

The effect of liquid grinding aids on the dry fine grinding of muscovite

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Abstract: This paper investigates the production of a micronized muscovite to a target product size of $d_{50} \sim 15 \mu\text{m}$ with a minimum energy consumption to suit the product requirements of the paint industry by a dry grinding process in a laboratory-scale vertical stirred ball mill. A series of batch dry grinding tests were conducted without and with two commonly used industrial liquid grinding aids, ethylene glycol (EG, $\text{C}_2\text{H}_6\text{O}_2$) and triethanolamine (TEA, $\text{C}_6\text{H}_{15}\text{NO}_3$). The results were evaluated based on particle size distribution (PSD), specific energy consumption, span value, and aspect ratio. The results showed that using liquid grinding aids resulted in a finer PSD, lower specific energy consumption, a narrower size distribution, lower span values, and a higher aspect ratio, which meant better delamination and improved grinding efficiency to that of no grinding aid. The interaction between grinding aids and ground muscovite surfaces was investigated by Fourier Transform Infrared Spectroscopy (FTIR). FTIR measurements revealed that EG and TEA were physically adsorbed on muscovite surfaces. Scanning Electron Microscopy (SEM) was also employed to determine differences between ground muscovite surfaces with and without grinding aids. SEM images indicated that grinding aids could prevent the agglomeration of ground muscovite particles while improving delamination. Adding grinding aids led to a decrease in muscovite agglomeration and an improvement in lamination owing to the adsorption of grinding aids on the particle surfaces.

Keywords: grinding aids, dry grinding, stirred ball mill, muscovite

1. Introduction

Hydrous aluminium silicate minerals that exhibit plate-like structures with different physical and chemical properties are referred to as mica. Muscovite, biotite, phlogopite, and lepidolite are the best-known minerals in the mica group. Most mica used today is in micronized form, and the mica of commerce is principally muscovite. Muscovite, $\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{F},\text{OH})_2$, has a perfect plate-like structure and can be easily separated into soft and elastic thin sheets. Muscovite, in the form of very thin sheets, is transparent, colourless, or light grey, and has a pearl luster (Chevalier, 2008). As an alternative material to environmentally harmful asbestos, micronized muscovite use is rising because of the latest developments in industrial raw materials (Willett, 2012).

Plastic fillers, insulators, condensers, pearlescent pigments, coatings, polymers, equipment, and devices used in the aeronautical industry are a few examples of the specialized uses for micronized muscovite. Its primary end uses are wallboard joint cement, coatings, automotive, plastics, and well-drilling fluids. Micronized muscovite should have specific physical and physicochemical properties to achieve ideal performance in the mentioned industries. Firstly, the shape factor of particles, namely the aspect ratio, is defined as the ratio of the diameter of the base plane to the thickness; the higher this ratio, the better the lamination and hence the improving reinforcing properties of muscovite-filled polymer matrices. Secondly, the size distribution should be uniform to avoid zones of dissimilarity and hence weakness. Finally, the surface properties of particles should be suitable for ideal dispersion and interaction with the matrix (Papirer et al., 1990). It is essential to retain or enhance the fundamental

features of the muscovite through the grinding process. Generally, muscovite grinding has been performed in impact, stirred, jet, and planetary mills, either dry or wet (Orumwense and Forssberg, 1990). Considering the importance of water resources and the need to use them more efficiently, dry grinding has become increasingly important, and studies in the related literature are at an early stage. Muscovite is mostly dry milled in Turkey using energy-intensive jet mills for fine sizes.

Stirred ball mills have been utilized efficiently for fine and ultra-fine grinding of numerous materials due to their simple operation, ease of construction, energy conservation, and increased grinding rate compared with other fine grinding machines (Altun et al., 2013; Bilir and Halil, 2022; Cayirli and Gokcen, 2021; Choi et al., 2010; Gao and Forssberg, 1995; Kwade, 1999; Rácz and Csóke, 2016; Zheng et al., 1996). Therefore, the dry grinding of muscovite in a stirred ball mill might be advantageous in terms of water and energy consumption and in improving the properties of muscovite mentioned above; furthermore, it will also contribute to the literature. Especially in dry grinding applications, depending upon the product and fineness range, the agglomeration phenomena of ground particles occur due to Van der Waals and electrostatic attraction forces, which results in poor grinding efficiency due to the formation of agglomerates and coatings on grinding media and the mill liners (Bilir, 2022; Gokcen et al., 2015; Zhang et al., 2015). There are ways to improve grinding efficiency, and one of them is to use grinding aids.

