Title: METHOD FOR MAKING ABRASIVE GRAIN

Abstract: Method of making alpha alumina-based abrasive. The abrasive grain can be incorporated into abrasive products such as coated abrasives, bonded abrasives, non-woven abrasives, and abrasive brushes.
METHOD FOR MAKING ABRASIVE GRAIN

Field of the Invention

This invention pertains to a method of making abrasive grain. The abrasive grain can be incorporated into a variety of abrasive articles, including bonded abrasives, coated abrasives nonwoven abrasives, and abrasive brushes.

Description of Related Art

In the early 1980’s a new and substantially improved type of alumina abrasive grain, commonly referred to as “sol gel” or “sol gel-derived” abrasive grain, was commercialized. This new type of alpha alumina abrasive grain had a microstructure made up of very fine alpha alumina crystallites. The grinding performance of the new abrasive grain on metal, as measured, for example, by life of abrasive products made with the grain was dramatically longer metal than such products made from conventional, fused alumina abrasive grain.

In general, sol gel abrasive grain are typically made by preparing a dispersion or sol comprising water, alumina monohydrate (boehmite), and optionally peptizing agent (e.g., an acid such as nitric acid), gelling the dispersion, drying the gelled dispersion, crushing the dried dispersion into particles, calcining the particles to remove volatiles, and sintering the calcined particles at a temperature below the melting point of alumina. Frequently, the dispersion also includes one or more oxide modifiers (e.g., CeO₂, Cr₂O₃, CoO, Dy₂O₃, Er₂O₃, Eu₂O₃, Fe₂O₃, Gd₂O₃, HfO₂, La₂O₃, Li₂O, MgO, MnO, Na₂O, Nd₂O₃, NiO, Pr₂O₃, Sm₂O₃, SiO₂, SnO₂, TiO₂, Y₂O₃, Yb₂O₃, ZnO, and ZrO₂), nucleating agents (e.g., α-Al₂O₃, α-Cr₂O₃, and α-Fe₂O₃) and/or precursors thereof. Such additions are typically made to alter or otherwise modify the physical properties and/or microstructure of the sintered abrasive grain. In addition, or alternatively, such oxide modifiers, nucleating agents, and/or precursors thereof may be impregnated into the dried or calcined (typically calcined particles) material.

Examples of boehmite taught in the art to be useful in making abrasive grain include those described in U.S. Pat. Nos. 4,202,870 (Weber et al.) and 4,676,928
(Leach et al.), as well as those commercially available under the trade designations “DISPERAL” from Condea Chemie, GmbH of Hamburg, Germany, and “DISPAL” (including “DISPAL 23480”) and “CATAPAL” (including “CATAPAL A,” “CATAPAL B,” and “CATAPAL D”) from Condea Vista Company of Houston, TX. These aluminum oxide monohydrates are in the alpha form, and include relatively little, if any, hydrated phases other than monohydrates (although very small amounts of trihydrate impurities can be present in some commercial grade boehmite, which can be tolerated). They typically have a low solubility in water, and have a high surface area (typically at least about 180 m²/g). Boehmite typically includes at least about 2-6 percent by weight free water (depending on the humidity) on its surface, and such water contributes to the amount of liquid medium in the dispersion. Typically, it is preferred that the boehmite has an average ultimate crystallite size of less than about 20 nanometers (more preferably, less than about 12 nanometers), wherein “crystallite size” is determined by the 120 and 031 x-ray reflections.

Details regarding sol gel abrasive grain, including methods for making them, can be found, for example, in U.S. Pat. Nos. 4,314,827 (Leitheiser et al.), 4,518,397 (Leitheiser et al.), 4,623,364 (Cottringer et al.), 4,744,802 (Schwabel), 4,770,671 (Monroe et al.), 4,881,951 (Wood et al.), 4,960,441 (Pellow et al.) 5,011,508 (Wald et al.), 5,090,968 (Pellow), 5,139,978 (Wood), 5,201,916 (Berg et al.), 5,227,104 (Bauer), 5,366,523 (Rowenhorst et al.), 5,429,647 (Larmie), 5,547,479 (Conwell et al.), 5,498,269 (Larmie), 5,551,963 (Larmie), 5,725,162 (Garg et al.), and 5,776,214 (Wood). One of these patents, U.S. Pat. No. 5,011,508 (Wald et al.), reports tumbling dried gel or calcined particles to increase the overall surface area of the resulting sintered abrasive grain. Although not wanting to be bound by theory, it is believed that the increased surface area may improve the adhesion of the abrasive grain to binder materials used to construct abrasive articles (e.g., coated abrasive articles) and/or vice versa. Over the past fifteen years sintered alumina abrasive grain, in particular sol gel-derived abrasive grain, have been used in a wide variety of abrasive products (e.g., bonded abrasives, coated abrasives, and abrasive brushes) and abrading applications, including both low and high pressure grinding applications.
In general, the grinding performance (e.g., the substrate removal rate and the useful life) of an abrasive product is typically better for an abrasive grain made from relatively expensive raw materials than for abrasive grain made from relatively inexpensive raw materials. There is need for high performance abrasive grain made from cheaper raw materials and processes, as well as a need for abrasive grain that provide improved grinding performance.

Summary of the Invention

In one aspect, the present invention provides a method for making alpha alumina-based ceramic abrasive grain, the method comprising:

dry milling (e.g., ball milling, attritor milling, jet milling, roll crushing, and combinations thereof) boehmite for a time sufficient to increase the average crystallite size of the boehmite by at least ten percent (preferably, at least 25 percent, more preferably, at least 50 percent);

preparing a dispersion by combining components comprising a first liquid medium, peptizing agent, and the dry milled boehmite;

converting the dispersion to particulate alpha alumina-based ceramic abrasive grain precursor material; and

sintering the precursor material to provide alpha alumina-based ceramic abrasive grain.

In another aspect, the present invention provides a method for making alpha alumina-based ceramic abrasive grain, the method comprising:

preparing a first dispersion by combining components comprising liquid medium and boehmite;

drying the first dispersion to provide first alpha alumina-based precursor material;

dry milling the first alpha alumina-based precursor material for a time sufficient to increase the average crystallite size of the boehmite by at least ten percent (preferably, at least 25 percent, more preferably, at least 50 percent);
preparing a second dispersion by combining components comprising a first liquid medium, peptizing agent, and the dry milled first alpha alumina-based precursor material;

converting the second dispersion to particulate alpha alumina-based ceramic abrasive grain precursor material; and

sintering the precursor material to provide alpha alumina-based ceramic abrasive grain.

In this application:

“Milling” refers to any process, technique, or operation to crush or otherwise comminute a material.

“Dry”, with regard to milling, means the milling environment is a non-liquid medium such as ambient air or other gaseous atmosphere (e.g., argon, nitrogen, and combinations thereof), and the material being milled contains less than 10 percent by weight (preferably less 5 percent by weight, 3 percent, or even 1 percent by weight) liquid medium (including water), not including bound water.

“Converting”, with regard to making the precursor material, refers to any step or series of steps that provide the precursor material, including deliquifying (typically drying).

"Ceramic precursor material" or "unsintered ceramic material" refers to deliquified or dried alumina-based dispersion (i.e., deliquified or dried ceramic precursor material) or calcined alumina-based dispersion (i.e., calcined ceramic precursor material), which is typically in the form of particles that have a density of less than 80% (typically less than 60%) of theoretical and are capable of being sintered and/or impregnated with an impregnation composition and then sintered to provide alpha alumina-based ceramic material.

"Alpha alumina-based ceramic abrasive grain" as used herein refers to sintered, polycrystalline ceramic abrasive grain that have been sintered to a density of greater than 90% (preferably, at least 92%, more preferably, at least 94%, or even at least 95% or 97%) of theoretical, and contain, on a theoretical metal oxide basis, at least 60% by weight Al₂O₃, wherein at least 50% by weight of the Al₂O₃ is present as alpha alumina.
"Dispersion" refers to a solid-in-fluid (liquid and/or liquid and gas (e.g., air)) system wherein one phase comprises finely divided particles (in the colloidal size range) distributed throughout a fluid, and/or the fluid is distributed throughout the particles.

Abrasive grain made according to the methods of the present invention can be incorporated into abrasive products such as coated abrasives, bonded abrasives, non-woven abrasives, and abrasive brushes.

**Brief Description of the Drawing**

FIG. 1 is a fragmentary cross-sectional schematic view of a coated abrasive article including abrasive grain made according to the method of the present invention;

FIG. 2 is a perspective view of a bonded abrasive article including abrasive grain made according to the method of the present invention;

FIG. 3 is an enlarged schematic view of a nonwoven abrasive article including abrasive grain made according to the method of the present invention; and

FIGS. 4 and 6 are elevational plan views of an extruder useful in the methods according to the present invention, while FIG. 5 is an enlarged top plan of the extruder feed port;

FIG. 7 is a digital micrograph of a commercially available boehmite referred to in Comparative Examples A, B, F, and I;

FIG. 8 is a digital micrograph of the commercially available boehmite shown in FIG. 7 after being ball milled as described in Example 1;

FIG. 9 is a digital micrograph of the commercially available boehmite shown in FIG. 7 after being attritor milled as described in Example 6; and

FIG. 10 is a digital micrograph of the commercially available boehmite shown in FIG. 7 after being jet milled as described in Example 9.

