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Surface coating of micronized calcite ($CaCO_3$) with stearic acid via an attritor mill

Mekanik kuru kaplama yoluyla mikronize kalsitin ($CaCO_3$) stearik asit ile yüzey modifikasyonu

Ahmad Farid Ehsan[1], **Öner Yusuf Toraman**[2*]

[1] *Niğde Ömer Halisdemir University, Graduate School of Natural and Applied Sciences, 51240, Niğde Türkiye*
[2] *Niğde Ömer Halisdemir University, Mining Engineering Department, 51240, Niğde, Türkiye*

Abstract

In this study, the surface coating (modification) of micronized calcite ($CaCO_3$, d_{50}=135 µm) in a stirred media (bead) mill with stearic acid was investigated. As a result of 15 min grinding and 5 min coating experiments, a product with d_{50}=2.15 µm and specific surface area of 3.21 m^2/cm^3 was obtained. The activation rate of this final product as an indicator of coating rate was 97.7%. According to the optimum coating results, the stearic acid rate was determined as 1%, the modification time was 7.5 min, the ball load was 900 g and the stirring speed was 600 rpm.

Keywords: Calcite, Stearic acid, Surface modification, Dry coating, Active ratio

Öz

Bu çalışmada mikronize kalsitin ($CaCO_3$, d_{50}=135 µm) stearik asitli karıştırmalı ortam (bilyalı) değirmende yüzey kaplaması (modifikasyonu) incelenmiştir. Yapılan 15 dak öğütme ve 5 dak kaplama deneyleri sonucunda d_{50}=2,15 µm ve özgül yüzey alanı 3.21 m^2/cm^3 olan bir ürün elde edilmiştir. Kaplama oranının bir göstergesi olarak nihai ürünün aktive oranı %97.7 elde edilmiştir. Optimum kaplama sonuçlarına göre stearik asit oranı %1, modifikasyon süresi 7.5 dak, bilya yükü 900 gr ve karıştırma hızı 600 rpm olarak belirlenmiştir.

Anahtar kelimeler: Kalsit, Stearik asit, Yüzey modifikasyonu, Kuru kaplama, Aktive oranı

1 Introduction

Calcite ($CaCO_3$) (calcium carbonate), known as the world's most useful (useful and versatile) mineral, is an industrial mineral that has a crystal structure in various shapes, has a glassy shine, is colorless, has medium hardness and low density, and is easily ground. Calcite, which is abundant in nature, is the main component of carbonate sedimentary rocks (chalks-limestones) and marbles formed as a result of their metamorphism. Calcite ($CaCO_3$), one of the important industrial minerals of our region (Niğde, Türkiye), is widely used in many areas of industry as a cheap filler and to give various properties to products. This industrial mineral, which is used especially in the paper, plastic, rubber and paint industries, is required to have some physical and physico-chemical properties, and features such as grinding to micronized dimensions (fineness), hydrophobic structure and high degree of whiteness stand out.

Today, in the coating of calcite, conventional mills/equipment such as Raymond mills, pin mills and heated stirring equipment are widely used. Moreover, there are also mills where surface coating is performed by mechanical activation (such as vibrating, jet, orbital and stirred ball mills). The mechanical activation process is carried out to create particles of certain sizes and shapes, to increase the surface area, and to encourage the formation of defects in the solids that will be necessary for subsequent processes such as chemical reactions. In industrial facilities, as the grain size decreases, the amount of energy consumed increases as the resistance of the grains to breaking increases. For this reason, ways to reduce the maximum size with the least amount of energy have been investigated. The term “high energy grinding” in mechano-chemistry is used to emphasize the characteristic of the applied grinding equipment. The mechanical energy provided by high-energy grinding turns into chemical energy and provides the interactions necessary to initiate a chemical reaction. Thus, with the deterioration of crystal structures, the number of particles increases, new active surfaces are formed, and the mass transfer required for solid state reaction inputs increases [1, 2].