Grinding aids are primarily high-polarity organic compounds, commonly consisting of glycols and amines. They have successfully been used in high-energy consuming dry fine and ultra-fine grinding operations (Hasegawa et al., 2006). Extensive studies have been conducted to determine the advantages of grinding aids. According to these studies, three mechanisms are principally responsible for the observed positive effects of grinding aids. The first is based on the decrease in the surface free energy of solids caused by the adsorption of surface active agents (Rehbinder, 1931), the second is attributed to changes in surface hardness induced by the influence of adsorbed species on the mobility of near-surface dislocations (Westwood and Goldheim, 1968), and the third is related to the role of reagents in dispersion and hence the flow of particles throughout comminution processes (Altun et al., 2015; Hanna and El Gamal, 1977; Klimpel and Manfroy, 1977; Prziwara et al., 2018a, b; Rose and Sullivan, 1958; Savage et al., 1974; Toprak and Benzer, 2019). These mechanisms are based either on the changes in mechanical properties of the solid or the flow properties of the ground suspension (El-Shall and Somasundaran, 1984a, b; Fuerstenau, 1995). Surface and mechanical property theories have failed to explain the effect of grinding aids. As a result, the dominant mechanism of effect is based on particle arrangement and material flow characteristics. At low flowability (grinding aid at low dosage), too much material is retained in the grinding zone, related to the stress energy, resulting in reduced grinding efficiency. At high flowability (grinding aid at high dosage), the amount of material retained in the grinding zone is insufficient, resulting in low efficiency regardless of the stress energy, implying that optimum flowability exists. Despite the absence of support for the surface and mechanical properties mechanism, the commonly reported reduction in surface energy remains a point of contention when grinding aids are used. Some studies have shown that using grinding aids reduces surface energy (Chipakwe et al., 2020; Prziwara et al., 2018a; Prziwara and Kwade, 2020). Paramasivam and Vedaraman (1992) investigated the effects of the physical properties of glycol-based grinding aids and reported that grinding aids increased the fineness of the ground particles and powder flow. Hasegawa et al. (2006) also demonstrated that liquid additives (three alcohols and two glycols with different alkyl groups) employed as grinding aids are beneficial due to the improved flowability and manipulation of reagglomeration due to micro-fine particles. In clinker grinding, Jolicoeur et al. (2007) studied the effects of glycols and compared the results with triethanolamine. They indicated no improvement in powder fluidity relative to triethanolamine was found with the ethylene glycol series at a dosage of 0.1%. Katsioti et al. (2009) investigated the effects of triethanolamine and triisopropanolamine on Portland cement clinker and found that grinding aids increased the specific surface area and the grindability index. Toprak et al. (2014) reported that grinding aids increased the cement grinding circuit's production rate by 15-24%. In addition, a recent study by Toprak et al. (2020) demonstrated that grinding aids increased the cement particle discharge rate (i.e., decreased mill residence time). As a result, by eliminating overgrinding, a substantial improvement in inefficient energy use was realized.

This study investigates the effects of two liquid grinding aids commonly used in industry (Bilir, 2022; Chipakwe et al., 2020; Kobya et al., 2022; Prziwara et al., 2019; Prziwara and Kwade, 2020), which have different chemical functional groups; glycol-based, ethylene glycol (EG, C₂H₆O₂) and amine-based, triethanolamine (TEA, C₆H₁₅NO₃), on the dry fine grinding of muscovite using a vertical stirred ball mill. The effects of grinding aids were evaluated in terms of particle size distribution, specific energy consumption, and span value, in addition to their effect on muscovite delamination, i.e., aspect ratio. To the best of the authors' knowledge, such effects of grinding aids on the dry fine grinding of muscovite have not been investigated before, especially in conjunction with FTIR and SEM analyses.

2. Materials and methods

2.1. Materials

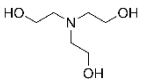
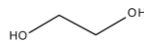
The muscovite sample (d₅₀ = 183 μm) was obtained from Kaltun Mining Company (Turkey), and its density was determined to be 2.71 g/cm³. The sample's chemical analysis (by X-ray fluorescence) is illustrated in Table 1. The sample was muscovite, of rather high purity.

Table 1. Chemical analysis of the sample

Oxides (%)	SiO ₂	Al ₂ O ₃	K ₂ O	Na ₂ O	MgO	CaO	Fe ₂ O ₃	TiO ₂	P ₂ O ₅	LOI
	62.32	22.75	5.97	2.81	1.23	0.88	0.85	0.33	0.50	2.35

Two liquid grinding aids commonly used in industry, glycol-based, ethylene glycol (EG, HOCH₂CH₂OH, Merck) and amine-based, triethanolamine (TEA, N(CH₂CH₂OH)₃, Merck), were used as the liquid grinding aids in their pure forms (Table 2). The dosages of grinding aids were 1000, 2000, and 4000 g/t. The dosage of 4000 g/t (0.4% by weight) was selected to investigate the upper limit of the grinding aids needed in the dry fine grinding of muscovite. It is known that the liquid grinding aids added in cement grinding usually not exceeding 0.25% by weight.

