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Investigation of grinding-aid effect on the fineness, particle size distribution, surface area and color properties of calcite powder in dry vertical stirred mill

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Abstract In this study, the effect of some chemical additives such as methanol, ethanol, sodium oleat and chloroform on the dry ultrafine grinding of calcite powder (X_{50}= 33 µm, Sv=0.95 m^2/cm^3) was investigated by using a stirred mill. The experiments were carried out by a batch operation, and the change in average particle size (X_{50}), particle size distribution (PSD) width, surface area (Sv) and color properties (lightness, whiteness) of calcite powder. The results show that the lightness (*L)* values of the ground calcite products slightly increased from 97.67 to 97.94 with grinding aids (methanol and ethanol) increased from 0.25% to 1%. The whiteness index (WI) value of the ground calcite products satisfactorily increased from 93.88 to 97.51 with grinding aids (ethanol) at a rate of 0.5%.

Keywords Stirred mill, calcite, grinding-aid, color properties

Introduction

It is known that grinding operation is used for the size reduction of materials, production of large surface area and/or liberation of valuable minerals from their matrices. It is also widely used in the manufacture of cement, pigments, paints, ceramics and pharmaceuticals [1]. However, at the same time, it is one of unit operations with the lowest energy efficiency [2]. The need for fine particles has increased in the field of preparing raw powders and high value added products in many industries such as mineral, ceramic, pigments, paint and pharmaceutical.

Stirred media mills have been used in recent years for grinding particles to micron and submicron sizes due to their easy operation, simpler construction, higher grinding rate and lower energy consumption compared with other fine grinding machines [3]. On the other hand, it is known that particle aggregation/agglomeration causes poor flowability of dry material to be ground in a mill. Moreover, grinding media and liner coating result in a poor dry grinding efficiency due to the cushioning effect [4]. Grinding aids (chemical additives) have been used successfully for decades in many industries such as mineral, cement, ceramics, pigments etc. They which can improve the efficiency of the grinding remarkably with a small amount addition should more positively be applied to the grinding operations, especially to dry ultrafine grinding with higher energy consumption [2]. Moreover, the penetration of grinding aid into a crack within a particle could promote propagation or the crack, resulting in easier breakage of the particle [3]. On the other hand, grinding aids should even more positively be applied to ultrafine grinding operations with higher energy consumption. However, not only in ultrafine grinding operations, but also in fine ones in fields other than the cement industry, grinding aids have scarcely been utilized because the undesirable contamination of the product occurs with the use of the aids. When it is used a grinding aid, it must be selected an appropriate one that has no detrimental effect on downstream processing or the final product [5]. If it is actually used a grinding aid at the present technical level, it must be empirically determined the variety and quantity of the grinding aid based on experimental data [6]. In most of the studies on grinding aids, the effect of moisture [7] and grinding aids [8-12] have been discussed to get the fine powders in wet grinding method for calcite/limestone, but there are only a few reports in dry conditions for calcite/limestone [5,13]. In these studies, analyses of product consist of specific surface area, fineness, particle size distribution, crystalline structure and specific energy consumption. Nevertheless, effects of grinding aids on colour properties of ground products were not found in the literature.

The colour of the calcite surface is the first quality parameter evaluated by consumers and 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 [14]. Color is an easily perceived physical characteristic of materials, and wields great importance for manufacturers [15]. 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 [16].

The main purpose of this study was to systematically investigate the effects on fineness, particle size distribution (PSD) width, surface area and color properties of some chemical additives such as methanol, ethanol, sodium oleat and chloroform on dry fine grinding of calcite powder in dry vertical stirred mill.

Materials and Methods

Materials

Powder sample used in this study was calcite ($CaCO_3$) (X_{50}=33 µm) (Fig.1) from Micron'S Co. (Nigde, Turkey) and its density was 2700 kg/m^3.

