COMPARISON TiO_2 POWDERS FLOWABILITY TESTS

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Abstract

In this work, four different flowability powder tests - angle of repose measuring, flow from hopper simulation, classical tube method and evaluation of flow functions using FT4 powder rheometer - were compared. The TiO_2 powders with different content of nanoparticle were used for these comparisons. These powders were characterized by basic mechanical-physical parameters such as particle size distribution, density, moisture etc. The first flowability method (angle of repose measuring) uses stand with vibration feeder of fine powder material. Flow simulation method is based on powder flow from the hopper. Both mentioned test stands were created in Bulk Solids Centre Czech Republic. Third classical tube method is based on free pouring of powder on the pad. These three methods named above are evaluated on a static angle of repose. The fourth test is based on the calculation of the flow function as ratio major principal stress and unconfined yield strength measured using FT4 powder rheometer. Flowability methods of TiO_2 powder have been compared. The advantages and disadvantages of the individual methods and the areas of their use have been identified.

Keywords: Flow, powders, angle of repose, titanium white, FT4 powder rheometer

1. INTRODUCTION

Flowability, one of the basic parameters of bulk materials, indicates the ability of bulk material to flow. In determining this parameter, the angle of repose was used, classifying the flow of bulk material into individual modes. This parameter was determined by three methods. Flowability was also determined using the shear device - powder rheometer Freeman FT4. The obtained data were evaluated, discussed and compared. This study was conducted on four samples of titanium white (A, B, C a D).

2. MATERIALS AND METHODS

2.1. Materials

Titanium white is a chemical compound of oxygen and titanium. Around the world, titanium dioxide is most commonly found in three mineral forms, and titanium white is produced by their treatment. The three basic forms of titanium dioxide are rutile, anatase, and brookite [1]. These minerals are very brittle, with a composition of Ti 59.9% and O 40.06%, insoluble in acids.

Rutile is a tetragonal mineral. It has the most stable nanoparticle system above 35 nm, with a density of about 4.2-4.3 $g.cm^{-3}$. This mineral has a perfect cleavage according to (101) and less perfect according to (100), the fracture being uneven and shelly.

The second one of these minerals is anatase. Anatase is also a tetragonal mineral. It has the most stable nanoparticle system close to 11 nm, with a density of about 3.9 $g.cm^{-3}$. This mineral has a perfect cleavage according to (101), while the fracture is shelly.

The last of these minerals is brookite. This mineral is rhombohedral. It has the most stable nanoparticle system in the range of 11-35 nm, with a density of about 4.1 g.cm^{-3}. This mineral has an imperfect cleavage according to (120), while the fracture is semi-shelly [2].

Titanium white is used in the cosmetic (creams, sunscreens), pharmaceutical (medicines, tablets, toothpaste, etc.) and food (E171) industries. It absorbs UV radiation and transforms it into harmless heat, and is used as a pigment, for its distinctive brightness and high refractive index. It is highly hydrophobic and therefore it is used to make car glass and spectacles. Suitably modified titanium oxide can be also used as a photocatalyst. It is also used in some types of solar cells; in medicine it allows the adhesion of implants to bones.

For testing of flowability, four samples A, B, C, D with different crystallography and particle size distribution were used. The particle size was measured on a CPS DC24000 Disk Centrifuge.

3. METHODS

For this type of study, three methods for determining the angle of repose and two methods for determining the flowability were used, and also the measuring device for determination of granulometry, a CPS DC24000 Disk Centrifuge

3.1. Particle size distribution method

Particle distribution was performed on the above mentioned device, a CPS disk Centrifuge RPS 24000 with a measurement range of 0.01 to 40 microns. This device evaluates the distribution using the centrifugal sedimentation principle. By using several layers of liquid of different density, a so-called density gradient is created in a transparent measuring cell. Through this gradient, the measured particles pass and are slowed down by the density difference of the liquid in the gradient layers and accelerated by the centrifugal force of the rotating cell. The particle size and concentration are detected by a laser located on the outer edge of the rotating cell [3].

