

EFFECT OF SAMPLE PREPARATION ON TiO₂ NANOPARTICLES SIZE DISTRIBUTION

ŽÍDEK Martin^{1,2}, JEZERSKÁ Lucie^{1,2}, ZEGZULKA Jiří^{1,2}, ZÁDRAPA František^{1,2}

¹VŠB - Technical University of Ostrava, Faculty of Mechanical Engineering, Institute of Transportation, Ostrava, Czech Republic, EU

²VŠB - Technical University of Ostrava, ENET Centre, Bulk Solids Centre Czech Republic, Ostrava, Czech Republic, EU

martin.zidek@vsb.cz

Abstract

The method of sample preparation is a widespread problem in all types of measurements from nanoparticles to coarse material. This article focuses on a specific method of sample preparation namely on determination of TiO₂ nanoparticles size distribution. The treatment of sample comprising a higher number of nanoparticles is complicated. Nanoparticles often cluster together and thereby affect the course and the results of measurement. Therefore, a brief comparative study examining the effect of vibration on the degradation of nanoparticles and demolition of submicron agglomerates. Experimental work was carried out using a vibration exciter and the size of TiO₂ nanoparticles was then measured on the CPS Disc Centrifuge DC24000 in the laboratory of Bulk Solid Centre Czech Republic. The study was performed on four different TiO₂ samples, compared and evaluated for several time vibration periods. From the first results can be seen that slight changes in the composition of the sample greatly affect the degree of particles clumps comminution in the measuring liquid.

Keywords: Titanium white, TiO₂, nanoparticles, nanoparticles size, vibration

1. INTRODUCTION

Preparation of samples containing large quantities of nanoparticles is often very complicated and demanding process. The problem arises in case of nanoparticles clumps formation that can affect measurement and evaluation. In this experiment was used vibratory excitation for separation of nanoparticles clumps, which allows to interrupt energetic bonds between particles and particles clumps. Set of four TiO₂ samples was selected for measurement. This set was exposed to vibratory excitation in the time interval. In this interval were agglomerates separated and measured with CPS DC24000 Disk Centrifuge device. Since the measuring device CPS DC24000 Disk Centrifuge is a rotational rheometer, working with throughput of particles through so called density gradient, consisting of several layers of liquid with different density, it is necessary to create also the liquid mixture (suspension) for measuring and separation of the sample.

2. MATERIALS

Titanium white as a substance is a chemical compound of oxygen and titanium. This substance occurs in the world mostly in three mineral forms whose modification is titanium white. Anatase, Rutile and Brookite [1]. Other forms also exist, but not in such large quantities [2]. These minerals are very fragile, with a composition of 59.9 % Ti and about 40.06 % O and is insoluble in acids.

Anatase is a mineral having a tetragonal structure. It has the most stable structure of nanoparticles approaching 11 nm with a density of about 3.9 g/cm³. This material has a perfect cleavage according to (101) while the fracture is conchoidal.

Second of these minerals is Rutile. Rutile is also a mineral having a tetragonal structure. It has the most stable structure of nanoparticles above 35 nm with a density of about 4.2 - 4.3 g/cm³. This material has a perfect cleavage according to (101) worse according to (100) while the fracture is uneven and conchoidal.

Last of these minerals is Brookite. This mineral has rhombohedral structure. It has the most stable structure of nanoparticles between 11 - 35 nm with a density of about 4.1 g/cm³. This material has a perfect cleavage according to (120) with half-conchoidal fracture [2].

The most common usage is as a pigment for its brightness and large refractive index. It absorbs UV radiation and transforms it into harmless heat. It is used in cosmetics (creams, sun creams), pharmaceuticals (medicines, tablets, toothpastes), food (E171), it is highly hydrophobic (water-repellent), therefore it is used to manufacture windshields, glasses. Suitably modified titanium dioxide can be also used as a photocatalyst. It is also used in some types of solar cells and in medicine allows growing together bones with the implants. Selected samples were labeled A, B, C, D. Where the samples A, B, D are Rutile type and sample C is Anatase type.