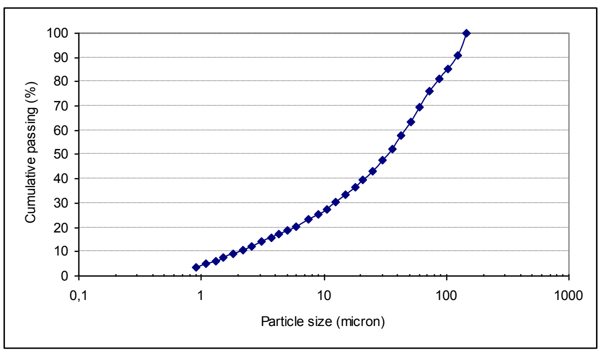


Figure 1: Particle size distribution in the feed sample

Chemical properties of sample are shown in Table 1. Volumetric surface area (S_V) of the calcite before grinding was 0.95 m^2/cm^3. The grinding media selected for the tests was 3.5-4.0 mm alumina (Al_2O_3) beads. The physical properties of grinding media are presented in Table 2. Four kinds of additives were used as grinding aids, as shown in Table 3.

Table 1: Chemical composition of the calcite sample (wt%)

$CaCO_3$	$MgCO_3$	Fe_2O_3	SiO_2	Al_2O_3	Total
99.5	0.2	0.01	0.01	0.02	99.74

Table 2: Physical properties of grinding media

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

Table 3: Physical properties and addition amount of grinding aids used

Additives	**Density (g/cm^3)**	**Chemical formula**	**Molecular weight (g/mol)**	**Additive dosage (wt%)**
Methanol	0,792	CH_3OH	32,0	0.25, 0.5, 1, 2
Ethanol	0,789	C_2H_5OH	46,1	0.25, 0.5, 1, 2
Sodium oleate	0,900	$C_{18}H_{33}NaO_2$	304,4	0.25, 0.5, 1, 2
Cloroform	1,49	$CHCl_3$	119,4	0.25, 0.5, 1, 2

These additives were special grade reagents (Merck and Sigma-Aldrich Corporation, St. Louis, MO, USA) and used without further purification. Summary of experimental conditions is also shown in Table 4.

Table 4: Summary of experimental conditions

Item	Experimental conditions
Bead filling ratio	0.70
Sample filling ratio	0.05
Rotation speed of stirrer	600 rpm
Grinding time	10 min
Internal volume of grinding pot	750 ml
Temperature	Room temperature
Material of grinding media	Alumina
Grinding media size	3.5-4 mm
Powder sample (calcite)	
Density	2.7 g/cm^3
Feed size	-150 µm
Surface area	0.95 m^2/cm^3

Methods

Grinding tests were carried out in a vertical type stirred media mill Standard-01 Model manufactured by Union Process (U.S.A.) which was reported in our previous study [17]. In order to investigate the effect of grinding aid on fineness and surface area of the products, a series of experiments were carried out. Sympatec HELOS (H0983) laser diffraction analyser (Sympatec GmbH, Clausthal-Zellerfeld, Germany) was used for the analysis of the feed and the ground products. Each test was repeated three times and the values reported are a mean average.

Several methods have been used to describe the particle size distribution (PSD) width [18]. An additional property is the "steepness" of the particle size distribution curve, defined by the "steepness factor" (SF) [19]. This value is the quotient of the X_{50} and the X_{20} values. A value with SF greater than 2 is described as "broad" and curves with a factor of less than 2 as "'narrow" or "steep" [20]. The SF value is calculated from X_{50}/X_{20}.

An organization called Commission Internationale del'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* (Lightness) represents the difference between light (“pure white”) (where L*=100) and dark (“black”) (where L*= 0); a* (Redness-Greenness) represents the difference between green (−a*) and red (+a*); and b* (Yellowness-Blueness) represents the difference between yellow (+b*) and blue (−b*) [21]. The CIELAB values are calculated from the red green and blue filters of the colorimeters and are particularly suited to describing near white samples according to the following equations [22]:

$$L^* = 116\,(Y/Y^n)^{1/3} - 16 \quad (1)$$

$$a^* = 200[((X/X^n)^{1/3} - (Y/Y^n)^{1/3}] \quad (2)$$

$$b^* = 200[((Z/Z^n)^{1/3} - (Y/Y^n)^{1/3}] \quad (3)$$

where X, Y and Z are the tristimulus values for the samples arising from the colorimetric system and X^n, Y^n and Z^n are those of a surface colour chosen as the nominal white stimulus. Accordingly, the perfect colourless white has the values L*=100, a*=0 and b*=0 in theory. Using this system and colour that corresponds to a place on the Cylindrical CIELAB colour space system was shown in Fig. 2.

