Article

Effects of Grinding Aids Used in Grinding Calcium Carbonate (CaCO₃) Filler on the Properties of Water-Based Interior Paints

Orkun Ersoy ^{1,*} , Dilek Güler ² and Murat Rençberoğlu ²

¹ Department of Geological Engineering, Faculty of Engineering, Hacettepe University, Ankara 06800, Turkey

² R&D Department, Niğtaş Corporation, Niğde 51100, Turkey; arge2@nigtas.com (D.G.); kalitekontrol3@nigtas.com (M.R.)

* Correspondence: oersoy@hacettepe.edu.tr

Abstract: Grinding aid chemicals which are used in the grinding of calcium carbonate (CaCO₃) to prevent agglomeration are chemisorbed on the surfaces of particles, and the compatibility of them with the solvent, water, or organic resin affects the dispersion of the minerals and ultimately down-stream product properties in consumer industries such as paint, papermaking, and plastic. This study tries to explain the effects of triethanolamine (TEA) and monoethylene glycol (MEG), which are most commonly used as grinding aids, on the behavior of CaCO₃ in water-based paints and on the properties of the paints. The powder properties of CaCO₃ (grain size, color, surface area, oil absorption capacity, zeta potential, etc.) were characterized, and the changes in the can stability, ease of application, and optical properties (gloss, opacity) of the paints were revealed with rheological and optical analysis. It was observed that amine compounds remained in higher amounts on the CaCO₃ surface and created negative results in the paint. On the other hand, glycol compound adhered less on the CaCO₃ surface and affected the properties of the final product less than the amine compound. Therefore, CaCO₃ ground without using any chemicals gives the best results in terms of long-term stability, ease of application, and visibility of the paint.

Keywords: water-based paints; calcium carbonate; grinding aids; opacity; gloss; rheology

Citation: Ersoy, O.; Güler, D.; Rençberoğlu, M. Effects of Grinding Aids Used in Grinding Calcium Carbonate (CaCO₃) Filler on the Properties of Water-Based Interior Paints. *Coatings* **2022**, *12*, 44. <https://doi.org/10.3390/coatings12010044>

Academic Editor: Xiaolong Wang

Received: 11 November 2021

Accepted: 25 December 2021

Published: 31 December 2021

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

In the cement and industrial mineral grinding technologies, liquid grinding aids are used to prevent the coating-effects on grinding media and mill equipment, agglomeration of fine particles, to increase the grinding performance, fineness of the product, and energy efficiency [1,2]. Amine and glycol compounds are the most widely used grinding aids. Triethanolamine (TEA) contains both amine and hydroxyl groups, all of which have the chemical properties of amines and alcohols. Monoethylene glycol (MEG), a polyol compatible with water and numerous organic compounds, contains non-dissociated and hydrophilic hydroxyl groups [3]. Studies involving molecular simulations have shown that the adsorption of grinding aids on the surface of the ground particles happens with their polar parts [4]. Thus, hydrogen bonds and other polar interactions connect the particle surface with the grinding aid functional groups. As a result, an adsorption layer is formed that keeps the particles at a distance where the effect of short-range attractive particle-particle forces is reduced [2]. The adsorption layer decreases the surface energy of the particle, so the agglomeration energy between the particles is strongly reduced during grinding in the mill. However, the performance of the grinding aid depends on both the type and the amount used in the grinding process [5]. Different types and amounts of grinding aids affect the properties of the final products in which the ground particles are used as filler since they are chemisorbed on the fresh surface of particles created by the grinding [6]. The compatibility of the grinding aid grafted on the mineral surface with the solvent, water or organic resin will affect the dispersion of the minerals and ultimately down-stream product

properties such as gloss, opacity, viscosity and storage stability in consumer industries such as paint, papermaking, and plastic [3,7].

