the 1st, 2nd, and 3rd washing process, respectively (Table 6).

Table 6. The solubility values of the ABX powders after the triple washing tests.

Processing period (min.)	Amount of SA (wt. %)	Solubility (wt. %)		
		after the 1st washing	after the 2st washing	after the 3st washing
0	0	*39.70*	*76.80*	*95.33*
30	0.5	13.50	38.03	80.30
	1.0	13.95	40.70	74.49
	2.0	13.75	33.87	68.01
60	0.5	12.18	33.44	74.22
	1.0	11.63	35.75	73.60
	2.0	4.59	29.04	67.28
120	0.5	10.89	34.45	72.22
	1.0	11.43	29.15	72.95
	2.0	10.97	31.43	73.92

Considering the variations in the weight losses obtained after the triple washing process for the ABX powders, the solubility values of the surface-treated powders appeared to decrease compared to that of untreated one. The obtained weight loss values after each washing process indicated that the lowest mass loss and thereby the minimum solubility was achieved with the SA amount of 2 wt. % at a period of 60 min. After the 3rd washing process, more than 67 % of the surface-treated ABX powders were dissolved in water, and this indicated that the coating integrity fades away under difficult physical conditions, i.e., a repeated washing process. As a result, the best coating durability was obtained in the ABX powders treated with 2 wt. % SA for 60 min as in the coating yield results.

Consequently, the triple washing tests prove that the SA powders were coated to the surface of the ABX powders, as their hydrophobic effects are maintained even after they were washed. The deterioration in the coating properties resulting from the repeated washing treatments indicates that the coating is achieved by the mechanism of physical adsorption rather than by chemical bonding.

Surface wettability of the surface-treated ABX powders

The contact angle measurements, as the surface wettability indicator, of the samples processed for each set of parameters are listed in Table 7. As indicated in the table, the contact angles of the ABX powders were in the range 25°-96.84° and the highest value was measured for the samples surface-treated with 2 wt. % SA for 60 min. The high measured values of the contact angles for all the surface-treated samples revealed significant hydrophobicity compared with that of the untreated ABX. This is because the stearic acid effectively reduces the free energy of the ABX surfaces because of the existence of the $-CH_2$ groups on the surface of the ABX.

It is understood that the contact angles of the ABX powders treated with 2 wt. % SA for 60 and 120 min were greater than 90°, i.e., the surfaces are hydrophobicised. Under the other processing conditions, it was concluded that the contact angles of the ABX powders were less than 90°, and, therefore, they were partially hydrophobicised.

Considering the above results, among all the processing conditions applied for the surface treatment of the ABX, the SA amount of 2 wt. % and processing period of 60 min yielded the best results in terms of the coating yield and durability, and also the surface hydrophobicity. Consequently, the compatibility of the experimental results indicates the reliability of the findings in the coating success.

Rheological stabilisation of the hard porcelain suspension

Figure 2 shows the rheological flow curves of the suspensions prepared without the use of the surface-treated ABX that contain different concentrations of both dispersants. It is seen that the flow behaviour reasonably depends on the amount and type of the dispersant used.

Table 7. The contact angles of the surface-treated and untreated ABX powders.

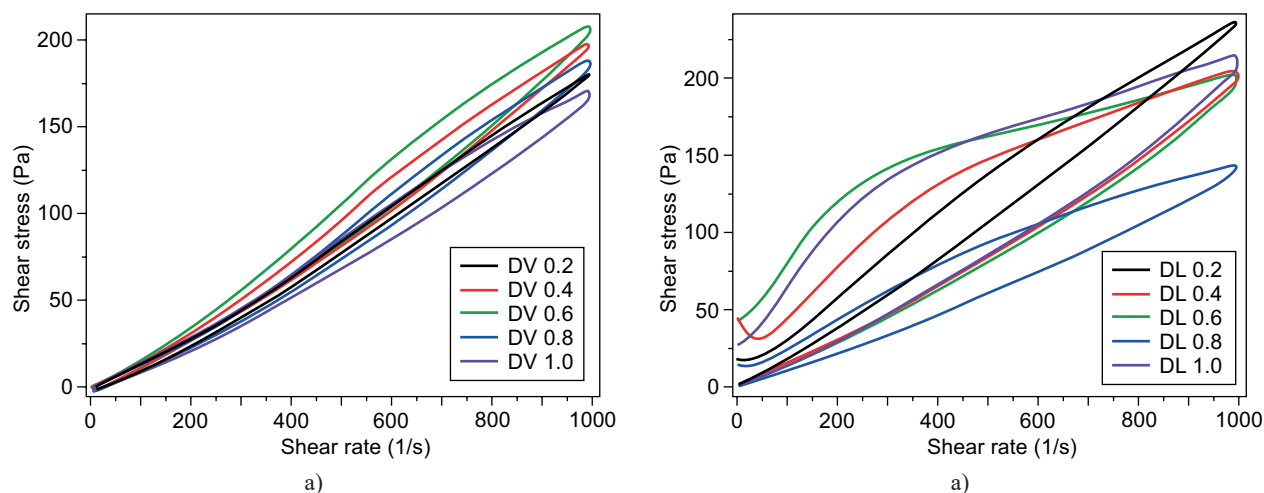| Processing period (min.)	Amount of SA (wt. %)			
	0	0.5	1.0	2.0
30	25 ± 0.74	84.13 ± 0.85	89.80 ± 1.36	84.57 ± 0.50
60	25 ± 0.74	81.47 ± 0.62	88.12 ± 1.14	96.84 ± 0.77
120	25 ± 0.74	76.39 ± 1.08	83.32 ± 1.80	91.75 ± 1.42