Table 2. Information about the liquid grinding aids used

Functional Group	Name	Molecular formula/structure	Purity (%)	Molar mass (g/mol)	Boiling point [°C]	Viscosity mPas (cP)
Amine	Triethanolamine (TEA)	C ₆ H ₁₅ NO ₃ 	≥99.0	149.19	360	609
Glycol	Ethylene glycol (EG)	C ₂ H ₆ O ₂ 	≥99.0	62.07	197.6	16.1

2.2. Stirred ball mill

Grinding tests were performed in a laboratory vertical stirred ball mill, Model HD-01 (Union Process Inc., USA). The mill consists of a 0.75-liter ceramic (99.9% alumina) grinding tank embedded in a water-cooled jacket for cooling, a plastic-coated stainless steel shaft with four slotted ZrO₂ arms, and a two-piece plastic cover. The alumina balls produced by Union Process were employed as grinding media. The balls were 99.9% pure, and their density was 3.9 g/cm³. The grinding experiments were conducted in batch mode, where samples were removed from the grinding tank at predetermined time intervals. After each test, the media were screened out of the ground products.

The impacts of various parameters on the dry fine grinding of muscovite were previously explored in depth by the current author (Cayirli, 2014). The aim was to obtain a target product size of d₅₀~15 μm with a minimum energy consumption to suit the product requirements of the paint industry. The optimum grinding time required to reach a target product size of d₅₀~15 μm was determined to be 105 minutes under the predetermined grinding conditions summarized in Table 3. The effects of EG and TEA dosages were tested under those conditions to determine particle size distribution, specific energy

consumption, span value, and aspect ratio. Additional grinding tests were also performed to determine the specific energy (i.e., grinding time) required to achieve the same target product size of $d_{50} \sim 15 \mu\text{m}$ with grinding aids.

Table 3. Grinding test conditions

Parameters	Conditions
Stirring speed (rpm)	600
Ball filling (%)	72
Ball amount (g)	1002.5
Interstitial filling (%)	58
Material amount (g)	162
Media material	Alumina
Media size (mm)	5
Grinding time (min.)	105

The results were assessed as specific energy consumption. Energy consumption was measured by torque (Jimenez, 1981). Torque was reported by the MINT WorkBench Program (MN 1262 Version 4, Baldor Ltd.) on a PC. Specific energy consumption was calculated using Eq. (1):

$$E = \frac{94,8 \times \text{Torque(Nm)} \times \text{Velocity(rpm)} \times \text{Time(h)}}{\text{Amount of samples(g)}} \quad (1)$$

where E is energy consumption (kWh/t).

3. Analysis

3.1. Particle size distribution (PSD)

The median particle sizes x_{50} and PSD of the feed and the ground products are most commonly used to describe and characterize the fineness of products in a wide range of industries. The PSD of the feed and the ground products were measured using a wet laser diffraction particle size analyser, Malvern 2000 Ver. 2.00, with a Hydro 2000 MU attachment (Malvern Ltd., UK). The particle size measurement range of the device is between 0.002 and 2000 μm . A representative number of samples were dispersed in water by ultrasound before the measurement. Each test was conducted three times, and the average was recorded. The mean error was calculated to be about ± 2 .

3.2. Span

Span is an indication of the width of the PSD. A narrower product PSD is often desirable in the powder processing industry. The span is expressed as the ratio of $(d_{90}-d_{10})/d_{50}$, where d_{90} , d_{50} , and d_{10} are the quantiles at 90%, 50%, and 10%, respectively.

3.3. Aspect ratio

The aspect ratio of ground products was also measured using a wet laser diffraction particle size analyser, Malvern 2000 Ver. 2.00 with Hydro 2000 MU attachment (Malvern Ltd., UK). The detailed mathematical theory behind the aspect ratio measurement using this device was described in an application note published by the device manufacturer and in the literature (Baudet et al., 1993; De Ridder et al., 2000; Ma et al., 2000). The aspect ratio was briefly defined as the ratio between the actual volume concentration (c) introduced to the device and the calculated volume concentration (real volume) by the software program. Eqs. (2) and (3) were used to calculate the actual and real volumes. When using the particle size analyser to determine the aspect ratio, the user inputs the weight of the sample added and the volume of water used. The density of the sample must also be entered. The software program then performs all the measurement steps and appropriate calculations to obtain the aspect ratio Eq. (4). Also, the particle thickness is calculated by dividing the mean particle size of

$$c = \frac{100 \log_e(1 - \text{Obscuration})}{\frac{-3}{2} b \sum \frac{V_i Q_i}{d_i}} (\%) \quad (2)$$

the surface distribution, $D_s(0.5)$, by the aspect ratio (Eq. 5). In Eq. (2) c is actual volume concentration, b is beam length, V_i is volume in size band Q_i is extinction coefficient of size band i and d_i is a mean diameter of size band i .

$$\text{real volume concentration} = \frac{\text{weight of sample}}{\text{density of the sample} \times \text{volume of water}} \times 100 (\%) \quad (3)$$

$$\text{aspect ratio} = \frac{c}{\text{real volume}} \quad (4)$$

$$\text{thickness} = \frac{D_s(0.5)}{\text{aspect ratio}} (\mu\text{m}) \quad (5)$$

3.4. Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR spectra of tested liquid grinding aids and ground products obtained with and without grinding aids were collected using a Perkin Elmer 2000 spectrometer equipped with its own Universal Attenuated Total Reflectance (UATR) and Diffuse Reflectance Infrared Fourier Transform (DRIFT) accessories. A deuterated triglycine sulfate (DTGS) detector was used to take an average of 200 scans in the spectral range of 4000-500 cm^{-1} with a resolution of 4 cm^{-1} .