**Detailed Description**

"Boehmite" as used herein refers to alpha alumina monohydrate and boehmite commonly referred to in the art as "pseudo" boehmite (i.e., Al₂O₃·xH₂O, wherein x=1 to 2). Suitable boehmites include those commercially available under the trade
designation "HIQ" (e.g., "HIQ-10," "HIQ-20," "HIQ-30," and "HIQ-40") from Alcoa Industrial Chemicals, and those commercially available under the trade designations of "DISPERAL" from Condea Gmbh, Hamburg, Germany, and "DISPAL 23N480" and CATA PAL D" from Condea Vista Company, Houston, TX. These boehmites or alumina monohydrates are in the alpha form, and include relatively little, if any, hydrated phases other than monohydrates (although very small amounts of trihydrate impurities can be present in some commercial grade boehmite, which can be tolerated). They have a low solubility in water and have a high surface area (typically at least about 180 m²/g). Preferably the dispersed boehmite used to make abrasive grain according to the present invention has an average crystallite size of less than about 20 nanometers (more preferably, less than 12 nanometers). In this context, "crystallite size" is determined by the 120 and 031 x-ray reflections.

Applicant has discovered that the use of dry milled boehmite can provided sol-gel derived alpha alumina-based abrasive grains with improved grinding performance. Although not wanting to be bound by theory, it is believed that dry milling breaks up agglomerated boehmite particles thereby reducing the number of defects in the resulting abrasive grain. Surprisingly, several dry milled boehmite powders, although decreasing in particle size when milled were found to decrease in surface area. This observation is contrary to what one of ordinary skill in the art would expect (see, e.g., Powder Surface Area and Porosity, S. Lowell and J. E. Shields, 2nd ed. 1984, p. 3, wherein it is taught that subdivided matter must be accompanied by an increase in surface area). Further, Applicant has discovered that the crystallite sizes of many of the dried milled boehmites, which were expected to subdivide with decreased milled particle size (see, e.g., Latin American Research, 21, pp. 63-68, 1991 and Thermochimica Acta, 170, pp. 41-50, 1990), were unexpectedly found to increase in size.

Under the present invention, boehmite is dry milled (e.g., ball milled, attritor milled, jet milled, roll crushed, and combinations thereof) for a time sufficient to increase the average crystallite size of the boehmite by at least ten percent (preferably, at least 25 percent, more preferably, at least 50 percent). The median particle size of commercially available boehmite powders is typically greater than 30 micrometers. The median particle size of such boehmite powders after dry milling as described herein is
typically less than 15 micrometers, preferably less than 10 micrometers, more preferably, less than 5 micrometers, and even more preferably, less than 3 micrometers.

In another aspect, the surface area of boehmite dry milled according to the present invention typically has an average surface area of greater than 180 m²/g, preferably, greater than 200 m²/g, and more preferably, greater than 220 m²/g.

Types of dry milling that have been found to be suitable in practicing the present invention include dry ball milling, dry jet milling, and dry attritor milling. Other types of dry milling that may be suitable include roll crushing, vibratory mills, and tumble millings (of which ball milling is one type) such as pebble milling, rod milling, tube milling, and compartment milling. Other suitable milling techniques may be apparent to those skilled in the art after reviewing the disclosure of the present invention.

Ball mills are included in a class of mills called tumbling mills, which include pebble, rod, tube and compartment mills. Ball mills typically consist of a cylindrical jacket containing a charge of ball or cylindrical shaped media. The cylindrical jacket is rotated about its axis so that size reduction or pulverizing of the material to be milled is effected by the tumbling of the balls on the material between them.

Attritor mills typically comprise a cylindrical tank with a stirrer that mixes the milling media and material to be comminuted. Size reduction or pulverizing is achieved as the media hits and slides against the material to be milled during mixing.

Vibratory mills typically use a cylindrical shell containing a charge of milling media and the material to be ground. The milling action results when the shell is vibrated or oscillated.

The milling media is most commonly in the form of balls or cylinders. The media can be composed of any of a number of materials, including steel, glass, alumina, and zirconium silicate, and zirconia. The size of the media selected generally varies depending on the desired final particle size of the material to be comminuted. Smaller media will result in finer grinding due to greater surface area. Composition of media should be chosen carefully to minimize harmful contamination of the material to the ground. For example, Si contamination from glass media may to have a detrimental effect on the densification of some sol-gel abrasive grain formulations.
Jet mills are generally of three types. The simplest form of jet mill is the spiral jet mill such as those available under the trade designations “MICRONIZER JET MILL” from Sturtevant, Inc. of Hanover, MA; “MICRON-MASTER JET PULVERIZER” from The JET Pulverizer Co. of Moretown, NJ; and “MICRO-JET” from Fluid Energy Aljet of Plumsteadville, PA. In a spiral jet mill a flat cylindrical grinding chamber is surrounded by a nozzle ring. The material to be ground is introduced inside the nozzle ring by an injector. The jets of compressed fluid expand through the nozzles and accelerate the particles, causing size reduction by mutual impact.

The second type of jet mill is known as a fluidized-bed jet mill. Such jet mills are available, for example, under the trade designations “CGS FLUIDIZED BED JET MILL” from Netzsch Incorporated of Exton, PA; and “ROTO-JET” from Fluid Energy Aljet of Plumsteadville, PA. This type of jet mill is equipped with mechanical classifier for finer products and allows for better control of the final particle size than does the spiral jet mill. The lower section of this type of machines is the grinding zone. A ring of grinding nozzles within the grinding zone is focused toward a central point, and the grinding fluid accelerates the particles. Size reduction takes place within the fluidized bed of material, and this technique can greatly improve energy efficiency. The partially reduced product is carried with the expanded grinding fluid upward toward a classifier. The oversize particles are rejected and the remaining fine particles leave the machine.

The third type is the opposed jet mill. Such jet mills are available under the trade designation “FLUIDIZED BED OPPOSED JET MILL AFG” from Hosokawa Alpine of Summit, NJ. This type of jet mills is similar to the fluidized-bed jet mill, except at least two opposed nozzles accelerate particles, causing them to collide at a central point. A mechanical classifier is used to separate the oversize particles from particles with the right size.

Examples of other commercially available jet mills include those available under the trade designations “JET-O-MIZER” and “THERMAJET” from Fluid Energy Aljet.

Roll crushers provide size reduction by crushing agglomerates or particles between two counter-rotating rolls (i.e., the material is crushed between at least two surfaces). Typically, the rolls are either smooth or profiled. The latter is commonly used
with coarser materials. Examples of roll crushers include those available under the trade designations “CONCEPT 21 MODULAR ROLL CRUSHER” from Gundlach Crushing Equipment, Belleville, IL; and “MARCY 6000 6-1/2"X6" DOUBLE ROLL CRUSHER” from GENEQ Inc., Montreal, QC, Canada.

After the milling step, a boehmite dispersion, sometimes referred to as a sol, is formed. Preferably, the (boehmite) dispersion is made by combining or mixing components comprising liquid medium, and dry milled boehmite, and optionally unmilled boehmite and/or metal oxide and/or metal oxide precursor (including nucleating material). The components for making the dispersion also typically include a peptizing agent (e.g., an acid such as nitric acid). The liquid medium in which the boehmite is dispersed is typically water (preferably deionized water), although organic solvents, such as lower alcohols (typically C_{1-6} alcohols), hexane, or heptane, may also be useful as the liquid medium. In some instances, it is preferable to heat the liquid medium (e.g., 60-70°C) to improve the dispersibility of the boehmite.

The peptizing agent(s) is generally a soluble ionic compound(s) which is believed to cause the surface of a particle or colloid to be uniformly charged in a liquid medium (e.g., water). Preferred peptizing agents are acids or acid compounds. Examples of typical acids include monoprotic acids and acid compounds, such as acetic, hydrochloric, formic, and nitric acid, with nitric acid being preferred. The amount of acid used depends, for example, on the dispersibility of the boehmite, the percent solids of the dispersion, the components of the dispersion, the amounts, or relative amounts of the components of the dispersion, the particle sizes of the components of the dispersion, and/or the particle size distribution of the components of the dispersion. The dispersion typically contains at least, 0.1 to 20%, preferably 1% to 10% by weight acid and most preferably 3 to 8% by weight acid, based on the weight of boehmite in the dispersion.

In some instances, the acid may be applied to the surface of the boehmite particles prior to being combined with the water. The acid surface treatment may provide improved dispersibility of the boehmite in the water.

The boehmite containing dispersions typically comprise greater than 15% by weight (generally from greater than 20% to about 85% by weight; typically greater than 20% to about 80% by weight; more typically greater than 30% to about 80% by weight)
solids (or alternatively boehmite), based on the total weight of the dispersion. Certain preferred dispersions, however, comprise 35% by weight or more, 45% by weight or more, 50% by weight or more, 55% by weight or more, 60% by weight or more and 65% by weight or more by weight or more solids (or alternatively boehmite), based on the total weight of the dispersion. Weight percents of solids and boehmite above about 80 wt-% may also be useful, but tend to be more difficult to process to make the abrasive grain provided by the method according to the present invention.