The driving force for the development of water-borne coatings has been environmental [8]. At the end of the road started in the mid-1960s to reduce volatile organic compounds (VOCs) and toxic chemicals in traditional solvent-based paints, today water-based paints have become the most widely used paints globally [9]. Waterborne paints use water as a solvent, which is cheap and non-toxic to human beings and the environment, making this type of paint one of the ideal choices for paint manufacturing in the modern coating market [10]. However, there are still technical problems in manufacturing water-based paints that can cause aesthetic issues and application disadvantages [11]. Pigment dispersion is one of these problems [7]. The state of the pigment dispersion affects paint properties (gloss, opacity, viscosity, storage stability) [7,12]. The dispersion process involves three major states; (i) wetting of the pigment, (ii) disagglomeration of the pigment assembly by mechanical disruption, and (iii) stabilization of the pigment [7,13]. Wetting of the pigment is one of the most important stages of pigment dispersion. In wetting, pigment is wetted, and the absorbed air on the pigment surface is replaced by an aqueous resin solution [7,12]. Due to water's much higher surface tension, water reducible-paints have more technical problems in wetting than conventional solvent-based paints [7]. It is understood that pigment surface chemistry and wetting characteristics directly affect the most critical properties of paints [7,12,14,15]. After wetting and mechanical disruption, a particle-particle repulsive force must be introduced to achieve stabilization [7,12]. Dispersion stabilization can be achieved by one of the following mechanisms: steric stabilization, electrostatic stabilization [7,12], or electrosteric stabilization, which combines the first two mechanisms [16,17]. Electrosteric stabilization is usually achieved by means of ionic surfactants. Polyelectrolytes bearing a polar head-group capable of forming an electrical double layer and a lipophilic side chain capable of providing steric repulsion can be used for this purpose as polymeric surfactants [17]. As the pigment volume concentration (PVC) values increase, the effects of fillers (pigments) and dispersants on the properties of the paint become more complex.

In this study, the effects of amine and glycol compounds remaining on the surface of the CaCO_3 particles on the properties of high PVC water-based interior paints were investigated. Powder characteristics of CaCO_3 ground using TEA and MEG were determined, and the viscosity, pH, electrokinetic, rheological properties, thinness, gloss, and opacity of water-based interior paints containing these powders as fillers were compared.

2. Materials and Methods

Water-based interior paints were prepared according to an industrial recipe. AKAKRIL-ADC500 (Argon Kimya, İstanbul, Turkey), APEO (Alkylphenol Ethoxylates)-free anionic-nonionic aqueous dispersion (emulsion) based on styrene and acrylic acid ester served as a binder, ECODIS-P90 (Arkema, İstanbul, Turkey), polyacrylate ammonium salt, as a dispersing agent, Eastman Texanol ester alcohol (Aker Kimya, İstanbul, Turkey), as a film former, ANTIFOAM XL (Kimsel Kimya, İstanbul, Turkey), as an anti-foaming agent, NATRASOL 250 HHR (Aker Kimya, İstanbul, Turkey), a water-soluble hydroxyethylcellulose, as a viscosity modifier. Mains water was used in paint preparation, and CALGON PT (Ataman Kimya, İstanbul, Turkey) was used as a water softener. Commercial grade triethanolamine (TEA) and monoethylene glycol (MEG) were supplied from Polivin Kimya (İstanbul, Turkey) with boiling points of 310°C and 200°C , respectively. Calcium carbonate (CaCO_3) powders, which were ground by adding 0.7% TEA and MEG by weight and ground without using any grinding aid, were obtained from Niğtaş company (Niğde, Turkey) as mineral filler. Di-iso-octyl Phthalate (DOP) (Zag Kimya, İstanbul, Turkey) and the linseed oil (Tito, İstanbul, Turkey) with pH values of 6.03 and 4.44, respectively, were used for oil absorption capacity tests.

The grafting ratio (%) of the grinding aid chemicals on the surfaces of CaCO_3 was calculated after the furnace test. Five grams of CaCO_3 samples were kept at 105°C for half an hour and dehumidified. Next, we heated the dehumidified coated CaCO_3 samples

to 405 °C in a furnace and allowed them to stand at this temperature for 1 h. The weight loss at 405 °C was used to calculate the amount of chemical grafted onto the surface of the micronized CaCO₃ particles.

The particle size distributions of the CaCO₃ powder samples were analyzed using a laser particle size diffraction analyzer (Mastersizer 2000, Malvern Instruments Ltd., Worcestershirecity, UK). The colors of the powders were determined using a color spectrophotometer (Elrepho, DataColor, Trenton, NJ, USA) as defined by the Commission Internationale de l'Eclairage (CIE), L* indicates lightness, a* is the red/green coordinate, and b* is the yellow/blue coordinate [18].