Various modification studies of calcium carbonate have been carried out in a stirred ball mill under wet conditions through mechano-chemical surface modification. Rezaei et al. [3] investigated the effect of sulphate ions on the surface modification of calcite with three different fatty acids. Then, the adsorption values of fatty acid types were examined and TGA analysis was used to evaluate the experimental results. Rezaei et al. [4] performed modification experiments on mica and calcite samples using four different fatty acids. TGA was used to evaluate the experimental results. Mihajlovic et al. [5] conducted surface modification studies of a calcite sample with a total surface area of 4.8 m^2/g using stearic acid. The products were examined by performing analyses such as TGA, DTA and SEM on the experimental products obtained from all stearic acid ratios studied. They concluded that 1.5-2% stearic acid would be sufficient for calcite coating in the proposed process. In the study carried

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[*] Sorumlu yazar / Corresponding author, e-posta / e-mail: otoroman@ohu.edu.tr (O. Y. Toraman)

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out by Uçurum and Malgır [6] using micronized calcite with d_{50}=2.45 µm, the activation rate of five different stearic acid types, which is an important indicator in coated calcite, as well as the coating rate, color parameters and tap densities were used for comparative analysis in a vertical stirred ball mill. There are also successful coating studies performed with different mill types in the literature. In a study conducted by Toraman and Eren [7], a coating efficiency of up to 88% was obtained in coating studies carried out in a high-speed (3000 rpm) stirred mill. In a study conducted by Toraman et al. [8], mechano-activated surface modification with stearic acid and sodium oleate mixture as modification reagent incorporated with dry ultra-fine grinding in a tumbling ball mill was investigated. In another study conducted by Toraman et al. [9], the results obtained indicate that the hydrophilic surface of calcite becomes hydrophobic with 1% stearic acid by planetary ball milling.

In this study, calcite was treated with different amounts of stearic acid by the dry coating method. The aim of these investigations was to determine the influence of the modification method by using stirred media mill on the coating properties of obtained products.

2 Materials and methods

2.1 Materials

Calcite ($CaCO_3$) powders of purity 98% was supplied by Mertaş Co. (Turkey). The particle size of the as-received calcite powders is under 250 µm and the d_{50} value (average particle size) of powders is about 135 µm (Figure 1). Stearic acid, as coating reagent, is a fine, white, greasy and cohesive powder widely used in the pharmaceutical formulation as a lubricant (Table 1).

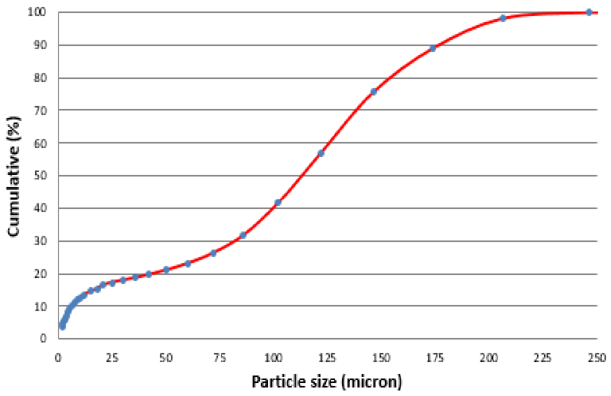

Figure 1. Particle size distribution (PSD) in the feed sample

Table 1. Chemical reagent used in the study

Reagent	Density (g/cm^3)(20^{o}C)	Molecular formula	Molecular weight (g/mol)
Stearic acid	0.94	$C_{18}H_{36}O_2$	284.5

Some physical and general properties of the calcite sample taken from Mertaş Co. (Niğde, Türkiye) are given in Table 2. According to these values, the whiteness of calcite is 98.5%, its brightness is 97%, its pH is 8.7 and its oil absorption rate is 18 g/100g. As can be seen from the table, the calcite used in experimental studies shows low hardness, low density, low moisture, high whiteness and brightness properties.

Table 2. Physical and general properties of the calcite sample

Parameter	Value
Moh's hardness	3
Density	2.7 g/cm^3
Whiteness	98.5%
Brightness	97%
pH	8.7
Humidity	0.3%
Oil absorption	18 g/100 g
DOP oil absorption	34 g/100 g

The elemental contents of calcite are listed in Table 3. It can be concluded that calcite mainly consists of around 98.4% $CaCO_3$ and other minor impurities. Although there is a small amount of MgO in the sample, components such as Fe, which reduce its color and purity, are at very low levels. The Si content in the sample should also be very low, so it does not complicate the grinding process and does not cause wear problems.

Table 3. Chemical characteristics of the calcite sample

Chemical assay	Calcite
CaO, %	55.4
MgO, %	0.3
Fe_2O_3, %	0.02
SiO_2, %	0.06
Al_2O_3, %	0.02
TiO_2, %	0.04
LOI, %	42.4

Table 4 shows the physical properties of the grinding media. Beads formed from a mixture of alumina and silica contain predominantly Al_2O_3. Its specific gravity is 3.6 t/m^3 and HV hardness is around 1200 kg/mm^2.