Optionally, the boehmite dispersion includes metal oxide (e.g., particles of metal oxide which may have been added as a particulate (preferably having a particle size (i.e., the longest dimension) of less than about 5 micrometers; more preferably, less than about 1 micrometer) and/or added as a metal oxide sol (including colloidal metal oxide sol)) and/or metal oxide precursor (e.g., a salt such as a metal nitrate, a metal acetate, a metal citrate, a metal formate, or a metal chloride that converts to a metal oxide upon decomposition by heating). The amount of such metal oxide and/or metal oxide precursor (that is in addition to the alumina provided by the boehmite) present in a dispersion or precursor (or metal oxide in the case of the abrasive grain) may vary depending, for example, on which metal oxide(s) is present and the properties desired for the sintered abrasive grain. For dispersions containing such metal oxides (and/or precursors thereof), the metal oxides (that are in addition to the alumina provided by the boehmite) are typically present, on a theoretical metal oxide basis, up to about 10 or even 15 percent by weight (preferably, in the range from about 0.1 to about 10 or even 15 percent; more preferably, in the range from about 0.5 to about 10 or even 15 percent by weight), based on the total metal oxide content of the abrasive grain; although the amount may vary depending, for example, on which metal oxide(s) is present.

Examples of such other metal oxides include: praseodymium oxide, dysprosium oxide, samarium oxide, cobalt oxide, zinc oxide, neodymium oxide, yttrium oxide, ytterbium oxide, magnesium oxide, nickel oxide, manganese oxide, lanthanum oxide, gadolinium oxide, dysprosium oxide, europium oxide, hafnium oxide, and erbium oxide, as well as manganese oxide, chromium oxide, titanium oxide, and ferric oxide which may or may not function as nucleating agents.
Metal oxide precursors include metal nitrate salts, metal acetate salts, metal citrate salts, metal formate salts, and metal chloride salts. Examples of nitrate salts include magnesium nitrate (Mg(NO$_3$)$_2$·6H$_2$O), cobalt nitrate (Co(NO$_3$)$_2$·6H$_2$O), nickel nitrate (Ni(NO$_3$)$_2$·6H$_2$O), lithium nitrate (LiNO$_3$), manganese nitrate (Mn(NO$_3$)$_2$·4H$_2$O), chromium nitrate (Cr(NO$_3$)$_3$·9H$_2$O), yttrium nitrate (Y(NO$_3$)$_3$·6H$_2$O), praseodymium nitrate (Pr(NO$_3$)$_3$·6H$_2$O), samarium nitrate (Sm(NO$_3$)$_3$·6H$_2$O), neodymium nitrate (Nd(NO$_3$)$_3$·6H$_2$O), lanthanum nitrate (La(NO$_3$)$_3$·6H$_2$O), gadolinium nitrate (Gd(NO$_3$)$_3$·5H$_2$O), dysprosium nitrate (Dy(NO$_3$)$_3$·5H$_2$O), europium nitrate (Eu(NO$_3$)$_3$·6H$_2$O), ferric nitrate (Fe(NO$_3$)$_3$·9H$_2$O), zinc nitrate (Zn(NO$_3$)$_3$·6H$_2$O), erbium nitrate (Er(NO$_3$)$_3$·5H$_2$O), zirconium nitrate (Zr(NO$_3$)$_4$·5H$_2$O), and zirconium hydroxynitrate. Examples of metal acetate salts include zirconyl acetate (ZrO(CH$_3$COO)$_2$), magnesium acetate, cobalt acetate, nickel acetate, lithium acetate, manganese acetate, chromium acetate, yttrium acetate, praseodymium acetate, samarium acetate, ytterbium acetate, neodymium acetate, lanthanum acetate, gadolinium acetate, and dysprosium acetate. Examples of citrate salts include magnesium citrate, cobalt citrate, lithium citrate, and manganese citrate. Examples of formate salts include magnesium formate, cobalt formate, lithium formate, manganese formate, and nickel formate.

Colloidal metal oxides are discrete finely divided particles of amorphous or crystalline metal oxide typically having one or more of their dimensions within a range of about 3 nanometers to about 1 micrometer. The average metal oxide (including in this context silica) particle size in the colloidal is preferably less than about 150 nanometers, more preferably less than about 100 nanometers, and most preferably less than about 50 nanometers. In some instances, the particles can be on the order of about 3-10 nanometers. Typically, the colloidal comprises a distribution or range of metal oxide particle sizes. Preferably, the colloidal metal oxide sols are a stable (i.e., the metal oxide solids in the sol or dispersion do not appear by visual inspection to begin to gel, separate, or settle upon standing undisturbed for about 2 hours) suspension of colloidal particles (preferably in a liquid medium having a pH of less than 6.5). Metal oxide sols for use in methods according to the present invention include sols of ceria, silica, yttria, titania, lanthana, neodymia, zirconia, and mixtures thereof. Metal oxide (including silica) sols are available,
for example, from Nalco of Naperville, IL; Nyacol Products, Inc. of Ashland, MA; Eka Nobel of Augusta, GA; Rhone-Plouenc of Shelton, CT; Transelco of Penn Yan, NY; and Fujimi Corp. of Japan. Silica sols include those available under the trade designations “NALCO 1115,” “NALCO 1130,” “NALCO 2326,” NALCO 1034A,” and “NALCOAG 1056” from Nalco Products, Inc. of Naperville, IL, wherein the latter two are examples of acidic silica sols; and “NYACOL 215” from Eka Nobel, Inc. For additional information on silica sols see, for example, U.S. Pat. Nos. 5,611,829 (Monroe et al.) and 5,645,619 (Erickson et al.). For more information on ceria, silica, or zirconia sols, see, for example, U.S. Pat. Nos. 5,429,647 (Larmie), 5,498,269 (Larmie), 5,551,963 (Larmie), 5,611,829 (Monroe et al.), and 5,645,619 (Erickson et al.).

Typically, the use of a metal oxide modifier may decrease the porosity of the sintered abrasive grain and thereby increase the density. Certain metal oxides may react with the alumina to form a reaction product and/or form crystalline phases with the alpha alumina which may be beneficial during use of the abrasive grain in abrading applications. For example, the oxides of cobalt, nickel, zinc, and magnesium typically react with alumina to form a spinel, whereas zirconia and hafnia do not react with the alumina. Alternatively, the reaction products of dysprosium oxide and gadolinium oxide with aluminum oxide are generally garnet. The reaction products of praseodymium oxide, ytterbium oxide, erbium oxide, and samarium oxide with aluminum oxide generally have a perovskite and/or garnet structure. Yttria can also react with the alumina to form $Y_2Al_5O_{12}$ having a garnet crystal structure. Certain rare earth oxides and divalent metal cations react with alumina to form a rare earth aluminate represented by the formula LnMAI₁₁O₁₉, wherein Ln is a trivalent metal ion such as La⁺³, Nd⁺³, Ce⁺³, Pr⁺³, Sm⁺³, Gd⁺³, Er⁺³, or Eu⁺³, and M is a divalent metal cation such as Mg⁺², Mn⁺², Ni⁺², Zn⁺², or Co⁺². Such aluminates have a hexagonal crystal structure. For additional details regarding the inclusion of metal oxide (and/or precursors thereof) in a boehmite dispersion see, for example, in U.S. Pat. Nos. 4,314,827 (Leitheiser et al.), 4,770,671 (Monroe et al.), 4,881,951 (Wood et al.) 5,429,647 (Larmie), and 5,551,963 (Larmie).

Optionally, the boehmite dispersion contains nucleating material (i.e., material that enhances the transformation of transitional alumina(s) to alpha alumina via extrinsic nucleation). The nucleating material can be a nucleating agent (i.e., material
having the same or approximately the same crystalline structure as alpha alumina, or otherwise behaving as alpha alumina) itself (e.g., alpha alumina seeds, α-Fe₂O₃ seeds, or α-Cr₂O₃ seeds, TiₓOᵧ (having a trigonal crystal structure), MnO₂ (having a rhombic crystal structure), LiₓO (having a cubic crystal structure), titanates (e.g., magnesium titanate and nickel titanate) or precursor thereof. Typically, nucleating material, if present, comprises, on a theoretical metal oxide basis (based on the total metal oxide content of the calcined precursor material before sintering (or the sintered abrasive grain)), in the range from about 0.1 to about 5 percent by weight. Additional details regarding nucleating materials are also disclosed, for example, in U.S. Pat. Nos. 4,623,364 (Cottringer et al.), 4,744,802 (Schwabel), 4,964,883 (Morris et al.), 5,139,978 (Wood), and 5,219,806 (Wood).

A preferred nucleating material for practicing the present invention include is iron oxide or an iron oxide precursor. Sources of iron oxide, which in some cases may act as or provide a material that acts as a nucleating material, include hematite (i.e., α-Fe₂O₃), as well as precursors thereof (i.e., goethite (α-FeOOH), lepidocrocite (γ-FeOOH), magnetite (Fe₃O₄), and maghemite (γ-Fe₂O₃)). Suitable precursors of iron oxide include iron-containing material that, when heated, will convert to α-Fe₂O₃. For additional details regarding the addition of iron sources to the dispersion or ceramic precursor material see, for example, U.S. Pat. Nos. 5,611,829 (Monroe et al.) and 5,645,619 (Erickson et al.).

General procedures for making sintered alpha alumina-based abrasive grain are also described, for example, in U.S. Pat. Nos. 4,518,397 (Leitheiser et al.), 4,770,671 (Monroe), 4,744,802 (Schwabel), 5,139,978 (Wood), 5,219,006 (Wood), and 5,593,647 (Monroe), and applications having U.S. Serial Nos. 09/407,672, 09/406,952, 09/407,671, and 09/407,781.