The spectra of grinding aids were obtained by using the UATR accessory. A drop of grinding aids was placed on the diamond top-plate of the UATR, then the spectra were recorded. The spectra of ground muscovite and muscovite ground with grinding aids were obtained by using the DRIFT accessory. A 0.01 g sample of air-dried ground muscovite was mixed gently with 0.10 g of spectroscopic grade KBr using an agate pestle and mortar, then embedded in a macro sampling cup before being positioned in a DRIFT accessory chamber for analysis. The KBr powder served as a background. The same procedure was applied to the muscovite powder ground with grinding aids.

3.5. Scanning Electron Microscopy (SEM)

Muscovite samples ground with and without a liquid grinding aid were first air-dried and then bonded to sample holders with conducting glue, followed by a 30-minute sputter of carbon. The images of prepared samples were obtained using a Zeiss Supra 50 VP scanning electron microscope (SEM). Images were taken under a 20 kV accelerating voltage and a magnification of 20-100 KX with a tungsten filament.

4. Results and discussion

4.1. Particle size distribution (PSD) and energy consumption

The effects of EG and TEA dosages on cumulative undersize (U/S) at a fixed grinding duration of 105 minutes, which was the predetermined optimum grinding time required to reach a target product size of $d_{50} \sim 15 \mu\text{m}$ without grinding aids, are illustrated together with the feed sample in Fig. 1. It can be seen that finer product sizes are obtained with increasing grinding aid dosages compared to grinding without any aid. Furthermore, finer products are obtained using TEA compared to EG, especially at 2000 and 4000 g/t dosages.

Similar effects of grinding aids have been noticed in the literature (Engelsen, 2008; Forssberg et al., 1995; Gokcen et al., 2015; Hasegawa et al., 2006; Jolicoeur et al., 2007; Katsioti et al., 2009; Paramasivam and Vedaraman, 1992; Rao, 2003; Toprak et al., 2014; Wang and Forssberg, 2007). Forssberg et al. (1995) determined that adding 0.1 wt.% of berolamine (a mixture of triethanolamine, diethanolamine, and monoethanolamine) as a grinding aid to the Sala agitated media mill (SAM) resulted in increased product fineness (<10 μm particles increased by 20%) and decreased energy consumption in dolomite grinding. Since the use of grinding aids resulted in relatively finer sizes than grinding with no aids at a fixed grinding time of 105 minutes, further grinding tests were performed under the same grinding aid conditions to determine the specific energy consumptions (i.e., grinding times) required to achieve the same target product size ($d_{50} \sim 15 \mu\text{m}$). Fig. 2 compares specific energy consumption values calculated based on the grinding times (the numbers on the bars) for both grinding aids at different dosages.

As seen in Fig. 2, specific energy consumption values decrease with increasing dosages of both grinding aids compared to no aids. It can also be observed that less specific energy (i.e., shorter grinding

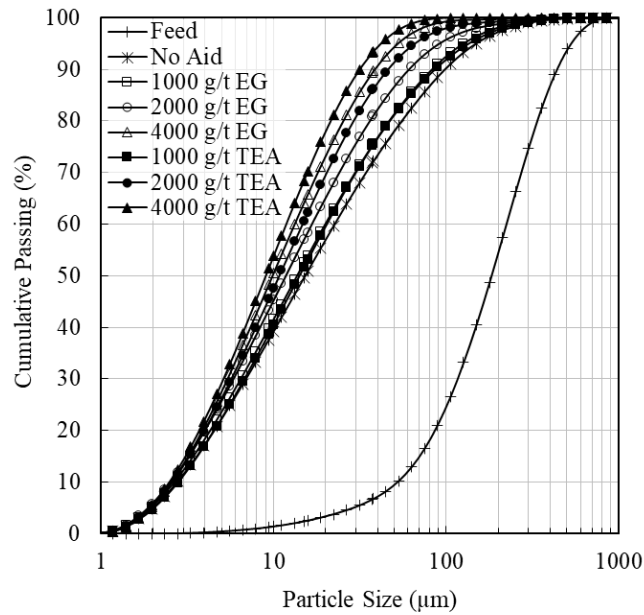


Fig. 1. The effect of grinding aid dosages on cumulative U/S (Grinding time: 105 min.)