3. METHODS AND EQUIPMENT USED DURING THE EXPERIMENT

For this research was used laboratory equipment of Bulk Solid Center of the Czech Republic located on the campus of VSB - Technical University of Ostrava, which participates in the European subsidy program GENET. Test samples were separated using FRITSCH ultrasonic-cleaner Laborette 17 device and measurement using rotational rheometer CPS disk centrifuge RPS 24000. Subsequently the results were evaluated and compared.

3.1. Separation of particles

Test samples were separated using FRITSCH ultrasonic-cleaner Laborette 17. This device works with a combination of the frequency generator (35 kHz) and the liquid bath (diameter 24.5 cm, height 13 cm) with a capacity of 5.6 liters. The ceramic oscillator generates from underneath the spa highly energetic vibrations and in a liquid bath arises so called cavitation effect, which cleans the necessary tools or loosens particles put in the requested suspension. In this case was used the second option of this device.

In laboratory test tubes were prepared 20 ml suspensions (H₂O - 90%, Ethanol p.a. - 10%). Into these suspensions was added 0.5 g of the measured material (Formula A, B, C, D). The test tube was then inserted into the bath of Fritsch ultrasonic - cleaner laborette 17 device using the stand for flasks. The bath was filled with water in an amount of 5 liters. After the frequency generator start began to spread through water frequency of oscillation with frequency of 35 kHz. This effect caused separation of the sample. Gradually were taken samples (2 ml) in the time horizon 10, 20, 30, 40, 50 and 60 minutes of the cavitation excitation duration. Subsequently was measured and analysed particle distribution of samples using the CPS disc centrifuge CPS DC24000 device.

3.2. Particle size distribution

The particle size distribution was carried out using already mentioned CPS disc centrifuge CSF 24000 device, whose measurement range is 0.01 to 40 microns. This device works on the principle of centrifugal sedimentation. In the transparent rotary cell is formed so called Density gradient, which consists of several layers of liquids of different density. Throughout this gradient pass measured particles, which are accelerated by the centrifugal force of the rotating cell and decelerated with difference of fluid density in layers of gradient. The size and concentration of particles is detected by a laser places on the outer edge of the rotating cell [3]. Before measurement it is important to calibrate the measurement method using the calibration standard, which defines the possible defects during measuring and enter parameters required for the materials used in the tracking software DCCS (The Disc Centrifuge Control System), which enables analysis and data collection,

setting of the rotational speed of the rotating cell dependent on the measured material and specified particle size range of the measured material. The results are graphs and measurement sheets with analysis of measured sample particle distribution. Parameters of measured samples were determined as follows with standard tables. Titanium white: Anatase, Measured range 0.05 - 1.2 micrometres, Particle Density 3.9 g/ml, Particle refractive index 2.49. Particle Absorption 0.075 K, Non-Sphericity Factor 1. Rutile, Measured range 0.05 - 1.2 micrometres, Particle Density 4.25 g/ml, Particle refractive index 2.9, Particle Absorption 0.075 K, Non-Sphericity Factor 1. Calibration Standard Parameters: PVC in DI water, Peak Diameter 0.377 micrometres, Half Height Peak Width 0.2 micrometres, Particle Density 1.385 g/ml. Solvent parameters: Fluid Density 0.997 g/ml, Fluid Refractive Index 1.349, Fluid Viscosity 1.02 cps.

4. MEASUREMENT AND EVALUATION OF RESULTS

Preparation of samples A, B, C, D is described in sub-chapter 3.1. After removing the sample is always prepared the set of 5-7 measurements for the credibility of the resulting values. These data were evaluated and entered into subsequent graphs and tables.

Density gradient was created according to the recommended tables for the material using per cent distribution of the necessary elements (**Table 1** and **Table 2**).