The (initial) mixture is typically prepared by adding the various components and then mixing them together to provide a homogenous mixture. For example, boehmite is typically added to water that has been mixed with nitric acid. The other components are added before, during, or after the boehmite is added. However, the dispersion is to include a nucleating material and silica sol, and the nucleating material is an aqueous, acidic dispersion of iron oxyhydroxide and the silica source is a basic colloidal silica sol, it is preferable not to add the two together, but rather to add each
individually to acidified water prior to, preferably, after other components, such as the boehmite, have been added to the acidified water.

A high solids dispersion is typically, and preferably, prepared by gradually adding a liquid component(s) to a component(s) that is non-soluble in the liquid component(s), while the latter is mixing or tumbling. For example, a liquid containing water, nitric acid, and metal salt may be gradually added to boehmite, while the latter is being mixed such that the liquid is more easily distributed throughout the boehmite.

Suitable mixers include pail mixers, sigma blade mixers, ball mill and high shear mixers. Other suitable mixers may be available from Eirich Machines, Inc. of Gurnee, IL; Hosokawa-Bepex Corp. of Minneapolis, MN (including a mixer available under the trade designation “SCHUGI FLEX-O-MIX”, Model FX-160); and Littleford-Day, Inc. of Florence, KY.

The dispersion may be heated to increase the dispersibility of the alpha alumina monohydrate and/or to create a homogeneous dispersion. The temperature may vary to convenience, for example the temperature may range from about 20°C to 80°C, usually between 25°C to 75°C. Alternatively, the dispersion may be heated under a pressure ranging from 1.5 to 130 atmospheres of pressure.

The dispersion typically gels prior to, or during, drying. The addition of most modifiers may result in the dispersion gelling faster. Alternatively, ammonium acetate or other ionic species may be added to induce gelation of the dispersion. The pH of the dispersion and concentration of ions in the gel generally determines how fast the dispersion gels. Typically, the pH of the dispersion is within a range of about 1.5 to about 4.

The dispersion may be extruded. It may be preferable to extrude a dispersion where at least 50 percent by weight of the alumina content is provided by particulate (e.g., boehmite) including in this context a gelled dispersion, or even partially deliquified dispersion. The extruded dispersion, referred to as extrudate, can be extruded into elongated precursor material (e.g., rods (including cylindrical rods and elliptical rods)). After firing, the rods may have an aspect ratio between 1.5 to 10, preferably between 2 to 6. Alternatively the extrudate may be in the form of a very thin sheet, see for example U.S. Pat. No. 4,848,041 (Kruschke). Examples of suitable extruders include ram
extruders, single screw, twin screw, and segmented screw extruders. Suitable extruders are available, for example, from Loomis Products of Levitown, PA, Bonnot Co. of Uniontown, OH, and Hosokawa-Bepex of Minneapolis, MN, which offers, for example, an extruder under the trade designation “EXTRUD-O-MIX” (Model EM-6).

Preferably, the dispersion is compacted, for example, prior to or during extrusion (wherein the extrusion step may inherently involve compaction of the dispersion). In compacting the dispersion, it is understood that the dispersion is subjected to a pressure or force such as experienced, for example, in a pellitizer or die press (including mechanical, hydraulic and pneumatic or presses) or an extruder (i.e., all or substantially all of the dispersion experiences the specified pressure). In general, compacting the dispersion reduces the amount of air or gases entrapped in the dispersion, which in turn generally produces a less porous microstructure, that is more desirable. Additionally the compaction step results an easier means to continuously feed the extruder and thus may save on labor producing the abrasive grain.

If the elongated precursor material is a rod, it preferably has a diameter such that the sintered abrasive grain will have a diameter of, for example, about 150-5000 micrometers, and preferably, an aspect ratio (i.e., length to width ratio) of at least 2.5:1, at least 4:1, or even at least 5:1. The rod may have any cross sectional shape including a circle, an oval, a star shape, a tube and the like. The rod abrasive grain may also be curved.

A preferred apparatus for compacting the dispersion (gelled or not) is illustrated in FIGS. 4-6. Modified segmented screw extruder 40, has feed port 41 and auger 42 centrally placed within barrel 44. FIG. 5 is a view of the interior of extruder 40 looking through feed port 41. Barrel 44 has grooves (not shown; generally known as “lands”) running parallel down its length. Pins 48 extend centrally into barrel 44. Further, helical flight 46 extends the length of auger 42. Flight 46 is not continuous down the length of auger 42 but is segmented so that flight 46 on auger 42 does not come into contact with pins 48.

The dispersion (including in this context gelled dispersion) (not shown) is fed in feed port 41. Packer screw 43 urges the dispersion against auger 42 so that the dispersion is compacted by auger 42 and extruded through die 50. Die 50 can have a
variety of apertures or holes therein (including a single hole or multiple holes). The die apertures can be any of a variety of cross sectional shapes, including a circle or polygon shapes (e.g., a square, star, diamond, trapezoid, or triangle). The die apertures can be any of a variety of sizes, but typically range from about 0.5 mm (0.02 inch) to 1.27 cm (0.5 inch), and more typically, from about 0.1 cm (0.04 inch) to about 0.8 cm (0.3 inch).

The extruded dispersion can be be cut or sliced, for example, to provide discrete particles, and/or to provide particles having a more uniform length. Examples of methods for cutting (or slicing) the dispersion include rotary knife, blade cutters and wire cutters. The compacted dispersion can also be shredded and/or grated.

In general, techniques for drying the dispersion are known in the art, including heating to promote evaporation of the liquid medium, or simply drying in air. The drying step generally removes a significant portion of the liquid medium from the dispersion; however, there still may be a minor portion (e.g., about 10% or less by weight) of the liquid medium present in the dried dispersion. Typical drying conditions include temperatures ranging from about room temperature to over about 200°C, typically between 50 to 150°C. The times may range from about 30 minutes to over days. To prevent salt migration, it may be desirable to dry the dispersion at low temperature.

After drying, the dried dispersion may be converted into precursor particles. One typical means to generate these precursor particles is by a crushing technique. Various crushing or comminuting techniques may be employed such as a roll crusher, jaw crushe, hammer mill, ball mill and the like. Coarser particles may be recrushed to generate finer particles. It is also preferred that the dried dispersion be crushed, as, for example, it is generally easier to crush dried gel versus the sintered alpha alumina based abrasive grain.

Alternatively, for example, the dispersion may be converted into precursor particles prior to drying. This may occur for instance if the dispersion is processed into a desired grit shape and particle size distribution. For example, the dispersion may be extruded into rods that are subsequently cut to the desired lengths and then dried. Alternatively, the dispersion may be molded into a triangular shape particle and then dried.

Additional details concerning triangular shaped particles may be found in U.S. Pat. No. 5,201,916 (Berg et al.).
Alternatively, for example, the dried dispersion is shaped into lumps with a high volatilizable content which then are explosively comminited by feeding the lumps directly into a furnace held at a temperature above 350°C, usually a temperature between 600°C to 900°C.

Typically, the dried dispersion is calcined, prior to sintering, although a calcining step is not always required. In general, techniques for calcining the dried dispersion or ceramic precursor material, wherein essentially all the volatiles are removed, and the various components that were present in the dispersion are transformed into oxides, are known in the art. Such techniques include using a rotary or static furnace to heat dried dispersion at temperatures ranging from about 400-1000°C (typically from about 450-800°C) until the free water, and typically until at least about 90 wt-% of any bound volatiles are removed.

It is also within the scope of the present invention to impregnate a metal oxide modifier source (typically a metal oxide precursor) into a calcined precursor particle. Typically, the metal oxide precursors are in the form metal salts. These metal oxide precursors and metal salts are described above with respect to the boehmite dispersion.

Methods of impregnating sol gel-derived particles are described in general, for example, in U.S. Pat. Nos. 5,164,348 (Wood). In general, ceramic precursor material (i.e., dried alumina-based dispersion (or dried ceramic precursor material), or calcined alumina-based dispersion (or calcined ceramic precursor material)) is porous. For example, a calcined ceramic precursor material typically has pores about 5-10 nanometers in diameter extending therein from an outer surface. The presence of such pores allows an impregnation composition comprising a mixture comprising liquid medium (typically water) and appropriate metal precursor to enter into ceramic precursor material. The metal salt material is dissolved in a liquid, and the resulting solution mixed with the porous ceramic precursor particle material. The impregnation process is thought to occur through capillary action.

The liquid used for the impregnating composition is preferably water (including deionized water), an organic solvent, and mixtures thereof. If impregnation of a metal salt is desired, the concentration of the metal salt in the liquid medium is typically in the range from about 5% to about 40% dissolved solids, on a theoretical metal oxide basis.
Preferably, there is at least 50 ml of solution added to achieve impregnation of 100 grams of porous precursor particulate material, more preferably, at least about 60 ml of solution to 100 grams of precursor particulate material.

After the impregnation, the resulting impregnated precursor particle is typically calcined to remove any volatiles prior to sintering. The conditions for this calcining step are described above.

After the precursor particle is formed or optionally calcined, the precursor particle is sintered to provide a dense, ceramic alpha alumina based abrasive grain. In general, techniques for sintering the precursor material, which include heating at a temperature effective to transform transitional alumina(s) into alpha alumina, to causing all of the metal oxide precursors to either react with the alumina or form metal oxide, and increasing the density of the ceramic material, are known in the art. The precursor material may be sintered by heating (e.g., using electrical resistance, microwave, plasma, laser, or gas combustion, on batch basis or a continuous basis). Sintering temperatures are usually range from about 1200°C to about 1650°C, typically, from about 1200°C to about 1500°C. The length of time which the precursor material is exposed to the sintering temperature depends, for example, on particle size, composition of the particles, and sintering temperature. Typically, sintering times range from a few seconds to about 60 minutes (preferably, within about 3-30 minutes). Sintering is typically accomplished in an oxidizing atmosphere, although inert or reducing atmospheres may also be useful.