3.2. Titanium white flow parameters determination

The first method determines the flow function using the Freeman FT4 powder rheometer [3]. The flowability is then evaluated by the Jenike theory [4], where the value of the flow function is given as ratio major principal stress and unconfined yield strength. This flow function is based on the Mohr circles and the stress state of the bulk material. The second method was determination of the flow character of the bulk material by determining the angle of repose. The flow character is then determined from the following **Table 1**.

Table 1 Powder flow classification according to angle of repose (left) [5] and flow function (right) [4]

Powder flow	Angle of repose [°]
Excellent	25-30
Good	31-35
Fair	36-40
Passable	41-45
Poor	46-55
Very poor	56-65
Very, very poor	> 66

Powder flow	Flow function
Free flowing	> 10
Easy flow	4-10
Cohesive	2-4
Very cohesive	1-2
Hardened	0-1

3.3. Angle of repose determination methods

The angle of repose was determined by three methods. The dynamic angle of repose measured on a stand - rotating drum, the static angle of repose measured on the Zenegero measuring device and by simply pouring the volume of bulk material onto a horizontal pad. The device for determination of the dynamic angle of repose and the Zenegero device were created in the labs of the Bulk Solid Center Czech Republic [3].

Determination of the dynamic angle of repose

This parameter was determined by stand - rotating drum. This device consists of a rotating drum on supports, drive and frequency converter. The measured material is loaded into the drum and the drum speed is adjusted using the frequency converter. For this study, drum speeds of 12 and 18 rpm were used. An optical device (camera) captures images of the shifted material in the drum, and the angles of the material are read before (α) and after (β) loading during rotation of the drum. The dynamic angle of repose is then the mean value (φ) of the above angles of slope [6].

