APPLICABILITY OF STATISTICAL PROCESS CONTROL FOR SURFACE MODIFICATION PLANT AND PROPERTIES OF COATED CALCITE

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Abstract: Due to its low surface energy, easy dispersion, high homogeneity and whiteness, coated (modified) calcite has increasingly been used in many industries, particularly in the plastics. The demand for this product will most likely increase in the years to come. Surface modification of calcite with a fatty acid would lead to a great expansion of industrial applications. The color values of coated calcite products are the first quality parameter. Therefore, it is very important to monitor the variations in the color characteristics of the coated calcite products. It is well known that statistical process control (SPC) techniques have been widely used in the many industries. In the present study, the surface of micronized calcite was coated with stearic acid by a pin mill. X-R control graphics and process capability index were applied for monitoring variations in quality control based on color parameters (L*, a* and b*) for the pin mill plant. In addition, active ratio, particle size distribution, whiteness parameters, BET, FTIR, TGA-DTA and SEM were then determined on a coated calcite sample. The results show that the pin mill plant seems under control and the coating technology is very effective in modifying the surface of micronized calcite products.

Introduction

Finely ground calcium carbonate has been widely applied as a filler material. However, it is essential to make the hydrophilic calcium carbonate particles compatible with the matrix, such as plastics, rubber and adhesives. Surface modification, a key process in functional powder preparation, is commonly used to achieve this purpose. Surface modification of fillers in plastics, rubber and adhesives

may improve their mechanical and physicochemical properties, increase filler loading in the matrix, and lower producing cost. The conventional surface modification technology, consisting of the heating mix modification and the packing modification method, has been applied widely in treatment of the fillers and pigments (Ding et al., 2007). Pin mills are also used to treat the surface of mineral fillers. The calcite coating process consists of three main stages. The first of these is the stearic acid melting unit, the second is the micronized calcite feeding unit and the third is the pin mill unit in which the micronized calcite and melted stearic acid are mixed together and the coating process takes place. The modification of calcite includes coating stearic acid on the surface of calcite particles to improve the homogenization, dispersion etc. powder of the mineral according to the application requirements.

The aspect and color of the calcite surface is the first quality parameter evaluated by consumers and is critical in the acceptance of the product. Industrial applications require specific properties and characteristics. Among the most valuable characteristics is the color, a function of the parent rock and its alteration (Murray, 2002). In polymineral natural samples with complex crystallochemistry, the study of color is more complicated than in minerals of high purity (or even synthetic ones) where diffuse reflectance spectroscopy techniques are employed (Burns, 1993). An organization called the Commission International Eclairage (CIE) determined the standard values that are used worldwide to measure color. The values used by CIE are called $L*$, $a*$, and $b*$, and the color measurement method is called CIELab. Symbol $L*$ represents the difference between light (where $L* = 100$) and dark (where $L* = 0$) $a*$ represents the difference between green ($-a*$) and red ($+a*$), and $b*$ represents the difference between yellow ($+b*$) and blue ($-b*$) (Sharafudeen, 2012).

In the mineral industry, quality control procedures are primarily concerned with the quality of conformance which aims at meeting consumer desired specification limits. The problem of quality control is of decisive importance in the mining industry due to inhomogeneous formation of ore deposits. Particularly in the cases of ore deposits which are formed under complex geological phenomena, the process of mineralization largely affects the grade distribution. This leads to formation of deposits which are usually characterized by wide variation of ore types and grades. The task of a quality control practitioner is to homogenize the different ore qualities during extraction in order to satisfy consumer's quality requirements. To facilitate their operations, the use of statistical quality control techniques including control charts has been proved to be a major contributing factor in achieving required quality and improving productivity. Through the application of control charts, various assignable causes of quality variation are identified. Many quality control operations in mining deal with controlling more than one variable for meeting the quality specifications. In such cases, an application of the univariate control charts is unsatisfactory as it fails to consider the problem in multivariate situation ignoring correlation structures amongst the variables. Hence, multivariate control charts should be constructed to identify an out of control condition (Bhattacherjee and Samanta, 2002).

Statistical process control (SPC) concept has become very important in chemical and manufacturing industries. Its objective is to monitor the performance of a process over time in order to detect any special events that may occur. By finding assignable causes for them, improvements in the process and in the product quality can be achieved by eliminating the causes or improving the process or its operating procedures (Theodora et al., 1996). The use of statistical process control techniques in mineral processing plants is as important as in many other industries, as management aims for a certain quality, which will enhance reputation and future progress. Control charts are among the most effective means for controlling process control systems via statistical methods in an economical and secure way. Control charts are used for determining quantitative and qualitative variations that occur in a process over a certain time frame (Ipek et al., 1999). To use a control chart such as the X-chart to monitor the process mean or the R-chart to monitor variability, samples are taken over time and values of a statistic are plotted (Woodall, 2000). Control chart type X-R is a very important quality tool. Its determined statistical measures are recorded properties of products obtained as a result of inspections taken randomly from the samples of products in the determined place of the process. The aim of control chart type X-R is to observe and register the changing ability of the characteristics of the researched element of the production process. The example of implementing control chart type X-R shows the possibility of monitoring parameters of the production process according to an idea of defect prevention. Using this method allows monitoring the production process, provides opportunities for cost reduction, and maintains the production process stability (Dudek-Burlikowska, 2011).