Zeta potential is a physical property that is exhibited by any particle in suspension. The magnitude of the zeta potential indicates the potential stability of the colloidal system [19]. Electrophoretic mobility of the powder and paint samples was measured by a zeta potential measurement system (Zetasizer Nano ZS90, Malvern, UK). The velocity of a particle in a unit electric field is referred to as its electrophoretic mobility [19,20]. Electrophoretic mobility was converted to zeta potential by using Smoluchowski's approximation. The zeta potential values of CaCO₃ powders were measured in triple distilled water at a solid-to-liquid ratio of 0.05 gr/100 cc. Powders were measured at equilibrium pH 8.4 after acid/base addition. The zeta potentials of the paints were measured at their inherent pH values.

Brunauer–Emmett–Teller (BET) measurements were used to assess the precise surface areas of the CaCO₃ powders using a surface-area analyzer (Quadrachrome-Evo, Quantachrome, Boynton Beach, FL, USA).

The oil absorption values of the CaCO₃ powder samples were determined according to the ASTM D 281 standard [21]. A stiff, putty-like paste was formed by the dropwise addition of dioctyl phthalate (DOP) oil or linseed (flax) oil to CaCO₃ powder under thorough rubbing with a spatula. The amount of oil required to achieve the desired endpoint was used to calculate the oil absorption value.

Three different paints were prepared using ground calcite without using any grinding aid (UC), ground calcite using TEA (TC), and ground calcite using MEG (MC). All paint components were added in the order in the industrial recipe and mixed with the help of a multipurpose disperser (VBR-12, Yokes, Turkey). The paint is prepared to contain 60% CaCO₃, 17% binder dispersion, 20% water, and 3% dispersing, anti-foaming, rheological agents. pH measurements of paints were made using a benchtop pH meter (Mettler Toledo, Columbus, OH, USA). Paints were applied with the help of a film applicator to Leneta charts and glass slides, with a thickness of 200 µm. The fineness of the grind of paints was measured using grind gauge (2020, Elcometer, Manchester, UK).

The color values of the paint films in the black and white regions of the Leneta chart were measured as tristimulus values (X, Y, and Z) using a color spectrophotometer (Ci-64, X-rite, MI, USA). The contrast ratio was calculated, which is defined in ASTM D 2805 as the ratio of the reflectance (Y) of a film on a black surface to that of an identical film on a white substrate. Opacity (%) was calculated, which is simply the Contrast Ratio multiplied by 100 to get a percentage, where 100% is complete hiding. Gloss is an essential aspect of our visual perception of objects. The perception of gloss can relate to a product's finish, texture, and how a sample is illuminated and viewed. Surfaces with high reflectance are perceived as glossy, shiny, or lustrous, while less reflective surfaces are perceived as semi-gloss or matt. Glossmeter (Elcometer, Manchester, UK) was used to measure the gloss of paint surfaces using 60° and 85° angles. The gloss values were expressed as gloss units (GU).

Rheological measurements were performed using a rotational rheometer (Kinexus Lab+, Netzsch, Germany) and the rSpace software. A parallel plate geometry with a diameter of 20 mm was used. The Viscosity-Shear rate measurements at a specific temperature (25 °C) were conducted with a controlled shear rate from 1 s^{−1} to 3750 s^{−1}.

The morphologies of paint films on glass slides were characterized by scanning electron microscopy (SEM, EVO50, Zeiss, Oberkochen, Germany) using a back-scattered electron detector (BSD). The film surfaces were coated with a layer of gold prior to SEM imaging to avoid charging.

3. Results

The results of the analysis of the CaCO_3 powder samples used as fillers in the paints are given in Table 1. Grain size analyzes show that the powders used are of the same grain size. They have median particle diameters (d_{50}) of about 3 μm and maximum grain sizes (d_{100}) of about 20 μm . The color measurement results show that all CaCO_3 powders used have high lightness with L^* values near 100. The a^* and b^* values both approaching zero shows that CaCO_3 powders contain no red, green, yellow, or blue colors. These color values of CaCO_3 enable the preparation of white paint formulations. Although the grinding aid chemicals did not cause a significant change in the color of the powders, the L value of the powders decreased slightly (Table 1).

