Retsch® Solutions in Milling & Sieving

the sample

Customer Magazine | Issue 39

part of VERDER scientific

HIGH ENERGY BALL MILLS

GRINDING AND PARTICLE SIZING ON A NANOSCALE

2,000 min^{-1} max. speed

unique liquid cooling

10^{-9}m

10^{-6}m

10^{-3}m

HIGH ENERGY BALL MILL
E_{max}

PLANETARY BALL MILL
PM 100

MIXER MILL
MM 400

CRYOMILL

PLANETARY BALL MILL
PM 400

EDITORIAL

Dear Readers, Customers and Business Partners,

"Nano" is a big issue these days as products containing nanoscale particles have become part of our everyday lives. Ultrafine particles are found in sunscreen, textiles, drugs or paint, to only name a few examples. Nanotechnology is the reason why these materials and products gain new properties and are further improved.

RETSCH and RETSCH TECHNOLOGY have also put their focus on nanotechnology! **The revolutionary design of the new high energy ball mill E_{max} allows for producing nanoscale particles in a fraction of the time required by comparable mill types.** The E_{max} can be operated with a maximum speed of 2,000 min^{-1} which is an absolute novelty for a ball mill. In this issue of "the sample" you will learn how RETSCH engineers **combined maximum pulverization energy with an innovative water cooling system** in the E_{max} – with the result that the mill can be used for continuous grinding without breaks!

Grinding down to the nano size range can also be achieved with RETSCH's well-proven planetary ball mills. We not only present our range of ball and mixer mills in this issue but also describe how to successfully carry out **high energy applications such as mechanical alloying and colloidal grinding.**

We hope you enjoy reading this issue of "the sample"!

Yours

Dr. Juergen Pankratz
CEO VERDER SCIENTIFIC

CONTENT

SMALL PARTICLES – HUGE EFFECTS: GRINDING DOWN TO THE NANOMETER RANGE

Nanotechnology is one of the most innovative developments of our time which revolutionizes industries such as materials science, pharmaceutics, food, pigments or semi-conductor technology. Nanotechnology deals with particles in a range from 1 to 100 nm. These particles possess special properties due to their size, as their surface is greatly enlarged in relation to their volume (so-called "size-induced functionalities"). Ultrafine particles are, for example, harder and more break-resistant than larger particles. Nanotechnology brings effects which occur in nature to a commercial scale, such as, for example, the lotus effect: nanocoated fabrics or paints are water- and dirt-repellent just like the lotus flower.

NANO

How are nano particles produced? The "bottom-up" method synthesizes particles from atoms or molecules. **The "top-down" method involves reducing the size of larger particles to nanoscale, for example with laboratory mills.** Due to their significantly enlarged surface in relation to the volume, small particles are drawn to each other by their electrostatic charges.

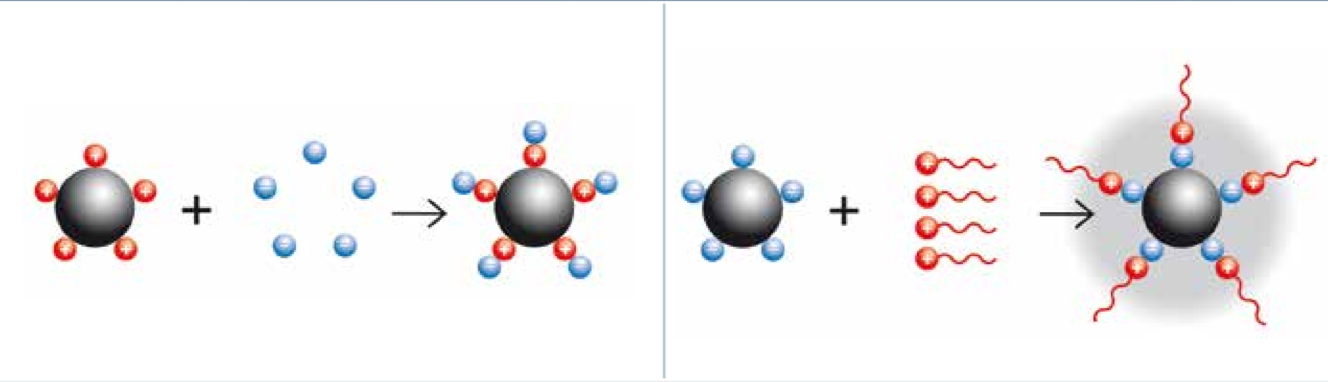
Nano particles are produced by colloidal grinding which involves dispersion of the particles in liquid to neutralize the surface charges. Both water and alcohol can be used as dispersion medium, depending on the sample material. In some cases the neutralization of surface charges is only possible by adding a buffer such as sodium phosphate or molecules with longer uncharged tails such as diaminopimelic acid (electrostatic or steric stabilization).

With the **planetary ball mills and the high energy ball mill E_{max}** RETSCH possesses **suitable mills** and the required know-how for the production of nano particles. The most important criteria for this application are:

- material of the grinding tools
- grinding ball size
- grinding balls/sample/dispersant ratio
- grinding time
- energy input

A big advantage of the E_{max} is the innovative cooling system which discharges a great part of the frictional heat generated during the grinding process.

The "comfort" grinding jars used with the planetary ball mills are ideally suited for colloidal grinding processes. Thanks to the tight o-ring sealing no liquid escapes, not even when there is a high pressure build-up inside the jar. Gripping flanges ensure easy transportation. Special safety closures make the use of the "comfort" jars particularly safe.



Neutralization of charged particles by adding a buffer (electrostatic stabilization, left) or by adding long-chained molecules (steric stabilization, right)

E_{max}

THE REVOLUTION IN ULTRAFINE GRINDING

The E_{max} is an entirely new type of ball mill which was specifically designed for high energy milling. The impressive speed of 2,000 min^{-1}, so far unrivaled in a ball mill, in combination with the special grinding jar design generates a vast amount of size reduction energy. The unique combination of impact, friction and circulating grinding jar movement results in ultrafine particle sizes in the shortest amount of time. Thanks to the new liquid cooling system, excess thermal energy is quickly discharged preventing the sample from overheating, even after long grinding times.

The high energy ball mill E_{max} is ideally suited for continuous grinding. The mill does not require cooling breaks which reduces the grinding time significantly compared to conventional planetary ball mills. The extremely high energy input at 2,000 min^{-1} together with the unique liquid cooling system provides perfect conditions for mechanical alloying and colloidal grinding down to the nanometer range.

Fig. 1: The E_{max} has two grinding stations.