The longest dimension of the alpha alumina-based abrasive grain is typically at least about 1 micrometer. The abrasive grain described herein can be readily made with a length of greater than about 50 micrometers, and larger abrasive grain (e.g., greater than about 1000 micrometers or even greater than about 5000 micrometers) can also be readily made. Generally, the preferred abrasive grain has a length in the range from about 100 to about 5000 micrometers (typically in the range from about 100 to about 3000 micrometers), although other sizes are also useful, and may even be preferred for certain applications. In another aspect, abrasive grain according to the present invention, typically have an aspect ratio of at least 1.2:1, or even 1.5:1, sometimes, at least 2:1, and alternatively, at least 2.5:1.
Dried, calcined, and/or sintered materials provided during or by the method according to the present invention, are typically screened and graded using techniques known in the art. For example, the dried particles are typically screened to a desired size prior to calcining. Sintered abrasive grain are typically screened and graded prior to use in an abrasive application or incorporation into an abrasive article.

It is also within the scope of the present invention to recycle unused (typically particles too small in size to provide the desired size of sintered abrasive grain) deliquified dispersion) material as generally described, for example, in U.S. Pat. No. 4,314,827 (Leitheiser et al.). For example, a first dispersion can be made as described above, dried, crushed, and screened, and then a second dispersion made by combining, for example, liquid medium (preferably, aqueous), boehmite (dry milled, unmilled or a combination thereof), and deliquified material from the first dispersion, and optionally metal oxide and/or metal oxide precursor. Alternatively, for example, the first dispersion can be made using unmilled boehmite, and the second dispersion made using, in part, dry milled boehmite. Further, for example, the deliquified material from a first dispersion, which may include unmilled boehmite, can be dry milled as discussed above for boehmite, and such dry milled material used to prepare a second dispersion. The recycled material may provide, on a theoretical metal oxide basis, for example, at least 10 percent, at least 30 percent, at least 50 percent, or even up to (and including) 100 percent of the theoretical Al₂O₃ content of the dispersion which is deliquified and converted (including calcining and sintering) to provide the sintered abrasive grain.

Screening and grading of abrasive grain made according to the method of the present invention can be done, for example, using the well known techniques and standards for ANSI (American National Standard Institute), FEPA (Federation Européenne des Fabricants de Products Abrasifs), or JIS (Japanese Industrial Standard) grade abrasive grain.

It is also within the scope of the present invention to coat the abrasive grain with a surface coating such as described in U.S. Pat. Nos. 1,910,440 (Nicholson), 3,041,156 (Rowse), 5,009,675 (Kunz et al.), 4,997,461 (Markhoff-Matheny et al.), and 5,042,991 (Kunz et al.), 5,011,508 (Wald et al.), and 5,213,591 (Celikkaya et al.).
Abrasive grain made by a method according to the present invention can be used in conventional abrasive products, such as coated abrasive products, bonded abrasive products (including vitrified and resinoid grinding wheels, cutoff wheels, and honing stones), nonwoven abrasive products, and abrasive brushes. Typically, abrasive products (i.e., abrasive articles) include binder and abrasive grain, at least a portion of which is abrasive grain made by a method according to the present invention, secured within the abrasive product by the binder. Methods of making such abrasive products are well known to those skilled in the art. Furthermore, abrasive grain made by a method according to the present invention can be used in abrasive applications that utilize slurries of abrading compounds (e.g., polishing compounds).

Coated abrasive product generally include a backing, abrasive grain, and at least one binder to hold the abrasive grain onto the backing. The backing can be any suitable material, including cloth, polymeric film, fibre, nonwoven webs, paper, combinations thereof, and treated versions thereof. The binder can be any suitable binder, including an inorganic or organic binder. The abrasive grain can be present in one layer or in two layers of the coated abrasive product. Methods of making coated abrasive products are described, for example, in U.S. Pat. Nos. 4,734,104 (Broberg), 4,737,163 (Larkey), 5,203,884 (Buchanan et al.), 5,378,251 (Culler et al.), 5,417,726 (Stout et al.), 5,436,063 (Follett et al.), 5,496,386 (Broberg et al.), and 5,520,711 (Helmin).

An example of a coated abrasive product is depicted in FIG. 1. Referring to this figure, coated abrasive product 1 has a backing (substrate) 2 and abrasive layer 3. Abrasive layer 3 includes abrasive grain 4 secured to a major surface of backing 2 by make coat 5 and size coat 6. In some instances, a supersize coat (not shown) is used.

Bonded abrasive products typically include a shaped mass of abrasive grain held together by an organic, metallic, or vitrified binder. Such shaped mass can be, for example, in the form of a wheel, such as a grinding wheel or cutoff wheel. It can also be in the form, for example, of a honing stone or other conventional bonded abrasive shape. It is typically in the form of a grinding wheel. Referring to FIG. 2, grinding wheel 10 is depicted, which includes abrasive grain 11, at least a portion of which is abrasive grain made by a method according to the present invention, molded in a wheel and mounted on
hub 12. For further details regarding bonded abrasive products, see, for example, U.S. Pat. Nos. 4,997,461 (Markhoff-Matheny et al.) and 4,898,597 (Hay et al.).

Nonwoven abrasive products typically include an open porous lofty polymer filament structure having abrasive grain distributed throughout the structure and adherently bonded therein by an organic binder. Examples of filaments include polyester fibers, polyamide fibers, and polyaramid fibers. In FIG. 3, a schematic depiction, enlarged about 100×, of a typical nonwoven abrasive product is provided. Such a nonwoven abrasive product comprises fibrous mat 50 as a substrate, onto which abrasive grain 52, at least a portion of which is abrasive grain made by a method according to the present invention, are adhered by binder 54. For further details regarding nonwoven abrasive products, see, for example, U.S. Pat. No. 2,958,593 (Hoover et al.).

Useful abrasive brushes include those having a plurality of bristles unitary with a backing (see, e.g., U.S. Pat. No. 5,679,067 (Johnson et al.)). Preferably, such brushes are made by injection molding a mixture of polymer and abrasive grain.

Suitable organic binders for the abrasive products include thermosetting organic polymers. Examples of suitable thermosetting organic polymers include phenolic resins, urea-formaldehyde resins, melamine-formaldehyde resins, urethane resins, acrylate resins, polyester resins, aminoplast resins having pendant α,β-unsaturated carbonyl groups, epoxy resins, and combinations thereof. The binder and/or abrasive product can also include additives such as fibers, lubricants, wetting agents, thixotropic materials, surfactants, pigments, dyes, antistatic agents (e.g., carbon black, vanadium oxide, graphite, etc.), coupling agents (e.g., silanes, titanates, zircoaluminates, etc.), plasticizers, suspending agents, and the like. The amounts of these optional additives are selected to provide the desired properties. The coupling agents can improve adhesion to the abrasive grain and/or filler.

The binder can also contain filler materials or grinding aids, typically in the form of a particulate material. Typically, the particulate materials are inorganic materials. Examples of particulate materials that act as fillers include metal carbonates, silica, silicates, metal sulfates, metal oxides, and the like. Examples of particulate materials that act as grinding aids include: halide salts such as sodium chloride, potassium chloride, sodium cryolite, and potassium tetrafluoroborate; metals such as tin, lead, bismuth, cobalt,
antimony, iron, and titanium; organic halides such as polyvinyl chloride and
tetrachloronaphthalene; sulfur and sulfur compounds; graphite; and the like. A grinding
aid is a material that has a significant effect on the chemical and physical processes of
abrading, which results in improved performance. In a coated abrasive product, a grinding
aid is typically used in the supersize coat applied over the surface of the abrasive grain,
although it can also be added to the size coat. Typically, if desired, a grinding aid is used
in an amount of about 50-300 g/m² (preferably, about 80-160 g/m²) of coated abrasive
product.

The abrasive products can contain 100% abrasive grain made by a method
according to the present invention, or they can contain a blend of such abrasive grain with
conventional abrasive grain and/or diluent particles. However, at least about 5% by
weight, and preferably about 30-100% by weight, of the abrasive grain in the abrasive
products should be abrasive grain made by a method according to the present invention.
Examples of suitable conventional abrasive grain include fused aluminum oxide, silicon
carbide, diamond, cubic boron nitride, garnet, fused alumina zirconia, and other sol-gel
abrasive grain, and the like. Examples of suitable diluent particles include marble,
gypsum, flint, silica, iron oxide, aluminum silicate, glass, and diluent agglomerates.
Abrasive grain made by a method according to the present invention can also be combined
in or with abrasive agglomerates. An example of an abrasive agglomerate is described in
U.S. Pat. Nos. 4,311,489 (Kressner), 4,652,275 (Bloecher et al.), and 4,799,939 (Bloecher
et al.).

Objects and advantages of this invention are further illustrated by the
following examples, but the particular materials and amounts thereof recited in these
examples, as well as other conditions and details, should not be construed to unduly limit
this invention. All parts and percentages are by weight unless otherwise indicated.

Examples

Any reference to the percent solids levels of the dispersion used in the
following examples are the approximate solids levels, as they do not take into account the
2-6% water commonly found on the surface of boehmite, nor the solids provided by any non-boehmite additives.