Statistical process control studies form the basic tool for obtaining the required process capability confidence levels. The various process capability indices are defined. The term C_p denotes the process potential capability index, and similarly, the term C_{pk} denotes the process performance capability index. C_p gives an indication of the dispersion of the product dimensional values within the specified tolerance zone during the manufacturing process. Similarly, index C_{pk} denotes for the centering of the manufacturing process with respect to the mean of the specified dimensional tolerance zone of the product. Index C_{pk} gives us an idea on whether the manufacturing process is performing at the middle of the tolerance zone or nearer the upper or lower tolerance limits (Sharma and Rao, 2013).

The purpose of this study is to apply statistical process control techniques for a pin mill plant in Turkey, Mikrokal Co. For this purpose, control chart type X-R and process capability indexes were used to color parameters such as L*, a* and b*. The specifications of the coated calcite, on a randomly selected coated calcite sample used in the statistical process control work, were then determined by some tests and analyses (active ratio, particle size distribution, whiteness parameters, BET, FTIR, TG-DTA and SEM).

Experimental

Materials

Turkish calcites are very good with respect to quality and reserves. The most important specification of these is the high $CaCO_3$ percentage and a very low ratio of silica and iron in impurities. The whitest composition of Turkey comprises the calcite reserves in the Nigde-Turkey region. The experimental sample was a finely ground calcite powder (micronized) obtained from the Mikrokal Limited Company, Nigde-Turkey. X-ray diffraction analysis verified that calcite was the sole mineral in the ore. Chemical analysis indicated that the ore was composed of 54.85% CaO and 42.70% CO_2 (Table 1). It is well known that the main impurities of calcite ores are generally silica, iron and magnesium. The material in this experiment has a very low percentage of the impurities such as 0.70% SiO_2, 0.05% Fe_2O_3 and 0.47 MgO. According to the XRD and XRF results, the calcite had a high purity as a starting compound. The mean size (d_{50}) of the sample was 2.45 μm, the specific surface area 5.66 m^2/g. Whiteness measurement of the micronized calcite yielded values of L* = 98.84, a* = −0.01 and b* = 0.67.

Table 1. Chemical composition of calcite

Species	wt.%
SiO_2	0.70
CaO	54.85
MgO	0.47
Fe_2O_3	0.05
Al_2O_3	0.05
Na_2O	0.01
K_2O	0.02
SO_3	≤0.01
CO_2	42.70
LOI	43.20

Methods

In the present study, stearic acid $CH_3(CH_2)_{16}COOH$ was used for the surface modification of calcite powder. The surface modification was performed in an industrial scale pin mill constructed of stainless steel and approximately 75 cm in diameter. The whole surface modification process consists of three steps: stearic acid melting unit, micronized calcite feeding unit, pin mills unit where a small amount (1%) of melting stearic acid and heated micronized calcite are added simultaneously. The main steps of the surface modification process are shown in Fig. 1. Here, although the melting temperature of stearic acid is 69 °C, it is melted at 110 °C to reduce viscosity.
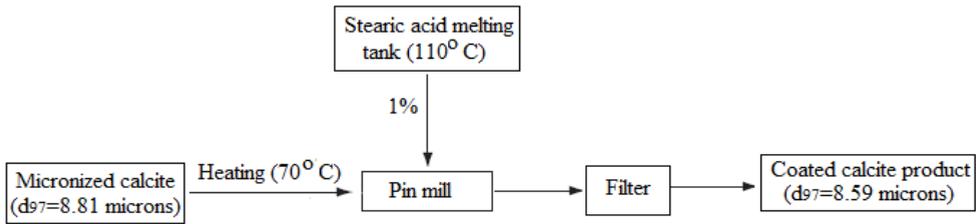
Fig. 1. The modification process main steps of coated calcite with stearic acid

The purpose of this study is to apply statistical process control techniques for a surface modification process (pin mill plant). In the experiment, X and R control chart was established in order to determine whether the results from color analysis coated calcite in a pin mill were under control or not. One day total of 4 samples were collected during consecutive 28 days and the color analysis were conducted so that X and R control charts for L*, a* and b* values of coated calcite products could be formed. By using these color analysis results, the parameters needed to establish X and R control charts were calculated.

Grant and Leavenworth (1980) showed that the X and R control charts should be prepared as follows:

-statistical parameters related to characteristics are computed for each subgroup,
-the averages of ranges of the subgroups are computed as the parameters of a group,
-the three parameters for *X* and *R* control charts are calculated as Central Line *(CL)*, Upper Control Limit *(UCL)* and Lower Control Limit *(LCL)*,
-the X and R control chart is drawn.

Control limit formulas for the most widely used charts are given in Table 2 (Elevli, 2006). These formulas are based on ±3 standard deviations (i.e., 3σ) and use a central line equal to the average of the data used in calculating the control limits. A_2, D_3 and D_4 are factors used in computation of upper and lower control limits depending on the number of items in the sample (Deniz and Umucu, 2010). The factors are taken from Table 2.