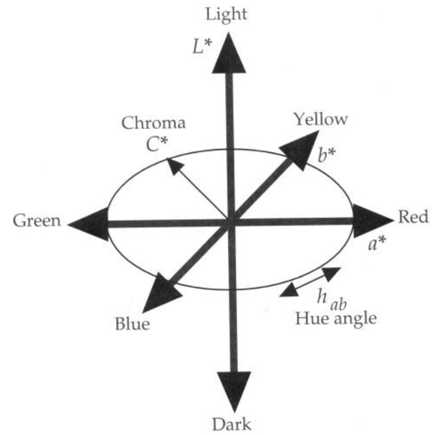


Figure 2: Cylindrical CIELAB color space [19]

Another useful parameter for describing white, which is given in the BS 3900 [23] is delta E (Δ*E)*. The total colour difference (Δ*E)* was calculated using the measurements and Equation 4, by using *L*, a** and *b** values [24, 25]. The colour parameters (L*a*b*) of ground products were measured using a Datacolour Elrepho SF450X spectrophotometer in the study.

$$\Delta E = [(L_0 - L^*)^2 + (a_0 - a^*)^2 + (b_0 - b^*)^2]^{0,5} \quad (4)$$

where subscript "0" refers to the colour reading of the control feed sample used as the reference, and a larger Δ*E* indicates greater colour change from the reference sample. Delta E represents the magnitude of the difference in colour, but does not indicate the direction of the colour difference [20]. If this value is positive, this means that the product is lighter than the reference sample or vice versa. Table 5 shows total colour difference values (Δ*E)*. If this value is positive, this means that the product is lighter than the reference sample or vice versa.

Table 5: Total color difference values [27]

(ΔE)	**0**	**1**	**2**	**3**	**4**	**5**
total color difference	no	very low	low	medium	high	very high

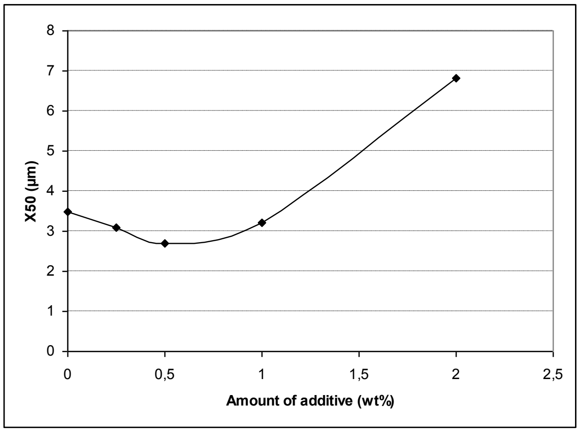
Moreover, a whiteness index (WI) has been described based on the distance of a color value from a nominal white point, represented in CIELAB color space as L*=100, a*=0 and b*=0. In spectral terms a white material is one whose reflectance across the visible wave length range is constant and high (i.e. close to 100% or reflectance factor of 1). Varying shades of gray to black have a constant reflectance with the perfect black having a reflectance of 0% [26].

