

Surface Modification of Anhydrous Borax with Stearic Acid by Wet Coating Method

Cansu Kurtuluş¹, Recep Kurtuluş²

¹Afyon Kocatepe University, Faculty of Engineering, Department of Materials Science and Engineering, Afyonkarahisar, Turkey, (ORCID: 0000-0002-0758-5844), cansudemir@aku.edu.tr

²Afyon Kocatepe University, Faculty of Engineering, Department of Materials Science and Engineering, Afyonkarahisar, Turkey, (ORCID: 0000-0002-3206-9278), rkurtulus@aku.edu.tr

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Abstract

The wet coating of anhydrous borax powders with stearic acid (SA) to reverse their inherent hydrophilic surface properties was investigated. The coating procedure was based on the results from a previous study that revealed that the stearic acid solution (2 wt. % SA) mixed for 60 minutes at 750 rpm on the magnetic stirrer was sufficient for the surface modification of anhydrous borax. For the experiments, stearic acid powders were first dissolved in water at 80 °C. The mixture obtained by adding anhydrous borax powders to this solution was vigorously mixed on a magnetic stirrer to initiate and complete the surface modification. Each of these solutions was then filtered using a filter paper to separate the undissolved particles, and the residue on paper was dried at 50°C for 48 h until constant weighing was obtained. Wettability has been accepted as a key parameter for success in wet coating treatment. This parameter gained via the experimental characterization technique was used for an evaluation of the powder properties. The degree of wettability of anhydrous borax powders was measured and compared both after their surfaces were coated with stearic acid and after they were treated with water for a certain period of time in an aqueous environment. The stearic acid coating made the powder hydrophobic and this property was highly preserved after washing.

Keywords: Surface modification, Anhydrous borax, Stearic acid, Wet Coating, Solubility.

Susuz Boraksın Stearik Asit ile Islak Kaplama Yöntemi ile Yüzey Modifikasyonu

Öz

Susuz boraks tozlarının doğal hidrofilik yüzey özelliklerini tersine çevirmek için stearik asit (SA) ile ıslak kaplanması araştırılmıştır. Kaplama prosedürü, manyetik karıştırıcı üzerinde 750 rpm'de 60 dakika süreyle karıştırılan stearik asit çözeltisinin (ağırlıkça% 2 SA) susuz boraksın yüzey modifikasyonu için yeterli olduğunu ortaya çıkaran önceki bir çalışmanın sonuçlarına dayanmaktadır. Deneyler için, stearik asit tozları önce 80°C'de suda çözülmüştür. Bu çözeltiye susuz boraks tozlarının ilave edilmesiyle elde edilen karışım, yüzey modifikasyonunun başlatılması ve tamamlanması için manyetik bir karıştırıcı ile kuvvetli bir şekilde

karıştırılmıştır. Daha sonra bu çözeltilerin her biri, çözünmemiş parçacıkları ayırmak için bir filtre kağıdı kullanılarak süzölmüş ve kağıt üzerindeki tortu, sabit tartım elde edilene kadar 48 saat boyunca 50 ° C'de kurutulmuştur. Islanabilirlik, ıslak kaplama işleminde başarı için anahtar bir parametre olarak kabul edilmiştir. Deneysel karakterizasyon tekniği ile elde edilen bu parametre, toz özelliklerinin değerlendirilmesi için kullanılmıştır. Susuz boraks tozlarının ıslatılabilirlik derecesi hem yüzeyleri stearik asit ile kaplandıktan sonra hem de sulu ortamda belirli bir süre su içerisinde bekletildikten sonra ölçölmüş ve karşılaştırılmıştır. Stearik asit kaplamasını tozu hidrofobikleştirmiş ve yıkama sonucunda da bu özellik yüksek oranda korunmuştur.

Anahtar Kelimeler: Yüzey modifikasyonu, Susuz boraks, Stearik asit, Islak kaplama, Çözünürlük.

1. Introduction

Boron-bearing compounds are commonly utilized in many industrial areas such as glass, ceramics, refractories, cement, metallurgy, agriculture, pharmaceuticals, cosmetics, automotive, and communications [1, 2]. Due to its promising novel advantages, research to expand the application areas of boron and its derivatives is gradually increasing. Minerals containing boron are named with different names in terms of alkaline, alkaline earth, boron oxide (B_2O_3) and water content, and crystal structures. However, only some of them (tincal, ulexite, colemanite, etc.) are of commercial importance [3, 4]. Refined borates (penta- and deca- hydrate borax, anhydrous borax, boric acid, etc.) are chemically processed run of mine boron minerals, which are aggregates or concentrates of raw minerals those further dehydrated with the heating process to obtain final products [5], [6].

