

US00RE45923E

(19) **United States**
 (12) **Reissued Patent**
Pujari et al.

(10) **Patent Number: US RE45,923 E**
 (45) **Date of Reissued Patent: *Mar. 15, 2016**

(54) **HIGH SOLIDS HBN SLURRY, HBN PASTE, SPHERICAL HBN POWDER, AND METHODS OF MAKING AND USING THEM**

(75) Inventors: **Vimal K. Pujari**, Northboro, MA (US);
William T. Collins, Auburn, MA (US);
Jeffrey J. Kutsch, Oxford, MA (US);
Thomas M. Clere, Orchard Park, NY (US);
Eugene A. Pruss, Hamburg, NY (US)

(73) Assignee: **Saint-Gobain Ceramics & Plastics, Inc.**, Worcester, MA (US)

(*) Notice: This patent is subject to a terminal disclaimer.

(21) Appl. No.: **11/266,751**

(22) Filed: **Nov. 3, 2005**

Related U.S. Patent Documents

Reissue of:

(64) Patent No.: **6,645,612**
 Issued: **Nov. 11, 2003**
 Appl. No.: **09/923,994**
 Filed: **Aug. 7, 2001**

(51) **Int. Cl.**

B01F 17/54 (2006.01)
B32B 18/00 (2006.01)
C04B 35/5833 (2006.01)
C08K 3/38 (2006.01)
H01L 23/34 (2006.01)
C01B 21/064 (2006.01)
C04B 35/626 (2006.01)
C04B 35/63 (2006.01)

(52) **U.S. Cl.**

CPC **C01B 21/064** (2013.01); **C04B 35/6263** (2013.01); **C04B 35/6264** (2013.01); **C04B 35/6265** (2013.01); **C04B 35/6303** (2013.01)

(58) **Field of Classification Search**

USPC 428/325, 323, 402; 257/717; 423/290; 501/96.4; 516/33, 78; 524/404; 264/13
 See application file for complete search history.

(56) **References Cited**

U.S. PATENT DOCUMENTS

2,991,508 A 7/1961 Reuben et al.
 3,125,547 A 3/1964 Blatz et al.
 3,351,690 A 11/1967 Stover
 3,617,358 A 11/1971 Dittrich
 3,720,740 A 3/1973 Muta et al.
 3,954,483 A 5/1976 Prochazka
 4,097,293 A 6/1978 Komeya et al.
 4,107,276 A 8/1978 Schwetz et al. 423/290
 4,188,194 A 2/1980 Corrigan 51/307
 4,195,002 A * 3/1980 Radtke et al.
 4,394,170 A 7/1983 Sawaoka et al.
 4,412,008 A 10/1983 Miyamoto et al.
 4,514,370 A 4/1985 Inoue et al. 423/344
 4,634,640 A 1/1987 Hunold et al. 428/704
 4,642,298 A 2/1987 Kuramoto et al.
 4,731,311 A 3/1988 Suzuki et al. 429/213
 4,784,978 A 11/1988 Ogasawara et al.
 4,801,445 A 1/1989 Fukui et al. 424/69
 4,863,881 A 9/1989 Ahrens et al. 501/92
 4,869,954 A 9/1989 Squitieri 428/283

4,882,225 A 11/1989 Fukui et al. 428/405
 4,927,587 A 5/1990 Takahashi et al.
 4,971,779 A 11/1990 Paine, Jr. et al.
 4,997,633 A * 3/1991 Koshida et al. 423/290
 5,001,091 A 3/1991 Pujari et al. 501/103
 5,011,870 A 4/1991 Peterson 523/220
 5,039,435 A 8/1991 Hanano
 5,063,184 A 11/1991 Tsuyoshi
 5,064,589 A * 11/1991 Ichikawa et al. 264/65
 5,098,609 A * 3/1992 Iruvanti et al. 524/404 X
 5,116,589 A 5/1992 Hoenig 423/298
 5,120,688 A 6/1992 Hsieh
 5,194,480 A * 3/1993 Block et al. 524/404
 5,213,868 A 5/1993 Liberty et al. 428/131
 5,229,339 A 7/1993 Pujari et al. 501/96
 5,234,712 A 8/1993 Howard 427/215
 5,273,558 A 12/1993 Nelson et al.