Table 1. Properties of CaCO_3 powders used in this study.

Sample Code	Grinding Aid (%)	Grafting Ratio (%)	d_{50}/d_{100} (μm)	$L^*/a^*/b^*$	Surface Area (m^2/g)	DOP/Linseed Oil Absorption ($\text{g}/100 \text{ g}$)	Zeta Potential (mV)
UC	-	-	2.97/19.95	98.91/0.00/0.60	4.28	28.42/17.67	10.30
TC	0.7	0.52	3.11/19.95	98.86/0.01/0.65	5.79	25.48/16.74	0.18
MC	0.7	0.12	2.94/17.14	98.83/0.02/0.66	5.56	27.44/16.74	0.00

It was observed that the grinding aids adhere to the surface of the CaCO_3 grains, increasing their surface area but decreasing their oil absorption capacity (Table 1). CaCO_3 powders (TC and MC) obtained from grinding using grinding aid chemicals have higher surface areas than powder ground without using chemicals (UC). It is thought that TEA can bind to the CaCO_3 surface with a physical bond [22] more strongly than MEG. The result of the furnace test also revealed that TEA binds to the CaCO_3 surface in more significant amounts than MEG (Table 1). The grafting ratio (%) for TC and MC samples was 0.52% and 0.12%, respectively. Considering that 0.7 wt.% of grinding aid chemical is added during grinding, the efficiency of grafting of chemicals on CaCO_3 was calculated after Yang et al. [23] and Ersoy et al. [24]. A total 74.3% and 17.1% grafting efficiencies were calculated for TC and MC, respectively. It is seen that the surface area increases as the amount of grinding aid on CaCO_3 increases. This finding is similar to the results obtained in previous studies [6,25–27]. The fact that CaCO_3 grains show less oil absorption despite their increased surface area can be explained by the surface chemistry change due to the grinding aid chemicals grafted onto the CaCO_3 surfaces. The oil demands of minerals explained by the acid-base interaction are attributed to the acidic or basic functional groups on the mineral surface [28]. It is thought that the chemicals grafted onto the CaCO_3 surface alter the basic sites on the surface and reduce the interaction between the CaCO_3 surface and the acidic groups in the oil molecules.

The effects of the grinding aids on the surface charges of the CaCO_3 particles were revealed as a result of the zeta potential measurements (Table 1). The zeta potential of the CaCO_3 powder ground without using any chemicals (UC) was measured as 10.3 mV, and the zeta potentials of the CaCO_3 powders with TEA (TC) and MEG (MC) were measured as 0.18 and 0.00, respectively. This change in the surface charges of the CaCO_3 grains indicates the presence of chemicals on the surface, changing the surface properties. In previous studies, it is known that organics adsorbed on the CaCO_3 surface render the surface potential less positive or even negative regardless of their composition and structure [29–32]. In this study, amine and glycol compounds grafted onto the CaCO_3 surface changed the surface charge of the grain in a more negative direction. Thus, the presence of these compounds on the surface has changed the pH value for CaCO_3 , where the zeta potential is zero (isoelectric point). This shows that the dispersion stability of the colloidal systems (e.g., paints) including UC, TC, and MC can be achieved at different pH values.

The zeta potentials of the paints were measured at their inherent pH values (Table 2). PUC has a higher pH value than other paints. The more acidic character of the PTC and PMC paints can be attributed to the fact that the basic functional groups on the CaCO_3

surface are altered by the grinding-aid chemicals, as discussed above. According to zeta potential theory, the magnitude of the zeta potential indicates the potential stability of the colloidal system. No significant difference was observed in the zeta potentials of the paints at their inherent pH values. However, when evaluated together with all their ingredients as a colloidal system, it was observed that the paints were far from the isoelectric point (zeta potential = 0) at their inherent pH values and were relatively stable.

Table 2. Properties of prepared paints.