Table 4. Physical properties of grinding media (alumina beads)

Composition	Specific gravity (kg/m^3)	Hardness, Hv (kg/mm^2)
Al_2O_3 (95%) +SiO_2 (5%)	3600	1200

2.2 Methods

2.2.1 Grinding and coating studies

In this study, a dry procedure as a one-step handy route was once desired for grinding and coating powders concurrently through the usage of a stirred media mill (attritor) (Figure 2). This laboratory-scale milling device has the working chamber with a jar (750 ml) filled with alumina balls (3-4 mm diameter) and positioned on the rotating basis plate (Figure 3).

2.2.2 *Characterization*

2.2.2.1 *Measurement of PSD*

Particle-size distribution analysis of coated and uncoated $CaCO_3$ powder samples was performed using a laser diffraction particle size analyser (Malvern Instruments Ltd, Malvern, UK). Wet or liquid dispersion is the most common method of sample dispersion for laser diffraction particle size measurements. Wet method was applied in particle size measurements in this study.

Figure 2. Stirred bead mill used in the experiments

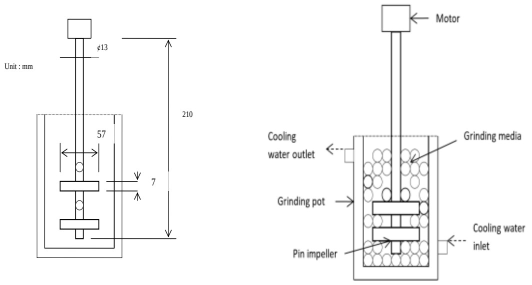

Figure 3. Dimensions and shape of grinding mill pot of stirred bead mill

Experimental conditions are shown in Table 5.

Table 5. Experimental conditions

Mill type	Union Process S01 attritor
Mill capacity	750 ml
Rotation speed of stirrer	600 rpm (shaft)
Mill material	Ceramic (Al_2O_3)
Shaft material	Stainless steel with Colmonoy arms
Diameter of the balls	3.5-4 mm
Ball mass per milling run	1000 g
Ball-to-powder ratio	17:1
Sample mass	60 g
Stearic acid	1%
Calcite:	
Density	2700 kg/m^3
Hardness, Mohs	3
Size range	-250 µm
Volumetric surface area, Sv	0.39 m^2/cm^3
Temperature	Room temperature

2.2.2.2 *Measurement of color properties*

It was used a Datacolor Elrepho device for color properties of coated and uncoated $CaCO_3$ powder samples.

2.2.3 *Determination of the coating efficiency*

The active ratio used to be derived through measuring the quantity of suspended $CaCO_3$ in accordance to the together one of-a-kind polar-nonpolar appeal when modified $CaCO_3$ used to be delivered to deionized water. It was derived using the following equation (Equation 1):

$$A = M_f / (M_f + M_s) \times 100\% \quad (1)$$

where A (%) denotes the active ratio; M_f denotes the weight of $CaCO_3$ from the upper suspended layer (g); and M_s denotes the weight of $CaCO_3$ from the lower sediment layer (g) [10].

3 Results and discussion

3.1 *Grinding studies*

Stirring speed and grinding time are effective parameters in grinding with a stirred ball mill. For grinding and coating, the highest speed (600 rpm) was used because the mill used in the experimental studies was a low speed. Grinding time was taken as 10-20 minutes and coating time was taken as 5 minutes.

As a result of 10-20 minutes of grinding in the stirred ball mill, it was understood that 15 minutes of grinding gave optimum results. Under these conditions, d_{50}=2.3 µm and the specific surface area was 3.1 m^2/cm^3. Table 6 shows the properties of $CaCO_3$ powders obtained after grinding. Three experiments were performed for each parameter and the average was taken. The size distribution curves of the products obtained depending on the grinding time for uncoated products are shown in Figure 4.