Figure 2. The rheological behaviour of the porcelain suspensions: a) dispersed with Darvan 821A, b) dispersed with Dolapix CE-64.

The initial viscosity of the suspensions dispersed with Darvan 821A, as seen in Figure 2a, increased with the increasing dispersant amount of up to 0.6 wt. %. With the further increase in dispersant addition to 0.8 wt. %, it slightly decreased. The viscosity reached the lowest value with the 1.0 wt. % Darvan 821A addition, where forces of repulsion dominate the suspension; thus, it is stabilised, and consequently, the viscosity is decreased. At this level of dispersant amount (1.0 wt. % Darvan 821A), the surface coverage of the adsorbent increased, the repulsion force increased accordingly and eventually attained a level that is strong enough to overcome van der Waals forces.

When the suspensions were dispersed with Dolapix CE-64 (Figure 2b), it is observed that the initial viscosity of the suspensions decreases steadily with the increasing dispersant amount of up to 0.8 wt. % and it reaches the lowest value with this level of addition, where the repulsion forces dominate the suspension. The further increase in the amount of the dispersant led to an increase in viscosity. As the excess amount of Dolapix CE-64 was not adsorbed on the surface of the particles in the suspension, the repulsion of the particles was weakened.

The flow curves of the suspensions containing both types of dispersant, in terms of the thixotropic behaviour, were compared and the increments in the hysteresis loop width were interpreted as another different effect of the dispersant type. While the Darvan dispersant did not cause a significant variation on the thixotropic behaviour of the suspensions, the Dolapix dispersant increased the thixotropic tendency of the suspensions. This effect was seen for all the suspensions, except for the suspension prepared by using an optimum amount of the dispersant.

Taking the above results into account, among all the suspensions (P_0) dispersed with both dispersants, the suspensions having the best dispersion stability with sufficient fluidity were determined to contain 1.0 wt. % Darvan 821A and 0.8 wt. % Dolapix CE-64 dispersants, respectively.

On the other hand, when the anhydrous borax was incorporated into the porcelain slurry without it being surface-modified, it was observed that the slurry became more thixotropic due to the ion release of the dissolved borax. However, after surface modification, it was understood that the addition of borax does not cause any significant changes in the rheological properties of the suspensions of P_1, P_2, and P_3 due to the fact that no changes were observed in the mould-filling time (pouring time). Consequently, the suspensions of P_1, P_2, and P_3 were also prepared under the determined conditions for P_0.

Evaluation of the impact of
the surface-treated ABX addition on
the properties of porcelain

The linear shrinkage, water absorption, open porosity, and bulk density values of the fired bodies are presented in Table 8. The linear shrinkage values measured in the porcelain samples prepared using the P_0, P_1, P_2, and P_3 suspensions were in the range of 10.78 - 13.31 % and the highest value was measured for the samples prepared from the suspensions dispersed with Dolapix CE-64 and containing 1 wt. % surface-treated ABX. It is understood that the linear shrinkage values shown in the table vary depending on the dispersant type since Dolapix CE-64 caused more shrinkage than was observed with Darvan 821A. The linear shrinkage values of the fired bodies, prepared from the suspensions dispersed with both dispersants, increased at a 1 wt. % addition of the surface-treated ABX. A further increase in the amount of the surface-treated ABX resulted in a progressive decrease in the linear shrinkage values of the samples prepared from the suspensions using Dolapix CE-64, while it did not have an outstanding effect on those values of the samples prepared from the suspensions using Darvan 821A.

As indicated in Table 8, the water absorption values of the samples prepared with both dispersants decreased with the increasing surface-treated ABX amount of up to 2 wt. %, and it again increased with a further increase in the amount of surface-treated ABX. The progressive decrease in the water absorption values of the samples and followed by a slightly upward trend can be explained with the formation of the bubbles by the bloating of the melt phase resulted from excessive sintering. On the other hand, the water absorption values of the samples prepared from the suspensions dispersed with Dolapix CE-64 resulted in it being lower than that what was observed with Darvan 821A. This situation may be speculated that due to the packing density of the particles in the samples prepared using Dolapix CE-64, the increased shrinkage caused the particles to approach each other more and reduce the space between them, and thus, the water absorption values reduced.

Table 8. Some physical properties of the fired bodies depending on the dispersant type.