Table 1 Creation of density mixtures for the gradient

Density gradient of the mixture	H ₂ O (%)	Saccharose (%)	Ethanol p.a. (%)	Total weight of mixture (g)
Hight	83.7	7	9.3	32
Low	87.3	3	9.7	30

Table 2 Creation of gradient with combination of high a light liquid density

Injection	1	2	3	4	5	6	7	8	9
Hight (ml)	1.6	1.4	1.2	1.0	0.8	0.6	0.4	0.2	0
Low (ml)	0	0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6

To avoid contact of the measured material with the gradient, it is necessary to inject a liquid hydrocarbon dodecane, whose physical state closes gradient. Thus, when injecting the sample occurs, wrapping of the sample with dodecane and the sample passes through a gradient, without being in contact with it. Because of the gradient pollution, it was necessary to change the gradient approximately every second measurement.

After creation of the gradient, entering all parameters and starting the measurement it is necessary to calibrate the measurement. This is done before the sample measurement when prompted by the program. It is injected 0.1 ml of calibration standard. After calibration occurs measurement of the sample. It is injected again 0.1 ml of solvent with the measured sample, for our case, samples A, B, C, D (A - Rutile with 2.59% admixture, B - Rutile with 1.53% admixture, C - Pure Anatase, D - pure Rutile), which were taken during the separation ultrasonic in Fritsch - laborette cleaner 17 at intervals of 10, 20, 30, 40, 50 and 60 minutes.

Afterwards the measurement was evaluated and the resulting values are shown below (**Figure 1** and **Figure 2**).

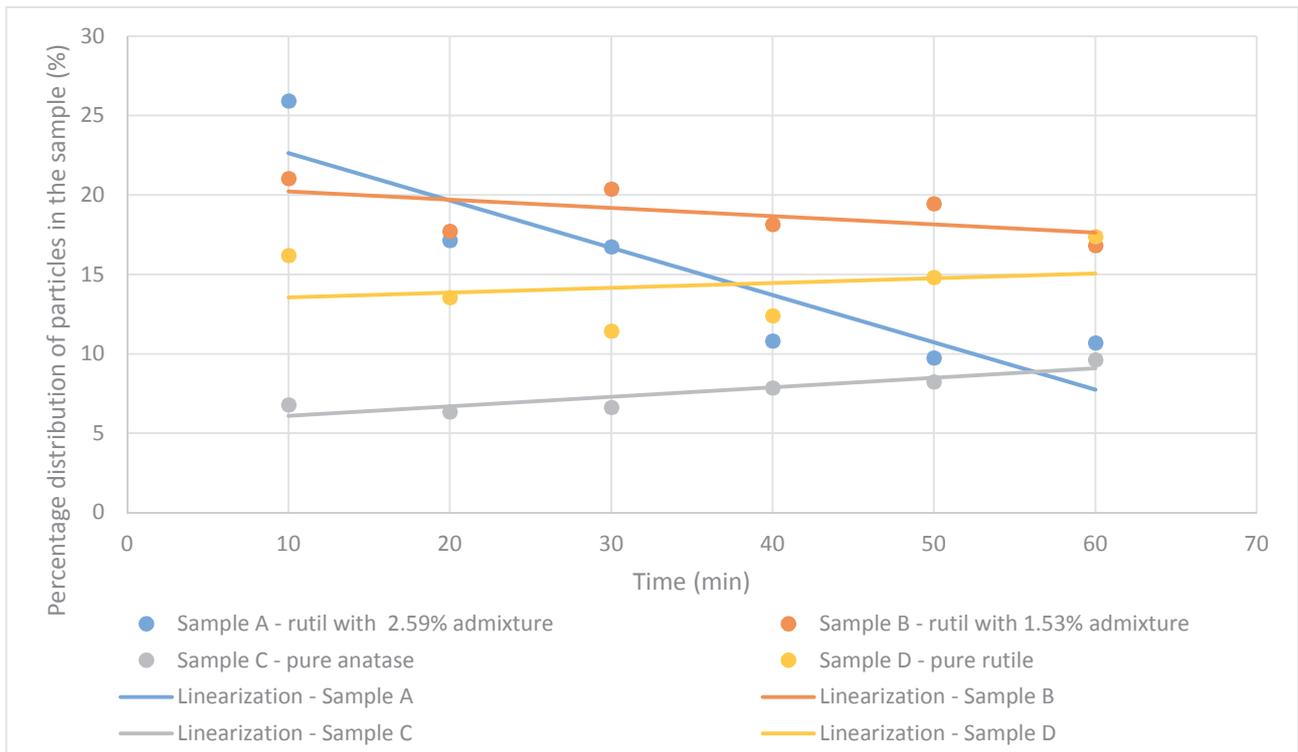


Figure 1 Percentage of particle size of TiO₂ between 244.9 and 336.4 mikron depending on the duration of frequency excitation in water bath