(Continued)

FOREIGN PATENT DOCUMENTS

AU 9067727 A 6/1991
 BR 9006359 A 9/1991

(Continued)

OTHER PUBLICATIONS

Chemical Abstracts, AN 130:96383, Columbus, OH, USA, corresponding to JP 11005907 A2, (Abstract) (copyright 2002—Month unavailable).*

Derwent Abstract on WPIX, London: Derwent Publications Ltd., AN 1998-476912, JP 10204300 A, (Mitsui Petrochem IND CO LTD), abstract, (1998—month unknown).*

Derwent Abstract on WPIX, London: Derwent Publications Ltd., AN 1997-359228, JP 09151324 A, (Fuji Kobunshi Kogyo KK), abstract, (1997—month unknown).*

Chemical Abstracts, AN 123:177515, Columbus, OH, USA, corresponding to JP 07157369 A2, (Abstract) (copyright 2002—Month unavailable).*

Chemical Abstracts, AN 118:127738, Columbus, OH, USA, corresponding to JP 04321506 A2, (Abstract) (copyright 2002—Month unavailable).*

Manual of Patent Examining Procedure Original Eighth Edition, Aug. 2001 Latest Revision Jul. 2008, U.S. Department of Commerce United States Patent and Trademark Office, Washington, DC 20402, MPEP § 1453, pp. 1-7.*

(Continued)

Primary Examiner — Ling Xu

(74) *Attorney, Agent, or Firm* — LeClairRyan, a Professional Corporation

(57) **ABSTRACT**

The present invention relates to a method for making a hexagonal boron nitride slurry and the resulting slurry. The method involves mixing from about 0.5 wt. % to about 5 wt. % surfactant with about 30 wt. % to about 50 wt. % hexagonal boron nitride powder in a medium under conditions effective to produce a hexagonal boron nitride slurry. The present invention also relates to a method for making a spherical boron nitride powder and a method for making a hexagonal boron nitride paste using a hexagonal boron nitride slurry. Another aspect of the present invention relates to a hexagonal boron nitride paste including from about 60 wt. % to about 80 wt. % solid hexagonal boron nitride. Yet another aspect of the present invention relates to a spherical boron nitride powder, a polymer blend including a polymer and the spherical hexagonal boron nitride powder, and a system including such a polymer blend.

34 Claims, 2 Drawing Sheets

(56)

References Cited

U.S. PATENT DOCUMENTS

5,283,542 A 2/1994 Ochiai et al. 335/6
 5,285,108 A 2/1994 Hastings et al. 257/712
 5,298,791 A 3/1994 Liberty et al. 257/707
 5,308,044 A 5/1994 Nakashima et al.
 5,312,571 A 5/1994 Pujari et al. 264/13
 5,320,989 A 6/1994 Chapman et al.
 5,332,629 A 7/1994 Sumiya et al.
 5,374,036 A 12/1994 Rogers et al. 266/45
 5,409,868 A 4/1995 Dasgupta et al.
 5,457,075 A 10/1995 Fukushima et al.
 5,466,269 A 11/1995 Corrigan et al. 51/307
 5,466,400 A 11/1995 Pujari et al. 264/13
 5,508,110 A 4/1996 Howard 428/402
 5,510,174 A 4/1996 Litman 428/261
 5,525,557 A 6/1996 Pujari et al. 501/97
 5,528,462 A 6/1996 Pendse 361/767
 5,536,485 A 7/1996 Kume et al.
 5,545,473 A 8/1996 Ameen et al. 428/283
 5,567,353 A * 10/1996 Bogan, Jr. 501/96 X
 5,571,760 A 11/1996 Pujari et al. 501/97
 5,591,034 A 1/1997 Ameen et al. 439/91
 5,593,773 A 1/1997 McKay et al. 428/328
 5,601,874 A 2/1997 Howard et al. 427/215
 5,610,203 A 3/1997 Buckmaster et al.
 5,614,319 A 3/1997 Wessels et al.
 5,660,917 A 8/1997 Fujimori et al. 428/195
 5,681,883 A * 10/1997 Hill et al. 524/404
 5,688,449 A 11/1997 Fox
 5,688,457 A 11/1997 Buckmaster et al. 264/211
 5,696,041 A 12/1997 Collins et al. 501/97
 5,716,665 A 2/1998 Vita et al.
 5,726,502 A 3/1998 Beddingfield
 5,738,936 A 4/1998 Hanrahan 428/313.5
 5,759,481 A 6/1998 Pujari et al. 264/655
 5,770,819 A 6/1998 Mehan
 5,781,412 A * 7/1998 de Sorgo 257/717 X
 5,783,308 A 7/1998 Leendersen
 5,849,316 A 12/1998 Mellul et al. 424/401
 5,854,155 A * 12/1998 Kawasaki et al. 501/96.4
 5,898,009 A 4/1999 Shaffer et al. 501/96.4
 5,898,217 A 4/1999 Johnston
 5,907,474 A 5/1999 Dolbear 361/705
 5,908,796 A 6/1999 Pujari et al. 501/97.1
 5,926,371 A 7/1999 Dolbear 361/704
 5,945,217 A 8/1999 Hanrahan
 5,945,478 A 8/1999 Buckmaster et al.
 5,950,066 A 9/1999 Hanson et al. 428/551
 5,962,122 A 10/1999 Walpita et al.
 5,981,641 A 11/1999 Takahashi et al. 524/428
 5,984,055 A 11/1999 Strasser et al.
 5,985,228 A 11/1999 Corrigan et al. 423/290
 6,048,511 A 4/2000 Shaffer et al. 423/290
 6,054,520 A 4/2000 Washio et al.
 6,096,671 A 8/2000 Kawasaki et al.
 6,110,527 A 8/2000 Brun et al. 427/214
 6,124,579 A 9/2000 Steinhauser et al.
 6,158,894 A 12/2000 Pujari et al. 384/492
 6,162,849 A * 12/2000 Zhuo et al. 524/404
 6,168,859 B1 1/2001 Mills et al. 428/329
 6,249,703 B1 6/2001 Stanton et al.
 6,251,513 B1 6/2001 Rector et al.
 6,255,376 B1 * 7/2001 Shikata et al. 524/404
 6,284,817 B1 9/2001 Cross et al. 523/220
 6,287,489 B1 * 9/2001 Rolander et al. 264/6
 6,300,607 B1 10/2001 Steinhauser et al.
 6,319,602 B1 * 11/2001 Fauzi et al. 423/290 X
 6,348,179 B1 * 2/2002 Paine et al. 423/277
 6,541,111 B2 4/2003 Fauzi et al.
 6,548,152 B2 * 4/2003 Nakatani et al. 428/325 X
 6,585,039 B2 7/2003 Sagal et al.
 6,645,612 B2 11/2003 Pujari et al.
 6,652,822 B2 11/2003 Phillips et al.
 6,660,241 B2 12/2003 Clere et al.
 6,676,893 B2 * 1/2004 Rolander et al. 419/8
 6,713,088 B2 * 3/2004 Lodyga et al. 424/489