$$WI = 100 - [(100 - L^*)^2 + a^{*2} + b^{*2}]^{0,5} \quad (5)$$

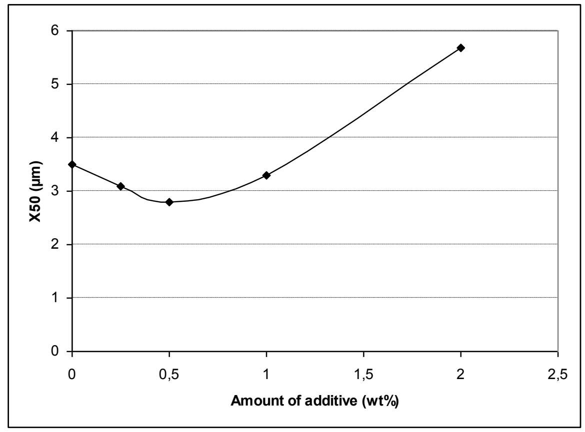
Results and Discussion

Influence of additive on the fineness, PSD width and surface area

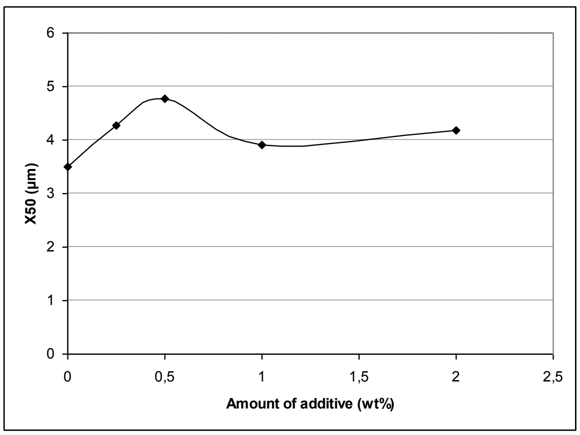
The effect of grinding aid on grinding performance has been explained mainly by two kinds of mechanism. One is based upon the alteration of surface and mechanical properties of individual particles, such as reduction of surface energy and modification of surface hardness, and the other is the change in arrangement of particles and their flow in suspensions [6]. Table 6 shows the summary of experimental results on product size (X_{10}, X_{50}, X_{90}). The median diameters (X_{50}) of ground products are decreased with the increase of additive dosage from 0.25% to 1% for methanol and ethanol. But, all X_{50} values are increased with sodium oleat and chloroform. In Fig.3, it can be seen the relationships between product size (X_{50}) and amount of additives.



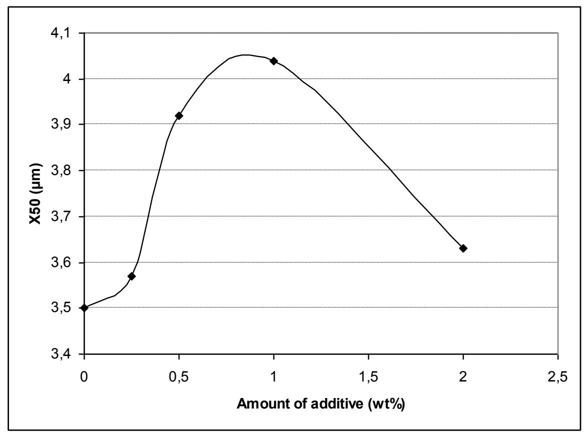
(a) methanol



(b) ethanol



(c) sodium oleat



(d) chloroform

Figure 3: Relationships between product size (X_{50}) and amount of additives

The steepness ratio (X_{50}/X_{20}) of calcite powder as received was about 9.4. It can be clearly shown that this value is decreasing with grinding and chemical additive. As mentioned in Section 2.2, this value with the greater than 2 is described as "broad", and those with the factor of less than 2 as "narrow" and "steep". Table 6 shows some SF values of feed material and final products. The SF value of the calcite powder at a rate of 1% ethanol was narrow (SF=1.9), with average particle size of 3.30 µm, while more than 90% of particles were less than 17.73 µm (Table 6).

Table 6 also shows the summary of results on surface area of product. The surface area (Sv) of ground products is increased with the increase of methanol and ethanol additive dosage from 0.25 to 1%. For >1, Sv values are decreasing. Also, all surface area (S_V) values are decreased with sodium oleat and chloroform from 0.25% to 2%. The decrease in the surface area is called as "negative grinding" and attributed to reagglomeration of the fine particles [12]. The surface area at the ethanol addition amount of 0.5% was about 0.1 times as large as the area without an additive, and about 3.35 times larger than that before grinding.