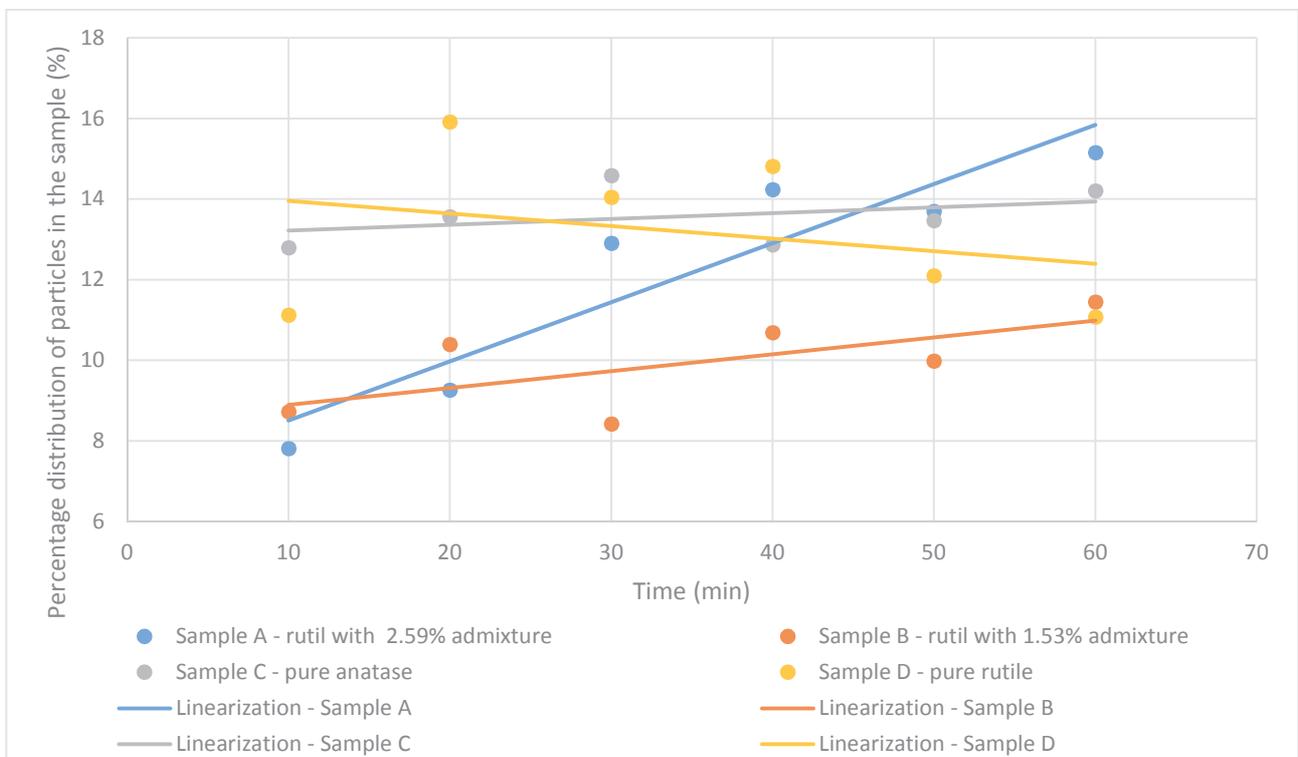


Figure 2 Percentage of particle size of TiO₂ between 68.8 and 94.5 nanometres depending on the duration of frequency excitation in water bath

