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Product Development, Formulation Screening and Quality Control

Business Unit
GRINDING & DISPERSING

PRODUCT DEVELOPMENT, FORMULATION SCREENING AND QUALITY CONTROL

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1. INTRODUCTION

The new NETZSCH grinding system for ultra-fine grinding of very small quantities *DeltaVita*® 1 enables simultaneous grinding of up to 40 different samples with different compositions or different grinding media. Mainly cost-effective standard sample containers are used, which can be disposed of after the test has been carried out, so that the cleaning effort, the solvent requirement and the time required can be revolutionarily minimized.

Especially in the field of research and development, for example for formulation development, raw material selection or process development, it is necessary to enable extensive screening with the smallest amounts of available substance. Ideally, several samples should be able to be processed simultaneously.

The quality control of raw materials for production is another important area of application for *DeltaVita*® 1.

2. DESIGN AND FUNCTION OF THE GRINDING SYSTEM FOR ULTRAFINE GRINDING OF VERY SMALL QUANTITIES

2.1. The *DeltaVita*® 1 grinding system for ultrafine grinding of very small quantities

The *DeltaVita*® 1 grinding system for ultrafine grinding of very small quantities operates according to the principle of a dual centrifuge (see Figure 1) that is based on the advanced development of a classic centrifuge. In contrast to a conventional centrifuge rotor, the rotor is equipped with two rotary plates. The rotary plates can be fitted with different plastic inserts, which are used to hold sample containers. Inserts for 2 ml twist-top vials - the ideal container for formulation development within the scope of nano grinding - as well as 10 ml injection vials, 15 ml and 50 ml Falcon tubes or 125 ml beakers are currently available as standard.

The type of sample motion depends on the geometry of the sample containers and their positioning in the dual centrifuge and, in the case of elongated containers, is to some extent comparable to the sample motion in a horizontal shaker (see Figure 2). However, even powerful laboratory shakers can only achieve a sample acceleration of fifty times the gravitational acceleration (*g*), while the grinding system for ultrafine grinding of very small quantities can achieve up to 1,000 x *g*, which results in a much higher energy input into the samples.

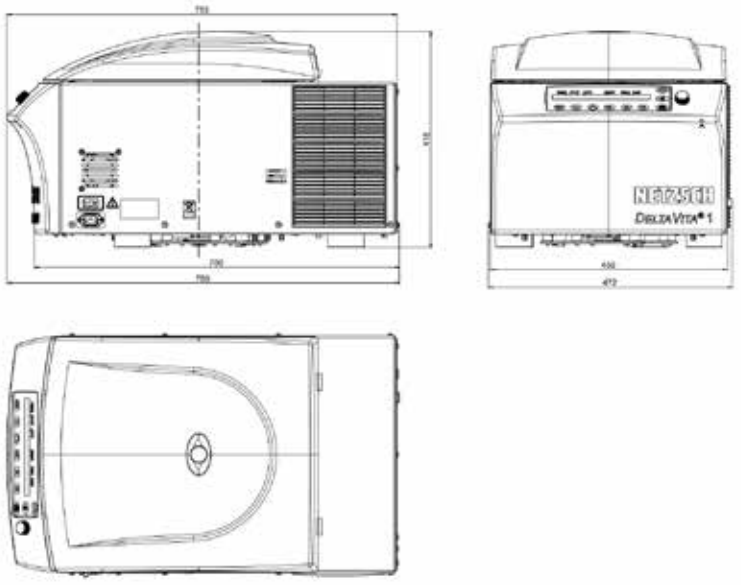
Due to the symmetrical arrangement of the rotary plates, this grinding system for ultrafine grinding of very small quantities can handle higher loads without the danger of becoming unbalanced. Thus, with fully loaded turntables, up to 40 samples of 2 ml volume can be processed in one run with the *DeltaVita*® 1.