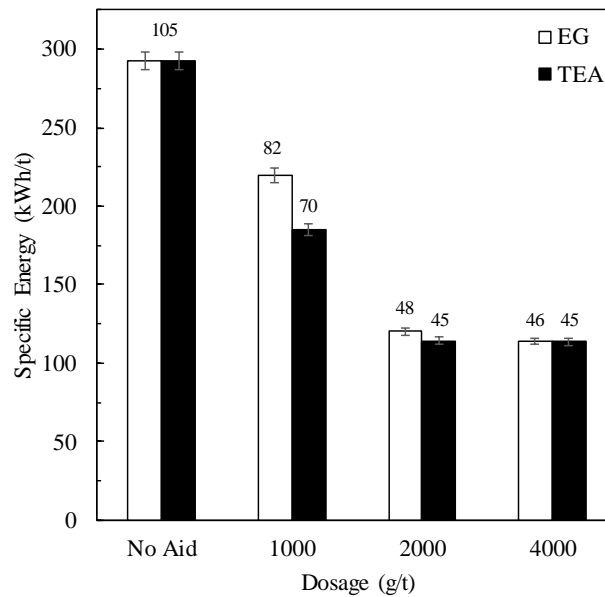


Fig. 2. The effect of grinding aids and their dosages on the specific energy (the numbers on the bars depict the grinding times in minutes to reach target grind size of $d_{50} \sim 15 \mu\text{m}$)

times) is consumed to reach the target product size when using TEA compared to EG at dosages of 1000 and 2000 g/t. It is also shown that no evident difference is observed between TEA and EG at a dosage of 4000 g/t. This could be explained by the fact that optimum flowability was attained at certain aid dosages; above this dosage, further improvement in flowability resulted in inefficient grinding. In other words, the grinding media did not have an adequate opportunity to capture the particles for efficient grinding (Prziwara et al., 2018c; Prziwara and Kwade, 2020). Finally, it can be concluded that the specific energy (i.e., grinding time) required to reach the target product size was significantly reduced by 25 to 61% using grinding aids. Rao (2003) noticed the positive effect of amine on fine calcite particles by affecting the mass transport in the mill and concluded that a decrease in energy consumption was probable despite the use of a small dosage of grinding aid concentration. Gokcen et al. (2015)

demonstrated that amine-based grinding aids decreased the energy consumption to reach the target grinding size ($d_{80} \sim 10 \mu\text{m}$) and were highly efficient for micro-fine grinding of feldspar.

The results obtained in Fig. 2 revealed that a grinding aid dosage of 2000 g/t is the optimum for efficient grinding since the further dosage increase did not result in sufficient energy consumption except for consuming double the amounts of grinding aids. PSDs and cumulative U/S of products of the same d_{50} size of $15 \mu\text{m}$ obtained at 2000 g/t TEA (i.e., 45 min.), 2000 g/t EG (i.e., 48 min.) and without grinding aids are shown in Figs. 3a and 3b, respectively. It can be inferred that the utilization of grinding aids resulted in lower energy consumption and a narrower PSD compared to the no aid condition. Furthermore, it can be deduced that the particle size distribution is slightly narrower with TEA than with EG, even at a slightly lower grinding time to reach the target product size of $d_{50} \sim 15 \mu\text{m}$. This could be attributed to the possible impacts of the molecular structure difference between TEA and EG, causing different tendencies to agglomeration (Cayirli, 2022; Prziwara and Kwade, 2020).