When examining the influence of the action of ultrasonic vibrations onto prepared samples were found that during the time period of action has changed the percentage of the particle size. On each sample acted the same effects, but the percentage of particle sizes varied differently. If we take the larger particles or agglomerates according to **Figure 3**, the largest proportion of these particles are in size from 244.9 to 336.4 nanometres, see **Figure 1**. X-axis of this chart is for clarity logarithmic and the relative number of particles was taken as a percentage of the maximum number of particles of all samples. It can be seen that the largest clumps were formed in sample A, which contained after 10 minutes of vibrations excitation 25.94% particles representation in the sample. After 60 minutes of vibrations excitation reduced the percentage of particles in the sample to 10.7%. In this sample, it was observed the highest percentage of clump of particles dilution 15.24%. In the other samples was also observed the percentage decrease of fraction /clumps of particles, but not so vigorous. In sample B 4.21%, sample C - 2.83% and Sample D - 1.18%. These values are average values measured in the range. The negative value indicates the increase and the positive decrease in the fraction /clump of particles in the measuring range.

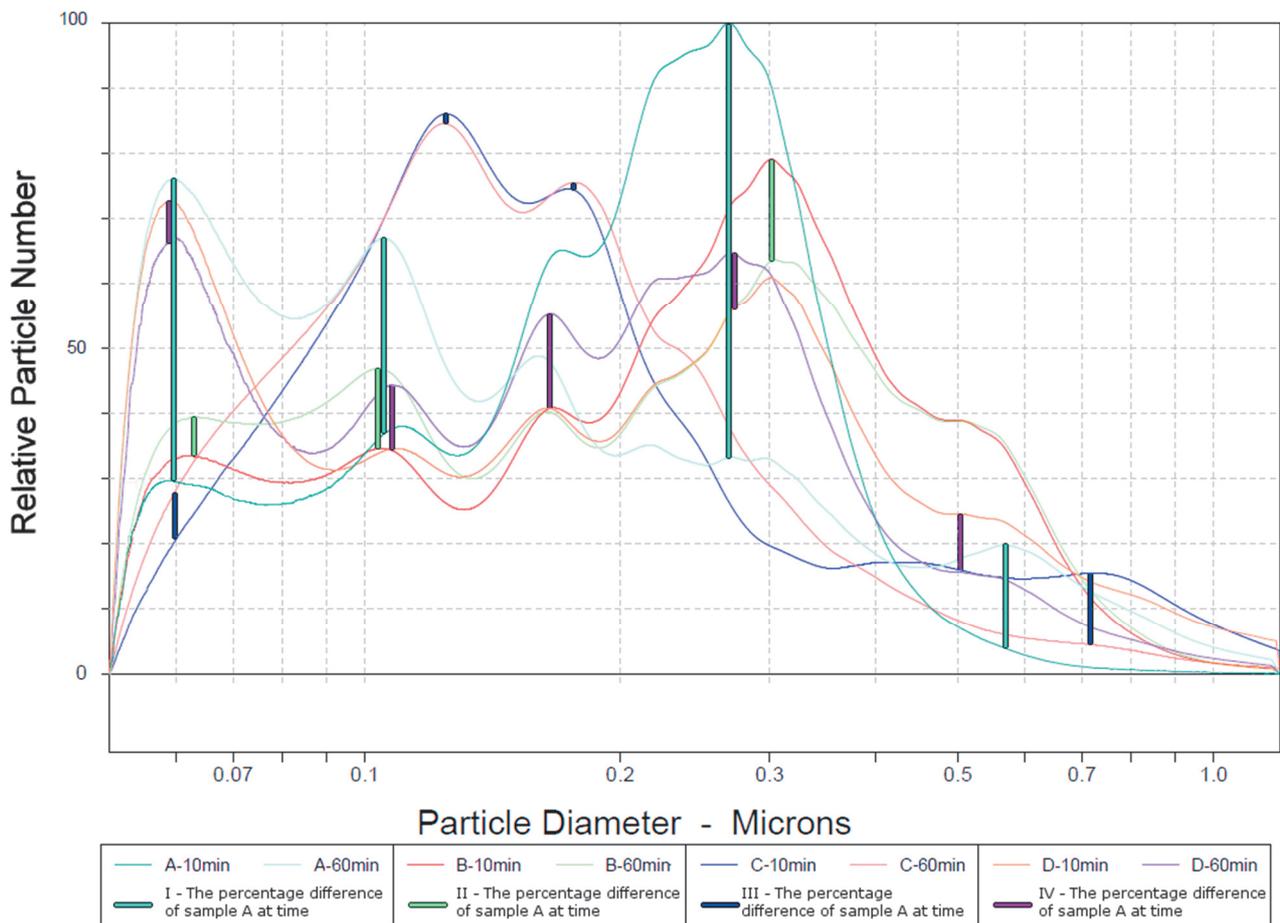


Figure 3 Relative percent difference in the sample time horizon of 10 and 60 minutes

The biggest percentage changes in number of particles were observed in the range from 68.8 to 94.5 nanometres, see **Figure 2**. Where again the largest percentage increase in the number of particles resulted in sample A -7.34%. In the other samples were also detected percentage changes in number of particles B - 2.72% C - 1.41% and 0.05% D. The percentage increase of the fine fraction particles was caused by dilution of clumps. Very interested is the sample C. It is special because in duration of the frequency excitation has changed its distribution curve minimally to almost nothing.

Table 3 Percentage of samples at specified intervals

Time (min)	The percentage representation of the fraction in the sample (%)							
	Fractions from 244.9 to 336.4 nanometers				Fractions from 68.8 to 94.5 nanometers			
	Sample A	Sample B	Sample C	Sample D	Sample A	Sample B	Sample C	Sample D
10	25.94	21.04	6.8	16.2	7.81	8.72	12.79	11.12
20	17.15	17.73	6.36	13.56	9.26	10.39	13.56	15.91