Table 6: Summary of results on each experimental condition

Grinding aids	**Additive dosage, %**	**Particle size (µm)**			**Surface area (m^2/cm^3)**	**SF value**
		X_{10}	X_{50}	X_{90}	Sv	X_{50}/X_{20}
Feed sample		*2.01*	*33.02*	*119.95*	0.95	9.4
Without grinding aids	0%	0.77	3.50	25.68	2.90	2.9

Methanol	0.25%	0.77	3.10	18.95	3.01	2.5
	0.5%	0.75	2.71	17.41	3.18	2.2
	1%	0.78	3.22	16.75	2.95	2.4
	2%	0.86	6.82	61.46	2.26	3.4
Ethanol	0.25%	0.77	3.09	18.20	3.01	2.2
	0.5%	0.75	2.79	15.39	3.17	2.1
	1%	0.78	3.30	17.73	2.93	1.9
	2%	0.82	5.68	72.59	2.44	3.7
Sodium oleate	0.25%	0.84	4.27	17.16	2.62	2.1
	0.5%	0.86	4.78	19.53	2.48	2.8
	1%	0.83	3.91	17.00	2.70	3.2
	2%	0.82	4.18	26.17	2.63	2.6
Cloroform	0.25%	0.76	3.57	48.69	2.89	2.7
	0.5%	0.77	3.92	49.36	2.81	3.2
	1%	0.77	4.04	48.97	2.79	3.4
	2%	0.76	3.63	49.59	2.89	3.3

Influence of additive on the colour properties

Table 7 shows the summary of results on colour properties of product. Whiteness is an important specification of micronized mineral filler products, and it is important for marketing purposes that whiteness be high (≥95%).

Table 7: Summary of results on each experimental condition

Grinding aids	Additive dosage, %	L*	a*	b*	ΔE*	WI
Feed material		94,69	0,42	3,01	0.00	93.88
Without grinding-aids	0	97,67	0,04	1,60	3.32	97.17
Methanol	0.25	97,53	0,03	1,59	3.24	97.06
	0.5	97,84	0,04	1,54	3.22	97.35
	1	97,64	0,04	1,53	3.32	97.19
	2	95,46	0,06	1,77	1.50	95.13
Ethanol	0.25	97,09	0,04	1,61	2.80	96.67
	0.5	97,88	0,05	1,53	3.54	97.51
	1	97,94	0,06	1,89	3.45	97.20
	2	96,33	0,16	2,18	1.86	95.73
Sodium oleat	0.25	97,54	0,08	1,58	3.21	97.08
	0.5	97,37	0,05	1,57	3.06	96.94
	1	97,42	0,05	1,83	2.99	96.84
	2	97,02	0,04	2,00	2.57	96.41
Chloroform	0.25	97,03	0,12	2,11	2.52	96.35
	0.5	96,74	0,13	2,17	2.23	96.08
	1	96,97	0,13	2,11	2.47	96.30
	2	96,83	0,14	2,14	2.33	96.17

The $L*$, $a*$, and $b*$ values of feed and ground calcite products are given in Fig. 4, 5 and 6. Notably, the $L*$ values of the ground calcite products slightly increased from 97.67 to 97.94 with grinding aids (methanol and ethanol) increased from 0.25% to 1%. Lightness (L*) is affected very slightly adversely both sodium oleat and chloroform. The value of $a*$ decreased significantly when the grinding aid increased to 1%, while $b*$, the second most important color value after $L*$, decreased from 1.60 to 1.53, revealing increased yellowness. The total color difference was calculated for grinding aids of 0.25, 0.50, 1, and 2%.