The power transmission for the rotation of the *DeltaVita*® 1 is not via a V-belt mechanism, which means that it takes a few seconds longer to accelerate up to the maximum target speed of 2500 rpm. In return, heat generation and contamination of the unit chamber, which would otherwise be caused by abrasion on the V-belts, have been minimized. In addition, the chamber of the *DeltaVita*® 1 is equipped with a powerful cooling system, so that samples can be tested for several hours without interruption. The unit chamber can be cooled down to temperatures as low as -20°C.

A novel feature is the positioning of the samples at an angle of approx. 40°. Similar to a planetary ball mill, the rotation on the primary path is superimposed by an additional rotation around the axis of

Fig. 1

NETZSCH *DeltaVita*® 1 grinding system for ultra-fine grinding of very small quantities



the rotary plates (see Figure 2). The combination of the sample positioning and the additional rotation causes the direction of the strong centrifugal acceleration in the sample containers to change very rapidly, which in turn causes the sample material to be accelerated continuously and at high frequency in a different direction (see Figure 3).

If the sample containers are now partially filled with grinding media, the result is a mill with freely moving grinding media, which delivers reproducible comminution results with minimum 1 ml of suspension and, which can be used for very efficient grinding processes.

Fig. 2

Positioning und motion pattern of *DeltaVita*® 1

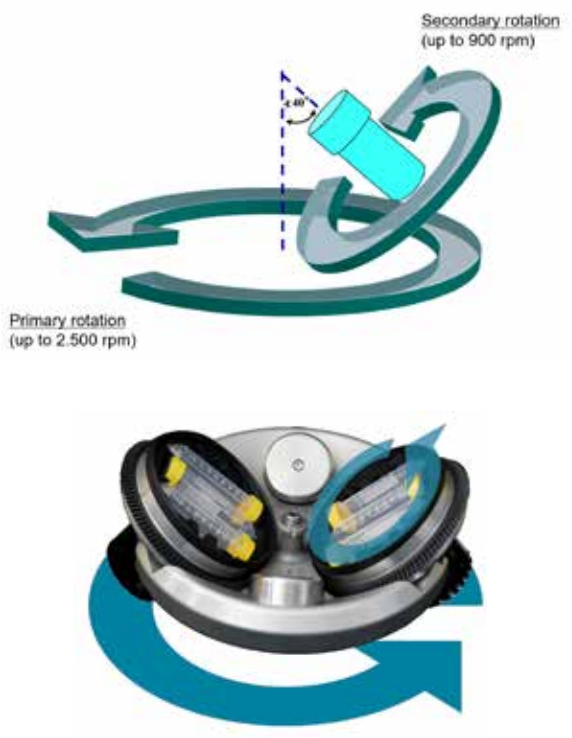


Fig. 3

Motion of the sample material in the sample containers

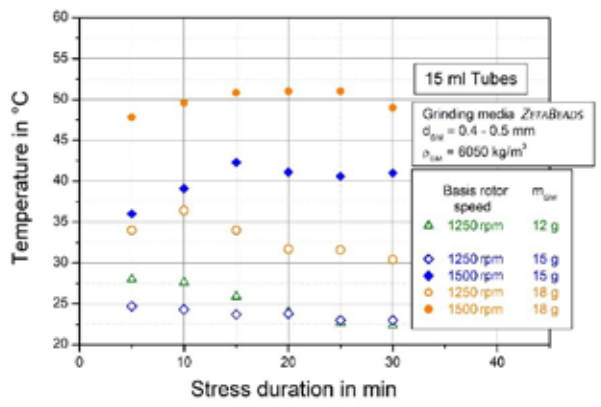
1.2. Effect of grinding media quantity and speed on the product temperature

Investigations regarding the development of the product temperature were carried out with the *DeltaVita*® 1 in 15 ml FalconTubes. Here, the amount of grinding media as well as the rotor speed were varied. The optimal amount of grinding media should always be determined in such a way that about 20% of the sample container is filled with a bulk volume of grinding media. When using yttrium stabilized zirconium oxide grinding media (*Zeta*®*Beads*) with a bulk density of approx. 3.65 kg/dm^3, the optimum filling quantity can thus be calculated with grinding media of approx. 11 g grinding media. If, on the other hand, glass grinding media with a lower bulk density of approx. 1.5 kg/dm^3 are used, the optimum filling quantity of only 4.5 g of grinding media results.