Table 2. Control chart limits (Elevli, 2006)

Chart type	Central line	Lower control limit	Upper control limit
Averages, $\bar{X}$	$\bar{X}$	$\bar{\bar{X}}$-A_2*R	$\bar{\bar{X}}$+A_2*R
Ranges, $\bar{R}$	$\bar{R}$	D_3*$\bar{R}$	D_4*$\bar{R}$

In control charts created for quality features of products, the following points are important (Ipek et al., 1999):

-two thirds of the point should be on the central line or near the central line,
-the number of points near control limits should be at minimum level,
-the points should randomly fall below or above central limits and should be balanced,

-there should be no points outside control limits.

Table 3. Constants for use in control limit calculation (Howard, 2003)

Sample Size	A_2	D_3	D_4
2	1.880	-	3.267
3	1.023	-	2.574
4	0.729	-	2.282
5	0.577	-	2.114

The highest and the lowest tolerance ranges were treated as the controlled upper and lower specification limits (USL and LSL, respectively) in the calculation of C_p and C_{pk} values. The indexes are given Eqs. 1 and 2.

$$Cp = \frac{USL-LSL}{6\sigma} \tag{1}$$

$$Cpk = \min[\frac{USL-\mu}{3\sigma}, \frac{\mu-USL}{3\sigma}] \tag{2}$$

where μ denotes the process mean. C_{pk} indicates, in addition, how well the distribution is centered about the nominal (target) value, a property that can better reveal the relationship between the mean and objective values (Chen et al., 2014). C_p controls only the distribution of the process, but C_{pk} controls both the distribution and the average. If C_p and C_{pk} values are below 1, it is obvious that the process is inadequate (Dudek-Burlikowska, 2005; Chase et al., 2008).

The effect of the surface modification was evaluated on a randomly selected coated calcite sample, used in the statistical process control work, by a series of analyses such as active ratio, particle size distribution, whiteness parameters, BET, FTIR, TG-DTA and SEM. In this study, the particle size distribution and values of whiteness color parameters (L*, a*, b*) were determined using Mastersizer 2000 (Malvern) and Elrepho 450x (Datacolor) in the laboratory of Mikrokal Co. Other analyses were performed at Mining Technical Research Institute (MTA) and The Scientific and Technological Research Council of Turkey-Marmara Research Center (TUBITAK-MAM). XRD analysis was made between 2-70° by Cu X-ray tube Bruker D8 advence device. The BET surface area, pore volume and pore diameter measurements in micronized and coated calcite samples were carried out with Nova 2200e Quantachrome. TG-DTA and SEM analyses were performed by using SII EXSTAR 6000 TG/DTA 6300 and FEI Quanta 400 MK2 instruments, respectively. The vibration modes of functional groups of the compound were determined by Fourier transforms infrared (FTIR) analysis. The FTIR spectra were measured in the range of 450–4000 cm^{-1} by the Perkin Elmer Spectrum One.

As a measure of hydrophobicity and surface modification, an active ratio of hydrophobic to non-hydrophobic particles was determined using Eq. 3. The floating test was performed as first characterization study for coated calcite. It is described by

Sheng et al. (2006) as follows: floating test is to measure the ratio of floated product to the overall weight of sample after mixing in water and stirring vigorously. The ratio is called active ratio. The higher the active ratio, the better the modification effect is:

$$AR \ (\%) = [(M_f/(M_s + M_f)] \cdot 100 \qquad (3)$$

where $AR \ (\%)$ is the active ratio, M_f the mass of the floated product and M_s the mass of the sink product (Sekulic et al., 2009).

It is well known that surface modification process is to produce the same size particles and steepness factor (SF) with feed calcite. These terms are of particular importance when considering fine extenders. An additional parameter is the "steepness factor" (SF) of the particle size distribution curve (Strauch et al., 1998). This is the quotient of the d_{50} and the d_{20} (the size of particle such that 20% are finer) values and it defines certain properties in the finished product. The SF can be calculated from the particle size distribution curve of the relevant extender using Equation 4. A curve with an SF greater than 2 is described as "broad", while one with a value less than 2 is "narrow" or "steep" (Werner, 2000)

$$SF = d_{50}/d_{20}. \qquad (4)$$

CIEL*a*b* color system illustration scheme is designed such a way that a constant difference in color, ΔE, is defined by its Euclidean distance, which represents a constant "perceived" color difference independent of the precise location in the color space. The smallest perceivable difference between two colored patches contacting one another is approximately 0.5–1.0 ΔE units (Joiner et al., 2008). ΔE is calculated using Eq. 5 by using L*, a* and b* values (ISO/DIS, 1996)

$$\Delta E = [(L_0 - L*)^2 + (a_0 - a*)^2 + (b_0 - b*)^2]^{0.5} \qquad (5)$$

where the subscript "$_0$" refers to the color reading of the reference sample.

Results

Application of statistical process control (SPC)

At the present time, statistical process control methods based upon the product quality data have been the standard approach to process monitoring. In order to analyze the variation in color parameters such as L*, a* and b* of the coated calcites delivered to the pin mill with control charts, data from 28 days have been gathered. The data arranged as $m = 28$ (number of sample) and $n = 4$ (subgroup) are given in the Table 4, 5 and 6. Control limits for $\bar{X}$ and R charts for color parameters were calculated by using Table 2 and Table 3. The results were given in Table 7.