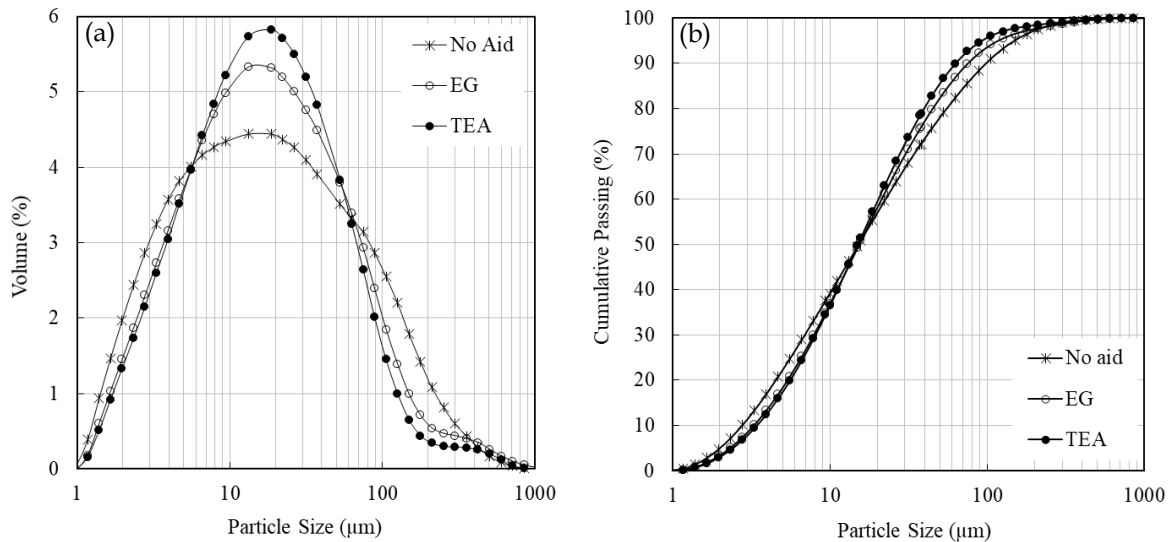


Fig. 3. PSDs (a) and cumulative U/S (b) at 2000 g/t

Table 4 also shows the quantiles and calculated span values obtained at 2000 g/t comparatively. As can be seen from the table, using grinding aids reduced the span values. TEA had the most significant improvement in span value compared to the EG and no aid conditions. Furthermore, research altering the span value by changing design and operating parameters has been reported in the literature (Karbstein et al., 1995; Nettet et al., 2006; Wang and Forssberg, 2000). Karbstein et al. (1995) pointed out that it changed the span value by changing the mode of circulation. Wang and Forssberg (2000) investigated the effect of media size and tip speed on the span value in a wet and dry-stirred mill. They found that the span value could be controlled by varying the media size and tip speed. The study using different stirred milling technologies by Nettet et al. (2006) showed that grinding media size affected the span value. It was also found that grinding media density and solid density also had a lesser effect on the span value.

According to the literature, the operating parameters of the mill affect the span. It is speculated that using a grinding aid changes the span value. In this case, the grinding aid, which is one of the operating parameters of the mill, is in line with this idea.

Table 4. The changes in span at 2000 g/t

	No Aid	EG	TEA
d_{90}	99.08	75.77	63.09
d_{50}	15.25	15.36	15.09
d_{10}	2.77	3.28	3.44
Span	6.32	4.72	3.95

4.2. Aspect ratio

The shape of the particles (particularly the thickness of particles) creating the mineral in a specified particle size distribution can be an essential factor in assessing the efficacy of the final use in the case of flaky minerals such as muscovite. Many researchers have applied different particle size measurement techniques to determine the aspect ratio (Blott and Pye, 2006; Bowen, 2002; Califice et al., 2013; Erdoğan et al., 2010; Gantenbein et al., 2011; Hogg, 2015; Li et al., 2005; Ma et al., 2001; Tinke et al., 2008; Xu and Di Guida, 2003). The laser diffraction method, one of the particle size measurement techniques, ensures a quick and trustworthy sample comparison tool that may be satisfactory if the primary purpose of the research is to create dimensional or provisional trends in particle size properties. Naito et al. (1998) point out that the size distribution is wide during the evaluation of anisotropic samples by the laser diffraction and scattering method due to particle alignment and the shear flow direction. This principle can be used to determine the aspect ratio. In addition, some studies show that the laser measurement technique will be a cumulative average of all the orientations of the particles rather than that each particle will be weighted with the longest dimension (Erdoğan et al., 2010; Li et al., 2005; Tinke et al., 2008; Xu and Di Guida, 2003).

When minerals such as muscovite are ground, delamination and breaking coincide (Balard et al., 1997). In order to investigate the change in delamination after the milling process, the aspect ratio and thickness of the products were calculated (Table 5). As seen in Table 5, the aspect ratio increases, and the thickness decreases with the increasing amount of both grinding aids. The use of grinding aids may increase powder flow, allowing shearing forces to be more effective. Recent studies show that the use of grinding aids increases the powder flow (Prziwara et al., 2018a, b, 2019; Prziwara et al., 2018c).

Table 5. The changes in aspect ratio and thickness at 2000 g/t

	No Aid	EG	TEA
Aspect Ratio	2.39	2.80	3.01
Thickness (μm)	6.38	5.48	5.01

The effect of grinding aids on the specific energy consumption could only be speculated due to the surface activity of grinding aids without direct evidence from surface characterization techniques. FTIR measurements were done on samples ground with and without grinding aids.

4.3. FTIR measurements

Fig. 4 shows the FTIR spectra of ground muscovite, EG, and muscovite ground with 2000 g/t EG (Muscovite + EG). In the spectrum of ground muscovite, the peak at 3620 cm^{-1} corresponds to the OH group, which is between the tetrahedral and octahedral sheets of muscovite. At about 1020 cm^{-1} , the peak corresponds to the stretching and bending vibrational modes of Si-O bonds. In addition, the strong peaks at about 750 and 530 cm^{-1} are attributed to the Al-O-Al and Al-O-Si stretching vibrations, respectively. Furthermore, the peaks at about 800 and 828 cm^{-1} are responsible for Si-O deformation and Al-O stretching vibrations, respectively (Wang et al., 2014). In the spectrum of EG, stretching vibrations of ether groups (C-O-C) emerged at 1030 - 1150 cm^{-1} . Stretching vibrations of $-\text{CH}_2$ are responsible for a sequence of modest peaks between 1200 and 1500 cm^{-1} . Stretching vibrations (symmetric and asymmetric) of alkyl ($-\text{CH}_2$) from 2800 to 3000 cm^{-1} are also observed. With absorbance ranging from 3200 to 3600 cm^{-1} , hydroxyl group contribution is also seen (Mansur et al., 2004). New absorption peaks (depicted on the spectrum) at 2922 and 2865 cm^{-1} that appeared in the muscovite + EG spectrum account for the $-\text{CH}_2$ asymmetric and symmetric stretching vibration modes of the alkyl chain. The fact that these peaks are absent in the spectrum of the muscovite indicates that EG is physically adsorbed on the surface of the muscovite.