The investigations showed that the cooling of the device chamber could keep the sample temperature at a constant level even with longer stress times (see Figure 4).

Fig. 4

Effect of the rotor speed and the quantity of grinding media on the sample temperature, for 15 ml tubes



Tests with different product suspensions with various solids contents and viscosities have shown that the rheological properties of the suspension also have a strong influence on the product temperature reached.

Therefore, if sufficient quantities of substance are available, it is advisable to carry out some preliminary tests in which the rotor speed is initially set low and moderately increased if necessary.

Of equal importance as the grinding media charge, it must be remembered that a vial or tube must never be completely filled with the product suspension. 10 - 20% of the sample container must always remain unfilled. On the one hand, this prevents the vial or tube from bursting when the sample heats up and the sample volume expands; on the other hand, this has a positive effect on the sample and grinding media movement.

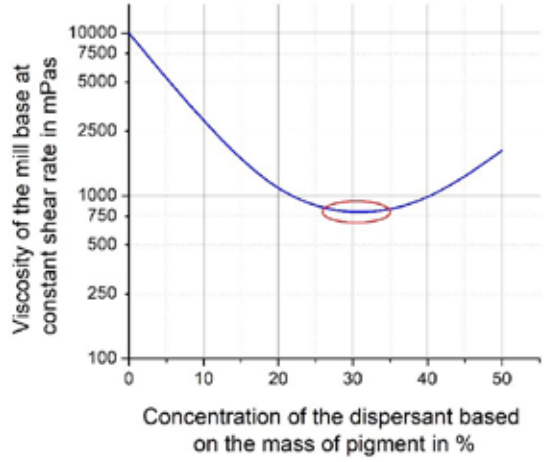
2.3. Formulation screening and optimization with the grinding system for the finest grinding of very small quantities *DeltaVita*® 1

The formulation, i.e. the proportions of pigment, solvent and binder, but above all the dispersant, has a decisive influence on the viscosity and stability of a preparation. In the present example, the optimal wetting and dispersant content should be determined in relation to the pigment.

For optimization, several samples with different concentrations of the dispersant must be processed. Comparing the viscosity of the samples produced then makes it possible to identify the optimal dispersant/pigment ratio, which is represented by the minimum viscosity and the corresponding formulation (see Figure 5).

Fig. 5

Determination of the optimal dispersant concentration



For this task, the preparation of 5-6 samples is required. With the *DeltaVita*® 1 grinding system for the finest grinding of very small quantities, only a small amount of pigment is required.

Furthermore, it is possible to process all samples simultaneously with the *DeltaVita®* 1. The time required is about 1.5 hours, including sample preparation, processing and all analyzes. Due to the use of disposable sample vessels, no cleaning is required.

Formulation		1	2	3	4	5
Binder/Water	%	77.2	75.2	73.2	71.2	69.2
Dispersant	%	2	4	6	8	10
Pigment	%	20	20	20	20	20
Defomer	%	0.1	0.1	0.1	0.1	0.1
Anti-setteling agent	%	0.5	0.5	0.5	0.5	0.5
Neutralizing agents	%	0.2	0.2	0.2	0.2	0.2
total	%	100	100	100	100	100
Dispersant concentration based on pigment	%	10	20	30	40	50