Table 4. Case study data for L* values

Number of sample	Subgroup 1	Subgroup 2	Subgroup 3	Subgroup 4	X_{mean}	R_{mean}
1	97.90	98.34	98.48	98.44	98.29	0.58
2	98.19	97.97	98.24	98.68	98.27	0.71
3	97.79	98.06	98.10	98.15	98.03	0.36
4	97.97	96.71	98.64	98.44	97.94	1.93
5	94.29	98.29	98.18	98.54	97.33	4.25
6	98.41	98.44	98.33	98.42	98.40	0.11
7	98.20	98.06	97.83	98.20	98.07	0.37
8	97.89	98.61	98.49	98.53	98.38	0.72
9	98.31	98.50	97.94	98.34	98.27	0.56
10	98.07	98.65	97.45	98.33	98.13	1.20
11	98.30	98.39	98.35	98.44	98.37	0.14
12	97.96	98.40	98.33	98.58	98.32	0.62
13	97.95	98.32	98.08	98.04	98.10	0.37
14	98.03	98.27	98.22	98.68	98.30	0.65
15	97.96	98.18	98.31	98.81	98.32	0.85
16	98.61	97.73	98.06	98.42	98.21	0.88
17	97.97	98.06	98.36	98.50	98.22	0.53
18	97.97	97.77	98.06	98.24	97.95	0.47
19	97.48	97.56	98.25	98.74	98.01	1.26
20	98.02	98.07	98.37	97.95	98.10	0.42
21	98.07	97.79	98.16	98.41	98.11	0.62
22	98.09	97.63	98.51	98.49	98.18	0.88
23	98.08	97.87	98.59	97.39	97.98	1.20
24	97.85	97.67	98.49	98.4	98.10	0.73
25	97.91	98.06	98.27	98.46	98.17	0.55
26	98.12	98.65	98.23	97.93	98.23	0.72
27	97.37	96.71	98.29	97.74	97.53	1.58
28	98.08	97.68	98.00	97.50	97.82	0.58
Mean					98.11	0.85

As it is seen in Fig. 2, on the X chart for L* value, most of the values are above or below the center line, exhibiting a random and balanced distribution. Two points on the outside of lower control limit. However, on the R chart for L* value in Fig. 3, only one point is seen on the outside of upper control limit and the other points are seen to display normal and regular distribution, near the center line. As seen in Fig. 4, on the X chart for a* value, most of the points are found above or near the center line and they show distribution randomly but wide range above and below the center line. It is seen that there are only two points at the hull of the upper and lower control limits and that there is except a point the control limits. On the R chart for a* value given in Fig. 5, just one point is seen outside the upper control limit, whereas almost all of the other

points are below the center line, and one point is at the hull of the upper control limit. X chart for b* value is given in Fig. 6. In this chart, only one point exists on the upper control limit whereas the other points exist among the upper and lower control limits. However, the distribution in this chart is seen to be relatively irregular. On the other hand, the R chart for b* value in Fig. 7 shows that two points exist on the outer part of the control limits and the other points exist among the upper and lower control limits.

Table 5. Case study data for a* values

Number of sample	Subgroup 1	Subgroup 2	Subgroup 3	Subgroup 4	X_{mean}	R_{mean}
1	0.07	0.03	0.09	0.04	0.06	0.06
2	0.09	0.02	0.03	0.01	0.04	0.08
3	0.04	0.05	0.03	0.04	0.04	0.02
4	0.04	0.00	0.06	0.05	0.04	0.06
5	0.30	0.07	0.06	0.03	0.12	0.27
6	0.09	0.06	0.01	0.07	0.06	0.08
7	0.11	0.07	0.05	0.09	0.08	0.06
8	0.09	0.06	0.08	0.06	0.07	0.03
9	0.04	0.04	0.01	0.05	0.04	0.04
10	0.02	0.06	0.02	0.07	0.04	0.05
11	0.01	0.05	0.00	0.05	0.03	0.05
12	0.03	0.06	0.03	0.08	0.05	0.05
13	0.03	0.06	-0.03	0.09	0.04	0.06
14	0.07	0.04	0.00	0.07	0.05	0.07
15	0.06	0.01	0.03	0.08	0.05	0.07
16	0.04	0.00	0.00	0.05	0.02	0.05
17	0.03	0.08	0.01	0.03	0.04	0.07
18	0.07	0.08	0.02	0.06	0.06	0.07
19	0.07	0.08	0.01	0.05	0.05	0.07
20	0.08	0.11	0.03	0.05	0.07	0.08
21	0.06	0.07	0.01	0.06	0.05	0.06
22	0.03	0.12	0.06	0.09	0.08	0.09
23	0.04	0.14	0.08	0.05	0.08	0.10
24	0.03	0.21	0.04	0.08	0.09	0.18
25	0.03	0.14	0.03	0.11	0.08	0.11
26	0.04	0.12	0.07	0.12	0.09	0.08
27	0.04	0.07	0.03	0.02	0.04	0.05
28	0.06	0.08	0.03	0.08	0.06	0.05
Mean					**0.06**	**0.08**