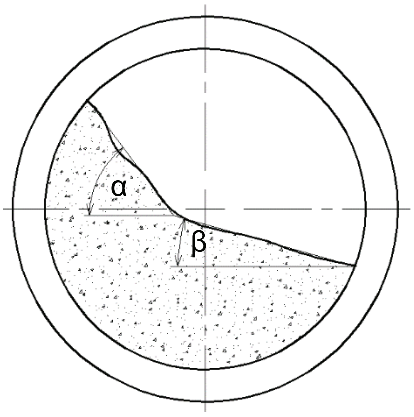


Figure 1 Measuring of dynamic angle of repose in rotating drum

Determination of the static angle of repose

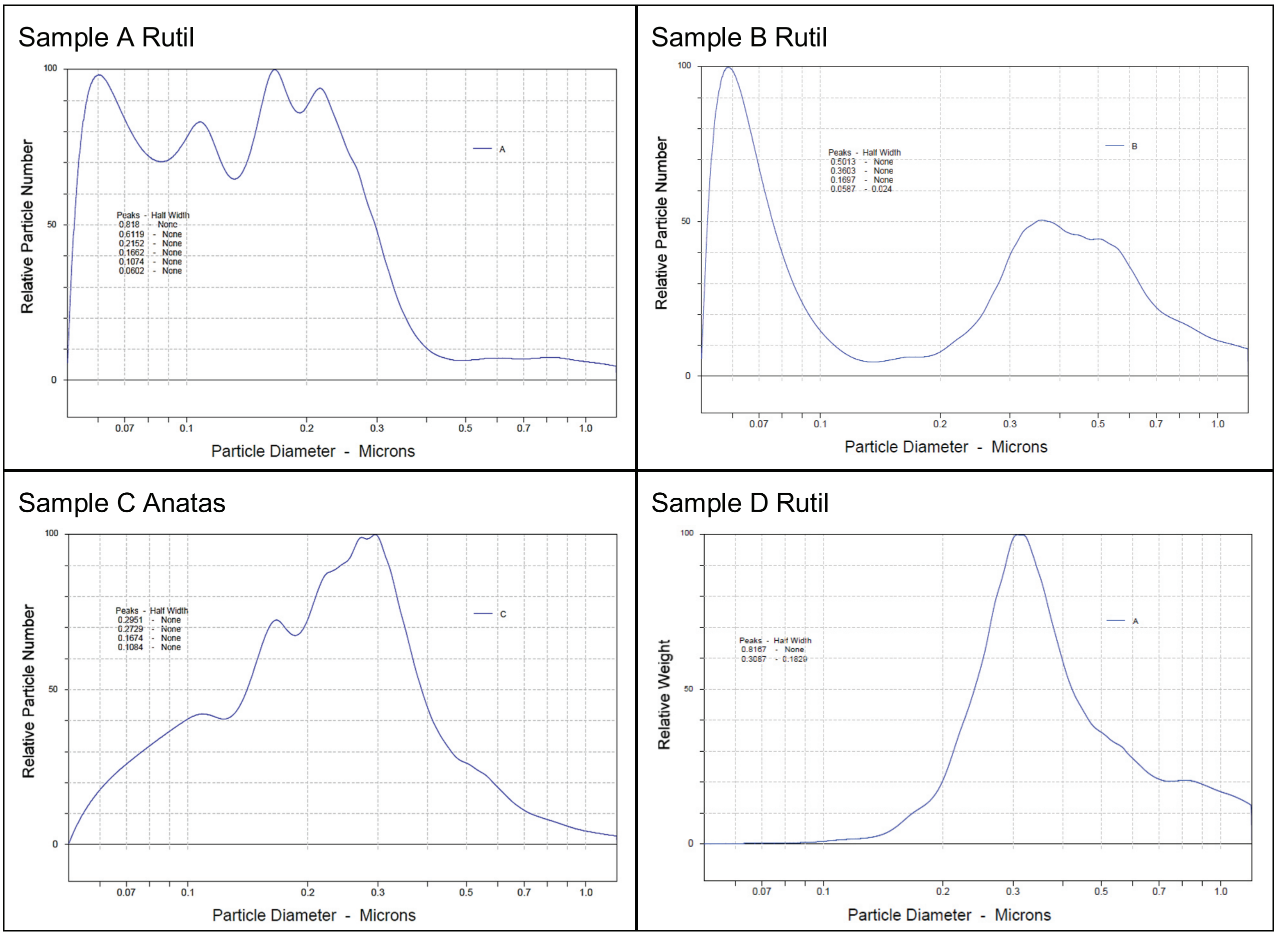
The static angle of repose was determined by pouring the volume of material on a horizontal pad (**Figure 2** left). For this purpose a measuring cylinder is used, filled with the measured sample. The cylinder is then carefully placed on the horizontal surface with by the bottom down and raised with continuous speed. The material begins to spill and lay on itself. After pouring, the angle of the material slope to the horizontal surface on which the material is piled is read out. The second method determines the static angle of repose using the Zenegero device (**Figure 2** right).

Figure 2 Left - static angle of repose determined by pouring of powder on a horizontal pad for sample A, right - static angle of repose determined by Zenegero method for sample C

The material is poured continuously by the vibratory feeder through a funnel onto the horizontal surface (tray). The excess material starts to spill out of the tray, leaving a pile of material on the tray. The static angle of repose is then determined as the angle of the slope to the horizontal surface of the tray.

4. RESULTS

The measurement results are shown below (**Figure 3**, **Table 2**, **Table 3**, **Table 4**). Particle size distributions of samples and crystal structures are shown at **Figure 3**.


Sample A Rutil

Sample B Rutil

Sample C Anatas

Sample D Rutil

Figure 3 Particle size distribution and crystal structure of samples A - D

Table 2 Measurement results of dynamic angle of repose

Sample	Average value of dynamic angle of repose [°]			Relative character of flow
	Rotation [rpm]		Average value	
	12	18		
A	50.27	40.64	45.45	Poor
B	49.28	46.63	47.95	Poor
C	51.48	60.01	55.75	Very poor
D	49.80	43.44	46.62	Poor

When evaluating the dynamic angle of repose it was determined that during the shifting a so-called cascade effect occurs that affects this measurement. It was found that for measurement of cohesive substances it is advisable to keep the lower speed of the drum for more accurate measurement and to try to eliminate this effect. It was further found that the rotation causes a lot of dusting of the particles for samples A, B and D. The dusting of sample C was minimal. This can be probably attributed to the mineral type and the perfect cleavage of crystals according to (101). Also for samples A, B and D the dynamic angle of reposes were greater at 12 rpm and for sample C at 18 rpm. The flow character was evaluated only relatively (**Table 2**). Currently, there is no classification of flow according to the dynamic angle of repose in the literature. This is most likely due to many factors that may affect the measurement. This measurement is not standardized.