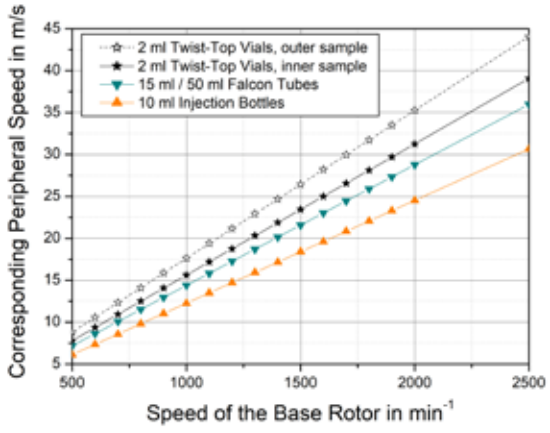
3. COMPARATIVE TESTS WITH DIFFERENT PRODUCTS

3.1. Transfer of operating parameters from the system for ultrafine grinding of very small quantities *DeltaVita*® 1 to agitator bead mills

Using the diameters of the base rotor (primary rotation) and the planetary rotor (secondary rotation), along with the speeds of the two rotors resulting from the transmission ratio, peripheral speeds can be determined for both rotors. The addition of these two speeds yields the maximum so-called corresponding peripheral speed of the samples (see Figure 6).

Fig. 6

Corresponding peripheral speeds of the sample as a function of the adapter geometry and the speed of the base rotor



The adapters for holding the different sample containers differ in their geometry, which results in different corresponding peripheral speeds at the same base rotor speed. This must be considered in comparative tests with different containers.

When grinding with freely moving grinding media, the decisive factor for comminution or dispersion is the kinetic energy of the grinding media when beads collide. While the grinding media in an agitator bead mill is more or less directly accelerated by an agitator, the cause of the grinding media acceleration in a *DeltaVita*® 1 is pure centrifugal acceleration.

Based on these considerations, it can be estimated that approximately twice the corresponding peripheral speed should be set in a *DeltaVita*® 1 compared to the peripheral speed in the agitator bead mill in order to achieve comparable stress energies and thus similar comminution results, if identical grinding media are used for the investigations.

3.2. Use of the *DeltaVita*® 1 grinding system for ultrafine grinding of very small quantities for pigmented systems

In order to demonstrate the transferability of crushing results, formulations of a titanium dioxide and a phtalocyanine blue PB15 were crushed with a laboratory agitator ball mill *LabStar Zeta*® or with an *Alpha*® *Lab Zeta*®. Subsequently, comparative studies were carried out with the same materials and identical formulations with the grinding system for the finest grinding of very small quantities *DeltaVita*® 1.

The *LabStar* and *Alpha*® *Lab Zeta*® *RS* laboratory agitator bead mills are multi-talented. These laboratory machines can be operated both as a classic disk agitator bead mill with the *Discus*® grinding system and with the pin grinding systems, *Zeta*® or *Neos*® (see Figure 7). Likewise, all possible modes of operation, such as circulation, passage or multi-passage operation, can be reproduced with these machines on a laboratory scale. The mills are available in different material designs such as steel, NELAST or various ceramics. In addition, they are also characterized by very user-friendly handling due to the swiveling grinding chamber. Thanks to an adapter system, it is possible to combine the grinding system of both the *Micro-* & *MiniSerie* with a grinding chamber volume of approx. 100 ml or 200 ml with the *LabStar* or the *Alpha*® *Lab Zeta*® *RS*. This makes these mills extremely flexible for all tasks in the area of research and development. In addition, the *Alpha*® *Lab Zeta*® *RS* can be operated with a separately driven open dynamic classifier system for the separation of grinding media. The *LabStar* and the *Alpha*® *Lab Zeta*® *RS* are the smallest agitator bead mills with which, based on lab tests, the specific energy requirement can be determined for each application reliably and reproducibly for scale-up calculations to production scale.