Sample Code	Filler CaCO ₃	The Thinness (Fineness) of Grind (μm)	pH	Zeta Potential (mV)	Gloss 60°/85°	Tristimulus Values on Black Region X/Y/Z	Tristimulus Values on White Region X/Y/Z	Opacity (%)
PUC	UC	20	8.34	21.97	2.10/11.50	72.55/76.69/82.95	83.96/88.64/95.28	87
PTC	TC	20	8.18	23.03	2.05/10.80	70.23/74.25/84.02	83.64/88.29/95.06	84
PMC	MC	20	8.05	24.03	2.10/10.90	71.91/76.07/82.19	83.51/88.17/94.66	86

The color values of paint films in the black and white regions of the Leneta chart and the gloss values of the films measured using 60° and 85° angles were given in Table 2. According to Master Painters Institute (MPI) standards, all paints have traditional matte finishes with gloss values below 5 at 60° [33] (Table 2). The opacity of the paints calculated according to ASTM D 2805 show that TEA and MEG grafted on the CaCO₃ surfaces reduce the hiding power of the paints (Table 2 and Figure 1). Calcite milled without using any chemicals (UC) had better hiding power than calcite milled using chemicals (MC and TC). TEA significantly negatively affected opacity, while MEG had less impact on opacity. Adverse effects of both chemicals were also observed on the gloss of paints (Table 2). The hiding power represents the ability of the CaCO₃ particles in the paint layer to cover the background light from the matrix.

Figure 1. PUC, PTC, and PMC films on the Leneta chart.

While the agglomeration of the pigment grains and their poor dispersion in the matrix decreases the hiding power, well-dispersed grains and optimized grain size increase the hiding power of the paint. In this study, no visible signs of agglomeration were observed in the paint films at the macro scale. The fineness of the grind of all paints was measured below 20 μm, consistent with the maximum grain size (d100) of CaCO₃ powders indicating that no agglomeration occurred in paints (Table 2 and Figure 2). Agglomeration was also

not observed at micro dimensions in SEM images (Figure 3). However, in UC, it was observed that the binder material (resin) between the grains was more abundant, the grains were in a binder on the paint film surface, the surface was smoother (Figure 3a), but in TC and MC, the grains were free on the paint film and gave a porous and rough surface appearance (Figure 3b,c). This difference in roughness, which can be observed at the microscale on the surfaces of paint films, is probably one of the crucial reasons affecting the opacity and gloss of the paints [13]. It is seen that UC, in which CaCO_3 grains are observed to be wetted by the binder, has a smoother surface and a higher gloss value than TC and MC. The fact that the binder is not evenly distributed to all particles (pigments) in the paint or cannot wet the pigments causes surface roughness in micro scales and thus a decrease in opacity and gloss [13]. It is thought that this deterioration in the optical properties of the paint is due to the inability of the resin to fully wet CaCO_3 grains due to the chemicals on the surfaces of the grains. Another possibility is the “frozen state” due to post-application water evaporation and coagulation of binder aggregates, which can be observed in high PVC water-borne (acrylic) dispersions as a result of poor stabilization, which can also be caused by poor wetting [11]. This instant “frozen state” limits the mobility of the binder, resulting in poor flow and leveling behavior of the paint.

Figure 2. Streaks of coatings on the grid gauge channels.

Figure 3. SEM micrograph images of (a) PUC, (b) PTC, and (c) PMC film surfaces on glass slides acquired using a back-scattered electron detector (BSD).

To prevent settling and instability during storage and transport, water-borne dispersion coatings must have high viscosities under low shears. However, they need low viscosities under high shears during application. This behavior is called shear-thinning or pseudo-plasticity [11,34,35]. It was understood from shear rate-dependent viscosity measurements that all the paints prepared in this study showed shear-thinning behavior (Figure 3). The power-law model was fitted to all viscosity curves ($R^2 > 0.99$) to compare the flow properties of the paints quantitatively. The power-law model is given by the following mathematical equation [36]:

$$\eta = K\dot{\gamma}^{(n-1)}, \quad (1)$$

where n is the power-law index, K is the consistency (with the strange units of Pa.sn).

The power-law index (n) gives information about the behavior in the high shear region, that is, shear-thinning and K give information about the behavior in the low shear area, that is, storage or in-can stability [36,37]. Smaller n values indicate more shear-thinning (pseudo-plastic) behavior, while smaller K values indicate lower viscosities in the low shear zone, i.e., low storage stability [37]. The viscosity of high PVC dispersions is more sensitive to small variations in particle properties [38], and these changes are evident with the power-law properties of paints (Table 3).