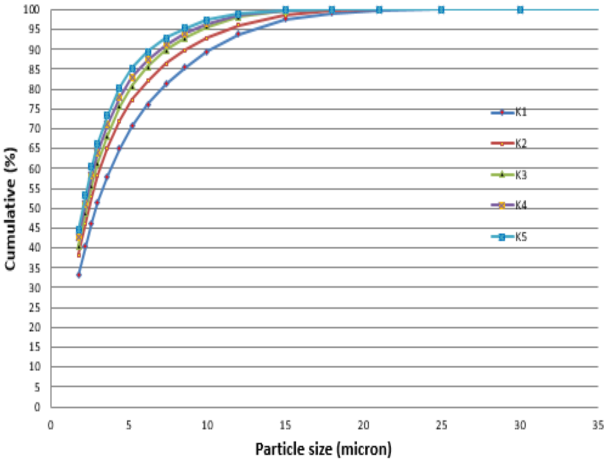

Figure 4. Variations in the PSD of uncoated products with grinding time

3.2 *Grinding + coating studies*

Table 7 shows the properties of $CaCO_3$ powders obtained after grinding + coating. As a result of 15-minute grinding and 5-minute coating experiments, a product with d_{50}=2.15 µm and specific surface area of 3.21 m^2/cm^3 was obtained, and the activation rate of this product was obtained as 94.75%. Three experiments were performed for each parameter and the average was taken.

Table 6. Characteristics of $CaCO_3$ powders

Sample code	Grinding time (min)	Particle size (µm)				Specific surface area, m^2/cm^3
		d_{10}	d_{50}	d_{97}	<2 µm, %	
K00	Feed material	5.99	134.99	240.89	4.28	0.39
K01	10.0	0.89	2.89	14.60	36.68	2.71
K02	12.5	0.84	2.43	13.17	42.24	2.98
K03	15.0	0.82	2.27	11.09	44.65	3.11
K04	17.5	0.81	2.14	10.48	46.91	3.21
K05	20.0	0.79	2.05	9.78	48.85	3.30

Table 7. Characteristics of $CaCO_3$ powders (coated)

Sample code	Grinding time (min)	Coating time (min)	Particle size (µm)				Specific surface area, m^2/cm^3	Active ratio, %
			d_{10}	d_{50}	d_{97}	<2 µm, %		
K06	10.0	5	0.83	2.30	10.73	44.05	3.09	94.30
K07	12.5	5	0.82	2.23	10.86	45.19	3.13	94.45
K08	15.0	5	0.81	2.15	10.06	46.84	3.21	94.75
K09	17.5	5	0.80	2.14	10.35	47.02	3.22	94.25
K10	20.0	5	0.79	2.04	9.90	49.17	3.32	91.20

The size distribution curves of the products obtained depending on the grinding time for coated products are shown in Figure 5.

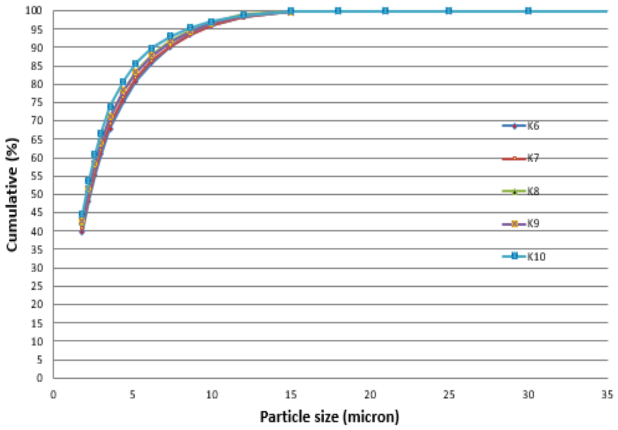

Figure 5. Variations in the PSD of coated products with grinding time

The color properties of micronized uncoated and coated calcite samples are shown in Table 8. As can be seen from the table, no negative effects were observed on color values after coating.

Table 8. Color characteristics of micronized (uncoated) and coated calcite samples

Sample code	C2 Ry brightness	E313 whiteness	E313 yellowness	CIE L*a*b*		
				L*	a*	b*
K03	96.47	93.65	1.18	0.83	2.30	10.73
K08	96.06	93.78	0.95	0.79	2.04	9.90

Figure 6 shows the differences in the PSD of coated product (K08) (15 min grinding time + 5 min coating time) and uncoated (K03) material (15 min grinding time).