Table 3 Measurement results of static angle of repose

Sample	Average value of static angle of repose [°]		Flow classification	
	ZENEGERO	Pouring of powder	ZENEGERO	Pouring of powder
A	34.71	28.38	Good	Excellent
B	42.59	31.79	Passable	Good
C	46.78	32.68	Poor	Good
D	41.51	30.55	Passable	Excellent

The flow character was determined by the static angle of repose using **Table 1**. This table determines the flow character using the static angle of repose. With the method using pouring of the bulk material on the horizontal pad there was a problem of the pulsating shocks that occurred during emptying the measuring cylinder. This affected the formation of the pile of bulk material, and the material was forced to move more widely into space. Therefore, the angle of the slope of the material with the horizontal plate was much smaller and the flow function was determined as better flowing. This was the reason behind the development of the Zenegero device which does not have those shocks. Here the material is poured by layers. Once the internal stresses in the bulk material have been overcome, the material is torn off and the excess overflows the tray. The static angle of reposes were read, evaluated and compared in the **Table 1**. The measured values are listed in **Table 3**.

The last measurement in this study was carried out on the Freeman FT4 powder rheometer. The values were evaluated based on **Table 1**and listed in **Table 4.**

Table 4 Flow classification according to flow function values measured by powder rheometer Freeman FT4

Sample	Flow function	Flow classification
A	1.18	Very cohesive
B	1.96	Very cohesive
C	1.05	Very cohesive
D	3.92	Cohesive

Due to the smaller number of the flow character zones, they were classified in the sectors of very poorly flowing and flowing with difficulty. In this case sample D had the best flow. This is probably due to the distribution of the particle size in the sample. This was the only sample not containing particles smaller than 200 nm. Thus the air pores are not filled with the dust fraction but with air and the material is more compressible. The shear strength of sample D is less than that of others and is better flowing.

5. CONCLUSION

The aim of the study was the comparison of methods for determination of the flow character of titanium white samples. Four methods were compared. Using a dynamic angle of repose, where the measurement was influenced by a cascade effect, it was found that for cohesive materials it is advisable to use lower speeds of the measuring drum. It was determined that for the 12 rpm setting the rutile titanium white exhibited a greater dynamic angle than for the 18 rpm setting. This was the opposite for the anatase titanium white. For this method, it was necessary to determine the flow character only relatively. In determining the flow character by means of a static pour angle, it was found that the method of emptying the volume of material on a horizontal pad is not sufficiently suitable for determining the flow character of titanium dioxide due to pulsating shocks during material discharge. This undesirable phenomenon affects the measurement and determination of the flow character of the material. Therefore the Zenegero device was used, where the material is gradually poured onto the tray and the static angle of repose is read after the stress state has stabilized in the bulk material. These angles were compared to the table for determination of the flow character, and it was found that the classification of sample C was the worst in this case, samples B and D were transported moderately "on average" and sample A was transported the best. The results of determining the flow character using the flow function measured with the Freeman FT4 powder rheometer were different compared to the other methods. By applying normal force, the material of sample D is probably more compressed because it does not contain the finer fraction of the particles as the others, there is lower shear strength of the sample and it is defined as the best flowing. This study found that the flow character of the titanium white sample was significantly influenced by size distribution and shape of the particles. When measuring the flow character using the dynamic angle of repose the effect of morphology prevails, and when measuring the flow character using the Freeman FT4 powder rheometer where material compression occurs, the effect of granulometry prevails.

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