Anhydrous borax, also referred to as disodium tetraborate, has a $Na_2B_4O_7$ chemical formula and melting point is 742.5 °C [7] and is produced by direct dehydration of borax followed by the fusion process at around 1000 °C. Boron utilization provides a process, which is less energy-intensive than traditional approaches for glass and ceramic industries due to the excellent fluxing agent and glass-forming properties of the element. The anhydrous form of borax dissolves in water more slowly than the hydrated forms. The solubility values of fine-sized crystalline anhydrous borax at 25 °C are 3.37 wt. % in water, 16.7 wt. % in methanol, and 30 wt. % in ethylene glycol [7].

The most coherent borates for utilization and discharging in the aqueous mediums are in the form of water-soluble inorganic complexes. Perborate-containing detergents, boronated fertilizers, additives to corrosion inhibitors in antifreeze formulations, biocides for cutting fluids, insecticides, and as buffers/preservatives for cosmetic and pharmaceutical preparations are the best examples of utilization in this manner [8]. However, their partial solubilities in aqueous systems, for instance, in glaze applications, cause some problems such as deterioration of suspension rheology, mass loss, etc. Besides partial solubility, they can absorb water from the atmosphere during storage due to their hygroscopic nature, resulting in the possibility of inaccurate amounts being placed into a glaze formula [9]. To prevent the above mentioned-failures for applications in aqueous systems, one must reveal a coating method for boron particles to avoid interaction with water.

Surface coating is a method that focuses on developing or changing some particular properties, which are not inherent in the powders. Today, surface coating or modification technologies are widely used for the production of functional materials, including ceramics, electronics, medicine, food, cosmetics, and special chemicals [10, 11]. Most of the commercial powder coatings are done by wet methods such as spray coating, dip

coating, spinning disc coating, chemical deposition, and sol-gel processes. The wet coating method is mainly used to create a film or barrier between the particles to be coated and their surroundings. The coating agents used for this purpose generally consist of substances that can be dissolved in an organic solvent [12]. A discrete or a continuous coating can be obtained depending on the preference of equipment and a variety of operating conditions, including processing time, the weight fraction of the modifier agent to particles to be coated, and the surface properties of the particles used [10, 11, 13, 14].

The industrial applications of water-soluble borates are limited in aqueous systems and cause some application failures unless preventive precautions against interaction with water are taken. The high-cost fritting process is the only industrial method currently applied to make water-soluble borates insoluble. Despite its commercial importance, an industrially alternative approach to the fritting process to prevent solubility of borates has not yet been found. However, a few studies on the production of lower-cost calcined borate, as an alternative approach, are available in the literature [15].

Although coating techniques have been identified as appropriate for the treatment of many oxides surfaces, there has been no study in the literature on the surface coating of borates until recently. On the other hand, the recent studies on the dry coating of anhydrous borax powders with magnesium stearate [16] and stearic acid [17] it has been found that promising results to overcome the above-mentioned restrictive conditions. However, to reduce the solubility of anhydrous borax in water, there is a still need in the coating process for improvement by adjusting the process parameters such as the modifier agent and its amount, and coating environment.

In this study, surface modification of anhydrous borax powders was studied to reduce their solubility in aqueous media. To achieve this goal, unlike our previous studies, stearic acid, which is cheaper and pure than magnesium stearate, as the modifying agent, and wet coating environment instead of a dry one, which causes some adverse effects on particle size and morphology of powders, was used as a coating medium. The main idea is that the coating with the dissolved stearic acid will delay the transformation of borates into hydrate forms, hence decreasing solubility and increasing the durability in aqueous systems. A constant amount of modifier agent and constant coating periods in the closed coating environment were used to accomplish this goal. The processed powders were characterized by their wettability properties.