Table 6. Case study data for b* values

Number of sample	Subgroup 1	Subgroup 2	Subgroup 3	Subgroup 4	X_{mean}	R_{mean}
1	1.14	1.19	1.41	1.00	1.19	0.41
2	1.21	1.09	0.97	0.85	1.03	0.36
3	1.05	1.36	1.04	1.00	1.11	0.36
4	1.09	1.09	0.96	1.06	1.05	0.13
5	2.95	1.24	0.99	0.99	1.54	1.96
6	1.20	1.33	1.39	1.16	1.27	0.23
7	1.15	1.15	1.25	1.23	1.20	0.10
8	1.14	1.02	1.05	1.11	1.08	0.12
9	1.29	0.94	1.16	1.13	1.13	0.35
10	1.08	1.04	0.84	1.06	1.01	0.04
11	0.89	1.22	0.85	1.16	1.03	0.37
12	0.72	1.25	1.24	1.06	1.07	0.53
13	0.97	1.12	0.76	1.11	0.99	0.36
14	0.99	0.99	0.88	1.16	1.01	0.28
15	1.07	1.13	0.90	1.39	1.12	0.49
16	1.12	0.79	1.83	1.25	1.25	1.04
17	0.98	1.30	0.94	1.55	1.17	0.53
18	1.55	1.34	0.91	1.16	1.22	0.54
19	1.07	0.98	0.75	0.86	0.92	0.32
20	1.19	1.28	0.78	1.10	1.09	0.50
21	1.29	1.1	0.99	1.12	1.13	0.30
22	1.09	1.1	1.13	1.12	1.11	0.04
23	0.95	1.19	1.05	1.2	1.10	0.25
24	1.17	1.53	1.01	1.4	1.28	0.52
25	1.16	1.01	1.07	1.26	1.13	0.25
26	1.13	1.36	1.08	1.10	1.17	0.28
27	1.03	1.02	1.35	1.09	1.12	0.33
28	0.97	1.29	1.01	1.63	1.22	0.66
Mean					**1.13**	**0.42**

Table 7. Control chart values of L*, a * and b* for $\bar{X}$ and R

	L*	a*	b*
$\bar{X}$ Chart	Lower Control Limit 98.11-(0.73*0.85) = 97.62	Lower Control Limit 0.06-(0.73*0.08) = 0.013	Lower Control Limit 1,13-(0.73*0.42) = 0.89
	Center Line 98.11	Center Line = 0.06	Center Line = 1.13
	Upper Control Limit 98.11+(0.73*0.85) = 98.60	Upper Control Limit 0.06+(0.73*0.08) = 0.1	Upper Control Limit 1,13+(0.73*0.42) = 1.37
R Chart	Lower Control Limit 0.85*0 = 0	Lower Control Limit 0.08*0 = 0	Lower Control Limit 0.42*0 = 0
	Center Line =0.85	Center Line = 0.08	Center Line = 0.42
	Upper Control Limit 2.28*0.85 = 1.94	Upper Control Limit 2.28*0.08 = 0.18	Upper Control Limit 2.28*0.42 = 0.96
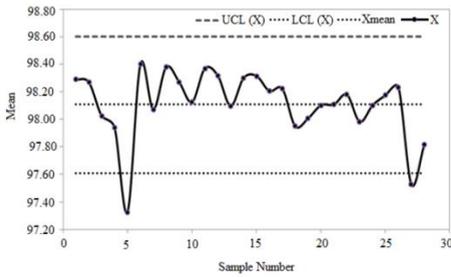
Fig. 2. X chart for L*
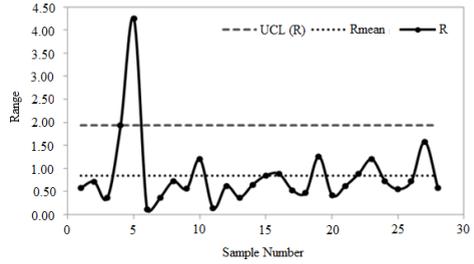
Fig. 3. R chart for L*
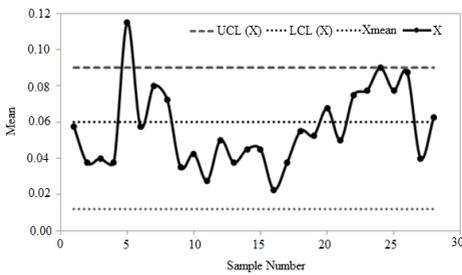
Fig. 4. X chart for a*
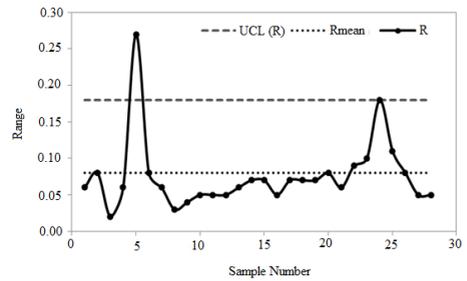
Fig. 5. R chart for a*
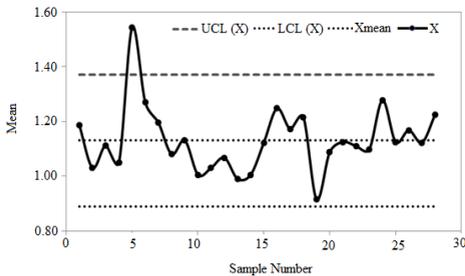
Fig. 6. X chart for b*
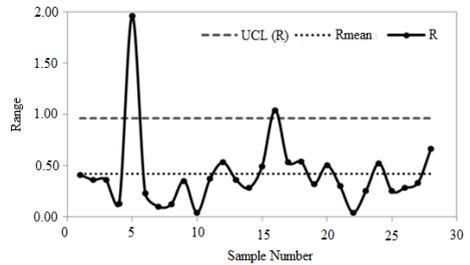
Fig. 7. R chart for b*