Product video E_{max} at www.retsch.com/emax

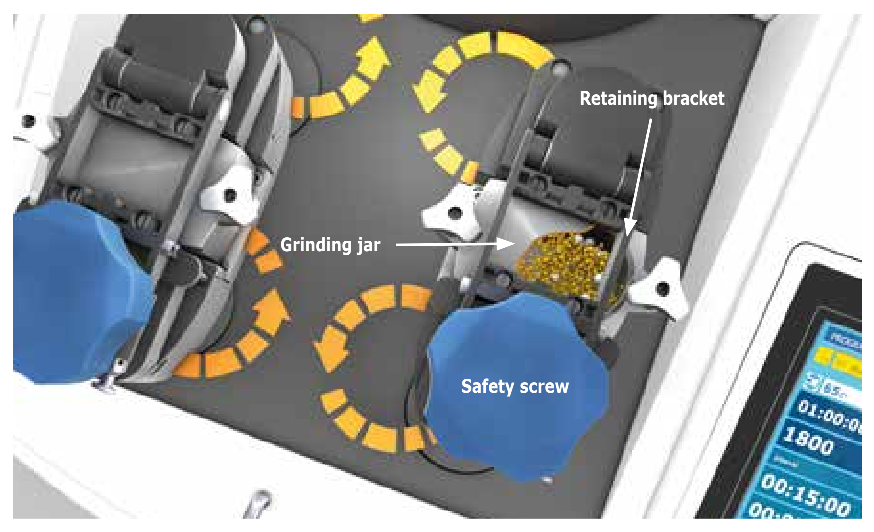


Fig. 2: The grinding jar brackets are mounted on two discs each which turn in the same direction. As a result, the jars move on a circular course without changing their orientation. The quadruple eccentric drive ensures the precise anti-synchronous movement of the grinding jars. Mass forces are eliminated by integrated counterbalances.

FUNCTIONAL PRINCIPLE

The novel size reduction mechanism of the **E_{max} unites the advantages of different mill types**: high-frequency impact (mixer mill), intensive friction (vibratory disc mill) and controlled circular jar movement (planetary ball mill) allow for unrivaled grinding performance. This unique combination is generated by the oval shape and the movement of the grinding jars. The grinding jar brackets are mounted on two discs each which turn in the same direction. As a result, the jars move on a circular course without changing their orientation. The interplay of jar geometry and movement causes strong friction between grinding balls, sample material and jar walls as well as rapid acceleration which lets the balls impact with great force on the sample at the rounded ends of the jars. This significantly improves the mixing of the particles resulting in smaller grind sizes and a narrower particle size distribution than achieved in ball mills.

Highlights

- Faster and finer grinding than with any other ball mill
- Speed of up to 2,000 min^{-1} provides ultra-fast pulverization of the sample
- Innovative water cooling permits continuous operation without cool down breaks
- Narrow particle size distribution thanks to special jar design which improves mixing of the sample
- Patented drive concept
- Jars with integrated safety closure
- Memory for 10 SOPs
- Range of jar materials ensures contamination free grinding

Fig. 3: The special jar geometry ensures a better mixing of the sample.

Technical Data

www.retsch.com/emax	
Applications:	size reduction, homogenization, nano grinding, mechanical alloying, colloidal grinding
Material feed size*:	<5 mm
Final fineness*:	<80 nm
Batch size / feed quantity*:	max. 2 x 45 ml
No. of grinding stations:	2
Grinding jar sizes:	50 ml / 125 ml
Speed:	300 – 2,000 min^{-1}
Cooling:	controlled integrated water cooling system option: external chiller
Type of grinding jars:	with integrated safety closure device, option: aeration covers
Material of grinding tools:	stainless steel, tungsten carbide, zirconium oxide
Storable SOPs:	10
Dimensions (W x H x D):	625 x 525 x 645 mm
*depending on feed material and instrument configuration/settings	

FASTER – FINER – E_{max}

Benchmark test: fineness and grinding time

Grind sizes at the nanoscale can only be achieved by wet grinding (see article on colloidal grinding, page 12). For this method a large number of grinding balls with 0.1 mm to 3 mm Ø is used to create as much friction as possible. **The resulting grinding energy is extended even further by the high speed of 2,000 min^{-1} in the E_{max}.** The high energy input is fully exploited as the unique liquid cooling system quickly discharges the frictional heat. Without effective cooling both sample and mill would overheat. Depending on the sample characteristics and grinding mode, cooling breaks of approx. 60 % of the total grinding time are recommended for conventional planetary ball mills to prevent overheating. The E_{max}, on the other hand, is suitable for continuous grinding without breaks thanks to its efficient liquid cooling system.

In a comparative trial, the pigment titanium dioxide was pulverized in the most powerful planetary ball mill and in the E_{max} (50 ml grinding jar of zircomium oxide, 110 g matching grinding balls 0.1 mm Ø, 10 g sample, 15 ml 1 % sodium phosphate).

After 30 minutes the d_{90} value of the E_{max} sample was 87 nm. The planetary ball mill achieved a grind size of only 476 nm after this time (excl. cooling breaks). Consequently, the E_{max} provided a 5 times higher final fineness than the planetary ball mill (fig. 4).

Titanium dioxide: 5 x finer

Grinding of titanium dioxide in the E_{max} and in a planetary ball mill

	d_{10}	d_{50}	d_{90}
E_{max} (after 30 min.)	57 nm	69 nm	87 nm
Planetary ball mill (after 30 min. excl. cooling breaks)	66 nm	105 nm	476 nm

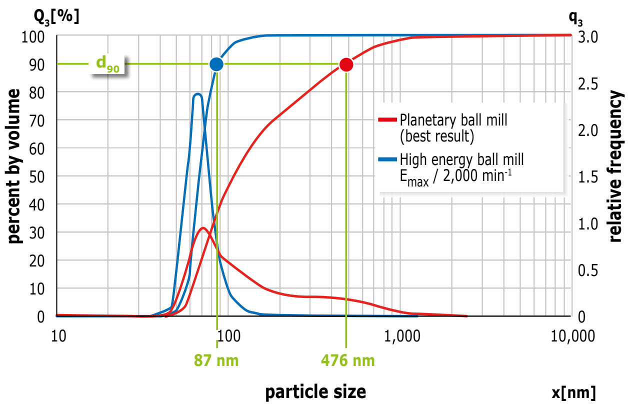


Fig. 4: The E_{max} pulverizes the sample not only faster and to a finer size, it also produces a significantly narrower particle size distribution.

Benchmark test: grinding time

The superiority of the E_{max} is even more visible when looking at the grinding time. Figure 5 shows the results of grinding graphite in the E_{max} at 2,000 min^{-1} (50 ml grinding jar of zirconium oxide, 110 g matching grinding balls 0.1 mm Ø, 5 g sample, 13 ml isopropanol) and in the most powerful planetary ball mill. Graphite is a lubricant and therefore requires a particularly high energy input for size reduction. **After only 1 hour of grinding 90 % of the E_{max} sample possessed a fineness of 13 microns. This grind size was achieved by the planetary ball mill only after 8 hours of grinding (excl. cooling breaks).** Regarding the final fineness achieved in the E_{max} after 8 hours of grinding, its superior performance again is quite apparent: With a d_{90} value of 1.7 µm the grind size is 7 times finer than the one achieved in the planetary ball mill (12.6 µm).