6,764,975 B1 7/2004 Clere
 6,794,435 B2 * 9/2004 Clere 524/404
 6,824,753 B2 11/2004 Paine et al.
 6,867,445 B2 3/2005 Jang
 6,951,583 B2 10/2005 Clere et al.
 7,189,774 B2 * 3/2007 Clere 524/404
 7,494,635 B2 * 2/2009 Pruss et al. 423/290
 7,557,054 B2 7/2009 Oda et al.
 7,914,886 B2 3/2011 Pruss et al.
 8,169,767 B2 5/2012 Pruss et al.
 2001/0004131 A1 6/2001 Masayuki et al.
 2001/0021740 A1 9/2001 Lodyga et al.
 2001/0048179 A1 12/2001 Stewart et al.
 2002/0004111 A1 1/2002 Matsubara et al.
 2002/0006373 A1 1/2002 Clere
 2002/0006511 A1 1/2002 Clere
 2002/0155052 A1 10/2002 Paine et al.
 2003/0038278 A1 2/2003 Ishihara
 2004/0041257 A1 3/2004 Tobita et al.
 2004/0077764 A1 * 4/2004 Lodyga et al. 524/445
 2004/0208812 A1 10/2004 Clere
 2005/0041373 A1 2/2005 Pruss et al.
 2006/0121068 A1 6/2006 Sane et al.
 2006/0127422 A1 6/2006 Lodyga et al.
 2006/0228542 A1 10/2006 Czubarow
 2007/0041918 A1 2/2007 Meneghetti et al.
 2007/0205706 A1 9/2007 Yamada et al.
 2008/0076856 A1 3/2008 Zhong et al.