Table 3. Power law properties of prepared paints.

Sample Code	Filler CaCO ₃	K (Pa.sn)	n
PUC	UC	218.12	−0.27
PTC	TC	67.45	0.26
PMC	MC	87.36	0.21

At low shear-rate range ($<10 \text{ s}^{-1}$), higher viscosity values indicate better in-can stability of PUC with 223.4% and 149.7% higher consistency indexes (K) than PTC and PMC, respectively. PUC seems to have higher dispersion and long-term storage stability than other paints. At a high shear-rate range ($>100 \text{ s}^{-1}$), PUC has the lowest viscosity suggesting that it is more advantageous in terms of application (painting, brushing, spreading). The particles in the paint are allowed to flow and orientate themselves during application due to the low viscosity behavior in the high shear-rate zone [37]. The more pseudoplastic behavior of PUC has also been seen from the power-law index (n) values (Table 3). PUC has 203.4% and 229.7% lower n values than PTC and PMC, respectively. Although PTC and PMC exhibit similar behavior, PMC appears to be somewhat more pseudo-plastic. At medium shear-rate ranges ($10\text{--}100 \text{ s}^{-1}$), the workability, which indicates the flow behavior during mixing, stirring, pouring, will be more difficult for PUC due to its relatively higher viscosity in this zone (Figure 4). Based on the effects of the grinding agents grafting on the CaCO₃ surface, it can be said that these chemical barriers preventing the wetting of the grains and the homogeneous distribution of the binder increase the grain–grain interaction in the paint. Since the wetting of the grains by the binder, which is the first stage of the dispersion process, is prevented by grinding aid chemicals, the behavior series that started with poor stabilization continued with high viscosity and application difficulties under high shear rates.

Figure 4. Shear rate-dependent viscosity of PUC, PTC, and PMC coatings.

4. Conclusions

The grinding aid chemicals used while grinding to the grain sizes required to be used as a filler mineral adhere to the surface of CaCO_3 and affect the properties of the final products. It was observed that amine compounds, one of these grinding aid chemicals, remained in higher amounts on the CaCO_3 surface and created negative results in the paint in which CaCO_3 was used as a filler. On the other hand, glycol compound adhered less on the CaCO_3 surface and affected the properties of the final product less than the amine compound. It has been observed that CaCO_3 ground without using any chemicals gives the best results in terms of long-term stability, ease of application, and visuality of the paint.

It is thought that the chemicals grafted on the CaCO_3 surface during grinding change the surface chemistry of the CaCO_3 grains, alter the functional groups that interact with the binder, and cause poor stabilization and application difficulties due to the lack of homogeneous distribution of the binder after poor wetting. Since it has been determined that grinding aid chemicals affect the behavior of the mineral fillers in the final product, it is understood that the companies producing filler minerals for industries such as paint and plastic need to use grinding aids that improve the properties of the final product. Considering that it is not technically possible to achieve effective dry grinding without the use of grinding aids, it is necessary for mineral producers to conduct research and development in order to be able to select grinding aids considering the end product properties.

Author Contributions: Methodology, O.E., D.G. and M.R.; investigation, supervision and writing, O.E.; sample preparation, powder analysis, paint analysis, O.E., D.G. and M.R. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by NİĞ TAŞ Corporation.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available in article.

Acknowledgments: We would like to thank NİĞ TAŞ Corporation for sharing the laboratory infrastructure used in this study.

Conflicts of Interest: NİĞ TAŞ Corporation permitted to use laboratory infrastructure to conduct this research and has financially supported the research. The authors D.G. and M.R. are the employees of the R&D department of NİĞ TAŞ Corporation. Author O.E. is the scientific consultant of NİĞ TAŞ Corporation.