The process capability study is a longer-term study. In addition to variation arising from the machine, all other external factors that influence the production process over a longer operating time must be taken into account (Parkash et al., 2013). Process capability indexes that are an overview and available statistic science for process performance gives us useful knowledge to analyze process capability or incapability. The USL_X and LSL_X as expected values for calculations indexes were obtained from the management of the plant. The calculated capability indexes for L*, a* and b* were given in Table 8. The Cp/Cpk values after performing the few iterations of data collection were greater than 1.0, and hence the process was declared as a capable process for important color parameters such as L* and b*. But, for a* value of

products, index values were under 1.0. In general, it was determined that the pin mill plant was adequate for surface modification of calcite minerals.

Table 8. Capability indexes for L*, a* and b*

	L*	a*	b*
USL_X	100	0.1	1.5
LSL_X	95	0.0	0.0
Cp	3.41	0.77	2.09
Cpr_1	2.58	0.67	1.02
Cpr_2	4.25	0.86	3.14

Properties of coated calcite

An index active ratio was employed to evaluate the surface modification effect. The test results showed that the active ratio of coated calcite increases by approximately 100% upon coating with 1% stearic acid using the pin mill process. Since is reported in literature that a greater active ratio implies better surface modification effects (Wu and Lu, 2003; Ding et al., 2007).

The particle population densities of the micronized and coated calcite samples are presented in Fig. 8. As may be noted, particle population density of the coated calcite do not become large different to be dependent on the pin mill coating process. In addition, d_{10}, d_{50} and d_{97} particle size values of micronized calcite were 0.80 μm, 2.45 μm and 8.81 μm, respectively. The coated calcite obtained from the pin mill had $d_{10} =$ 0.77 μm, $d_{50} = 2.74$ μm and $d_{97} = 8.59$ μm. SF values were calculated as 2.23 and 2.28 for the micronized and coated calcite. These results are very important for the coating process, and should be considered as an indicator of the quality of a coating technology. If a coating process causes major changes in the size distribution, a new classification of the products is required, resulting in a rise in costs and a decline in productivity.
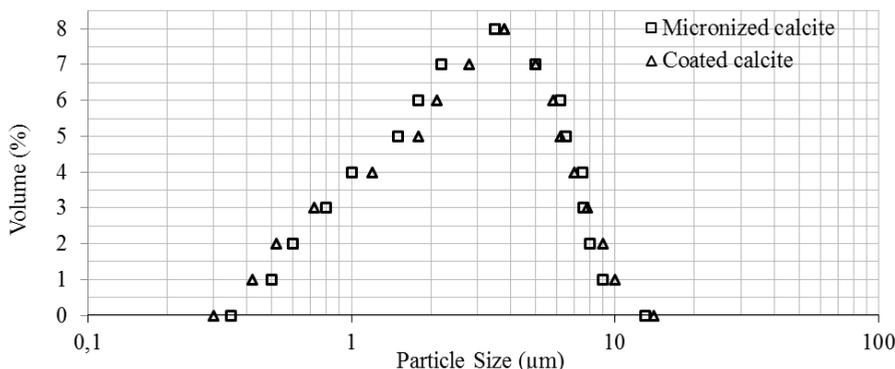
Fig. 8. The particle population density of the micronized and coated calcite

Whiteness is an important specification of coated calcite products, and it is important that this be high ($\geq$ 95%) for the product to be marketable. This property of coated calcite products is primarily a function of the whiteness of micronized calcite that is subjected to the coating process and the type and quantity of the fatty acid used in the coating process. The L*, a*, b* values of the coated calcite (randomly selected sample used in the statistical process control work) in this study were 97.97, 0.07 and 1.55, respectively. When these results are compared with the results from micronized calcite (98.84, -0.01, 0.67), it is understood that there is a decrease in L* which is the whiteness value (-0.87). The increase of value a* from -0.01 to 0.07 shows that the coating turns the calcite very slightly from green to red, while b*, the second most important color value after L*, increases from 0.67 to 1.55, revealing that there is an increase in the yellowness value. The total color difference was calculated as $\Delta E = 1.24$. As this value is greater than 1, there is a slight a color difference between micronized and coated calcite products, which is considered to be a natural result of the coating process.

Textural characteristics such as specific surface area, cumulative pore volume and pore size analysis carried out for micronized and coated calcite samples in this study. For coated calcite, the total surface area is a fairly important parameter to the quality of the coverage. BET surface area analysis shows that the micronized calcite has a surface area of 5.67 m^2/g and that the surface area increases to 7.26 m^2/g when it is coated in the pin mill using 1% stearic acid. As there is no significant grinding in a pin mill, the increase in the total surface area is clearly due to surface modification. In addition, pore volume and pore diameter of micronized calcite were 0.027 cm^3/g and 0.83 nm and the values were obtained for coated calcite as 0.019 cm^3/g and 1.44 nm, respectively. As it can be seen from the results, surface modification decreased the pore volume but increased pore diameter.

