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PRODUCTION OF ULTRAFINE, HIGH-PURITY CERAMIC POWDERS USING THE U.S. BUREAU OF MINES DEVELOPED TURBOMILL

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ABSTRACT

Turbomilling, an innovative grinding technology developed by the U. S. Bureau of Mines in the early 1960's for delaminating filler-grade kaolinitic clays, has been expanded into the areas of particle size reduction, material mixing and process reaction kinetics. The turbomill, originally called an attrition grinder, has been used for particle size reduction of many minerals, including natural and synthetic mica, pyrophyllite, talc and marble. In recent years, an all-polymer version of the turbomill has been used to produce ultrafine, high-purity advanced ceramic powders such as SiC, Si_3N_4, TiB_2, and ZrO_2. In addition to particle size reduction, the turbomill has been used to produce intimate mixtures of high surface area powders and whiskers. Raw materials, TiN, AlN, and Al_2O_3, used to produce a titanium nitride/aluminum oxynitride (TiN/AlON) composite were mixed in the turbomill, resulting in strength increases over samples prepared by dry ball milling. Using the turbomill as a leach vessel, it was found that 90.4 pct of the copper was extracted from the chalcopyrite during a 4-hour leach test in ferric sulfate versus conventional processing which involves either roasting the ore for Cu recovery or leaching the ore for several days.

INTRODUCTION

The Bureau of Mines turbomill has evolved over a period of 30 years. The original patent granted to the Bureau was for a process to produce paper coating grade clays from lower grade kaolins [1]. Following this work, the Bureau conducted numerous other studies on grinding of industrial minerals. A Bureau of Mines Bulletin highlighting the kaolin research and information on the grinding of industrial minerals was published in 1980 [2]. This Bulletin also describes several commercial applications of the turbomill grinding technology.

In the early 1980's, research to determine the feasibility of using the turbomill to produce ultrafine, high-purity powders for advanced ceramics was undertaken [3]. In his study, Wittmer found that preparing SiC in the original steel mill yielded powders with iron levels above the acceptable range. A variety of polymers was tested as mill construction materials with ultra-high molecular weight (UHMW) polyethylene exhibiting the best wear resistance. Use of the all-polymer mill produced α-SiC powders of higher purity. Wittmer also evaluated the use of autogenous milling, in which the milling medium and the material to be milled are of the same or similar composition. Other ceramic materials, such as Si_3N_4 and ZrO_2, were milled with favorable results.

The turbomill also has been used to produce intimate homogeneous mixtures of high surface area powders and whiskers. SiC whiskers have been dispersed in alumina and silicon nitride powders [4]. Mixing the raw materials for preparation of a TiN/AlON composite in the turbomill resulted in strength increases over samples prepared by dry ball milling the components.

Rice, Cobble, and Brooks reported the use of the turbomill as a leaching vessel. Chalcopyrite was ground and leached simultaneously with ferric sulfate [5]. They found that 90.4 pct of the copper was extracted from chalcopyrite during a 4-hour leach test. Conventional processing technology for the recovery of Cu from chalcopyrite involves either roasting the chalcopyrite ore or leaching the ore for extended periods of time.

THE TURBOMILL

The turbomill consists of three main parts: a rotor, composed of vertical bars fixed to upper and lower disks (the upper one attached to the drive shaft); a cagelike stator composed of vertical bars attached to rings at the top and bottom; and a cylindrical container. A frame holds the motor which is attached to the rotor drive shaft and the machine components. The turbomill has been scaled up to sizes as large as 50.8-cm-diam for use in the laboratory. Industry has used mills as large as 132-cm-diam for production of ultrafine powders. The mill in use at the Tuscaloosa Research Center (TURC) is a 12.7-cm-diam. mill with the rotor, stator, and container constructed of UHMW polyethylene (shown in figures 1 and 2).

The slurry to be milled is placed in the container and consists of a milling liquid (typically water, kerosene, or alcohol), the milling medium (spherical balls or coarse granular material), and the material to be milled. A dispersant and/or antifoaming agent is typically added to aid in milling efficiency. The rotor operates at speeds which range from 1,400 to 1,700 rpm. Run times needed to reach the desired particle size range from 30 min to 4 hours.