Fig. 7

LabStar laboratory agitator bead mill

Grinding Chamber	Agitator and Ginding Chamber Lid
Cr-Ni-Steel	
NELast	
Polyamide	
NETZSCH *Ceram Z*	
NETZSCH *Ceram Z*	*NELast*
NETZSCH *Ceram Z*	Polyamide
NETZSCH *Ceram C*	NETZSCH *Ceram N*
NETZSCH *Ceram Z*	*NELast*

ZetaBeads® 0.1 mm diameter yttrium-stabilized zirconia grinding media from NETZSCH were used for both titanium dioxide and for grinding a phtalocyanine blue PB15 pigment.

3.3. Comminution of titanium dioxide (PW 6)

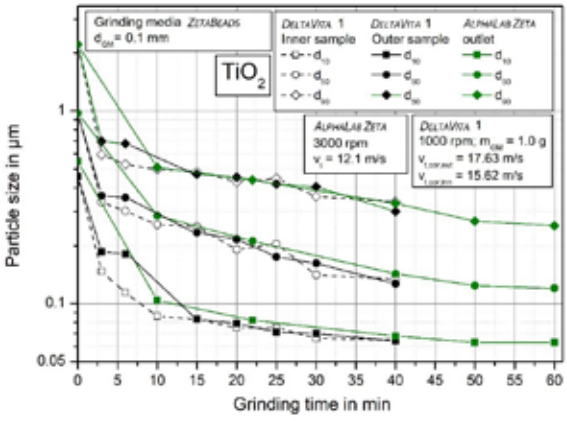
The titanium dioxide, TiO2, was ground with the *Alpha*® *Lab Zeta*® as well as the *DeltaVita*® 1 laboratory agitator bead mill with a mass solids concentration of 10 Ma%. For both tests, the formulation was identical, and a stabilizing agent was used.

The batch size in the *Alpha*® *Lab Zeta*® laboratory agitator bead mill was 1.7 kg. The suspension was ground in circulation mode with a suspension throughput of approx. 30 kg/h and an agitator shaft peripheral speed of approx. 12.1 m/s.

The tests on the *DeltaVita*® 1 were carried out in 2 ml vials. Here, two identical samples were prepared and, for comparison purposes, placed in the inner and outer positions in the sample adapters (see Figure 8). The vials were each filled with 1.0 g of grinding media and 1 ml of product suspension. The comminution tests were run at a base rotor speed of 1 000 rpm.

Fig. 8

Characteristic values of particle size distribution $d_{10}(x)$, $d_{50}(x)$ and $d_{90}(x)$ as a function of grinding time for the comminution of titanium dioxide in an *Alpha*® *Lab Zeta*® laboratory agitator bead mill and in the *DeltaVita*® 1



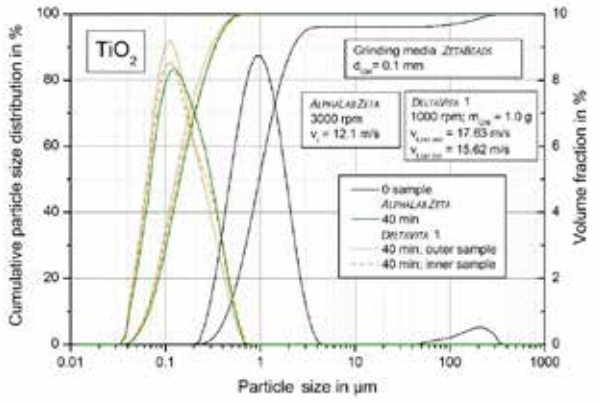
The results from both series of tests are plotted in Figure 8, with the characteristic values of the particle size distribution $d_{10}(x)$, $d_{50}(x)$ and $d_{90}(x)$ shown as a function of the grinding time. Coincidentally, there was very good agreement between the test results with similar grinding times.

A Malvern Mastersizer 3000 was used for particle size characterization in all cases.

Figure 9 shows the particle size distributions of the initial suspension and the product suspension for comminution of titanium dioxide in the laboratory agitator bead mill and for comminution with the *DeltaVita*® 1 after every 40 min of grinding time.