2. Material and Method

Anhydrous borax (ABX) powders with a fineness of less than 500 microns and high purity (99 %) were supplied from Eti Mining Plants. Before the coating process, ABX powders were ground via dry milling to get the particles less than 100 μm . Their measured d_{10} , d_{50} , and d_{90} values were 6.5 μm , 40.6 μm , and 100.6 μm , respectively, and BET surface area was 1.00 m^2/g . The fatty acid used as a coating agent was stearic acid (SA), which is a fine-sized lubricous and cohesive powder widely used in the pharmaceutical formulation as a lubricant and was supplied by As Kimya (İstanbul). SA was directly used without any enrichment, purification, or grinding. The main characteristics of the SA powders are given in Table 1.

Table 1. Technical data of stearic acid

Property	Value
Formula	$\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$
M_w (g/mol)	284.47
Boiling point (°C)	383
Melting point (°C)	69.08
Density (gr/cm ³)	0.941
Solubility in water (g/100 mL) at 25 °C	0.034

2.1. Wet Coating of ABX Powders with SA

The following procedure was carried out for surface modification of ABX powders by a wet coating method. SA powders were dissolved in water first in order to perform the coating process. The SA powders included in 100 mL of water in a beaker were placed on a hot plate of a magnetic stirrer and then mixed at 750 rpm and 80 °C to dissolve the SA. 10g ABX powder was added to the mixture of SA powders of solution and stirring was continued for 1 hour at 80°C 750 rpm. After the coating took place, the solutions were filtered with filter paper, and the powders deposited on the filter paper were dried at 50°C for 48 hours. The dried powders were shaped with the help of a hydraulic press and then analyzed. The coating durability of the surface-treated powder was measured by the washing test. The schematic presentations of the experimental set-ups used in the experiments are shown in Figure 1.

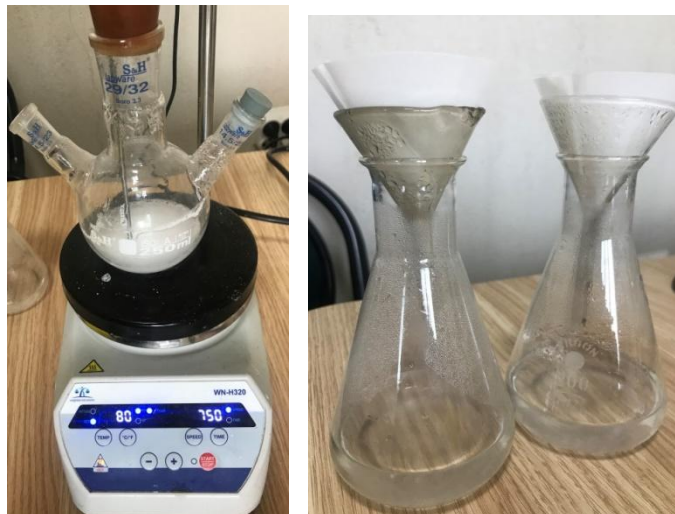


Figure 1. Experimental set-ups for wet-coating process and filtration process

In this research study, surface wettability was accepted as a success criterion for surface modification of anhydrous borax powders by a wet coating method. The contact angle measurements for surface wettability were performed.

2.2. Characterization of Surface-Coated ABX Powders

2.2.1. Wettability measurements

In order to determine the effect of SA coating on mitigating the water interaction of ABX, the wettability tests were performed on ABX samples before and after wet coating treatment. The wettability of the samples was measured at 25 °C by the sessile drop method using an optical tensiometer (KSV Attension ThetaLite TL 101). Wettability measurements were carried out by measuring the contact angle of the water dropped onto the surfaces of the samples prepared by pressing from ABX powders as tablets. The tablet discs with a 1.5 cm diameter were made by compression under a load of 10 kN using a uniaxial manual hydraulic press and labeled discs were kept in a desiccator until contact angle measurements. The analyses were repeated three times for each sample, and average values were obtained. In the measurements, the contact angle values in the 2nd second were taken into consideration.

2.2.2. FTIR measurements

In order to detect possible structural changes after the dry coating and washing process, Fourier-transform infrared (FT-IR) was used. Infrared spectra of surface coated, uncoated, and washed ABX samples were imaged using a Perkin Elmer Spectrum BX spectrophotometer with a resolution of 4 cm⁻¹ from 4000 to 500 cm⁻¹.