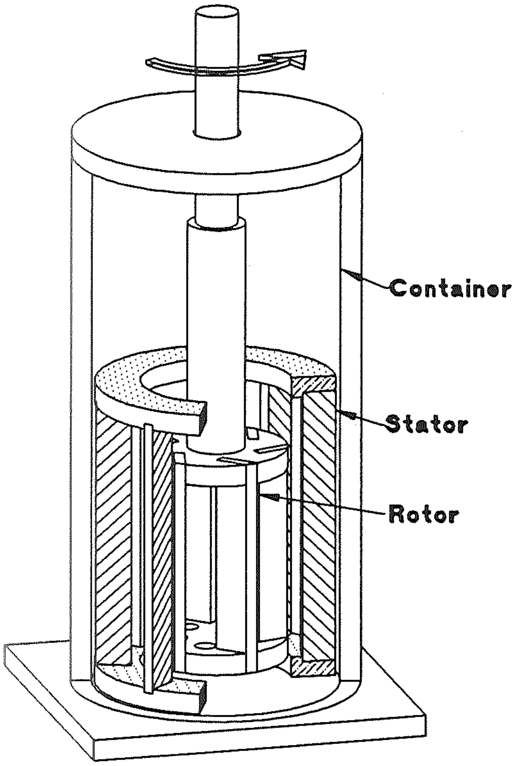

Figure 1. **Bureau of Mines turbomill.**

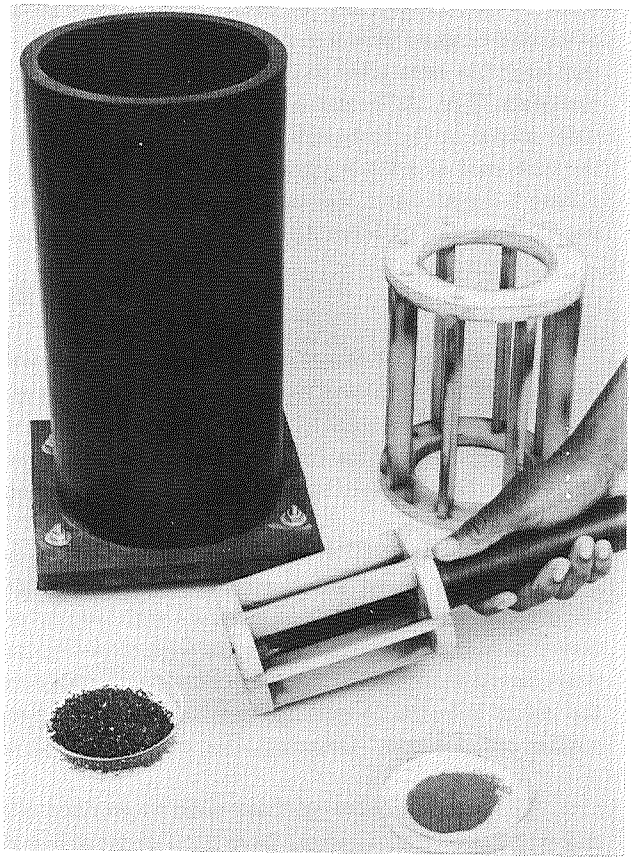

Figure 2. All-polymer container, stator, and rotor components of the turbomill.

GRINDING OF KAOLIN AND OTHER MINERALS

The efficiency of grinding kaolin using the turbomill was compared to the efficiency of other processes, including jar mills, colloid mills, and ultrasonics. In general, it was found that the turbomill produced more minus 2-μm equivalent spherical diameter (ESD) material than other methods in less time. It was also found that the milling efficiency increases when a large mill (25.4-cm-diam) is used versus a smaller mill (12.7-cm-diam).

A series of tests to develop continuous grinding using the turbomill considered both open- and closed-circuit systems [6-7]. In open-circuit turbomilling, the overflow material was collected and sized. In closed-circuit milling, the overflow material was collected, sized, and incompletely ground material was returned to the mill as part of the feed slurry. It was found that closed-circuit grinding achieved a slightly greater rate of particle size reduction and consumed less energy than open-circuit grinding. A later investigation to determine the effect of operating variables on the grinding efficiency of kaolin showed the greatest influences related to the type, size and shape of grinding media; the ratio of medium weight to clay weight; peripheral rotor speed; clay slime pulp density; density of pulp dispersion and the angular arrangement of the rotor and stator. [8].