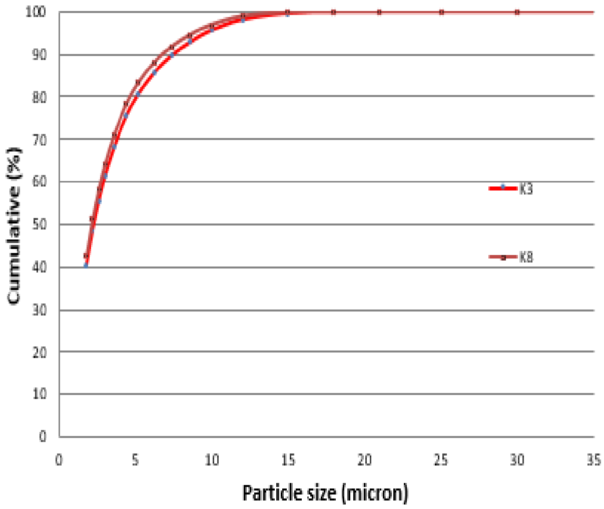

Figure 6. Differences in the PSD of coated product (K08) and uncoated (K03) material (15 min grinding time + 5 min coating time)

3.3 *Evaluation of coating*

Calcite coating parameters are shown collectively in Table 9. In studies where the amount of stearic acid, coating time, ball load and mixing speed were tested, the following ranges were tested: 0.6-1.4% stearic acid, 2.5-12.5 min coating time, 600-1000 g ball load, 200 g ball load and 600 rpm rotation speed was examined. Therefore, five levels were studied for each parameter.

In optimum conditions (K19), the active ratio was found to be approximately 97.66%. In experimental studies, first the stearic acid ratio was selected as a parameter, and then the modification (coating) time, ball charge and stirring speed were continued. Each parameter was evaluated by measuring the coating speed of the resulting product. Three experiments were performed for each parameter and the average was taken.

Table 9. Characteristics of $CaCO_3$ powders (coating parameters)

Sample code	Stearic acid (%)	Coating time (min)	Ball loading (gr)	Stirrer speed (rpm)	Active ratio, %
K11	1.4%	5	800	600	93.49
K12	1.2%	5	800	600	90.84
K08	1.0%	5	800	600	94.75
K13	0.8%	5	800	600	86.52
K14	0.6%	5	800	600	65.90
K15	1.0%	12.5	800	600	-
K16	1.0%	10	800	600	95.32
K17	1.0%	7.5	800	600	96.50
K08	1.0%	5	800	600	94.75
K18	1.0%	2.5	800	600	94.89
K08	1.0%	7.5	1000	600	96.50
K19	1.0%	7.5	900	600	97.66
K20	1.0%	7.5	800	600	97.35
K21	1.0%	7.5	700	600	96.17
K22	1.0%	7.5	600	600	96.32
K19	1.0%	7.5	900	600	97.66
K23	1.0%	7.5	900	500	95.34
K24	1.0%	7.5	900	400	95.15
K25	1.0%	7.5	900	300	-
K26	1.0%	7.5	900	200	-

Table 10. Optimal coating results (K19)

Parameters	Optimal conditions
Stearic acid	1%
Coating time	7.5 min
Ball loading	900 g
Stirrer speed	600 rpm

This final result additionally explains why stearic acid is one of the main chemical agents for the surface modification of $CaCO_3$, which has a heterogeneous surface with exposed polar cationic sites [11].

3.3.1 SEM results

SEM images of the products before and after coating are shown in Figure 7. The SEM image of the original calcite sample (Figure 7a) shows that the mineral is large in size (maximum 250 µm) and has a specific crystal shape (cubic). SEM image (K03) of the micronized product in the photo (d_{50}=2.27 µm) obtained after 15 min of grinding (without coating). SEM image of the (coated) product obtained after 5 minutes of coating (d_{50}=2.15 µm) (K08) in Figure 7b. Figure 7c is shown. It is seen that the crystal structure is partially disrupted by grinding and acquires an amorphous (irregularly shaped) structure. SEM images of the product (K19) obtained under optimum conditions (1% stearic acid, 7.5 min coating time, 900 g ball load, 600 rpm mixing speed) are also shown in Figure 7d.

4 Conclusion and suggestions

As a result of 10-20 minutes of grinding in the stirred ball mill, it was understood that 15 minutes of grinding gave optimum results. Under these conditions, d_{50}=2.3 µm and the specific surface area was 3.1 m^2/cm^3. As a result of 15-minute grinding and 5-minute coating experiments, a product with d_{50}=2.15 µm and specific surface area of 3.21 m^2/cm^3 was obtained, and the activation rate of this product was 97.7%.

According to the optimum coating results, the stearic acid rate was determined as 1%, the modification time was 7.5 minutes, the ball load was 0.9 kg and the mixing speed was 600 rpm.

After this, the thermal and mechanical properties of the composite obtained by using the coated calcite product as a mineral filler in the polymer matrix will be investigated.