3. Results and Discussion

3.1. Surface Wettability of SA-Coated ABX Powders

The contact angle measurements of the samples that are untreated; surface treated and washed for 60 min after coating are listed in Table 2 and Figure 2. As indicated in the table, the contact angles of untreated ABX powders were measured as 18°. Surface coated powders were measured to give a contact angle of 92°. The high measured value of contact angle for the surface-coated sample provided a significant increment in hydrophobicity compared with that of uncoated ABX. This situation is because stearic acid in an effective manner decreases the free energy of the ABX surfaces because of the entity of the -CH₂ groups on the surface of ABX. Considering the contact angle of the sample measured after washing, the coating integrity was not greatly affected. Consequently, after the washing process, the samples retained their hydrophobic properties.

Table 2. Contact angles of SA-coated, uncoated, and washed ABX powders

Processing Period (min.)	Amount of SA (wt.%)		Washing Process (60 min.)
	0	2	

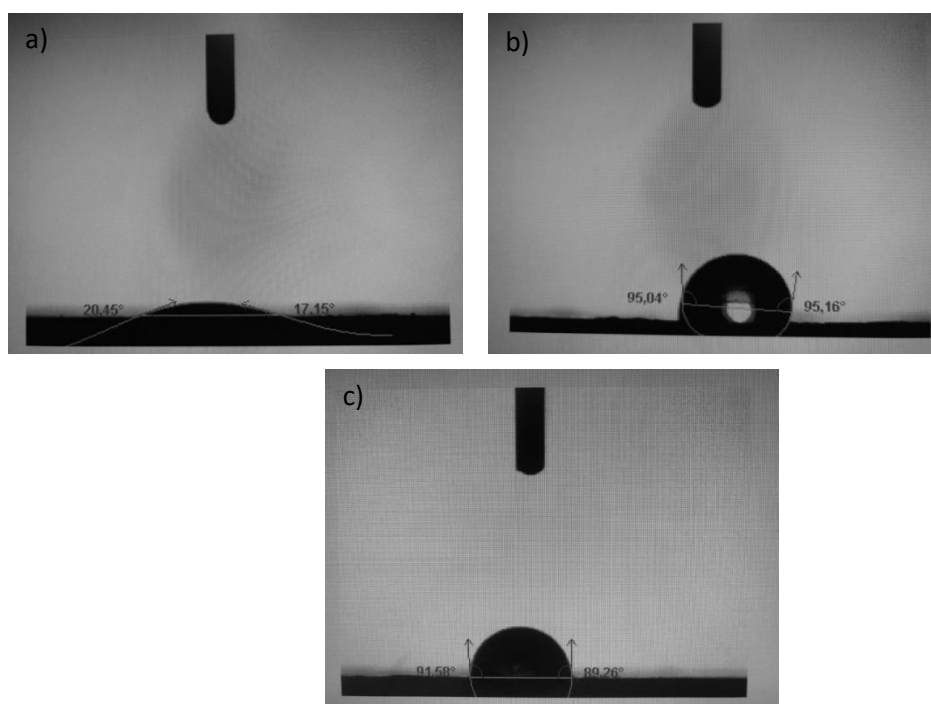


Figure 2. Contact angle measurements of a) untreated b) SA coated, and c) washed ABX specimens.

3.2 FT-IR Spectroscopy

FT-IR spectroscopy is a practical analysis instrument to examine the interaction between active groups at the molecular level. The FT-IR spectra of uncoated, surface-coated, and washed ABX samples are shown in Figure 3. The IR spectra of all samples expose the same bands in the wavelength between 700-1600 cm^{-1} , which are the distinctive vibrations of borax. The weak band at 709 cm^{-1} demonstrates the B-O-B ring bending. The bands at 825, 997, 1076, and 1132 cm^{-1} are assigned to the stretching of tetragonal (BO_4) units. The bands seen at 945, 1283, 1337, and 1426 cm^{-1} wavelengths are attributed to the stretching of trigonal boron (BO_3) groups. These assignments are coherent with the pertinent literature.