The following designations are used in the examples:

- **DWT:** Deionized water that was at a temperature of 20-25°C, unless otherwise specified.
- **HNO₃:** Nitric acid, 70% concentrated.
- **H-20:** An alpha-alumina monohydrate (boehmite) (obtained from Alcoa Industrial Chemicals, Houston, TX, under the trade designation "HIQ-20").
- **H-30:** An alpha-alumina monohydrate (boehmite) (obtained from Alcoa Industrial Chemicals, under the trade designation "HIQ-30").
- **H-40:** An alpha-alumina monohydrate (boehmite) (obtained from Alcoa Industrial Chemicals, under the trade designation "HIQ-40").
- **AAMH-R:** An alpha-alumina monohydrate (boehmite) (obtained from Condea Chemie, Hamburg, Germany, under the trade designation "DISPERAL RTM").
- **C-D:** Alpha-alumina monohydrate (boehmite); obtained from Condea Vista Company under the trade designation "CATAPAL D".
- **MEM:** A rare earth nitrate solution prepared by mixing a lanthanum, neodymium, and yttrium nitrate (having, on a theoretical metal oxide basis, 23% rare earth oxide (i.e., La₂O₃, Nd₂O₃, and Y₂O₃); available from Molycorp of Lourviers, CO) with a sufficient amount of magnesium nitrate (Mg(NO₃)₂·6H₂O) solution (having, on a theoretical metal oxide basis, 11% MgO; available from Mallinckrodt Chemical of Paris, KY) and cobalt nitrate (Co(NO₃)₂·6H₂O) solution (having, on a theoretical metal oxide basis 19% CoO; available from Hall Chemical of Wickliffe, OH) to provide a solution containing, on a theoretical metal oxide basis 5.8% La(NO₃)₃·6H₂O, 5.8% Nd(NO₃)₃·6H₂O, about 7.1% Y(NO₃)₃·6H₂O, about 14.4% Mg(NO₃)₂·6H₂O, about 0.4% Co(NO₃)₂·6H₂O, and the balance deionized water.
Example 1 and Comparative Example A

Approximately 1200 grams of H-40 powder was ball-milled at 70-80 rpm in a polyurethane lined vessel (30 cm (12 inch) ball mill jar obtained from Paul Abbe, Inc.) containing about 8000 grams of 1.27 cm (0.5 inch) zirconia media (obtained from U.S. Stoneware, East Palestine, OH) for 24 hours. After recovering the ball-milled powder, 1000 grams of the powder was mixed with an acid-water solution (prepared by mixing 60 grams of HNO₃ with 607.6 grams of DWT) by hand in a plastic wash-tub. The resulting powder material was allowed to stand over a weekend in sealed-plastic bags. The powdered material was then extruded through a single screw extruder containing a die with thirty six 2.54 mm (0.1 inch) openings. The extrudate was dried through a tunnel oven at a rate of 1 m/min. The tunnel oven had first zone, 2.43 meters in length, set at 71°C (160°F), and the second zone, 2.43 meters in length, set at 82°C (180°F). The dried extrudate as collected in aluminum pans and allowed to stand for 2 hours in a forced air oven set at 80°C.

The resulting dried material was crushed into particles using a pulverizer (having a 1.1 mm gap between the steel plates; obtained under the trade designation “BRAUN” Type UA from Braun Corp., Los Angeles, CA) and screened to sizes +30-16 mesh (+0.68 mm-1.44 mm) using a conventional screener (obtained under the trade designation “EXOLON SCREENER” from Exolon-ESK, Tonawanda, NY).

The retained particles were fed into a calcining kiln to provide calcined abrasive grain precursor material. The calcining kiln consisted of a 15 cm inner diameter, 1.2 meter in length, stainless steel tube having a 0.3 meter hot zone. The tube was inclined at a 3.0 degree angle with respect to the horizontal. The tube rotated at about 3.5 rpm, to provide a residence time in the tube of about 4-5 minutes. The temperature of the hot zone was about 650°C.

The calcined particles were impregnated with MEM, wherein the ratio of solution to particles was 60 ml of solution to 100 grams of particles. The impregnated particles were dried using a blow gun. The dried, impregnated particles were then calcined again at 650°C as described above to provide abrasive grain precursor particles.

The calcined abrasive grain precursor particles were fed into a rotary sintering kiln. The sintering kiln consisted of an 8.9 cm inner diameter, 1.32 meter long
silicon carbide tube inclined at 4.4 degrees with respect to the horizontal and had a 31 cm hot zone. The heat was applied externally via SiC electric heating elements. The sintering kiln rotated at 5.0 rpm, to provide a residence time in the tube of about 7 minutes. The sintering temperature was about 1400°C. The sintered abrasive grain exited the kiln into room temperature air where it was collected in a metal container and allowed to cool to room temperature.

The density of the abrasive grain was determined with a helium gas pycnometer (obtained under the trade designation "MICROMERITICS ACCUPYC 1330" from Micromeritics Instruments Corp., Norcross, GA). The density of the Example abrasive grain was 3.93 g/cm².

In coated abrasive products, “sharper” abrasive grains, in some abrading applications, abrade more metal than abrasive grains that are less sharp. One means to measuring the “sharpness” of an abrasive grain is by a bulk density measurement. The bulk density of the abrasive grain was determined using an apparatus consisting of a glass funnel with an inside diameter of 9.5 cm at the top and an inside diameter at the stem of 1.4 cm. The entire height of the funnel was about 11.5 cm (including stem). The funnel was placed on a ring-stand above a metal cup so that the base of the funnel stem was 7.6 cm (3 inches) above the top of the metal cup (10cc aluminum sample cup obtained from Micromeritics Instrument Corporation, Norcross, GA as Part No. 133/25805/00). The volume of the metal cup was determined by filling the cup with water from a graduated burette. The volume of the cup was calculated as 10.38 cc, SDn-1 = 0.09 cc.

To allow the funnel to be filed with the abrasive grain, the stem of the funnel was closed with a rubber ball attached to the outside of the funnel stem. Abrasive grain was poured into the funnel. The rubber ball was removed to allow the abrasive grain to empty into and eventually overflow the metal cup. Using a straight edge, the abrasive grain was carefully leveled to the top of the cup, tapped to allow the abrasive grain to settle in the cup and then weighed. The bulk density was determined by dividing the weight of the mineral and cup minus the weight of the cup by the volume of the cup (which was determined as described above to be 10.38 cc). The bulk density is reported an average of three independent measurements. The bulk density of the Example 1 abrasive grain was 1.66 +/- 0.01.
The sintered alpha alumina-based ceramic abrasive grain was graded to retain the -25+30 and -30+35 mesh fractions (U.S.A. Standard Testing Sieves). These fractions were blended in a 1:1 ratio and incorporated into coated abrasive discs, which were tested for grinding performance. The coated abrasive discs were made according to conventional procedures. The sintered abrasive grain were bonded to 17.8 cm diameter, 0.8 mm thick vulcanized fiber backings (having a 2.2 cm diameter center hole) using a conventional calcium carbonate-filled phenolic make resin (48% resole phenolic resin, 52% calcium carbonate, diluted to 81% solids with water and glycol ether) and a conventional cryolite-filled phenolic size resin (32% resole phenolic resin, 2% iron oxide, 66% cryolite, diluted to 78% solids with water and glycol ether). A KBF₄ supersize coating (as described in U.S. Pat. Nos. 5,556,437 (Lee) and 5,549,719 (Lee)) was applied on top of the size coat. The wet make resin weight was about 185 g/m². Immediately after the make coat was applied, the sintered abrasive particles were electrostatically coated. The make resin was then partially cured by heating the resulting construction of make resin and abrasive grain for 90 minutes at 88°C. The wet size weight was about 850 g/m². The size resin was precured for 90 minutes at 88°C, followed by a final cure of 10 hours at 100°C. The coated abrasive discs were flexed prior to testing.

Each coated abrasive disc was mounted on a beveled aluminum back-up pad, and used to grind the face of a pre-weighed 1.25 cm x 18 cm x 10 cm 304 stainless steel workpiece. The disc was driven at 5,000 rpm while the portion of the disc overlaying the beveled edge of the back-up pad contacted the workpiece at a load of 8 Kg. Each disc was used to grind individual workpiece in a sequence of one-minute intervals. The total cut was the sum of the amount of material removed from the workpieces throughout the 10 minute test period. The average total cut of four Example 1 discs was 295 grams.

Comparative Example A coated abrasive discs were prepared and tested as described for Example 1, except the H-40 powder was not ball milled. The density and bulk density of the Comparative Example A abrasive grain were determined as described for Example 1 to be 3.90 g/cm² and 1.54 +/- 0.01 g/cm², respectively. The average total cut of four Comparative Example A discs was 245 grams.
Example 2 and Comparative Example B

Example 2 coated abrasive discs were prepared and tested as described for Example 1 except two identical alumina ball mills (17.78 cm in height and 15.24 cm in diameter), each with 1500 grams 0.635 cm (0.25 inch) alumina media, were used, and the samples were milled for 18 hours. Each mill contained 600 grams of H-40 powder. The milled powder was combined into one sample.

The density and bulk density of the Example 2 abrasive grain were determined as described for Example 1 to be 3.89 g/cm² and 1.60 +/- 0.01 g/cm², respectively. The average total cut of four Example 2 discs was 293 grams.

Comparative Example B coated abrasive discs were prepared and tested as described for Example 2 except the H-40 was not ball milled. The density and bulk density of the Comparative Example B abrasive grain were determined as described for Example 1 to be 3.87 g/cm² and 1.53 +/- 0.01 g/cm², respectively. The average total cut of four Comparative Example B discs was 282 grams.