References

- Hoffmann, B.; Bernhardt, C. Zur energieeffektivität bei der mahlung von kalkstein mit monocarbonsäuren. *Powder Technol.* **1985**, *41*, 295–300. [\[CrossRef\]](#)
- Prziwara, P.; Breitung-Faes, S.; Kwade, A. Impact of grinding aids on dry grinding performance, bulk properties and surface energy. *Adv. Powder Technol.* **2018**, *29*, 416–425. [\[CrossRef\]](#)
- Wu, X.P.; Liu, C.; Liu, Y.; Hou, T.F.; Wu, Z. A Review: Research into Organic Surface Treatment of Titanium Dioxide Material. *Mater. Sci. Forum* **2018**, *914*, 193–201. [\[CrossRef\]](#)
- Mishra, R.K.; Flatt, R.J.; Heinz, H. Force Field for Tricalcium Silicate and Insight into Nanoscale Properties: Cleavage, Initial Hydration, and Adsorption of Organic Molecules. *J. Phys. Chem. C* **2013**, *117*, 10417–10432. [\[CrossRef\]](#)
- Prziwara, P.; Kwade, A. Grinding aids for dry fine grinding processes—Part I: Mechanism of action and lab-scale grinding. *Powder Technol.* **2020**, *375*, 146–160. [\[CrossRef\]](#)
- Hasegawa, M.; Kimata, M.; Yaguchi, M. Effect and behavior of liquid additive molecules in dry ultrafine grinding of limestone. *KONA Powder Part. J.* **2006**, *24*. [\[CrossRef\]](#)
- Kobayashi, T. Pigment dispersion in water-reducible paints. *Prog. Org. Coat.* **1996**, *28*, 79–87. [\[CrossRef\]](#)
- Elliott, P.T.; Glass, J.E. Water-borne Coatings. In *Applied Polymer Science: 21st Century*; Elsevier: Amsterdam, The Netherlands, 2000; pp. 563–588. [\[CrossRef\]](#)
- Javadi, A.; Cobaj, A.; Soucek, M.D. Commercial waterborne coatings. In *Handbook of Waterborne Coatings*; Elsevier: Amsterdam, The Netherlands, 2020; pp. 303–344. [\[CrossRef\]](#)
- Yang, F.; Chen, B.; Hashimoto, T.; Zhang, Y.; Thompson, G.; Robinson, I. Investigation of Three-Dimensional Structure and Pigment Surrounding Environment of a TiO₂ Containing Waterborne Paint. *Materials* **2019**, *12*, 464. [\[CrossRef\]](#)
- Kästner, U. The impact of rheological modifiers on water-borne coatings. *Colloids Surf. A Physicochem. Eng. Asp.* **2001**, *183*–185, 805–821. [\[CrossRef\]](#)
- Clayton, J. Pigment/dispersant interactions in water-based coatings. *Surf. Coat. Int.* **1997**, *80*, 414–420. [\[CrossRef\]](#)
- Tsutsui, K.; Ikeda, S. 10 years' progress in the characterization of state of dispersion. *Prog. Org. Coat.* **1982**, *10*, 235–250. [\[CrossRef\]](#)
- Balfour, J.G.; Hird, M.J. Flocculation-its measurement and effect on opacity in systems containing titanium dioxide pigments. *J. Oil Colour Chem. Assoc.* **1975**, *58*, 331–344.
- Heertjes, P.M.; Smits, C.I. The influence of adsorbed layers on the rheological behavior of titanium dioxide dispersions. *Powder Technol.* **1977**, *17*, 197–205. [\[CrossRef\]](#)
- Davies, J.; Binner, J.G.P. The role of ammonium polyacrylate in dispersing concentrated alumina suspensions. *J. Eur. Ceram. Soc.* **2000**, *20*, 1539–1553. [\[CrossRef\]](#)
- Ivanov, M.G.; Ivanov, D.M. Nanodiamond Nanoparticles as Additives to Lubricants. In *Ultrananocrystalline Diamond: Synthesis, Properties and Applications*, 2nd ed.; Elsevier: Amsterdam, The Netherlands, 2012; pp. 457–492. [\[CrossRef\]](#)
- Zarubica, A.; Miljkovic, M.; Purenovic, M.; Tomic, V. Colour parameters, whiteness indices and physical features of marking paints for horizontal signalization. *Facta Univ.-Ser. Phys. Chem. Technol.* **2005**, *3*, 205–216. [\[CrossRef\]](#)
- Hunter, R.J. *Zeta Potential in Colloid Science*; Elsevier: Amsterdam, The Netherlands, 1981; ISBN 978-0-12-361961-7.
- Misra, V.N.; Reddy, P.S.R.; Mohapatra, B.K. *Mineral Characterisation and Processing*; Sunil Sachdev: Bhubaneswar, India, 2004; ISBN 81-7764-615-X.
- ASTM International. *ASTM D281-12-Standard Test Method for Oil Absorption of Pigments by Spatula Rub-out*; ASTM International: West Conshohocken, PA, USA, 2016.
- Hiçyılmaz, C. *The Effects of Amines on the Surface Properties of Scheelite and Calcite*; Middle East Technical University: Ankara, Turkey, 1988.
- Yang, Z.; Tang, Y.; Zhang, J. Surface modification of CaCO₃ nanoparticles with silane coupling agent for improvement of the interfacial compatibility with styrene-butadiene rubber (SBR) latex. *Chalcogenide Lett.* **2013**, *10*, 131–141.
- Ersoy, O.; Köse, H. Comparison of the effect of reactive and nonreactive treatments on the dispersion characteristics of a calcium carbonate (calcite) filler in a polypropylene matrix composite. *Polym. Compos.* **2020**, *41*, 3483–3490. [\[CrossRef\]](#)
- Hasegawa, M.; Kanda, Y. The Effect of Alcohol Grinding Aids on the Ultrafine Grinding of Feldspar. *J. Soc. Powder Technol. Jpn.* **1993**, *30*, 570–575. [\[CrossRef\]](#)
- Hasegawa, M.; Kimata, M.; Shoji, T. Effect of Liquid Additives and Behavior of Alumina Powder in Ultrafine Grinding of Alumina. *J. Soc. Powder Technol. Jpn.* **2002**, *39*, 736–742. [\[CrossRef\]](#)
- Hasegawa, M.; Kimata, M.; Shimane, M.; Shoji, T.; Tsuruta, M. The effect of liquid additives on dry ultrafine grinding of quartz. *Powder Technol.* **2001**, *114*, 145–151. [\[CrossRef\]](#)
- Casanova, H.; Orrego, J.A.; Zapata, J. Oil absorption of talc minerals and dispersant demand of talc mineral non-aqueous dispersions as a function of talc content: A surface chemistry approach. *Colloids Surf. A Physicochem. Eng. Asp.* **2007**, *299*, 38–44. [\[CrossRef\]](#)
- Vdović, N. Electrokinetic behaviour of calcite-the relationship with other calcite properties. *Chem. Geol.* **2001**, *177*, 241–248. [\[CrossRef\]](#)
- Andersen, J.B.; El-Mofty, S.E.; Somasundaran, P. Using electrophoresis for determining the mechanism of amine, sulfate and oleate adsorption on calcite. *Colloids Surf.* **1991**, *55*, 365–368. [\[CrossRef\]](#)