Graphite: 8 x faster 7 x finer

Comparison of grinding time and fineness in the E_{max} and in a planetary ball mill

Grinding time				
E_{max}	1 h	2 h	4 h	8 h
Final fineness	13.0 µm	8.2 µm	5.5 µm	1.7 µm
Planetary ball mill (excl. cooling breaks)	1 h	2 h	4 h	8 h
Final fineness	25.0 µm	20.3 µm	16.2 µm	12.6 µm

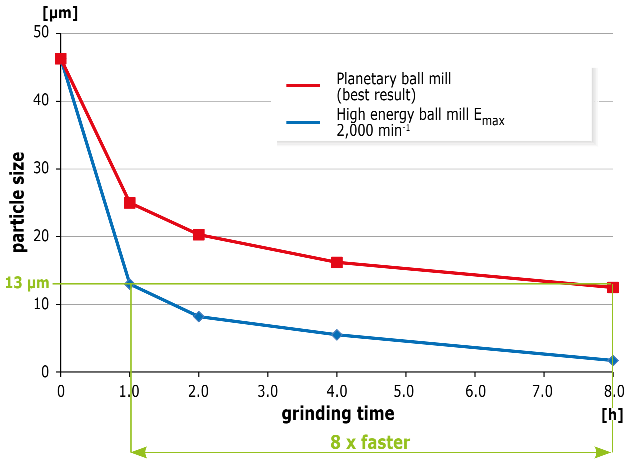


Fig. 5: Pulverization of graphite. The water-cooled E_{max} is highly superior to the planetary ball mill without cooling system both in speed and achieved final fineness.

HIGHLY EFFICIENT LIQUID COOLING

The grinding jars of the E_{max} are cooled by an **integrated water cooling system**. To further reduce the temperature, the mill can be connected to a heat exchanger or the tap. Figure 6 shows the cooling circuit of the E_{max}. The grinding jars are cooled via the jar. **The cooling system is very effective because heat is more easily discharged into water than into air.** The E_{max} software allows the user to carry out the grinding process within a **defined temperature range**, i.e. he can set a minimum and a maximum temperature. When the maximum temperature is exceeded, the mill automatically stops and starts again upon reaching the minimum temperature.

Cooling can be an essential advantage, especially if heat-sensitive samples are processed or if isopropanol has been added to the sample (fig. 7). Isopropanol evaporates at 82 °C which makes the pressure inside the jar rise considerably. If the temperature remains below this value, the pressure inside the jar and the stress on the sealing are reduced. Moreover, the grinding jar can be opened shortly after the grinding is finished.

Cooling circuit E_{max}

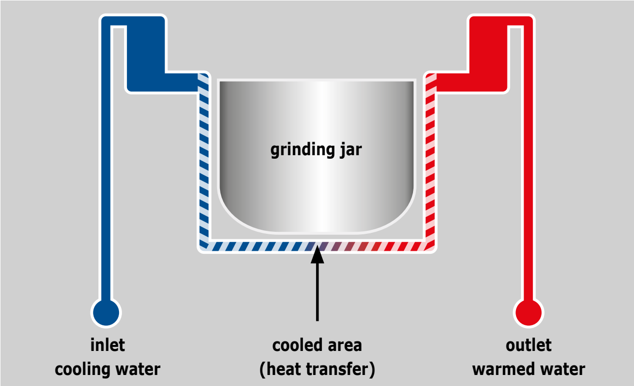


Fig. 6: The grinding jar is cooled via the jar brackets.

Wet grinding of graphite in the E_{max}

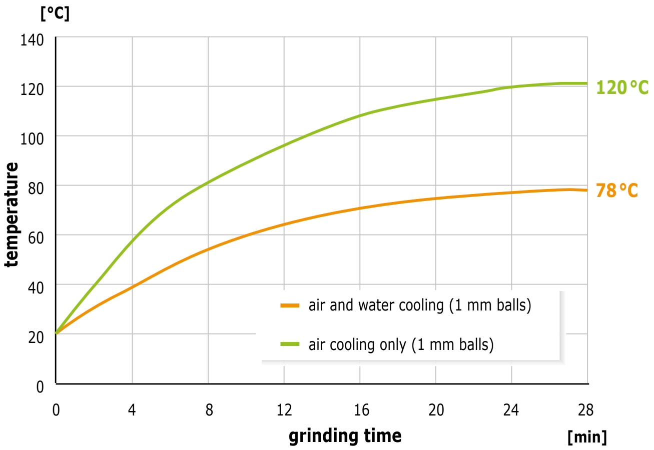


Fig. 7: When grinding graphite with isopropanol (50 ml jar, 1 mm balls, 5 g sample), the warming of the grinding jar could be limited to 78 °C thanks to the liquid cooling. Without water cooling the temperature was 120 °C.

MAXIMUM SAFETY

During product development of the E_{max} special attention was paid to operational safety. The position of the grinding jar is automatically monitored, so that the mill cannot be started if the position is not correct. **No counterweight is required** to operate the E_{max}. Possible imbalances are controlled at all times. If they become too strong the mill automatically stops. The remaining grinding time is displayed and the process can be re-started once balance has been restored.

Conclusion

The E_{max} opens up a new dimension in high energy milling. The unique combination of friction and impact as well as the revolutionary speed of 2,000 min^{-1} permit the production of ultrafine particles in the shortest amount of time. Thanks to the unrivaled liquid cooling system the E_{max} generates substantially more grinding energy than conventional planetary ball mills – without overheating. Moreover, the water cooling allows for a significant reduction of the grinding time compared to ball mills without cooling that require grinding breaks. The examples shown in this article impressively demonstrate that the E_{max} achieves the desired grind sizes in a fraction of the time required by comparative ball mills.

THE CLASSIC TOOLS FOR PULVERIZATION TASKS

PLANETARY BALL MILLS

RETSCH Planetary Ball Mills are used wherever highest demands are placed on speed, fineness, purity, and reproducibility. They pulverize and mix soft, medium-hard to extremely hard, brittle and fibrous materials and easily achieve final finenesses down to the lower micron range. For wet grinding, even grind sizes in the nanometer range are possible. In addition to classic grinding tasks, the mills also meet all requirements for colloidal grinding and have the necessary energy input for mechanical alloying.

HIGHLIGHTS

- Powerful and fast grinding down to the submicron range
- Reproducible results due to energy and speed control
- Suitable for long-term trials and continuous use
- Allows for both dry and wet grinding
- Wide choice of materials for neutral-to-analysis grinding

MODEL SELECTION & EXTENSIVE RANGE OF ACCESSORIES

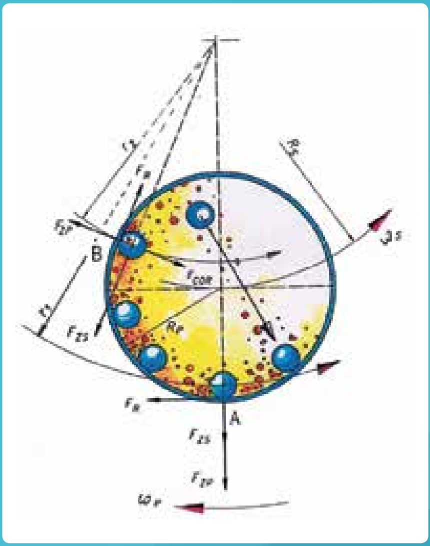
RETSCH offers an entire range of planetary ball mills. **The PM 100, PM 100 CM and PM 200 are benchtop models with one or two grinding stations.** The PM 100 CM operates in centrifugal mode, i.e. the speed ratio of the sun wheel to the grinding jar is 1: -1. This leads to a more gentle size reduction process with less abrasion. **The PM 400 is a floor model with two or four grinding stations,** which permits to grind up to eight samples simultaneously by stacking the grinding jars. To generate the high energy input which is required for mechanical alloying, the PM 400 is available as "MA" version with a speed ratio of 1: -2.5 or 1:-3.