Thermal characteristics of both samples were analyzed by TG-DTA in this study. Osman and Suter (2003) claimed that TG is an adequate technique to detect organic contaminations of the calcite surface and determine the optimal amount of surfactant necessary to coat it with an alkyl monolayer. This technique is also able to differentiate between chemisorbed, intercalated (local bilayer), and free acid molecules that may be present on the surface of calcite fillers. For calcite coated with fatty acids, two main steps are usually visible in the thermal curves in the temperature range of 25–600 °C. The third part starts at approximately 580 °C and corresponds to the decomposition of calcite (Gomari et al., 2006). DTA and TG results on micronized and coated calcite samples are presented in Fig. 9 and Fig. 10, respectively. It can be clearly seen that there is an exothermic reaction in the DTA result of the coated calcite. TG curves show different results for the micronized and coated calcite. While no weight loss was observed in the micronized calcite up to approximately 600 °C, in the coated calcite the slope of the curve shows a noticeable change. Thus, both the TG and DTA curves show that the coated calcite has a stearic acid coating upon it.
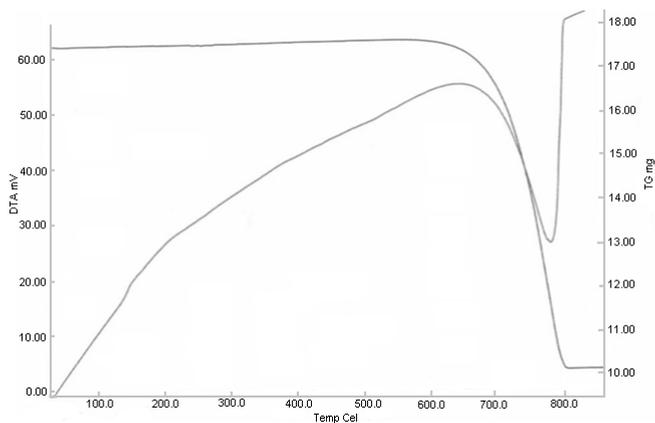
Fig. 9. TG and DTA analysis of micronized calcite
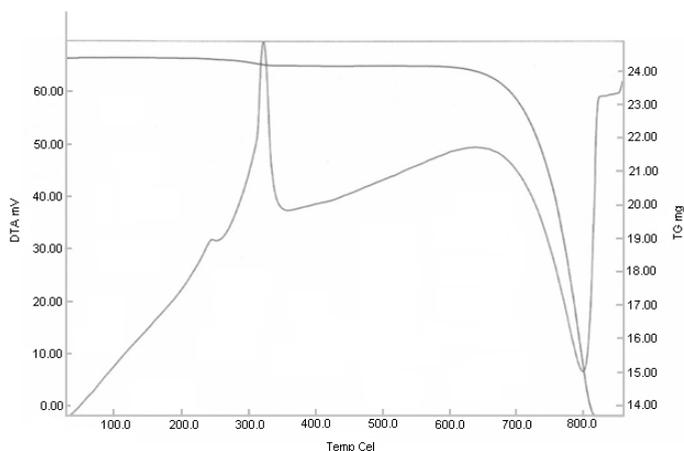
Fig. 10. TG and DTA analysis of modified calcite

As a further characterization method, FTIR spectral analysis was carried out on the micronized and coated calcite samples. Cifrulak (1970) showed that the vibration modes of calcium carbonate result in three active IR bands, 714 cm^{-1} (v4-in-plane bend), 879 cm^{-1} (v2-out-of-plane bend) and 1432 cm^{-1} (v3-antisymmetric stretching), and one inactive band at 1097 cm^{-1} (v1-symmetric stretching). FTIR analysis of micronized and coated calcite are shown in Fig. 11 and Fig. 12, respectively. It can be seen that the IR bands are overlapping with each other. The bands at 712 cm^{-1}, 875 cm^{-1} and 1427 cm^{-1} are diagnostic for calcite. In both spectra, the band observed at approximately 3435 cm^{-1} corresponds to –OH strain vibrations from H_2O on the surface of the calcite. However, the typical band of the hydroxyl bond stays at almost the same value after modification. The FTIR analysis results of the micronized and coated samples are very similar, showing that micronized calcite does not undergo any structural change when coated with stearic acid. The absence of deterioration in the

structure of the calcite during the coating process is important, as structured changes in the calcite are not desired by users.
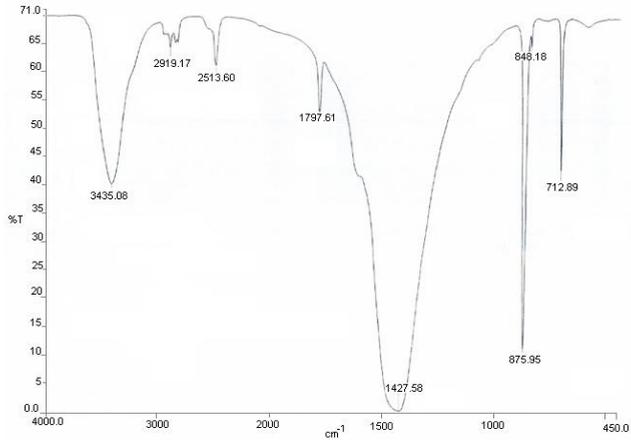
Fig. 11. FTIR analysis of micronized calcite
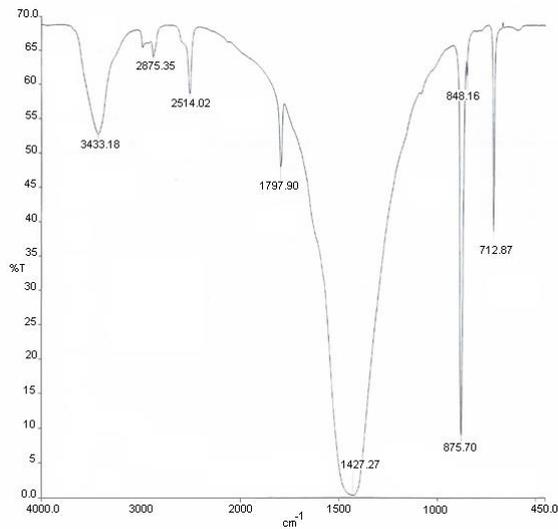
Fig. 12. FTIR analysis of coated calcite