Code	The linear shrinkage (%)		Water absorption (%)		Porosity (%)		Bulk density (g·cm⁻³)	
	Darvan	Dolapix	Darvan	Dolapix	Darvan	Dolapix	Darvan	Dolapix
P0	10.78 ± 0.12	11.93 ± 0.03	6.17 ± 0.05	5.11 ± 0.04	13.37 ± 0.08	11.14 ± 0.09	2.14 ± 0.03	2.18 ± 0.01
P1	11.59 ± 0.11	13.31 ± 0.03	1.31 ± 0.03	1.20 ± 0.08	2.97 ± 0.03	2.49 ± 0.06	2.30 ± 0.03	2.33 ± 0.04
P2	11.50 ± 0.09	12.37 ± 0.10	0.54 ± 0.04	0.44 ± 0.05	1.28 ± 0.05	1.02 ± 0.05	2.35 ± 0.04	2.33 ± 0.02
P3	11.49 ± 0.04	11.24 ± 0.03	0.65 ± 0.10	0.50 ± 0.10	1.48 ± 0.08	1.16 ± 0.11	2.35 ± 0.03	2.33 ± 0.03

Table 9. The bending strength of fired bodies depending on the dispersant type.

Dispersing agent	P0	P1	P2	P3
Darvan 821A	15.68 ± 0.52	20.25 ± 0.28	22.95 ± 0.30	29.39 ± 0.49
Dolapix CE-64	15.96 ± 0.40	29.08 ± 0.22	21.06 ± 0.21	20.38 ± 0.16

The porosity values measured in the porcelain samples prepared using the suspensions containing no surface-treated ABX that were dispersed with both dispersants were above 10 %. With the addition of the surface-treated ABX up to 3 wt. %, the porosity values gradually decreased to 1 % and increased again by the addition of the 3 wt. % surface-treated ABX. The lower porosity values were obtained in the samples of the Dolapix series compared to that of the Darvan series, as observed in the water absorption values.

The bulk density values were measured in the range of 2.14 - 2.35 g·cm⁻³ and 2.18 - 2.33 g·cm⁻³ in the samples prepared from the suspensions dispersed with Darvan 821A and Dolapix CE-64, respectively. With the addition of the surface-treated ABX up to 3 wt. %, the bulk density values in the samples of the Darvan series gradually increased from 2.14 to 2.35 g·cm⁻³ and then remained constant by the addition of the 3 wt. % surface-treated ABX. However, the bulk density values in the samples of the Dolapix series increased at the 1 wt. % addition of surface-treated ABX, and remained substantially constant at 2.33 g·cm⁻³ with a further increase in the amount of the surface-treated ABX.

Table 9 shows the results of the bending strength depending on the type of dispersant and the surface-treated ABX addition. Consistent with the other results reached from the characterisation tests, an increase in the strength values was also obtained with the addition of borax. The highest strength values were measured to be 29.39 MPa at 3 wt. % borax addition in the Darvan series and 29.08 MPa at 1 wt. % borax addition in the Dolapix series. From the table, it was clear that bending strength gradually increased from 15.68 to 29.39 MPa as the increase of the borax addition in the samples prepared from the suspensions dispersed with Darvan 821A. However, the bending strength values in the samples prepared from the suspensions dispersed with Dolapix CE-64 increased from 15.96 to 29.08 MPa at the 1 wt. % addition of the surface-treated ABX and after that consistently decreased by the addition of the surface-treated ABX.

The results obtained in this study are comparable to those of our previous studies where wollastonite [35] and calcined colemanite [19] additives were used. When compared to the results obtained from the experimental studies with those of the data obtained by these two additives, the findings can be summarised as follows: With the addition of the surface-treated borax, the values of the water absorption and porosity in the porcelain samples that were fired at 1200 °C were lower than those of the porcelain bodies containing wollastonite and calcined colemanite additives that were fired at 1250 and 1275 °C. However, the maximum values of the bending strength for the porcelain samples containing the surface-treated borax addition that was fired at 1200 °C were close to those of the porcelain bodies containing 3 wt. % of calcined colemanite and 5 wt. % of wollastonite additives that were fired at 1250 °C. All these results indicated that porcelain bodies could be produced with less borax addition and firing at a lower temperature by at least 50 °C.

CONCLUSIONS

The use of the surface-treated anhydrous borax in the hard porcelain bodies yielded a relatively high strength at lower firing temperatures. The surface modification reduced the weight loss of the anhydrous borax in an aqueous media and caused significant effects even when used in small amounts in the porcelain formulation. Both of dispersants used in the suspension preparation stage caused different effects on the viscosity and thixotropic properties, and as a result, even if the same amount of borax was used in the porcelain recipe, it was found that the bodies having different technological properties were obtained. Dolapix CE-64 rendered the suspensions, which offered porcelain bodies having a higher strength with relatively less modified borax additive compared to the suspensions dispersed with Darvan 821A. With the addition of 1 wt. % of the surface-treated ABX, the porcelain bodies can be produced at a much lower temperature, i.e., 1200 °C, than the traditional hard porcelain firing temperature.

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