The "comfort" range of grinding jars has been specially designed for extreme working conditions such as long-term trials, wet grinding, high mechanical loads, maximum speeds as well as for mechanical alloying. **A wide range of materials and sizes (12 ml - 500 ml),** also for the grinding balls, allows a largely neutral-to-analysis preparation adapted to the application requirements. Due to an O-ring seal, all "comfort" grinding jars are gas-tight and dust-proof.

For colloidal grinding, the use of a grinding jar with a special closure device is recommended. This permits a gas-tight handling inside and outside of the glove box and ensures safe transport of the grinding jar.

For grindings under inert conditions, **aeration covers** are available. These permit the introduction of gases like argon or nitrogen into the grinding jar.

THE "PLANETARY PRINCIPLE"



In the planetary ball mill, every grinding jar represents a "planet". This planet is located on a circular platform, the so-called sun wheel. When the sun wheel turns, every grinding jar rotates around its own axis, but in the opposite direction. Thus, centrifugal and Coriolis forces are activated, leading to a rapid acceleration of the grinding balls (see fig. 1).

The result is very high pulverization energy allowing for the production of very fine particles. The enormous acceleration of the grinding balls from one wall of the jar to the other produces a strong impact effect on the sample material and leads to additional grinding effects through friction. For colloidal grinding and most other applications, the ratio between the speed of the sun wheel and the speed of the grinding jar is 1: -2. For applications where a higher energy input has to be achieved, planetary ball mills with other ratios as well as high performance ball mills such as the E_{max} are the perfect choice.

Fig. 1: In the planetary ball mill, centrifugal and Coriolis forces permit grindings down to the submicron range.

FINAL FINENESS DOWN TO THE NANOMETER RANGE

Figure 2 shows the result of grinding of alumina (Al_2O_3) at 650 min^{-1} in the PM 100. After 1 hour of size reduction in water with 1 mm grinding balls, the mean value of the particle size distribution is 200 nm; after 4 hours it is 100 nm. In a further trial, the material was initially ground for 1 hour with 1 mm grinding balls and then for 3 hours with 0.1 mm grinding balls (see fig. 3). In this case, an average value of 76 nm was achieved. The grinding results show that planetary ball mills can produce particle sizes in the nanometer range. The choice of the right ball size plays a crucial role in the success of nanogrinding.

Colloidal grinding of alumina in the PM 100

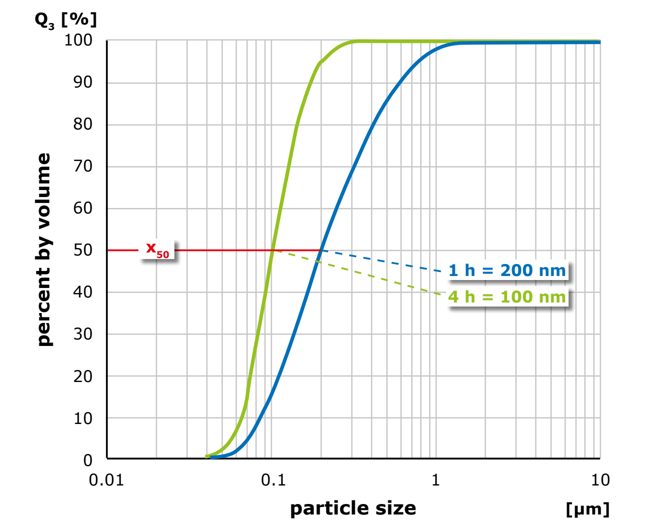


Fig. 2: Grinding of alumina in water with 1 mm grinding balls (left) after 1 hour (blue) and after 4 hours (green)

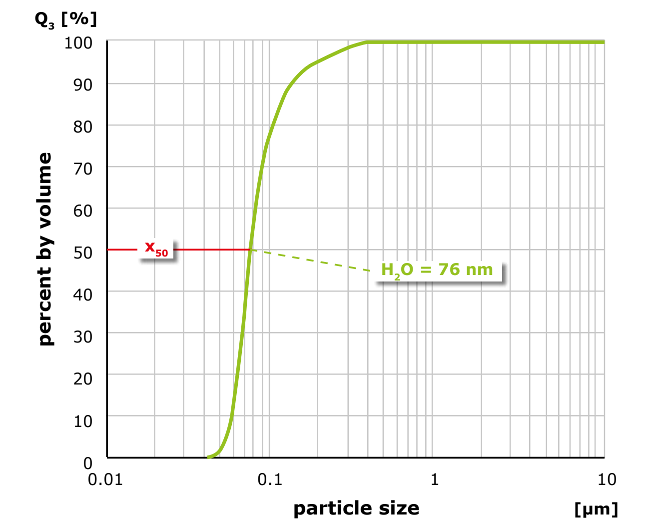


Fig. 3: Grinding of alumina with a 1 mm grinding ball (1 hour) and then with 0.1 mm balls (3 hours) in water

Conclusion

Planetary Ball Mills are ideally suited for classical mixing and size reduction processes in which a high energy input is required. They are suitable for both dry and wet grinding; with the latter even grind sizes down to the nanometer range can be achieved depending on the sample material. RETSCH offers various models and extensive accessories, making the PM product range universally applicable.

MECHANICAL ALLOYING

High Energy Ball Mill E_{max}

Planetary Ball Mill PM 400

Alloys such as amalgama in dental medicine or stainless steel are universally known and used. The traditional way to produce alloys is to fuse the components at very high temperatures. If only small quantities are required or if the alloys cannot be fused by melting mechanical alloying is an alternative. For this application ball mills are ideally suited. They provide a high energy input due to the impact and friction effects which occur during grinding. The mechanical impact is also advantageous in mechanochemistry, for example, to produce chemical reactions without using solvents.

WHAT HAPPENS DURING MECHANICAL ALLOYING?

The first alloys (bronze) were produced as early as 3,300 BC. Today, a huge variety of alloys exists which are characterized by optimized properties. Some components can be mixed when molten and remain dissolved in each other due to the formation of mixed crystalline structures. New properties, for example the improved hardness of the alloy, are a result of the atoms of the alloy element entering the crystal lattice of the basic element. Due to the different atom diameters, the lattice in the mixed crystals is distorted, the slip planes are disturbed and the metal becomes harder but also more brittle.