FOREIGN PATENT DOCUMENTS

CA 2031834 A1 6/1991
 CA 2389963 A1 6/2001
 CN 1269273 A 11/2000
 CN 1834167 9/2006
 DE 2629960 1/1978
 DE 0 279 769 A2 8/1988
 DE 39 17 726 A1 7/1990
 DE 4013025 10/1990
 EP 0 279 769 A2 8/1988
 EP 0396448 A1 11/1990
 EP 0 432 007 A1 12/1991
 EP 0717020 6/1996
 EP 0 896 031 A2 2/1999
 EP 0 939 066 A1 9/1999
 EP 0 479 387 A1 10/1999
 EP 0 982 391 A1 3/2000
 EP 1 053 973 A1 * 11/2000
 EP 1702907 9/2006
 FI 906048 A2 6/1991
 FR 2655638 A1 6/1991
 GB 870084 6/1961
 GB 1179156 1/1970
 GB 1241206 8/1971
 GB 2301818 A 12/1996
 JP 58060679 4/1983
 JP 58060680 4/1983
 JP 61132564 6/1986
 JP 61268763 A 11/1986
 JP 62123070 6/1987
 JP 63006093 1/1988
 JP 63040769 2/1988
 JP 63045104 2/1988
 JP 63045178 A 2/1988
 JP 63117966 A 5/1988
 JP 64-38424 A 2/1989
 JP 1065073 3/1989
 JP 1119564 5/1989
 JP 1122971 5/1989
 JP 1126661 A 5/1989
 JP 1131062 5/1989
 JP 1131065 5/1989
 JP 1131066 5/1989
 JP 1133982 5/1989
 JP 1239066 9/1989
 JP 01-54379 B 11/1989
 JP 1275471 11/1989
 JP 2044067 2/1990
 JP 2055766 2/1990

(56)

References Cited

FOREIGN PATENT DOCUMENTS

JP	2092868		4/1990
JP	2164433	A	6/1990
JP	3012316		1/1991
JP	3177361		8/1991
JP	3215364		9/1991
JP	4065366		3/1992
JP	4164805		6/1992
JP	4321506	A	11/1992
JP	5000853		1/1993
JP	5000854		1/1993
JP	5078106	A	3/1993
JP	5148038		6/1993
JP	06219714		8/1994
JP	06-321638		11/1994
JP	7041311		2/1995
JP	07-157369	A1 *	6/1995
JP	7157369	A	6/1995
JP	07204492		8/1995
JP	7315937		12/1995
JP	08-127793		5/1996
JP	08183906		7/1996
JP	2590908	B2	3/1997
JP	2590964	B2	3/1997
JP	9151324	A	6/1997
JP	9202663		8/1997
JP	11-134944	A	10/1997
JP	10194711	A	7/1998
JP	10204300	A	8/1998
JP	11005907	A	1/1999
JP	11-060215	A	3/1999
JP	11060215		3/1999
JP	11-116213	A	4/1999
JP	11-134944	A	5/1999
JP	11-209618		8/1999
JP	11-277515		10/1999
JP	2981002	B2	11/1999
JP	2000-34107		2/2000
JP	2000508259	T	7/2000
JP	2000279796	A	10/2000
JP	2001010867	A	1/2001
JP	2001-172604	A	6/2001
JP	2001172604		6/2001
JP	2002-080617	A	3/2002
JP	2002-097372	A	4/2002
JP	3290127	B2	6/2002
JP	2002-198619	A	7/2002
JP	2003518185	T	6/2003
JP	2005036016		2/2005
PT	96113	A	9/1991
SU	514796		5/1976
WO	97/37828	A1	10/1997
WO	WO 01/46313	A1	6/2001
WO	WO 01/83371		11/2001
WO	02/088234	A1	11/2002
WO	2005/021428	A1	3/2005
WO	2006023860		3/2006
WO	WO 2006/117117	A1	11/2006

OTHER PUBLICATIONS

G.L. Messing, "Calcination and Phase Transformation", pp. 887-893, Edited by Buschow et al (2001) Encyclopedia of Materials—Science and Technology, vols. 1-11, (Knovel release date Sep. 12, 2008), Elsevier, Online version @ http://www.knovel.com/web/portal/browse/display?_EXT_KNOVEL_DISPLAY_bookid=1871&VerticalID=0.*

Machine Translation of Publ. No. JP 07-157369, published Jun. 1995, Japan patent Office, Tokyo, Japan, obtained online @ <http://www19.ipdl.inpit.go.jp/PA1/cgi-bin/PA1INDEX> (Downloaded Oct. 25, 2011).*

Carborundum Boron Nitride Data Sheet, "Cosmetic Grade Boron Nitride Powders" (Jun. 1998).

Hagio et al., "Sintering of the Mechanochemically Activated Powders of Hexagonal Boron Nitride," *J. Am. Ceram. Soc.* 72(8):1482-84 (1989).

Jimenez, I. et al., "Core-level photoabsorption study of defects and metastable bonding configurations in boron nitride", *The American Physical Society*, 1997, pp. 12 025-12 037, vol. 55, No. 18.

Rosenbaum, E. et al., "Boron nitride as a processing aid for the extrusion of polyolefins and fluoropolymers", *Polymer Engineering & Science*, Jan. 2000, vol. 40, No. 1, pp. 179-190.