Example 3 and Comparative Example C

An alumina ball mill, measuring 17.78 in height (without cover) and 15.24 cm in diameter (obtained from U.S. Stoneware), was filled with 1200 grams of H-30 powder and 3300 grams of 0.635 cm (0.25 inch) alumina media (U.S. Stoneware). The sample was milled at 80 rpm for 48 hours. The milled powder was recovered from the mill. The median particle size of the milled powder was measured using a laser scattering particle size analyzer (obtained under the trade designation “HORIBA LA-910” from Horiba Laboratory Products, Irvine, CA) and found to be 7.3 micrometers.

A sol was prepared by combining 338 grams of the milled powder, 31 grams of HNO₃ and 1550 grams of DWT together in a conventional 4 liter, food grade blender (Model 34BL22(CB6), Waring Products Division, Dynamics Corp. of America, New Hartford, CT). The contents of the blender were mixed at low speed for one minute. The resulting sol was poured into a 23 cm (9 inch) x 30 cm (12 inch) glass pan (obtained under the trade designation “PYREX”). The sol was dried overnight in a forced air oven at 93°C (200°F). The resulting friable material was crushed into particles using the
pulverizer, screened, calcined, impregnated, re-calcined, sintered, and used to make coated abrasive discs as described in Example 1.

The density and bulk density of the Example 3 abrasive grain were determined as described for Example 1 to be 3.93 g/cm$^2$ and 1.89 +/- 0.01 g/cm$^2$, respectively.

The discs were ground as described in Example 1 except the grinding load was 4000 grams, and three discs were ground using 6-two-minutes intervals for each disc. The average total cut of three Example 3 discs was 117.8 grams.

Comparative Example C coated abrasive discs were prepared and tested as described for Example 3 except the H-40 was not ball milled. The milled powder was recovered from the mill. The median particle size of the milled powder was measured as described in Example 3 and found to be 31.7 micrometers.

The density and bulk density of the Comparative Example C abrasive grain were determined as described for Example 1 to be 3.91 g/cm$^2$ and 1.78 +/- 0.01 g/cm$^2$, respectively. The average total cut of three Comparative Example B discs was 109.1 grams.

**Example 4 and Comparative Example D**

An 18.9 liter metal pail with a polyethylene liner was charged with 2600 ml of DWT, 48 grams of HNO$_3$, and 800 grams of AAMH powder. The charge was dispersed at high speed for five minutes using a conventional homogenizer (obtained from under the trade designation “GIFFORD-WOOD HOMOGENIZER MIXER” from Greeco Corp., Hydson, NH). The resulting sol was poured into a 46 cm x 66 cm x 5 cm polyester-lined aluminum tray and dried in an air oven at 150°C, to provide to a friable solid. The dried material was crushed using the pulverizer described in Example 1. The crushed material was screened to -150 mesh using a USA Standard Testing Sieves.

An alumina-lined mill (24.13 cm (9.5 inch) in height without cover and 25.4 cm (10 inch) in diameter; obtained from U.S. Stoneware) was charged with 1,200 grams of the -150 mesh fines and 3,300 grams of 0.635 cm (0.25 inch) alumina media (U.S. Stoneware). The charge was ball-milled at 80 rpm for 26 hours. A thousand grams
of the milled powder was mixed by hand with 575 grams of DWT into the milled powder in a plastic tub. The resulting mixture was extruded using a 5.1 cm (2 inch) extruder (obtained under the trade designation “BONNET EXTRUDER” from Bonnet Co., Uniontown, OH) using a die which produced extrudate approximately 0.159 cm (1/16 inch) in diameter. The extrudate was allowed to dry overnight at room temperature in aluminum trays.

The dried extrudate was crushed using a roll crusher (obtained from Allis-Chalmers, Milwaukee, WI). About 400 grams of the -16+46 mesh (+0.68 mm-1.44 mm) material collected was screened (“EXOLON SCREENER”) through five 20 mesh screens (U.S.A. Standard Testing Sieves) for 5 minutes using a mechanical siever (obtained under the trade designation “ROTOTAP RX29” from U.S. Tyler, Inc., Mentor, OH. The rods retained on the bottom 20 mesh screen were retained. The retained rod-shaped particles were then calcined, impregnated, calcined, and sintered as described for Example 1.

The density of the Example 4 abrasive grain was determined as described for Example 1 to be 3.88 g/cm³.

The sintered abrasive particles were graded using a stack of five 40 mesh screens (USA Std. Testing Sieves). In this case, the sintered abrasive particles retained on the top screen were used to prepare coated abrasive discs. The coated abrasive discs were prepared and tested as described for Example 1, except the workpieces were made of 1018 mild steel, the load was 4.5 Kg, and the test length, with one-minute intervals, was 12 minutes. The average total cut of four Example 4 discs was 936 grams.

Comparative Example D coated abrasive discs were prepared and tested as described for Example 4 except the -150 mesh fines were not ball milled. The density of the Comparative Example A abrasive grain were determined as described for Example 1 to be 3.84 g/cm³. The average total cut of four Comparative Example D discs was 831 grams.

Example 5 and Comparative Example E

An alumina lined mill, measuring 24.13 cm (9.5 inch) in height without cover and 25.4 cm (10 inches) in diameter (U.S. Stoneware), was filled with 1000 grams of H-20 and 3,300 grams of 0.635 cm (0.25 inch) alumina media (U.S. Stoneware). The
material was ball-milled for 8 hours. After recovering the ball-milled powder, 1000 grams of the powder was mixed with an acid-water solution (prepared by mixing 60 grams of HNO₃ with 650 grams of DWT) by hand in a plastic wash-tub.

The resulting mixture was extruded, dried, crushed, screened crushed, calcined, impregnated, calcined, sintered, made into discs, and tested as described for Example 4.

The density of the Example 5 abrasive grain was determined as described for Example 1 to be 3.82 g/cm². The average total cut of four Example 5 discs was 892 grams.

Comparative Example E coated abrasive discs were prepared and tested as described for Example 4 except the H-20 was not ball milled. The density of the Comparative Example E abrasive grain was determined as described for Example 1 to be 3.80 g/cm². The average total cut of four Comparative Example D discs was 828 grams.

Example 6 and Comparative Example F

An attritor mill (obtained under the trade designation “SZEGVARI ATTRITOR MILL”, Model HSA1, from Union Process, Akron, OH) containing a polymer coated impellor and 3.8 liter (1 gallon) sized polymer-lined sample vessel was filled with 3000 grams of 0.635 cm (0.25 inch) cylindrically shaped zirconia milling media (obtained from U.S. Stoneware) and 600 grams of H-40 powder. The H-40 powder was milled by rotating the impellor at 250 rpm for 20 minutes. The resulting milled powder was separated from the media.

The surface area of the milled (Example 6) and unmilled (Comparative Example F) H-40 powder were determined using a nitrogen gas-sorption (obtained under the trade designation “NOVA 1000” from Quantachrome Corp. Boynton Beach, FL) and determined to be 196.3 m²/g and 228.4 m²/g, respectively. The median particle size of the milled and unmilled H-40 powders were measured using a laser scattering particle size analyzer (“HORIBA LA-910”) and found to be 4.5 micrometers and 46.6 micrometers, respectively.
Further, the average crystallite size for the milled and unmilled boehmite powders were determined as follows. The boehmite powder to be evaluated was placed on a glass microscope slide using a double sided adhesive tape. The excess powder was blown or brushed off to provide a monolayer of powder on the glass slide. The sample was then placed in an x-ray diffractometer (obtained under the trade designation “INEL CPS 120” from Inel of Stratham, NJ). The x-rays were generated using a conventional x-ray generator (obtained under the trade designation “PHILLIPS 3100” from Phillips of Mahwah, NJ). The average crystallite size of a sample was measured using the 120 peak for boehmite located at \( \theta = 28.3^\circ \), and the 031 peak located at \( \theta = 38.5^\circ \). This peak was scanned at a sufficiently slow rate to obtain greater than 10,000 counts under the 120 peak, or the 031 peak. The average crystal size of the boehmite was calculated using the formula:

\[
D = \frac{k \lambda}{\beta \cos \theta},
\]

wherein

- \( k \) is a constant = 0.89
- \( \lambda \) is the wavelength of the x-rays used to irradiate the sample (i.e. copper x-rays = 1.5418 Angstroms)
- \( \theta \) corresponds to the 120 peak for boehmite, \( \theta = 28.3^\circ \), \( \theta = 14.15^\circ \), or, for the 031 peak, \( \theta = 38.5^\circ \), \( \theta = 19.25^\circ \), and
- \( \beta = (\beta^2_{\text{measured}} - \beta^2_{\text{instrument}})^{0.5} \) where \( \beta_{\text{measured}} \) is the full width half maximum of the 120 peak, or the 031 peak, for the boehmite sample and \( \beta_{\text{instrument}} \) is a constant unique to each x-ray diffractometer calculated using a known standard sample of known crystal size. All \( \beta \) values are measured in radians.

The average crystallite size for the unmilled powder was 61 Angstroms; the milled powder, 99 Angstroms.