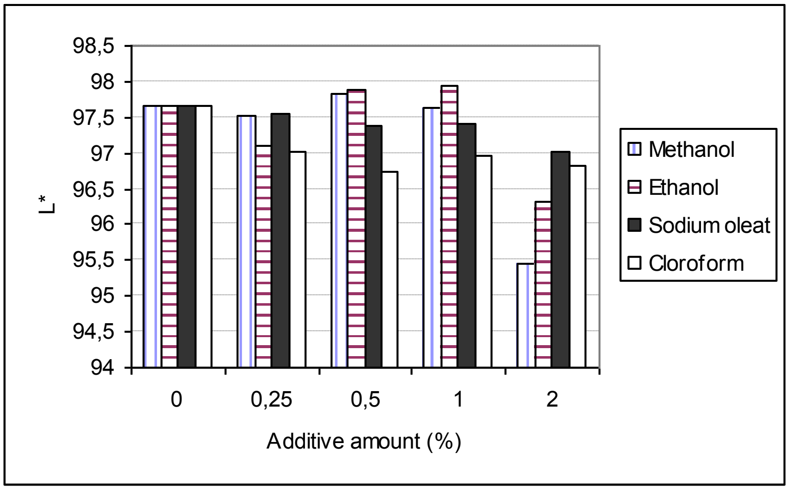


Figure 4: L values obtained with different amount of various grinding aid*

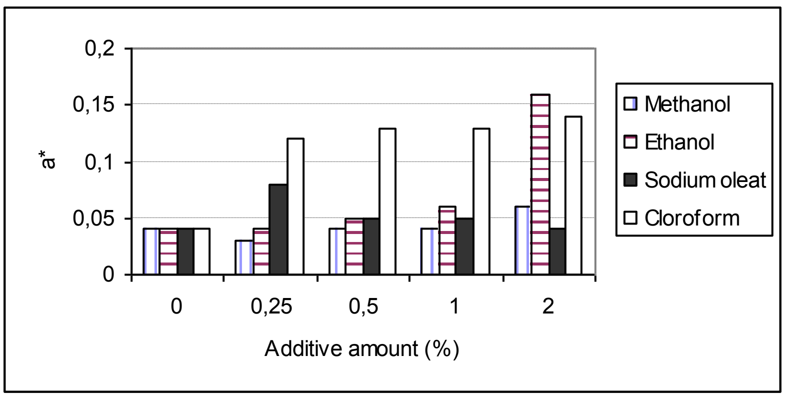


Figure 5: a values obtained with different amount of various grinding aid*

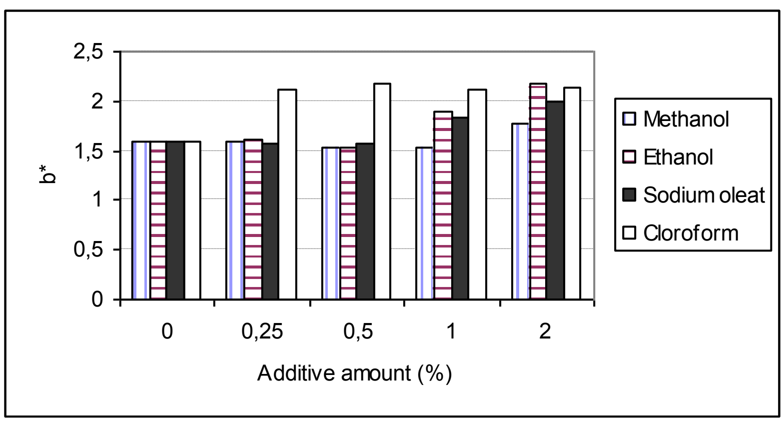


Figure 6: b values obtained with different amount of various grinding aid*

Similar trends are observed for ΔE, which increases with increasing amount of grinding aids from 0% to 0.5% for methanol and ethanol, indicating that the quality of colour of calcite heals (Fig. 7).