30	16.74	20.38	6.63	11.45	12.9	8.42	14.58	14.04
40	10.81	18.16	7.86	12.4	14.23	10.68	12.86	14.81
50	9.76	19.45	8.25	14.81	13.69	9.98	13.46	12.09
60	10.7	16.83	9.63	17.38	15.15	11.44	14.2	11.07

5. CONCLUSION

In this study was determined the effect of sample preparation for measurement of the TiO₂ nanoparticles size distribution. In this study it was found that the vibration affects particle size distributions (structure) of samples and agglomerates separation. It was found the influence of vibration on particle size distribution of particles during separation of samples A, B, C and D. The biggest impact of vibration excitation was recorded on the sample A, where the percentage of fraction with clumps decreased by 15.24% and the percentage of fine particle fraction increased by 7.34%. In the other sample was also seen decrease of agglomerates of particles and an increase in the fine fraction **Table 3**. Very interested is the sample C where the influence of vibration was minimal. Probably, it is due to the chemical purity of this sample. It is important to determine the appropriate time interval for sample preparation. The time interval at which to measurements will be satisfactory and representative. It is true that every material has its own specific characteristics and parameters. Because of this evaluation were divided into two results group - for titanium white with admixtures and chemically pure. Take account was taken of all measurements and percentages of particles. Therefore, it we recommend the mean value of the time interval for sample preparation. For titanium white with admixtures it is 40 minutes and commercially pure titanium white 20 - 30 minutes.

ACKNOWLEDGEMENTS

This paper was conducted within the framework of the project LO1404: Sustainable development of ENET Centre and within Student Grant Competition titled Process study of pneumatic conveying system SP2016/159.

REFERENCES

- [1] FUJISHIMA, A, X ZHANG a D TRYK. TiO₂ photocatalysis and related surface phenomena. *Surface Science Reports*, 2008, vol. 63, pp. 515-582.
- [2] DIEBOLD, Ulrike. The surface science of titanium dioxide. *Surface Science Reports*. 2003, vol. 48, pp. 53-229.
- [3] ZEGZULKA, J., JEZERSKÁ, L., HLOSTA, J., ŽÍDEK, M., NEČAS, J. Effect of SiO₂ nanoparticles on the mechanical/physical properties of SiO₂ microparticles mixtures. In *METAL 2015: 7th International Conference on Nanomaterials - Research & Application*. Brno, 2015, pp. 153-1158.