Fig. 9

Particle size distributions of the initial suspension and the product suspension for comminution of titanium dioxide in an *Alpha*® *Lab Zeta*® laboratory agitator bead mill after 40 min of grinding time and for comminution with a *DeltaVita*® 1 after 40 min grinding time



There were only minimal differences in the test results for the inner and outer sample positions for grinding in the *DeltaVita*® 1. In comparison to the *Alpha*® *Lab Zeta*® laboratory agitator bead mill, minor differences were also seen.

In general, however, the agreement in the particle size distribution is very good. This made it possible with initial investigations on the *DeltaVita*® 1 to make statements about grindability, the stability of the suspension, the optimum grinding media size and the achievable particle size.

3.4. Comminution of a blue pigment

The pigment phtalocyanine blue PB15 was ground with both the *LabStar Zeta*® laboratory agitator bead mill and the *DeltaVita*® 1 with a bulk solids concentration of 23 Ma%. The aqueous formulation was again identical in both tests. A customized stabilizing agent was also used here.

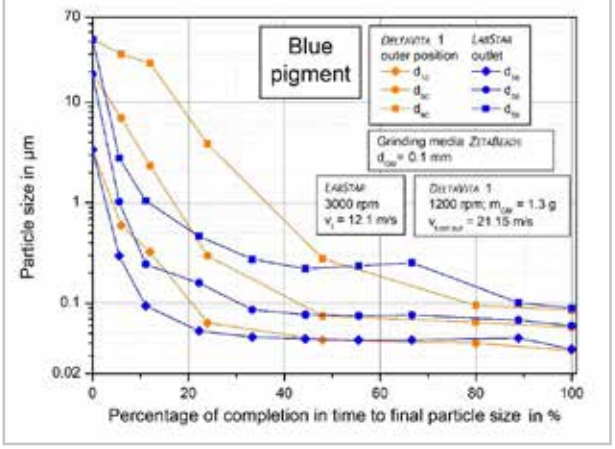
The batch size in the *LabStar Zeta*® laboratory agitator bead mill was 1.74 kg. The suspension was ground in circulation mode with a suspension throughput of approx. 30 kg/h and an agitator shaft peripheral speed of approx. 12.1 m/s.

The tests on the *DeltaVita*® 1 were also carried out in 2 ml vials. The samples were placed in the outer sample position only. The vials were each filled with 1.3 g of grinding media and 1 ml of product suspension. The comminution tests were run at a base rotor speed of 1200 rpm.

In most cases, the grinding results of *DeltaVita*® 1 cannot be transferred directly to the results of an agitator bead mill. If the grinding time in the process is related to the grinding time required to achieve the desired particle size distribution, the percentage of completion in time to final particle size is obtained.

Fig. 10

Characteristic values of the particle size distribution $d_{10}(x)$, $d_{50}(x)$ and $d_{90}(x)$ as a function of grinding time for the comminution of phtalocyanine blue PB15 pigment in an *Alpha*® *Lab Zeta*® laboratory agitator bead mill and in the *DeltaVita*® 1



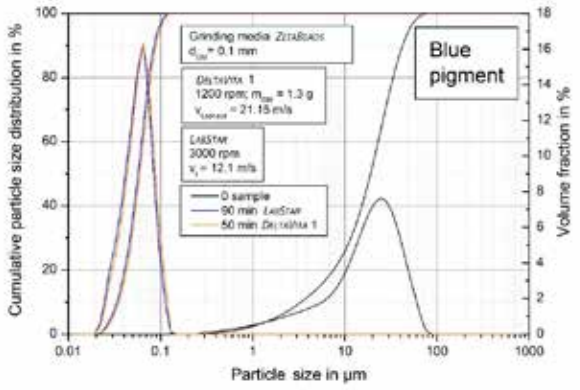
The results from both series of tests are plotted in Figure 10 with the characteristic values of the particle size distribution $d_{10}(x)$, $d_{50}(x)$ and $d_{90}(x)$ shown as a function of the percentage grinding time up to the desired product quality. According to the customer's specifications, the desired product particle size distribution should have a $d_{90}(x) < 100$ nm.