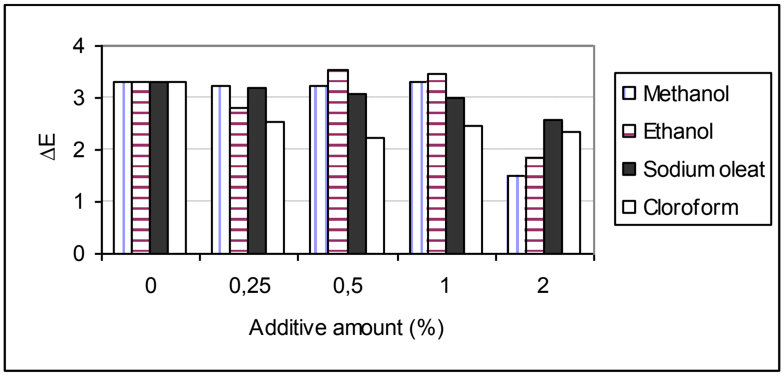


Figure 7: ΔE values obtained with different amount of various grinding aid

The results are reported in Fig. 7, which shows that ΔE increases with increasing grinding aid, apparently reaching a maximum at 3.54 for ethanol at a rate of 0.5%. With values >3, as it can be seen from Table 5, there is a medium color difference between the feed and micronized calcite products with grinding aid, which is considered to be a natural result of the grinding process and depends on the chemical additive type. The *WI* value of the ground calcite products slightly increased from 93.88 to 97.51 with grinding aids (ethanol) at a rate of 0.5% (Fig.8).

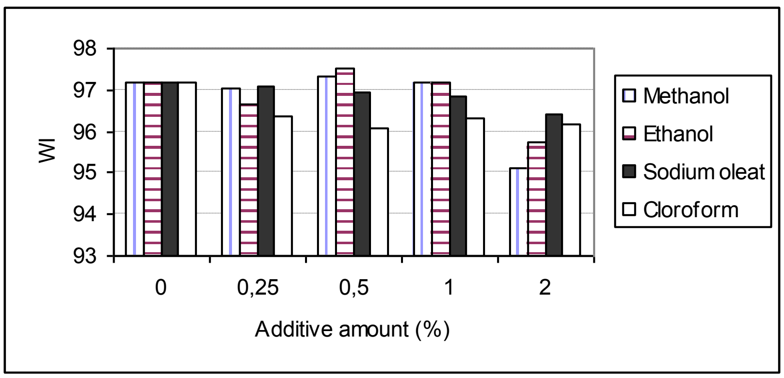


Figure 8: WI values obtained with different amount of various grinding aid

Conclusions

Experimental studies on grinding performance using calcite powder in dry vertical stirred mill have been carried out. The effects of grinding aid on the particle size, size distribution, surface area and color properties were examined. The followings were found out:

1. The median diameter (X_{50}) at the methanol addition amount of 0.5% was about 0.3 times as small as the particle size without an additive, and about 12 times smaller than that before grinding.
2. The use of 0.5% weight of grinding aid in the mill indicated enough beneficial effect on product size and volumetric surface area. The observed beneficial effect is due to the adsorption of grinding aid on fine calcite particles by influencing the mass transport.
3. It can be concluded that the increase in surface area is possible even with the use of small dosage of additive concentration by weight 0.5%.
4. The lightness (*L)* values of the ground calcite products slightly increased from 97.67 to 97.94 with grinding aids (methanol and ethanol) increased from 0.25% to 1%.
5. The total color difference (ΔE) increases with increasing grinding aid, apparently reaching a maximum at 3.54 for ethanol at a rate of 0.5%. This means that there is a medium color difference between the feed and micronized calcite products with grinding aid, which is considered to be a natural result of the grinding process and depends on the chemical additive type.

6. The whiteness index (WI) value of the ground calcite products which is one of the color properties satisfactorily increased from 93.88 to 97.51 with grinding aids (ethanol) at a rate of 0.5%.

Nomenclature

X_{10}	10% feed/product particle size
X_{50}	average particle size
X_{90}	90% feed/product particle size
S_v	volumetric surface area (m^2/cm^3)
L*	lightness of calcite
a*	redness-greenness of calcite
b*	yellowness-blueness of calcite
ΔE	the total color difference
WI	whiteness index

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