Following the grinding studies on kaolin, the Bureau determined the extent of particle size reduction obtained with other minerals [9]. A series of tests on mica showed that a sample with 11.1 pct minus 45-μm material was ground with sand to a product 100 pct minus 45-μm and 52.3 pct minus 2-μm material. The electrical energy consumed when grinding the mica sample at a feed pulp density of 50 percent solids was 1206.6 MJ/mt of dry feed (304 kW•h/st) of dry feed. A second sample of mica with 8 pct minus 45-μm material was ground to 100 pct minus 45-μm with 56.8 pct minus 2-μm material. Electrical consumption for the second sample was 1270 MJ/mt (320 kW•h/st) of dry feed. A large scale continuous open-circuit method for grinding mica was also developed. A feed with 9.2 pct minus 45-μm mica was ground to 51.3 pct less than 45-μm. Pyrophyllite, talc, marble, barite, and fluorite were also evaluated as part of this research.

BENEFICIATION APPLICATIONS

Other research focused on improved beneficiation of minerals including clay and olivine foundry sand. A study to improve the plasticity of a coarse kaolinitic clay for use as a bond clay in ceramic bodies was reported by Goode and Tyrrell [10]. An Alabama underclay was ground in the turbomill and compared to a standard ball clay used for whiteware bodies. The modulus of rupture of the fired body made using the ground underclay was increased by a factor of 1.7 over bodies made with the unground clay and was close to those made using the standard ball clay. The water absorption of the fired body made with turbomilled underclay was reduced by 35 pct when compared to the body made with the unground underclay.

A study to determine the feasibility of producing olivine for use as a foundry sand from dunite was reported in 1977 [11]. Dunite contains olivine and variable quantities of serpentine, talc, chlorite, actinolite, and vermiculite. The original products analyzed 2- to 3-pct loss on ignition (LOI) resulting from these impurities. After grinding using the turbomill, 200-mesh concentrates of the ground material met or exceeded the Steel Founder's Society of America specifications of a maximum 1.35 pct LOI for olivine aggregate and flour products. This beneficiation technique was patented by Davis in 1977 [12].

CERAMIC POWDERS

In the 1970's researchers at the Bureau's Tuscaloosa Research Center (TURC) investigated turbomilling of several ceramic oxide powders [13]. In general, the turbomilling process was more efficient than other processes such as ball milling. The increased particle size reduction yielded more reactive powders for sintering. For example, zirconia produced in the turbomill was sintered to 96 pct of theoretical density while commercial powders only sintered to 74 pct of theoretical [14].

Another research program was designed to demonstrate the catalytic properties of turbomilled silica [15]. Two crystalline forms of silica were ground and compared to two commercial silica catalysts used for n-hexane cracking and for dehydration of ethanol. The milled catalysts were more active than the commercial catalysts for n-hexane cracking; however, the ethanol dehydration activity was lower for the turbomilled silica. The differences were due to the different active sites required for dehydration.

Stanley, et al. describe a method for autogenous milling of SiC [16]. In these early tests, the mill was constructed of metal, resulting in iron contamination of the mill product. In 1980, a study to determine the feasibility of producing high purity α-SiC powders in the turbomill was undertaken [3]. Since iron is detrimental to the properties of sintered α-SiC, researchers redesigned the turbomill using a polymer as the construction material for the mill parts. Several polymers were tested and UHMW was selected for its wear resistance properties. Autogenous milling was used to eliminate contamination of the mill product by the milling media.

Autogenous turbomilling in the all-polymer turbomill successfully produced ultrafine α-SiC powders. Powders with Brunaur-Emmett-Teller (BET) surface areas of 30 to 35 m^2/g were obtained after 3 to 6 hours of milling. These powders, with iron contents less than the starting material, were hot pressed with 1 pct boron (B) and 1 pct carbon (C) additions. Theoretical density of >99 pct was achieved and properties comparable to those of commercially available α-SiC were obtained.

Based on these promising results, experiments to optimize the milling parameters for α-SiC were conducted. The starting material for the tests had an average diameter of 100 μm. Ninety-seven percent of the starting material was less than 150 μm in diameter and contained no material below 30 μm in diameter. The effects of dispersants, temperature, pH, and milling time on the particle size were investigated. The six dispersants used were: TSPP,[*] a sodium phosphate; Darvan No. 7,[†] a sodium salt; Marasperse N-22,[‡] a sodium lignosulfonate; Nopcosperse 44,[§] an ammonium salt; Aerosol OT,[¶] an anionic disodium sulfosuccinate; and Norlig NH,[**] an ammonium lignosulfonate.