Sols were prepared of the milled and unmilled H-40 powders by mixing 200 grams of the respective powders, 12 grams of HNO₃, and 1000 grams of DWT. The ingredients were thoroughly mixed using a blender (Waring Model 34BL22(CB6) at low
speed for one minute. The sols were poured into 23 cm (9 inch) x 30 cm (12 inch) glass
(“PYREX”) trays and placed in a forced air oven at 93°C (200°F) overnight. The
resulting friable materials were crushed, screened, calcined, impregnated, re-calcined, and
sintered as described in Example 1, except the crushed material was screened to sizes +46-
14 mesh (+0.68 mm-1.44 mm), and the ratio of MEM to particles was 70 ml of solution to
100 grams of particles.

The density of the resulting abrasive grains were as described in Example 1. The
density of the Example 6 and Comparative Example F abrasive grains were 3.85
g/cm³ and 3.87 g/cm³, respectively.

Example 7 and Comparative Example G

-150 mesh dried gel material as described in Example 4 was jet milled
(using a jet mill obtained under the trade designation “CCE FLUID BED JET MILL” from
CCE Technologies, Mendota Heights, MN) at a feed rate of 204 kg/hr (450 lb./hr.). The
median particle size of the milled (Example 7) and unmilled (Comparative Example G)
materials were measured using a laser scattering particle size analyzer (“HORIBA LA-
910”) and found to be 2.2 micrometers and 69.4 micrometers, respectively.

The average crystallite size for the unmilled and milled powders were
determined as described in Example 6, and found to be 123 Angstroms and 130
Angstroms, respectively.

Sols were prepared of the milled and unmilled material by mixing control
by mixing 280 grams of the respective materials, 8 grams of HNO₃, and 1000 grams of
DWT. The ingredients were thoroughly mixed using a blender (Waring Model
34BL22(CB6) at low speed for one minute. The sols were poured into 23 cm (9 inch) by
23 cm (9 inch) glass (“PYREX”) trays and placed in a forced air oven at 93°C (200°F)
overnight.

The resulting friable materials were crushed, screened, calcined, impregnated, re-calcined, and sintered as described in Example 6.

The density of the Example 7 and Comparative Example G abrasive grains,
as determined according to Example 1 were 3.89 g/cm³ and 3.85 g/cm³, respectively.
Example 8 and Comparative Example H

About 1000 grams of C-D powder was ball milled with 6000 grams of zirconia media (U.S. Stoneware, East Palestine, OH) in a plastic 3.8 liter (1 gallon), 25.4 cm high, 15 cm diameter jar for 24 hours at a rotation rate of 80 rpm. The average crystallite size for the unmilled powder (Comparative Example H) was 66 Angstroms; the milled powder (Example 8), 100 Angstroms.

The surface area of the milled (Example 8) and unmilled (Comparative Example H) were analyzed by nitrogen gas-sorption analyzer (obtained under the trade designation “NOVA 1000” from Quantachrome Corporation, Boynton Beach, FL). Surface areas were measured to be 244.6 m$^2$/g for the milled powder and 218.7 m$^2$/g for the unmilled powder. The median particle size of the milled and unmilled powders were measured using the laser scattering particles size analyzer (“HORIBA LA-910”) and found to be 11.4 micrometers for the milled powder, and 51.8 micrometers for the unmilled powder.

Example 9 and Comparative Example I

H-40 powder was jet milled by the manufacturer, Alcoa Industrial Chemicals. The average crystallite size for the unmilled powder (Comparative Example I) was 68 Angstroms; the milled powder (Example 9), 82 Angstroms. The average particle size of the milled and unmilled powders were 1.6 micrometers and 46.6 micrometers, respectively.

Various modifications and alterations of this invention will become apparent to those skilled in the art without departing from the scope and spirit of this invention, and it should be understood that this invention is not to be unduly limited to the illustrative embodiments set forth herein.
What is claimed is:

1. A method for making alpha alumina-based ceramic abrasive grain, said method comprising:
   dry milling boehmite for a time sufficient to increase the average crystallite size of said boehmite by at least ten percent;
   preparing a dispersion by combining components comprising a first liquid medium, peptizing agent, and the dry milled boehmite;
   converting said dispersion to particulate alpha alumina-based ceramic abrasive grain precursor material; and
   sintering said precursor material to provide alpha alumina-based ceramic abrasive grain.

2. The method according to claim 1 wherein said dry milling is ball milling.

3. The method according to claim 1 wherein said dry milling of said boehmite is conducted for a time sufficient to increase the average crystallite size of said boehmite by at least 25 percent.

4. The method according to claim 1 wherein said boehmite has an average surface area of at least 180 m²/g prior to said dry milling.

5. The method according to claim 1 wherein said boehmite has an average crystallite size of at least 25 Angstroms prior to said dry milling.

6. The method according to claim 1 wherein said converting includes extruding said dispersion.
7. The method according to claim 1 wherein the solids content of said dispersion is in the range from 30 to 85 percent by weight, based on the total solids content of said dispersion.

8. The method according to claim 1 wherein the solids content of said dispersion is in the range from 40 to 65 percent by weight, based on the total solids content of said dispersion.

9. The method according to claim 1 wherein between said converting and said sintering, said method further comprises (i) impregnating said precursor material with a mixture prepared by combining components comprising a second liquid medium and at least one of metal oxide or metal oxide precursor to provide impregnated precursor material; (ii) drying said impregnated precursor material; and (iii) calcining the dried, impregnated precursor material.

10. A method for making an abrasive article, said method comprising: dry milling boehmite for a time sufficient to increase the average crystallite size of said boehmite by at least ten percent; preparing a dispersion by combining components comprising a first liquid medium, peptizing agent, and the dry milled boehmite; converting said dispersion to particulate alpha alumina-based ceramic abrasive grain precursor material; sintering said precursor material to provide alpha alumina-based ceramic abrasive grain and combining at least a plurality of said alpha alumina-based ceramic abrasive grain with binder to provide an abrasive article.

11. The method according to claim 10 wherein said abrasive article is a coated abrasive article that includes a backing.
12. The method according to claim 11 wherein combining at least a plurality of said alpha alumina-based ceramic abrasive grain with binder includes combining fused alumina abrasive grain with said binder.

13. A method for making alpha alumina-based ceramic abrasive grain, said method comprising:

preparing a first dispersion by combining components comprising liquid medium and boehmite;

drying said first dispersion to provide first alpha alumina-based precursor material;

dry milling said first alpha alumina-based precursor material for a time sufficient to increase the average crystallite size of said boehmite by at least ten percent;

preparing a second dispersion by combining components comprising a first liquid medium, peptizing agent, and the dry milled first alpha alumina-based precursor material;

converting said second dispersion to particulate alpha alumina-based ceramic abrasive grain precursor material; and

sintering said precursor material to provide alpha alumina-based ceramic abrasive grain.

14. The method according to claim 13 wherein said dry milling is ball milling.

15. The method according to claim 13 wherein said dry milling of said boehmite is conducted for a time sufficient to increase the average crystallite size of said boehmite by at least 25 percent.

16. The method according to claim 13 wherein said boehmite has an average surface area of at least 180 m²/g prior to said dry milling.
17. The method according to claim 13 wherein said boehmite has an average crystallite size of at least 25 Angstroms prior to said dry milling.

18. The method according to claim 13 wherein said converting includes extruding said dispersion.

19. The method according to claim 13 wherein the solids content of said dispersion is in the range from 30 to 85 percent by weight, based on the total solids content of said dispersion.

20. The method according to claim 13 wherein the solids content of said dispersion is in the range from 40 to 65 percent by weight, based on the total solids content of said dispersion.

21. The method according to claim 13 wherein between said converting and said sintering, said method further comprises (i) impregnating said precursor material with a mixture prepared by combining components comprising a second liquid medium and at least one of metal oxide or metal oxide precursor to provide impregnated precursor material; (ii) drying said impregnated precursor material; and (iii) calcining the dried, impregnated precursor material.

22. A method for making an abrasive article, said method comprising: preparing a first dispersion by combining components comprising liquid medium and boehmite;

drying said first dispersion to provide first alpha alumina-based precursor material;

dry milling said first alpha alumina-based precursor material for a time sufficient to increase the average crystallite size of said boehmite by at least ten percent;

preparing a second dispersion by combining components comprising a first liquid medium, peptizing agent, and the dry milled first alpha alumina-based precursor material;
converting said second dispersion to particulate alpha alumina-based ceramic abrasive grain precursor material;

sintering said precursor material to provide alpha alumina-based ceramic abrasive grain; and

combining at least a plurality of said alpha alumina-based ceramic abrasive grain with binder to provide an abrasive article.

23. The method according to claim 22 wherein said abrasive article is a coated abrasive article that includes a backing.

24. The method according to claim 23 wherein combining at least a plurality of said alpha alumina-based ceramic abrasive grain with binder includes combining fused alumina abrasive grain with said binder.
Fig. 4

Fig. 5

Fig. 6
## INTERNATIONAL SEARCH REPORT

### A. CLASSIFICATION OF SUBJECT MATTER

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According to International Patent Classification (IPC) or to both national classification and IPC

### B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic database consulted during the international search (name of data base and, where practical, search terms used)

### C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<td></td>
<td>Y column 2, line 56 - line 67; claims 1-5; examples 3-7 9-12, 21-24</td>
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<td>Y WO 99 38817 A (MINNESOTA MINING AND MANUFACTURING COMPANY) 5 August 1999 (1999-08-05) 9-12, 21-24</td>
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<td>Y page 7, line 20 - line 27; claims 6-12; example 1 page 12, line 31 - page 16, line 17</td>
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Patent family members are listed in annex.

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**Date of the actual completion of the international search:**

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**Name and mailing address of the ISA**

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Hauck, H
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