With the *LabStar Zeta*® laboratory agitator bead mill, this product quality was achieved after a grinding time of 90 minutes, while with the *DeltaVita*® 1, a grinding time of only 50 minutes was required to achieve a comparable product quality.

Figure 11 shows the particle size distributions of the initial suspension and the product suspension for the comminution of a phtalocyanine blue PB15 pigment in aqueous formulation in the laboratory agitator bead mill after a grinding time of 90 minutes and for the comminution with the *DeltaVita*® 1 after 50 minutes of grinding time. The particle size distributions shown for the product suspensions are congruent.

Fig. 11

Particle size distributions of the initial suspension and the product suspension for comminution of phtalocyanine blue PB15 pigment in a *LabStar*® *Zeta* laboratory agitator bead mill after 90 min grinding time and for comminution with the *DeltaVita*® 1 after 50 min of grinding time



3.5. Studies on the optimization of product quality and manufacturing process of a yellow pigment preparation PY74

For a pigment preparation PY74 (yellow) with a known formulation, the aim was to assess whether dispersion by means of an agitator bead mill can significantly improve the quality compared to a product sample provided as a reference. A further goal was to determine which process parameters are required to achieve the desired quality increase.

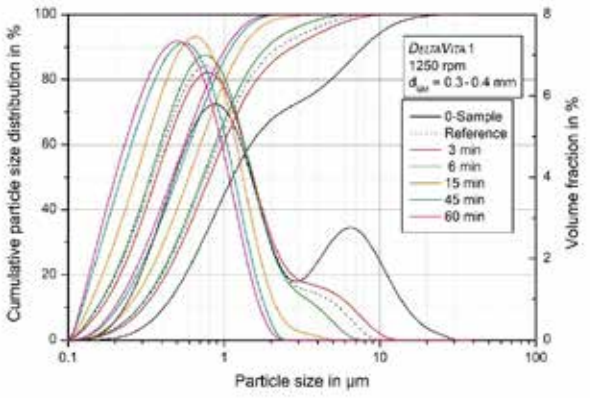
First, 6 small samples of 10 g each were taken from the premixed starting material, which had a total mass of approx. 10 kg. Each of these samples was prepared with 11 g of 0.3 - 0.4 mm diameter *ZetaBeads*® in 15 ml Falcon tubes. An additional 15 ml Falcon tube was filled with 21 g of a mixture of grinding media and water. The 6 product samples were arranged in the adapters and run together in the *DeltaVita*® 1 at a base rotor speed of 1250 min^{-1}. After 3 minutes, the *DeltaVita*® 1 was stopped for the first time. One product sample was removed and, to compensate, replaced with the water/grinding media tube, which in operation only serves to create a mass balance and thus ensure vibration-free operation. The cooling was set to -10°C.

Additional product samples were analyzed after runs of 6, 15, 45 and 60 minutes. After only 6 minutes of stressing in the *DeltaVita*® 1, a narrower particle size distribution was achieved than in the reference sample (see Figure 12). After 45 minutes of stressing, no significant progress in dispersion was observed. The product sample after 60 min exposure was additionally analyzed with a spectrophotometer (see Table 1). For this purpose, the sample was mixed in a ratio of 90:10 with a standardized water-dilutable 1K acrylic lacquer white. Subsequently, the mixtures were drawn with a squeegee on a film laminated test card of the company Byk with 120 µm. After drying in air 24h/NK (normal climate), color strength and hue were measured over black and white. The product temperature was measured in each case and was between 19 - 20°C for all samples taken.