Figure 13 shows scanning electron microscopy (SEM) images of micronized and coated calcium carbonate. It can be seen that the surface of calcite after modification appears smooth and uniform because of the coating with stearic acid.
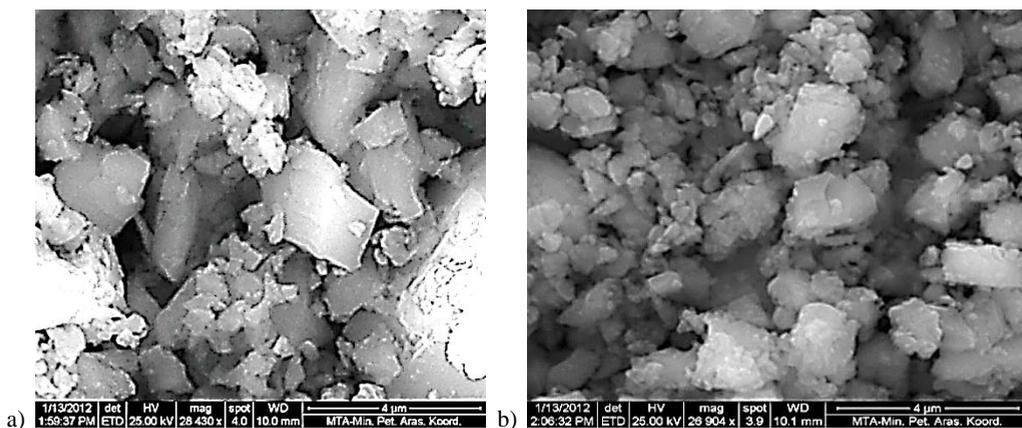
Fig. 13. SEM images of micronized (a) and coated (b) calcite

Conclusions

Several important conclusions can be drawn from the present study.

1. *X*-R control charts created with L*, a* and b* of coated calcite products in the pin mill are observed. It can be seen that the values of the color parameters are above and below the central line in general. The results show that the statistical process control is an effective means for controlling and improving the process quality. If process adequacy ratios are below 1, it means that the process is inadequate. However, the calculated C_p values (3.41 for L*, 0.77 for a*, 2.09 for b*) for important color parameters (L*, b*) of coated calcite products are upper than 1.0. Meanwhile, the C_{pr1} and C_{pr2} values are great than 1.0, except for a* like Cp. Therefore, it can be said that the process is adequate.

2. The active ratio of micronized calcite was increased from 0% to approximately 100% value with 1% stearic acid ratio by the pin mill surface modification process.

3. The particle size distribution of feed calcite had d_{10}, d_{50} and d_{97} values of 0.80 μm, 2.45 μm and 8.81 μm, while the coated micronized calcite had particle size values of d_{10} = 0.77 μm, d_{50} = 2.74 μm and d_{97} = 8.59 μm, respectively. SF values were calculated as 2.13 and 2.28 for micronized and coated calcite samples. These results show that there is no significant difference between micronized and coated calcite samples in terms of particle size and distribution. BET surface area analysis shows that the micronized calcite has of 5.67 m^2/g of surface area, which increases to 7.26 m^2/g via the coating process with stearic acid. Although the particle size does not significantly change after modification, there is a significant growth in the total surface area of the coated calcite, indicating that the calcite is very well coated with stearic acid by the pin mill process.

4. The L*, a*, and b* values of the coated calcite sample used in the study were determined to be 97.97, 0.07 and 1.55, respectively. When these results are compared

with the values of the micronized calcite color values of 98.84, -0.01, and 0.67, it is clear that there is a decrease in the L* parameter ($\Delta L^* = 0.87$). The a* value increased from -0.01 to 0.07, indicating a very change from green to red, and the b* value increased from 0.67 to 1.55, revealing an increase in the yellowness value. The total color difference (ΔE) was calculated as 1.24 for this study.

5. FTIR analysis showed that there is a chemical adsorption process between stearic acid and calcite. DTA results show that there was an exothermic reaction in the coated calcite. TG curves demonstrate that the coated calcite has a layer of stearic acid coating. Electron microscopy (SEM) images of micronized and coated calcium carbonate show that the surface of the calcite after modification appears smooth and uniform.

6. The pin mill technology is very effective in the modification of the surface of calcite.

Acknowledgements

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