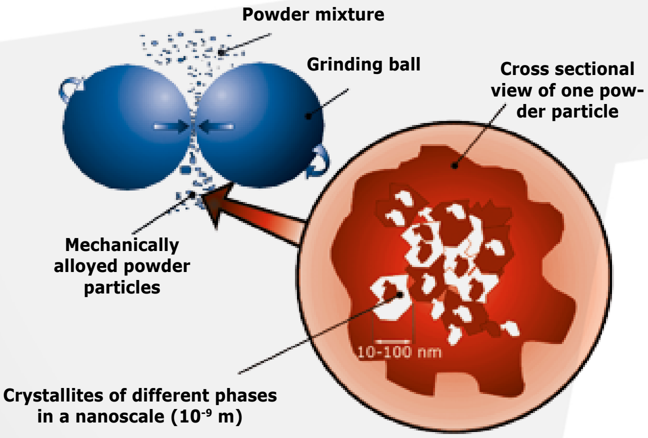


Fig. 1: Principle of mechanical alloying

MECHANICAL ALLOYING IN BALL MILLS

What if components cannot be alloyed by melting? If, for example, the melting temperatures differ so much that one component is already evaporated when the other is melting? In the late 1960s ferronickel alloys were first produced by mechanical alloying to obtain extremely temperature-resistant materials. Mechanical alloying uses intensive kinetic processes to fuse the components in the form of powders (fig. 1). **The planetary ball mills and the high energy ball mill E_{max} provide the required energy input by strong impact effects.** The powder particles are plastically deformed between the grinding balls and fused with each other by strong kinetic processes. The planetary ball mill PM 400 MA has a speed ratio of 1:-3 which further increases the impact effects and makes this mill ideally suited for mechanical alloying.

Initially, larger particles are produced this way. Increased defect structures such as dislocations, gaps and tension in the crystal lattices of the individual particles lead to an elevated diffusion rate of their atoms, resulting in increased embrittlement which promotes the formation of cracks and a subsequent breaking of the particle. The diffusion is supported by a temperature rise generated by frictional heat in the grinding jar. A model calculation showed that temperature peaks of 700 – 1,800 K and pressure peaks of a few thousand atmospheres occur in a planetary ball mill [1]. The process of fusion and folding continues until complete homogenization is achieved after a few minutes or several hours. Diminutive crystalline sections of adjacent initial components are formed in the powder particles which are called "nano crystallites" (fig. 2 and 3).

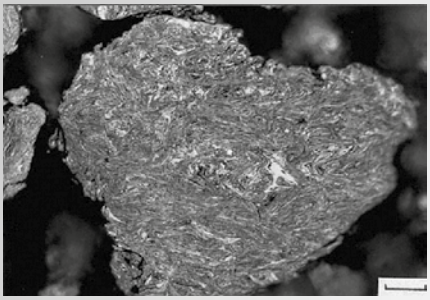


Fig. 2: Cross sectional optical micrograph of a mechanically alloyed iron-tantalum-copper (FeTaCu) powder particle after 5 h

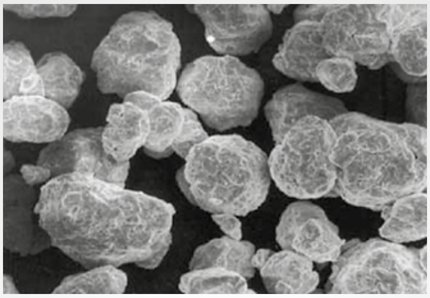


Fig. 3: Scanning electron microscopical (SEM) picture of a mechanically alloyed FeTaCu powder after 20 h (top view)

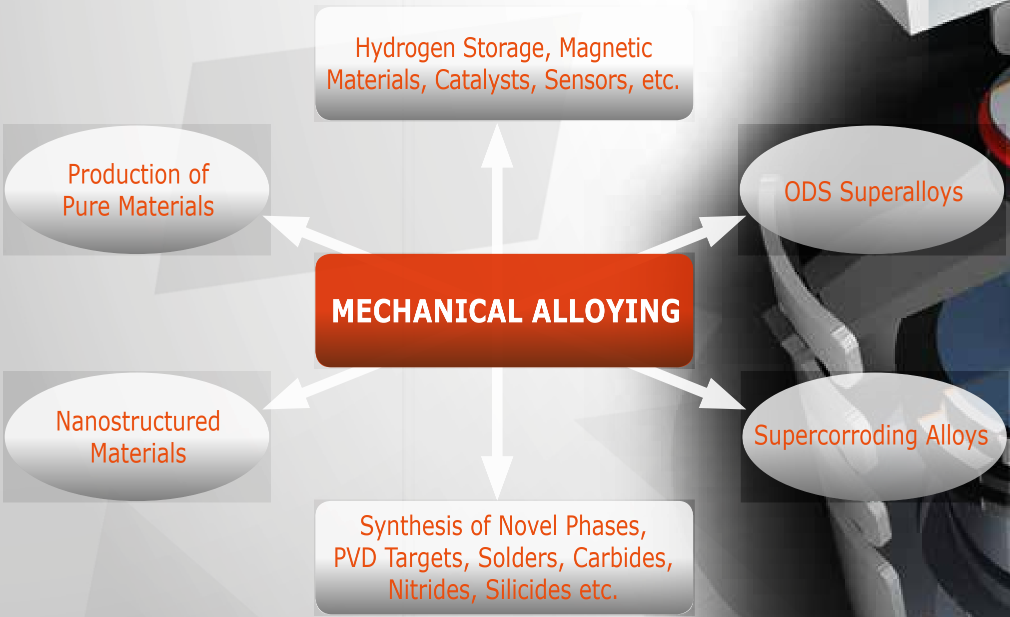
In this way it is possible to produce alloys which cannot be obtained by melting and casting. Any mixing ratio can be selected. RETSCH's ball mills provide the required energy input for mechanical alloying and can be operated with high speed ratios.

For reactions under controlled atmosphere or working under inert conditions the "comfort" grinding jars of the PM series can be equipped with safety closures and aeration lids. The high energy ball mill E_{max} also meets all requirements for mechanical alloying.

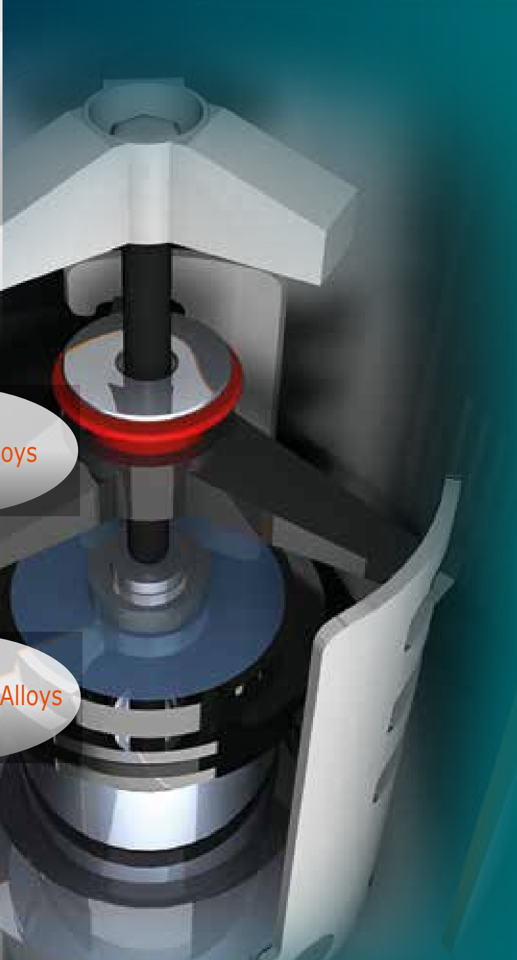
[1] Urakaev FK (2000), Powder Technology 200, 107, 93

MECHANOCHEMISTRY

The mechanical effects generated by a planetary ball mill are also highly suitable for the so-called mechanochemistry. **Mechanical impact provides the activation energy required for chemical reactions.** These complex reactions can be carried out without the use of solvents. The types of reactions vary greatly, from oxidative halogenations or Diels-Adler reactions to the formation of enamines, syntheses of glycosides or even simple regio-selective reactions. Mechanochemistry can be used, for example, for the dehalogenation of waste (DMCR) which would hardly be possible with conventional methods.