Dispersion tests were then carried out with the *LabStar* laboratory agitator bead mill with a Discus grinding system in passage mode. *ZetaBeads*® with a diameter of 0.3 - 0.4 mm were also used as the grinding media. The peripheral speed was set to

Fig. 12

Preliminary tests on the dispersion of a yellow pigment preparation with the *DeltaVita*® 1



approx. 10.4 m/s and the product throughput to approx. 20 kg/h. After 3 passes, the dispersion results were almost identical to those obtained with *DeltaVita*® 1 (see Figure 13). For comparison, a product sample was also mixed and analyzed with a spectrophotometer after sample preparation (see Table 1).

Fig. 13

Comparison of the dispersion results for a yellow pigment preparation run in the *LabStar* laboratory agitator bead mill and the *DeltaVita*® 1

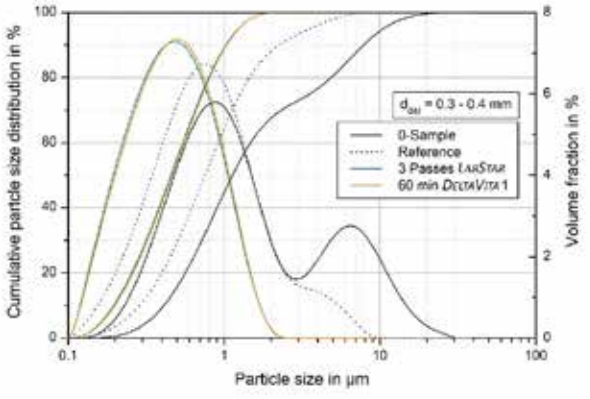


Table 1

Results of the spectrophotometer analyses

Sample	Reference sample	*LabStar* 3. Passage 0.3 - 0.4 mm	*DeltaVita*® 1 60 min. 0.3 - 0.4 mm
a* (D65)	2.88	1.89	1.98
b* (D65)	67.18	75.69	75.32
h (D65)	87.54	88.57	88.49
C* (D65)	67.25	75.72	75.57
dL* (D65)	-	- 0.36	- 0.37
da* (D65)	-	- 0.99	- 0.9
db* (D65)	-	8.51	8.14
Chroma	-	8.47	8.32
Hue	-	1.28 yellower	1.19 yellower
Color strenght	100 %	144.89 %	142.53 %
Gloss 85°	36.3	42.3	42.4

The tests have demonstrated that the *DeltaVita*® 1 not only achieved similar results with regard to particle size or particle size distribution. Both the results for the increase in the color strength, the gloss and the change in the color coordinates or the brilliance and the contrast ratio are very comparable.

This means that the *DeltaVita*® 1 grinding system for ultrafine grinding of very small quantities can be employed as a user-friendly laboratory machine for product and formulation development in the area of pigmented systems but is also ideally suited as a fast and reproducible method for the incoming goods inspection quality control of pigments.

4. CONCLUSIONS

With the *DeltaVita*® 1 grinding system for ultrafine grinding of very small quantities, feasibility studies, product and formulation development or sample preparation for analyses or quality control are possible for a wide variety of product groups.

This small handy machine is characterized by its intuitive operation. Only very small quantities of material are required for the tests to be performed. Different formulations or grinding media sizes can be tested simultaneously, so the results are available very quickly. A time consuming cleaning as with an agitator bead mill is not necessary here.

Due to the very efficient cooling of the device chamber and despite the high possible energy input, tests with long run times can also be carried out with no pauses, without fear of product overheating. Even temperature-sensitive pigments can be processed without any break time.

A direct prediction of required specific energy inputs or comminution times is not possible. Nevertheless, a good prediction of the optimal grinding media size or the necessary agitator shaft speed as well as the optimization of formulations can be realized with the *DeltaVita*® 1 using very small quantities of product and requiring minimal time and cleaning effort.

Based on a wide variety of tests with active pharmaceutical ingredients, nanomaterials or various pigmented systems, it has been demonstrated that the results obtained with the *DeltaVita*® 1 can be transferred very well to results obtained with agitator bead mills.

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