31. Cicerone, D.S.; Regazzoni, A.E.; Blesa, M.A. Electrokinetic properties of the calcite/water interface in the presence of magnesium and organic matter. *J. Colloid Interface Sci.* **1992**, *154*, 423–433. [[CrossRef](#)]
32. Vdović, N.; Bišćan, J. Electrokinetics of natural and synthetic calcite suspensions. *Colloids Surf. A Physicochem. Eng. Asp.* **1998**, *137*, 7–14. [[CrossRef](#)]
33. MPI Gloss Levels. Available online: http://mpi.arcomone.com/DT201arcom/Manuals_ASM/Misc/standards.asp (accessed on 7 September 2021).
34. Hester, R.D.; Squire, D.R. Rheology of waterborne coatings. *J. Coat. Technol.* **1997**, *69*, 109–114. [[CrossRef](#)]
35. Prideaux, J. Rheology modifiers and thickeners in aqueous paints. *Surf. Coat. Int.* **1993**, *76*, 177–183.
36. Barnes, H.A.; Hutton, J.F. Viscosity. In *An Introduction to Rheology*; Elsevier: Amsterdam, The Netherlands, 1989; Chapter 2.
37. Moolman, P.L. *Rheology of Coating Systems*; University of Stellenbosch: Stellenbosch, South Africa, 2003.
38. Larson, R.G. *The Structure and Rheology of Complex Fluids*; Topics in Chemical Engineering; Oxford University Press: Oxford, UK, 1999; ISBN 9780195121971.