Source: Suryanarayana et al. (2001), The science and technology of mechanical alloying, Materials Science and Engineering, A304–306 p151–158



PRODUCING NANO PARTICLES BY COLLOIDAL GRINDING

So-called colloidal or nano grindings are usually carried out as wet grindings. To reduce already small particles further in size by using mechanical force, a high energy input is required. This input is provided by RETSCH's E_{max} and planetary ball mills. Further important criteria for nano grindings are suitable grinding tools and optimum grinding ball fillings.

Grinding jar "comfort" for PM series with safety closure, aeration cover

PRELIMINARY GRINDING

Depending on the size of the initial sample material and desired final fineness, a preliminary size reduction step can be useful. A dry grinding process with grinding balls of >3 mm Ø is usually carried out by filling one third of the jar with grinding balls and one third with sample material. The obtained sample is then used for the actual colloidal process.

HOW TO CARRY OUT COLLOIDAL GRINDING IN A BALL MILL

With the planetary ball mills and the new E_{max}, RETSCH offers two types of ball mills which provide the required energy input for colloidal grinding down to the nanometer range. Grinding jars and balls made of an abrasion-resistant material such as zirconium oxide are best suited for this type of application. **60 % of the grinding jar volume is filled with grinding balls of 0.5 to 3 mm Ø**, providing a large number of frictional points. The actual sample fills about one third of the jar volume. By adding a suitable dispersant (e.g. water, isopropanol, buffer), **the consistency of the sample should become pasty** thus providing ideal preconditions for colloidal grinding. If a very high final fineness is required, it is recommended to proceed with a second colloidal grinding with 0.1 to 0.5 mm Ø grinding balls, particularly if 2 to 3 mm balls were used in the first process (the balls need to be 3 x bigger than the particle size of the initial material). To separate the sample from the grinding balls, both are put on a sieve (with aperture sizes 20 to 50 % smaller than the balls) with a collecting pan. For the subsequent colloidal grinding 60 % of the jar is filled with small beads. The suspension from the previous grinding is carefully mixed with the grinding beads until a pasty consistency is obtained.

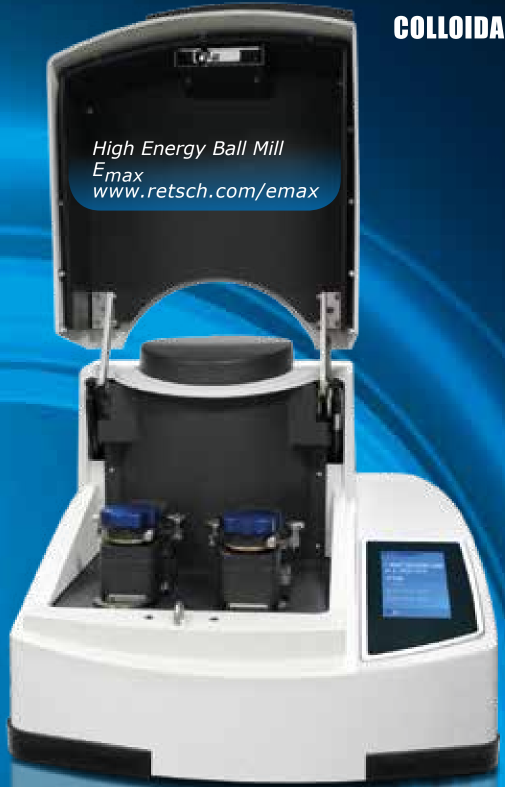
CONSISTENCY

If a sample tends to swell during wet grinding, the consistency of the sample-grinding ball mixture should be checked during the process to add more dispersant if required. If the material is known to swell easily, it should be diluted more strongly before the grinding is started.

REMOVAL OF GRINDING JAR

Care must be taken when removing the grinding jar from the planetary ball mill as it can have a temperature of up to 150 °C due to the heat generated during the grinding process. Moreover, pressure builds up inside the grinding jar. Therefore, it is recommendable to use the **optional safety closure** for the "comfort" grinding jars of the PM series which allows for safe removal of the jar. After the grinding process the jar should cool down for a while. The E_{max} jar already has an integrated safety closure. Moreover, the effective cooling system of the E_{max} prevents the jars from heating up too much. Both jars can be equipped with optional aeration covers which allow working under inert atmosphere.

Planetary Ball Mill PM 100 www.retsch.com/pm100



High Energy Ball Mill E_{max} www.retsch.com/emax

Selection of grinding tools: size and material of grinding jar and balls, grinding balls 3 x larger than biggest particle of the sample ►

Grinding jar filling: 60% grinding balls, 30% sample material, addition of dispersant until pasty consistency is obtained

◄ **Dispersion media:** e.g. isopropanol, ethanol, mineral turpentine, sodium phosphate, diaminopimelic acid

▼

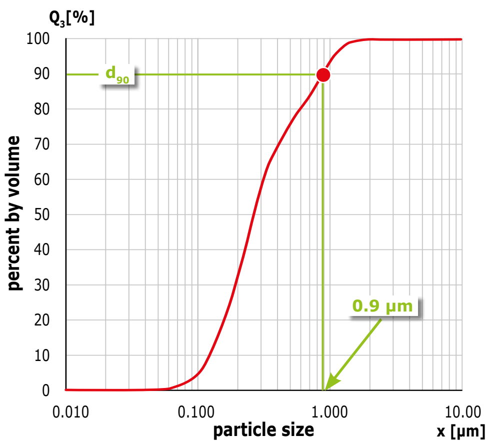
Grinding process

▼

Cooling down: grinding jar should not be opened until it has reached room temperature

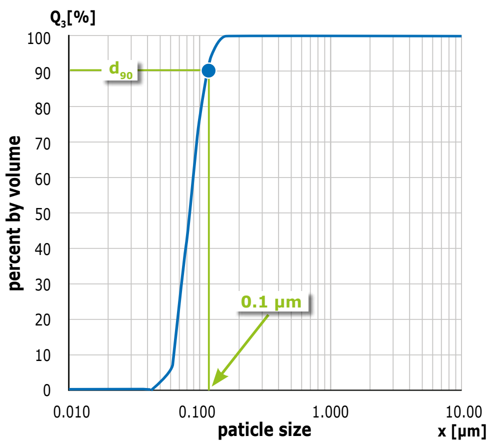
◄ **Particle size analysis**

Grinding of rocks (granite-like) in the PM 100



A 50 ml zirconium oxide jar was filled with 30 ml zirconium oxide balls of Ø 2 mm. 21 g sample material (which corresponds to one third of the jar volume) and 15 ml water were added and everything was mixed, resulting in a pasty consistency. After 2 hours of grinding in the PM 100 at 550 min^{-1}, the d_{90} value was 0.9 µm.