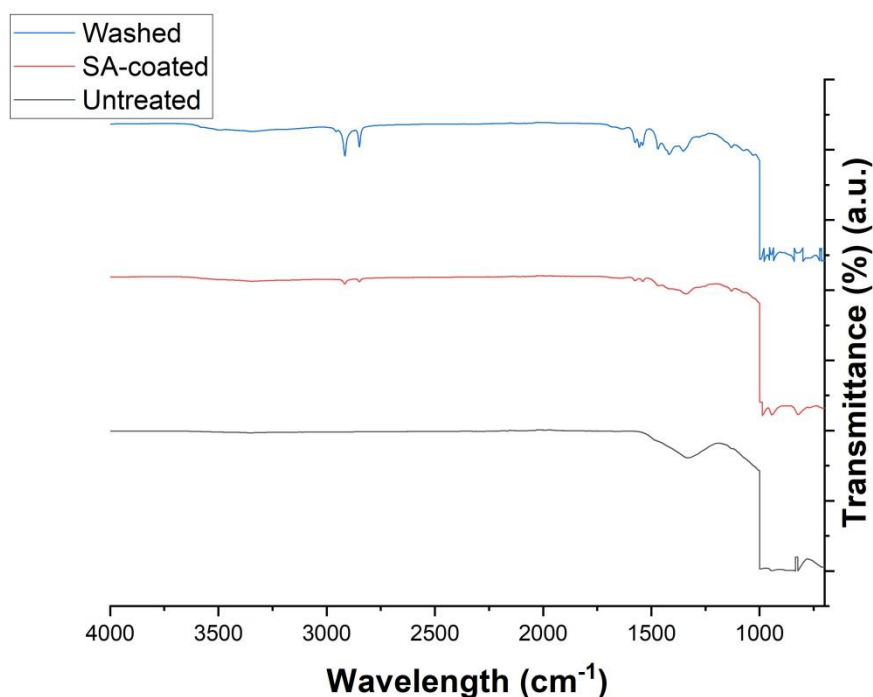


Figure 3. FT-IR spectra of surface-coated and uncoated and washed ABX samples.

Stretching vibrations seen at wavelengths of 2800-2950 cm^{-1} in coated and washed samples are indicative of the stearic acid coating on the surface of ABX powders. Stretching peaks became more clarified in the washed samples. Additionally, the bands at 1467 and 1561 cm^{-1} are assigned to stretching vibrations in the $\text{CH}_3(\text{CH}_2)_{16}\text{COO}^-$ groups. Stretching seen in these regions also proves that the stearic acid is on the ABX surface. These findings are consistent with the result obtained by Focke et al. [18] and Qing et al., [19] respectively. No additional and shifted bands were also monitored in the spectra of SA-coated ABX, and this remarks that there is no chemical interaction between SA and ABX, thus evidencing the inertness of ABX.

4. Conclusions and Recommendations

The experimental studies aimed to decrease anhydrous borax's solubility in water by covering it with hydrophobic stearic acid. The coating success was evaluated in terms of contact angle measurements. With the SA coating, the powders were given hydrophobic properties and the contact angle was increased from 18° to 95° .

The obtained findings have some differences from the results reported in the previous work [16], [17]. Studies of stearic acid and magnesium stearate coating on ABX powders' surfaces by the dry method have shown that it provides different physical properties than its pristine form. When wettability properties of ABX powders were evaluated together, the dry-coated ABX powders with 1 wt. % SA for 60 min and 1 wt. % Mg-St for 120 min were found to give the best results in both behaviors. The minimum solubility values for the same samples were measured at 8.6 % for stearic acid coating and 10 % magnesium stearate coating. This result showed that the stearic acid to reduce the water solubility of ABX would be better as a coating agent than magnesium stearate, and the lower solubility

values at the shorter processing times could be achieved with stearic acid than that of magnesium stearate. Anhydrous borax surfaces are also highly hydrophilic (25°), and their surface wettability was altered to hydrophobic via dry coating with stearic acid (99°) and magnesium stearate (115 °).

Notably, in comparison with the results of our previously presented dry coating of anhydrous borax [[16], [17], it was understood that when the stearic acid is coated on the anhydrous borax surfaces by the wet method, lower solubility values 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.

This study presents physical changes in the properties concerning the wet coating of anhydrous borax powders through stearic acid addition. Besides, this study presents changes in the physical properties of anhydrous borax powders after wet coating with the addition of stearic acid and after washing. Anhydrous borax is a water-soluble powder and could be altered to a poorly soluble state via wet coating with stearic acid. The washing test shows that the SA powders were coated to the ABX powders' surface, as their hydrophobic effects are maintained even after they were washed. The deterioration in the coating properties resulting from the washing treatments indicates that the coating is achieved by physical adsorption mechanism rather than by chemical bonding, and is proven by FTIR analysis. The contact angles of the ABX powders were treated with 2 wt. % SA for 60 were greater than 90°, i.e., the surfaces are hydrophobicised. After the washing process, although the hydrophobic properties are preserved, it decreases to 89° and there is a slight loss.

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