Table 1 lists average particle diameters, determined by laser beam diffraction, and ESD calculated from BET measurements of the α-SiC ground in water using the different dispersants. The average particle size produced using no dispersant, Marasperse N-22, Norlig NH, Aerosol OT, TSPP or Darvan No. 7 decreased gradually during 4 hours. Particle size did not change from 1 h to 4 h when Nopcosperse 44 was used as the dispersant; however, the ESD of the powder decreased. This indicates the formation of agglomerates during milling which was confirmed using scanning electron microscopy (SEM). Particle size distribution data, listed in table 2, for Marasperse N-22 indicates that the amount of material less than 1-μm was 55 pct after 1 hour of milling; the amount does not increase significantly during the next 3 hours.

Contamination of the α-SiC, determined by spectrographic analysis, was negligible. The iron content decreased with milling time. During milling, the surface of the SiC particles is scrubbed resulting in removal of the iron, which is a surface contaminant. As the iron is removed from the surface of the powders, it goes into solution. The decrease in iron content was advantageous because SiC must often be leached after grinding to reduce the iron content.

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[*] Fisher Scientific, Fair Lawn, NJ. Reference to a specific product does not imply endorsement by the Bureau of Mines.

[†] R. T. Vanderbilt Co., Norwalk, CT.

[‡] Reed Lignin, Inc., Atlanta, GA.

[§] Diamond Shamrock, Inc., Morristown, NJ.

[¶] American Cyanamid, New York, NY.

[**] Reed Lignin, Inc., Atlanta, GA.

Table 1. Effect of dispersant on particle size of α-SiC as determined by laser beam diffraction (average diameter) or by surface area measurement (ESD) after milling for 1 hour and 4 hours.

Dispersant	Average diameter, μm		ESD, μm	
	1 h[1]	4 h	1 h	4 h
None	2.13	1.81	0.21	0.13
TSPP	1.16	0.98	0.27	0.16
Darvan No. 7	1.54	0.99	0.22	0.16
Marasperse N-22	1.31	0.92	0.24	0.17
Nopcosperse 44	1.35	1.42	0.22	0.18
Aerosol OT	2.47	1.00	0.32	0.20
Norlig NH	3.22	1.92	1.05	0.28

[1] Milling time

Note.--Average diameter of starting material - 100 μm

Table 2. Effect of Marasperse N-22 dispersant on α-SiC particle size

Particle diameter, μm	Percent[1] less than indicated diameter			
	1 h[2]	2 h	3 h	4 h
2.21	84	90	96	96
1.30	71	80	86	86
0.80	51	59	65	65
0.55	30	34	38	38
0.39	12	12	13	13
0.30	3	3	3	3
0.20	1	1	1	1

[1] Percentages are for minus 325-mesh fraction of milled material.

[2] Milling time.

Note.--Average diameter of starting material - 100 μm

When Marasperse N-22 was used as the dispersant, the temperature of milling also played a major role in milling efficiency, as shown in table 3. As the temperature increased, the resulting average particle size did not change significantly. However, the grinding efficiency, as indicated by the amount of minus 325-mesh and submicrometer material, increased. The poor correlation between ESD values and the laser-measured particle diameters results from the fact that the laser technique measures agglomerates while BET techniques measure individual particles. Changes in pH also did not significantly affect the particle size (table 4); however, the efficiency of grinding was increased when the pH was slightly basic. The dispersing effect of Marasperse is affected by pH according to its manufacturers, with best results between pH 7 and pH 10. This increased dispersion effect results in greater particle/particle contact and increased grinding efficiency. The combined effects of Marasperse N-22, pH 9.5 and 50° C resulted in 80 pct <1-µm material after 4 hours of milling. The energy required was 2088.9 MJ/mt of feed (526.4 kW•h/st of feed).

Table 3. **Effect of temperature on 4 hour milling of α-SiC in water with Marasperse N-22**

Milling temperature, ° C	ESD, µm	Average diameter, µm	Percent less than		Contaminants, pct	
			325 mesh	1 µm	Fe	Na
25	0.18	0.87	60.6	43.8	0.18	0.13
50	0.19	0.76	78.0	57.5	0.05	0.14
70	0.15	0.73	82.1	63.1	0.00	0.19

Note.--Average diameter of starting material - 100 µm

Table 4. **Effect of pH on 4 hour milling of α-SiC in water with Marasperse N-22**

Milling temperature, ° C	pH	ESD, µm	Average diameter, µm	Percent less than	
				325 mesh	1 µm
25	3.6	0.22	0.90	63.0	49.9
25	6.5	0.18	0.87	60.6	43.8
25	9.5	0.20	0.82	86.5	67.9
50	9.5	ND	1.14	92.6	79.7