Grinding of alumina in the E_{max}



A 20 percent by weight suspension of alumina in 0.5% sodium phosphate was pulverized in the E_{max}. The initial material had a fineness of 1.2 µm (d_{90}). 30 g of the suspension were mixed in a 50 ml jar with 110 g grinding balls of Ø 0.1 mm and ground for 30 minutes at 2,000 min^{-1}. The obtained d_{90} value was 0.11 µm.

MIXER MILL MM400

THE "ALL-ROUNDER" FOR SMALL QUANTITIES

Grinding – Mixing – Cell Disruption

Mixer Mill MM 400
www.retsch.com/mm

Highlights

- Reproducible and efficient grinding, mixing and homogenization in seconds
- Powerful grinding with max. 30 Hz of up to 20 samples simultaneously
- Grinding jars with screw-top lid allow wet and cryogenic grinding
- Memory for 9 SOPs
- Grinding jar sizes from 1.5 ml to 50 ml, adapter for disposable vials
- KryoKit for cooling of grinding jars at -196 °C

No matter whether bone or tissue samples, hair, tablets, wood, plastics, minerals, or chemicals – the mixer mill MM 400, and the basic model MM 200, are proven "all-rounders" for grinding, mixing and homogenizing of small samples. They achieve grind sizes of up to 5 microns, and process hard, medium-hard, brittle as well as soft, elastic or fibrous samples quickly and reliably.

SAMPLE PREPARATION OF PLANT MATERIAL

Plants are used in many ways, for example, as food, in the paper manufacture or for the production of secondary fuels. Due to their ligneous components (such as lignin), plants are often fibrous. Lignin is a very stable substance which can cause problems, for example, in animal feed or in the production of bioethanol. In order to make specific improvements in these areas, researchers need to understand exactly how lignin is produced in plants. With a growing understanding of the production process of herbal substances, the content or the structure of lignin can be changed via targeted biotechnological manipulation. Plants with modified lignin may lead to better digestibility in cattle feeding; or the bleaching of these plants in the paper manufacture is easier, and thus more environmentally friendly. In research often only small amounts of plant material are available for analysis. The MM 400 is the ideal mill to prepare small sample volumes. Six pieces of the thale cress plant (Arabidopsis thaliana) were ground in the MM 400 to a final fineness of 100 microns for subsequent analysis. Even after a short grinding time, the sample was homogeneous, i. e. no coarse components or fibers could be found that might have interfered with the subsequent analysis.

arabidopsis thaliana 6 plants (approx. 2 g)

after manual preliminary size reduction

after fine grinding in the MM 400

50 ml grinding jar of stainless steel, 1x25 mm grinding ball of stainless steel, 30 Hz, 2 min

MIXER MILL TECHNOLOGY

The grinding jars oscillate in a horizontal bow movement. The inertia of the grinding balls in the oscillating jars leads to a powerful impact of the balls on the rounded ends of the jars. **The sample is pulverized in seconds to minutes and thoroughly mixed.** If many small balls are used, the effect of friction is amplified, so that it is even possible to disrupt biological cells.

FLEXIBILITY THANKS TO EXTENSIVE ACCESSORIES

Various grinding jar sizes and materials make the mixer mills highly versatile instruments. Jars made of stainless steel are available from 1.5 to 25 ml (MM 200) or 50 ml (MM 400). For applications in which neutral-to-analysis work is important, materials such as tungsten carbide, zirconium oxide, agate, or PTFE are used. The grinding jars for the MM 400 permit the **use under cryogenic conditions**, thanks to their gaskets and screw-top lids. For such applications, RETSCH offers the KryoKit, in which jars can be cooled at -196 °C in liquid nitrogen and the sample can be embrittled inside the jar. The mixer mills are frequently used for **cell and tissue disruption in DNA/RNA extraction**. For this application, adapter racks are available that can be fitted with up to 20 reaction vials. Grinding parameters such as frequency and grinding time can be set conveniently via the display. Up to 9 SOPs can be stored, in order to facilitate routine grinding processes.

Conclusion

The RETSCH mixer mills MM 200 and MM 400 are versatile, compact benchtop models that are specifically designed for grinding small amounts of sample. They mix and homogenize powders and suspensions in seconds and are also ideally suited for cell disruption.

CRYOMILL

ICE-COLD GRINDING

For ductile and elastic materials, as well as for samples of highly volatile ingredients, cryogenic grinding is the only way to achieve grind sizes required for many analyses. Through cooling with liquid nitrogen to -196 °C, the sample material is embrittled, which improves the breaking properties and allows grind sizes up to 5 microns. Volatile substances of the sample are preserved and can be detected quantitatively; furthermore, thermally induced decomposition is prevented.

Highlights

- Increased frequency of 30 Hz ensures high energy input and grind sizes up to 5 microns
- No direct contact with liquid nitrogen provides safe operation
- Autofill system guarantees low nitrogen consumption
- Memory for 9 SOPs
- Grinding at room temperature is possible

quick – safe – cryogenic

CryoMill
www.retsch.com/cryomill

SAFE AND FLEXIBLE

One particular advantage of the CryoMill is the high operating safety, since **the user is at no time in contact with the liquid nitrogen**. The nitrogen supply from the integrated autofill system is controlled by a temperature sensor so that LN_2 is always replenished in the exact amount that is needed to keep the temperature at -196 °C. The automatic cooling system guarantees that the grinding process will not start before the sample is thoroughly cooled – **this reduces consumption and guarantees reproducible grinding results.** With a vibration frequency of 30 Hz, the mill grinds a variety of materials very effectively in a few minutes. The main grinding mechanism is impact, but there is also friction, so that **much finer grind sizes** can be obtained compared with other cryogenic mills. At very high energy inputs, grinding can be interrupted at defined moments to dissipate frictional heat from the grinding jar. The mill can also be operated without nitrogen cooling.

Thanks to the wide range of accessories, the applications of the CryoMill are very diverse. For nitrogen supply, RETSCH offers a **50 liter LN_2 tank with safety valve**. The grinding jars from 5 to 50 ml can be screwed tightly, so that no sample material can escape. For neutral-to-analysis applications, 25 ml grinding jars made of zirconium oxide or PTFE are available. The offer is completed by different ball sizes and materials, as well as **adapters for the use of up to 6 x 2 ml reaction vials**.

In order to ensure the best possible adaptation to the different samples, pre-cooling, grinding time, and intervals are freely programmable. During the pre-cooling, the grinding jar is moved at 5 Hz, so that the grinding ball permanently stays in motion and does not freeze in humid samples. By storing up to 9 grinding programs (SOPs), routine processes are simplified. LEDs in the display allow to control at any time, which step is currently being processed.

Conclusion

The RETSCH CryoMill has proven to be a perfect instrument for grinding of temperature-sensitive materials with a glass transition temperature below room temperature. The final fineness is significantly higher than compared to other cryogenic mills. For materials with volatile components, the CryoMill is the ideal instrument for sample preparation.

GENTLE GRINDING OF PET

PET bottles are popular and widely used as light and robust beverage packaging. Mineral water and other beverages in PET bottles, however, can contain traces of the harmful compound acetaldehyde. The substance, even in small traces in the range of 10-20 ppb, has a negative effect on the taste. Therefore, the quality control process of packaging manufacturers and beverage bottlers involves time-consuming and elaborate quantitative test methods. Since acetaldehyde is a highly volatile compound, thermal stress on the PET sample must be avoided in any case before the analysis. **Cryogenic grinding at -196 °C is an ideal method for gentle, reproducible grinding of samples made of elastic materials.** A heat-induced loss of acetaldehyde during the grinding process is reliably prevented by cooling. The cryogenic grinding is ideal for sample preparation in the context of chromatographic routine checks in certified laboratories.