Fig. 5 shows the FTIR spectra of ground muscovite, TEA, and muscovite ground with 2000 g/t TEA. The stretching vibration band of $-\text{OH}$ is detected between 3000 and 3600 cm^{-1} in the FTIR spectrum of TEA, while the stretching vibration bands of $-\text{CH}_3$, $-\text{CH}_2$, and C-H are detected between 2800 and 3000 cm^{-1} (Katsioti et al., 2009; Zhao et al., 2015). The peaks at 1357 , 1406 , and 1454 are various modes of $-\text{CH}$ vibrations (scissoring and wagging). Stretching peaks for C-N (aliphatic amine) and C-O (primary

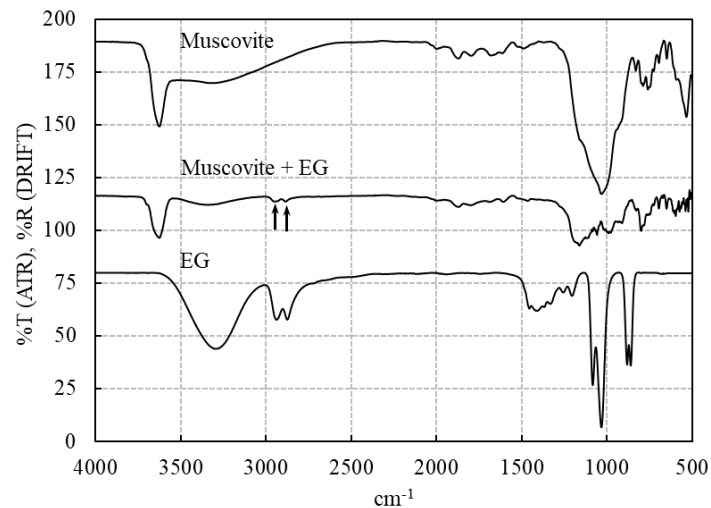


Fig. 4. FTIR spectra of ground muscovite, EG, and muscovite ground with EG

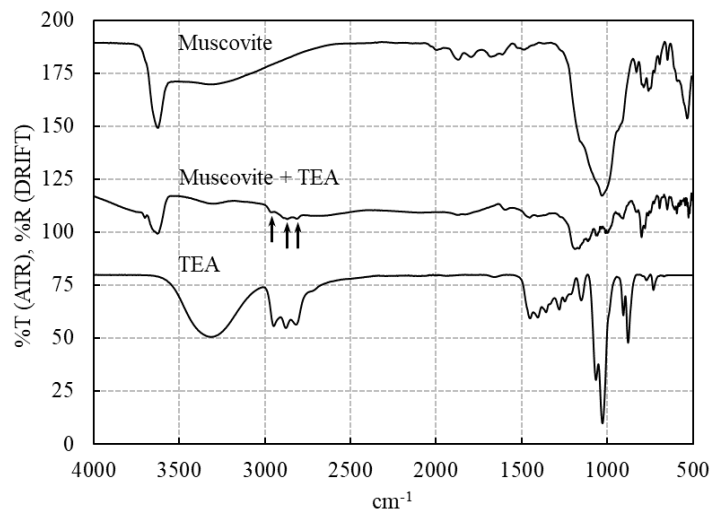


Fig. 5. FTIR spectra of ground muscovite, TEA, and muscovite ground with TEA

alcohol) can also be found at 1030 and 1070 cm^{-1} , respectively. In comparing the spectra of TEA and Muscovite + TEA, the observed three faint peaks (depicted on the spectrum), from 2815 to 2950 cm^{-1} , are assigned to the ethyl groups of the TEA physically adsorbed on the muscovite surface.

As surface-active reagents, grinding aids adsorb on the solid surfaces via their polar functional groups, lowering the surface energy or covering the outer surfaces of the finely dispersed particles, thereby hindering their agglomeration. Due to this physical adsorption, the particles coated by the grinding aid change the particle-particle as well as particle-media grinding actions, resulting in more effective grinding (Engelsen, 2008; Forssberg et al., 1995; Wang and Forssberg, 2007). The comparison of the Muscovite + EG (Fig. 4) and Muscovite + TEA (Fig. 5) FTIR spectra also revealed that TEA, having both amino and hydroxyl groups, has more functional groups that are oriented to the muscovite surfaces compared to EG. This might also explain why less energy is consumed to reach the target product size of d_{50} 15 μm with TEA compared to EG at the dosage of 2000 g/t (Wang et al., 2009; Zhao et al., 2015).