Note.--Average diameter of starting material - 100 µm

Several other materials used to produce advanced ceramics were also evaluated following turbomilling. Tables 5 and 6 list results for silica, two alumina materials, zirconia (ZrO_2), Al_2O_3-partially stabilized zirconia (APSZ), CaO-partially-stabilized-zirconia (CPSZ), silicon nitride (Si_3N_4), and TiB_2. These materials were ground in water using autogenous turbomilling. The average diameter and the amount of submicrometer material follow similar trends except for the larger Al_2O_3 material and the TiB_2. The particle size of the Al_2O_3 decreased rapidly and then increased and the percentage of submicrometer material decreased. The increase in particle size and decrease in the amount of submicrometer powder indicates agglomeration to form larger particles or breakdown of the milling media. SEM analysis confirmed the presence of agglomeration and a sieve analysis of the mill product showed a 15 pct reduction in the amount of coarse milling media. Grinding of TiB_2 did not produce a large amount of submicrometer material. Use of other dispersants, different milling media or other milling fluids might increase the efficiency for milling of TiB_2.

Table 5. Particle size of oxide ceramics

Material	Average diameter, μm				Percent less than 1-μm			
	0 h[1]	.5 h[2]	1 h	4 h	0 h	.5 h	1 h	4 h
SiO_2	16.3	ND	3.44	2.85	3	ND	14	28
Al_2O_3-1	102	ND	2.69	4.32	0	ND	31	4
Al_2O_3-2	34.2	1.96	ND	ND	0	24	ND	ND
ZrO_2	20	ND	3.09	2.73	0	ND	17	23
APSZ	21.1	5.22	3.11	ND	0	16	23	ND
CPSZ	14	6.68	3.48	ND	4	10	17	ND

[1] As-received particle size
[2] Milling time
ND-Not determined

The GTE Si_3N_4, listed in table 6, contained some whiskers. After 4 hours of milling, the whiskers were still present. The material was milled an additional 2 hours to determine if the whiskers would break down. After 6 hours, the powder no longer contained whiskers. Contamination of the powders was negligible as in the SiC studies.

Table 6. Particle size of nonoxide ceramics

Material	Average Diameter, μm				Percent less than 1-μm			
	0 h[1]	2 h[2]	4 h	6 h	0 h	2 h	4 h	6 h
Si_3N_4*	55	2.09	2.05	ND	0	54	51	ND
Si_3N_4‡	55	2.72	2.51	2.53	0	23	35	37
TiB_2§	55	5.52	3.99	ND	0	3	4	ND

[1] As-received particle size
[2] Milling time
*Ube Chemical Co., Ube, Japan.
‡GTE, Towanda, PA.
§Sohio Chemicals and Industrial Products, Co., Niagara Falls, NY.
ND-Not determined

ALTERNATIVE PROCESSING OF CERAMIC RAW MATERIALS

The turbomill has also been used to improve the dispersion of sintering aids in high-surface-area powders [4] and to mix high surface area powders for a ceramic matrix composite [17]. Boron and carbon were added to α-SiC during turbomilling. These powders were hot pressed and physical properties were compared to B- and C-doped SiC materials prepared with powders processed using traditional methods. The addition of B and C during turbomilling resulted in enhanced properties, likely due to the breakdown of agglomerates of carbon which serve as flaw origins in conventionally processed powders. The raw materials, TiN, AlN and Al_2O_3 powders, for a ceramic matrix composite were mixed in the turbomill. Comparison of hot pressed composites formed from ball milled and turbomilled powders showed that turbomilling is the preferred method for preparing the powders for the composite.

Many advanced ceramic materials have whiskers added as reinforcements to improve the fracture toughness of the matrix material. A uniform dispersion of the whiskers is essential to the production of a reliable composite. Wittmer [4] conducted studies sponsored by Martin Marietta Energy Systems-ORNL to determine the feasibility of using the turbomill to produce a SiC whisker reinforced alumina composite. Well dispersed mixtures with no whisker agglomerates were prepared in 30 min in the turbomill using partially stabilized zirconia beads as the milling media. No degradation of the whiskers was visible in the short milling time. The strength and fracture toughness of these composites exceeded the properties measured on composites prepared by conventional methods by 30 pct. Wittmer also demonstrated that the slurries prepared by turbomilling could be pressure cast to form green bodies which, when fired, had improved properties over those processed conventionally.