The **preliminary size reduction** of the flexible PET material takes place in a **cutting mill such as the RETSCH SM 300** which is ideally suited for this purpose. This mill ensures an adequate preliminary size reduction to a fineness of about 5 mm without thermal stress on the material. On this basis, the required final fineness of less than 0.5 mm can be easily achieved in a second grinding step in the CryoMill. The grinding of a sample of 6 g of pre-crushed preform PET material takes only 5 minutes.

*PET preforms **after preliminary size reduction in the SM 300** (center)* – 1200 min^{-1}, 6 mm sieve, parallel section rotor.

*After **fine size reduction in the CryoMill** (right) – 50 ml grinding jar of stainless steel, 1 x 25 mm grinding ball of stainless steel, 30 Hz, 2 x 2 min with 1 min intermediate cooling.*

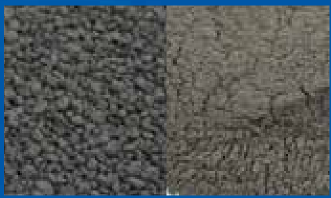
APPLICATION EXAMPLES

RETSCH's innovative ball mills meet and exceed all requirements for fast and reproducible grinding down to the submicron range. They are used for the most demanding tasks, from routine sample processing to colloidal grinding and advanced materials development.

PLANETARY BALL MILLS

Sample	Accessories	Parameters	Feed quantity	Final fineness
Ash	Grinding jar 500 ml zirconium oxide, 1100 g grinding balls 1 mm zirconium oxide, 120 ml water	600 min^{-1}, 2 h	100 g	<1.3 µm
Catalysts	Grinding jar 250 ml zirconium oxide, 15 x grinding balls 20 mm zirconium oxide	450 min^{-1}, 2 min	130 ml	<63 µm
Ceramics	Grinding jar 500 ml zirconium oxide, 25 x grinding balls 20 mm zirconium oxide, some drops of isopropanol	280 min^{-1}, 20 min	250 g	<20 µm
Effluent sludge	Grinding jar 500 ml stainless steel, 25 x grinding balls 20 mm stainless steel	500 min^{-1}, 8 min	172 g	<110 µm
Mangan-oxide	Grinding jar 250 ml zirconium oxide, 550 g grinding balls 2 mm zirconium oxide, 100 ml 0.5% $NaPO_3$	480 min^{-1}, 2 h	40 g	<0.7 µm
Mineral	Grinding jar 500 ml zirconium oxide, pre-grinding 8 x grinding balls 30 mm zirconium oxide, fine grinding 160 x grinding balls 30 mm zirconium oxide	400 min^{-1}, 3 min and 20 min	150 g	<45 µm
Semi-cristalline Polymer	Grinding jar 50 ml zirconium oxide, 110 g grinding balls 2 mm zirconium oxide, 20 ml water	530 min^{-1}, 2 h	2 g	<0.6 µm
Straw	Grinding jar 500 ml zirconium oxide, 160 x grinding balls 10 mm zirconium oxide	400 min^{-1}, 75 min	50 g	<50 µm
Super-absorber	Grinding jar 500 ml zirconium oxide, 160 x grinding balls 10 mm zirconium oxide	280 min^{-1}, 30 min	100 g	<50 µm






HIGH ENERGY BALL MILL E_{max}

Sample	Accessories	Parameters	Feed quantity	Final fineness
Al_2O_3	Grinding jar 50 ml zirconium oxide, 110 g grinding balls 0.1 mm zirconium oxide, in 0.5% sodium phosphate	2,000 min^{-1}, 15 min	23 g 20% by weight suspension	<0.14 µm
Coal	Grinding jar 125 ml steel, 54 x grinding balls 10 mm stainless steel	1,500 min^{-1}, 10 min	26 g	<17 µm
Graphite	Grinding jar 50 ml zirconium oxide, 110 g grinding balls 1 mm zirconium oxide, 13 ml isopropanol	2,000 min^{-1}, 8 h	5 g	<1.7 µm
Pigment TiO_2	Grinding jar 50 ml zirconium oxide, 110 g grinding balls 0.1 mm zirconium oxide, 15 ml 1% sodium phosphate	2,000 min^{-1}, 30 min	10 g	<0.087 µm
Quartz	Grinding jar 125 ml stainless steel, 18 x grinding balls 15 mm stainless steel	1,000 min^{-1}, 30 min	66 g	<16 µm

The RETSCH mixer mills are ideally suited for grinding and homogenizing a huge variety of different sample materials. Whether the products are hard, medium-hard, soft, brittle, elastic or fibrous, they can be ground in dry, wet or cryogenic mode.

MIXER MILL MM 400

Sample	Accessories	Parameters	Feed quantity	Final fineness
Cr-Alloy	Grinding jar 25 ml WC, 3 x grinding balls 20 mm WC	30 Hz, 2 min	20 g	<250 µm
Frog tissue	Grinding jar 50 ml stainless steel, 3 x grinding balls 12 mm stainless steel, sample and grinding jar pre-cooled in LN_2	30 Hz, 2 min	10 g	homogenized
Moss	Grinding jar 50 ml stainless steel, 3 x grinding balls 15 mm stainless steel	30 Hz, 3 min	1 g	<150 µm
Parts of insects	Adapter MM for 5 reaction vials 2 ml PTFE, 0.5 g balls of glass (0.75 – 1 mm)	30 Hz, 3 min	1-2 pieces	homogenized
Tablets	Grinding jar 50 ml stainless steel, 6 x grinding balls 12 mm stainless steel	30 Hz, 5 min	15 g	<150µm
Wood	Adapter MM for 5 reaction vials 2 ml PTFE, 3 x grinding balls 7 mm stainless steel	30 Hz, 3 min	1 piece	<200 µm




CRYOMILL

Sample	Accessories	Parameters	Feed quantity	Final fineness
Caoutchouc	Grinding jar 50 ml stainless steel, 1 x grinding ball 25 mm stainless steel, 10 min pre-cooling	30 Hz, 2 min	4 g	<1 mm
Chocolate	Grinding jar 50 ml stainless steel, 1 x grinding ball 25 mm stainless steel, 10 min pre-cooling	30 Hz, 2 min	1 piece	<0.5 mm
Paper	Grinding jar 50 ml stainless steel, 1 x grinding ball 25 mm stainless steel, 6 min pre-cooling	25 Hz, 8 x 2 min, 30 sec interval	4 g	<400 µm
PET granulate	Grinding jar 50 ml stainless steel, 1 x grinding ball 25 mm stainless steel, 10 min pre-cooling	25 Hz, 8 x 4 min, 30 sec interval	10 g	<350 µm
Shoe sole	Grinding jar 50 ml stainless steel, 1 x grinding ball 25 mm stainless steel, 10 min pre-cooling	30 Hz, 4 x 2 min, 1 min interval	6 g	<400 µm

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