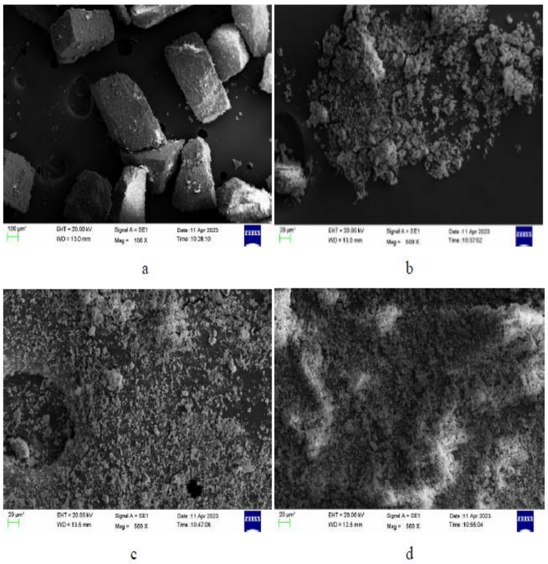

Figure 7. SEM images of calcite samples: Original calcite (uncoated) (a); ground uncoated (K03) (b); ground coated (K08) (c); ground coated (K19) (optimal) (d)

Conflict of interest

The author declares that there is no conflict of interest.

Similarity rate (iThenticate): 17%

References

[1] A. Nasser, U. Mingelgrin, Mechanochemistry: A review of surface reactions and environmental applications. Applied Clay Science, 67-68, 141-150, 2012. https://doi.org/10.1016/j.clay.2011.11.018.

[2] T. Tunç, H.Ö. Toplan, K. Yıldız, Thermal behavior of mechanically activated sepiolite. The Online Journal of Science and Technology, 3(2), 187-193, 2013.

[3] K. A. Rezaei Gomari, A. A. Hamouda, R. Denoyel, Influence of sulfate ions on the interaction between fatty acids and calcite surface. Colloids and Surfaces A: Physicochemical and Engineering Aspect, 287(1-3), 29-35,2006a. https://doi.org/10.1016/j.colsurfa.2006.03.018.

[4] K.A. Rezaei Gomari, R. Denoyel, A. A. Hamouda, Wettability of calcite and mica modified by different long-chain fatty acids (C_{18} acids). Journal of Colloid and Interface Science, 297(2), 470-479, 2006b. https://doi.org/10.1016/j.jcis.2005.11.036.

[5] S. Mihajlovic, Z. Sekulic, A. Dakovic, D. Vucinic, V. Jovanovic, J. Stojanovic, Surface properties of natural

calcite filler treated with stearic acid. Ceramics, 53(4), 268-275, 2009.

[6] M. Uçurum, E. Malgır, Stearik asit çeşidinin kalsit kaplama verimi üzerine etkisi. Çukurova Üniversitesi Mühendislik Mimarlık Fakültesi Dergisi, 32(2), 137-144, 2017. https://doi.org/10.21605/cukurovaummfd.358399

[7] Ö. Y. Toraman, E. Eren, Kalsitin Dikey Karıştırmalı Bilyalı Değirmende Kaplanması ve Plastik Kompozitte Performansının Araştırılması, II. International Eurasian Conference on Science, Engineering and Technology (EurasianSciEnTech 2020), p.1010-1022, 7-9 October 2020, Gaziantep-Turkey.

[8] O. Y. Toraman, O. Ersoy, H. Köse, Surface Modification of Calcium Carbonate by Tumbling Ball Milling with Stearic Acid, 6th International Conference on Materials Science and Nanotechnology for Next Generation (MSNG 2019), p.233-236, 6-18 October 2019, Niğde-Turkey.

[9] Ö. Y. Toraman, O. Ersoy, M. Uçurum, Mechano-Activated Surface Modification with Fatty Acid in Planetary Ball Mill, 16th International Mineral Processing Symposium (IMPS'18), Edited by M. Ü. Atalay, A. İ. Arol, N. E. Altun, p.13-20, 23-25 October 2018, Bodrum-Turkey.

[10] M.A. Osman, U.W. Suter, Surface treatment of calcite with fatty acids: Structure and properties of the organic monolayer. Chemistry Materials, 14(10), 4408-4415, 2002. https://doi.org/10.1021/cm021222u

[11] T. Ahsan, B.A. Colenutt, K.S.W. Sing, Gas chromatography of pure and surface-modified precipitated calcium carbonate. Journal of Chromatography A., 479, 17-25, 1989. https://doi.org/10.1016/S0021-9673(01)83313-6