MICROGRINDING OF COAL

The turbomill was used to produce microfine coal which could be used as a substitute for oil in firing steam boilers or as an addition to diesel fuel [18]. Three coals, each from a different seam, were ground in water using Ottawa sand, steel shot or coarse grain coal as the grinding media. Grinding with steel shot was the most efficient technique. A coal from the Pittsburgh seam (82 pct minus 75-μm) was reduced to 57 pct minus 2-μm in 15 min with energy requirements of 496.8 MJ/mt (138 kW•h/mt).

ALTERNATIVE LEACHING PROCESS FOR CHALCOPYRITE

Copper is traditionally recovered from chalcopyrite ore concentrates by roasting which results in sulfur dioxide emissions or by leaching the chalcopyrite ore for extended periods of time. In its efforts to develop new mineral processing technologies to enable cost-effective compliance with environmental requirements, the Bureau conducted research to improve the kinetics of chalcopyrite dissolution by simultaneous grinding-leaching in ferric sulfate solution [5]. The researchers proposed that during grinding, a chalcopyrite surface would be exposed, leached, and removed. Grinding of the surfaces in the turbomill would increase the number of fresh surfaces exposed to the leaching solution, reducing diffusion barriers for the reaction. Using minus 20- plus 30-mesh Ottawa sand as the grinding media, they found that the rate of leaching increased with increasing rotor speed and increasing solids content (by volume). They also found that the energy required for leaching passes through a minimum level as the amount of solids is varied. The minimum energy level for the conditions studied was 4,576 MJ/mt (1,153 kW•h/st) of copper extracted. This level occurred at 400 rpm and 35 vol pct solids at a recovery of 80 pct.

TECHNOLOGY TRANSFER AND COMMERCIAL APPLICATIONS

The turbomill developed by the U.S. Bureau of Mines has been used to produce materials for many different applications. It has been used in minerals processing. It has also been used to produce high-purity powders for use as raw materials for advanced ceramics. At the Tuscaloosa Research Center of the Bureau of Mines, a 12.7-cm-diam laboratory mill is available for evaluating different materials. Since 1987, the materials listed in table 7 have been milled in the turbomill. The Bureau of Mines can enter into various types of agreements in order to transfer this technology into different areas of interest. A Memorandum of Agreement (MOA) can be used to conduct work with private, state and academic organizations. An MOA outlines the work to be done and the costs involved. A Memorandum of Understanding (MOU) is similar to an MOA except it is an agreement with another federal agency. The Bureau can also use a Cooperative Research and Development Agreement (CRDA) with any non-Federal party. A CRDA is usually used when the cooperative work involves proprietary information and/or there is the possibility of a patentable invention.

Several small mills have been constructed by researchers around the world for use in their labs, while others have expressed interest in purchasing production size mills. Because these mills are built from schematic diagrams, the Bureau does not know how many units are in use worldwide. Turbomilling technology has been applied successfully on a commercial scale in the paper coating and titania pigment preparation industries. Georgia Kaolin Co. has designed and is operating 101.6-cm-diam production units, each capable of treating

1.81 mt of coarse kaolin/h (2 st of coarse kaolin/h). Kerr-McGee uses 132.1-cm-diam units with a combined capacity of 45,350 mt/yr (50,000 st/yr) to improve the particle size uniformity of TiO_2 for paint pigment.

Table 7. Materials evaluated in the Bureau of Mines turbomill

Material	Description/Application
Kaolin	Low grade, clay product. Desire to improve paper coating quality.
Alumina	Electrical applications
Graphite	Pencil Lead
Rutile waste	Desire to remove calcium carbonate from surface to allow TiO_2 recovery
Hematite	Paint pigment
Y_2O_3 stabilized ZrO_2	Skull melted
Al_2O_3/ZrO_2	Skull melted
Silica	Potential raw material for optical fiber or computer chip industry
B"-alumina	Electrolyte for use in fabrication of Na-S batteries
Indium oxide	Alloy manufacturing
Glass powders	Dielectric applications
Aluminum titanate	Paint pigment
Petroleum Coke	Residue from oil refinery. Recovery for use as particulate addition to rubber
Silica	Desire to produce silica flour from plus 100-mesh material
Silicon Nitride with MgO and Y_2O_3	Obtain intimate mixture of MgO and/or Y_2O_3 in Si_3N_4
Plastic film and chopped plastic bottles	Desire to scrub surface of plastics to remove adhesive and printing prior to recycling.
Glass frit	Reduce plus 200-mesh material with little contamination to <2-μm
Graphite fibers	Desire to reduce length from 0.25 in to 25-30 μm with no degradation of fiber properties

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