4.4. SEM analysis

The behavior of muscovite particles after grinding with and without grinding aids was studied using SEM. SEM images of ground muscovite and muscovite ground with 2000 g/t TEA are illustrated in Figs. 6a and 6b, respectively. By comparing SEM images, it can be seen that grinding aids are used to regulate the degree of aggregation and delamination in the ground muscovite particles. A large number

of fine particles that have agglomerated cover the surfaces of the large particles without grinding aid, as seen in Fig. 6a. The use of grinding aid, however, mitigates this effect (Fig. 6b). Furthermore, as can be seen in Fig. 6b, the grinding aid considerably enhanced the delamination of the muscovite particles, supporting the aspect ratio findings. It could be said that grinding aids decreased the agglomeration of fine particles (Hasegawa et al., 2006) and improved the delamination of the muscovite (i.e., increased aspect ratio).

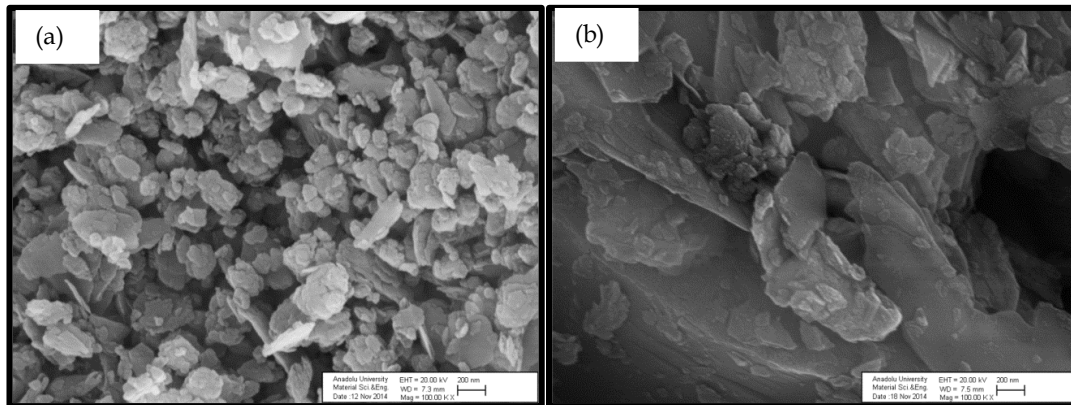


Fig. 1. SEM images of ground muscovite particles (a) Without; (b) With 2000 g/t TEA

5. Conclusions

This study aimed to produce a micronized muscovite with a target product size of $d_{50} \sim 15 \mu\text{m}$ with a minimum energy consumption to suit the product requirements of the paint industry by a dry grinding process in a laboratory-scale vertical stirred ball mill. Within the scope of the study, the effects of two industrially commonly used grinding aids with different chemical functional groups: Glycol based, ethylene glycol (EG) and amine-based, triethanolamine (TEA), liquid grinding aids (ethylene glycol, EG, and triethanolamine, TEA) and their dosages (1000, 2000, and 4000 g/t) were investigated.

The results showed that at a fixed grinding duration of 105 minutes, which was the predetermined optimum grinding time required to reach a target product size of $d_{50} \sim 15 \mu\text{m}$ without grinding aids, finer product sizes were acquired with EG and TEA, with TEA being finer than EG. The specific energy consumed (i.e., grinding times) to reach the target product size of $d_{50} \sim 15 \mu\text{m}$ was significantly reduced within the 25 to 61% range using both grinding aids. A grinding aids dosage of 2000 g/t was optimal for efficient grinding since the further dosage increase did not result in sufficient energy consumption except for consuming double the amounts of grinding aids. Less specific energy was consumed with TEA than with EG at lower dosages. In addition, narrower PSDs were obtained with TEA compared to EG. Furthermore, both grinding aids improved span values (i.e., the width of the PSDs) and aspect ratios. TEA was more effective than EG once again.

The effect of grinding aids on the dry fine grinding of muscovite could only be speculated based on the surface activity of grinding aids without direct evidence from the surface characterization techniques. FTIR measurements were performed on samples ground with and without grinding aids. According to FTIR measurements, EG and TEA were physically adsorbed on the particle surfaces of ground muscovite. FTIR spectra also revealed that TEA, having both amino and hydroxyl groups, has more functional groups oriented to the muscovite surfaces than EG. This explains the better grinding performance obtained with TEA than with EG. Furthermore, SEM images of the muscovite surfaces ground without and with a grinding aid indicated that the agglomeration and delamination of ground particles were controlled using a grinding aid. The addition of grinding aid decreased the agglomeration of fine muscovite particles while considerably improving the delamination of the muscovite particles, in line with the aspect ratio findings.

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