Rudin, "Fluorocarbon elastomer aids polyolefin extrusion", *Plastics Engineering*, Mar. 1, 1986, pp. 63-66, Society of Plastics Engineers, Inc., Greenwich, CT, US.

"Silicones & Silicon-Containing Polymers," Petrarch Systems Silanes and Silicones: Silicon Compounds Register & Review (1987).

Trice, Rodney. et al., "Investigation of the Physical and Mechanical Properties of Hot-Pressed Boron Nitride/Oxide Ceramic Composites", *J. Am. Ceram. Soc.*, 1999, pp. 2563-2565, vol. 82, No. 9.

Masters K: "Spray Drying Hand Book" 1985, Longman Scientific & Technical New York, XP002386938, p. 171, first paragraph.

"AlSiC Microwave Packages," *Microwave Journal* pp. 39(6):90,92,94 (1996), (Jun. 1996).

Bathe et al., "BN Protective Coating for High Temperature Applications," *Mat. Res. Soc., Symp. Proc.* 697:61-6 (2002).

Combat Boron Nitride Powders Specifications, Carborundum, p. 1 only (1990), (Jun. 1995).

"Boron," *Ceramic Industry Materials Handbook* pp. 62,64 (1997), (Jan. 1997).

Engler et al., "Hexagonal Boron Nitride (hBN)—Applications from Metallurgy to Cosmetics," *Ceramic Forum International* 84(12):E49-E53 (2007).

Georgeoni et al., "Sintered Materials Based on the Hexagonal and Cubic Boron Nitride," *Powder Metallurgy* pp. 247-249 (1994).

Hagio et al., "Sintered BN Products Obtained from a Ground BN Powder and Its Sintering Processes," *Journal of the Ceramic Society of Japan* 162(10):940-3 (1994).

Hagio & Yoshida, "Sintering and Crystallization of Ground Hexagonal Boron Nitride Powders," *Journal of Materials Science Letters* 13:653-5 (1994).

Itoh et al., "Effects of Added c-BN Seed Crystals on the Reaction Sintering of c-BN Accompanied by a Conversion from h-BN to c-BN," *Journal of Materials Science* 25:203-6 (1990).

Hubáček & Ueki, "Pressureless-Sintered Boron Nitride with Limited Content of Boric Oxide," *Materials Science Research International* 1(4):209-12 (1995).

Kabyshev et al., "Physical Properties of Polycrystalline Cubic Boron Nitride," *Inorganic Materials* 32(2):146-50 (1996).

Morgiel & Benko, "Microstructure of Boron Nitride Sintered with Titanium," *Materials Letters* 25:49-52 (1995), (Oct. 1995).

Ohsawa et al., "Sintering of hBN Using Polysilazane," *Journal of the Ceramic Society of Japan* 102:646-9 (1994).

Olszyna, "Deposition of BN Coatings by Spraying a Powder Accelerated Electrostatically in a Coaxial Pulse Plasma Generator," *Thin Solid Films* 277:79-82 (1996).

Dean et al., "Novel Thermal Interface Material with Aligned Conductive Fibers," Johnson Matthey Electronics, Spokae, WA, International Symposium on Microelectronics, SPIE Proceedings Series 3906:462-467 (1999).

International Preliminary Examination Report for International Patent Application No. PCT/US01/14041 (Nov. 16, 2002), PCT Appl. published as WO 0183371 A2.

International Search Report for International Patent Application No. PCT/US01/14041 (Dec. 7, 2001), PCT Appl. published as WO 0183371 A2.

International Search Report for International Patent Application No. PCT/US02/23396 (Dec. 13, 2002), PCT Appl. published as WO 03013845 A1.

International Search Report for International Patent Application No. PCT/US2004/026765 (Dec. 3, 2004), PCT Appl. published as WO 2005021428 A1.

Machine Translation of EP 0 396 448 A (Disclosure and Claims), obtained online @ <http://ep.espacenet.com/>, EP 0 396 448 A published Nov. 1990, Machine Translation downloaded Feb. 4, 2010.

Miyazaki et al., "Microstructure of Pressureless Sintered h-BN," *Journal of the Ceramic Society of Japan, Int. Edition* 99:566-9 (1991).

(56)

References Cited

OTHER PUBLICATIONS

- Rosenbaum et al., "A New Processing Additive Eliminating Surface and Gross Melt Fracture in the Extrusion of Polyolefins and Fluoropolymers," ANTEC (1998).
- Rosenbaum et al., "Boron Nitride as a Processing Aid for the Extrusion of Polyolefins and Fluoropolymers," Rapra Abstracts, Pergamon Press Ltd:Oxford, GB p. 168 (Jun. 2000).
- Seth et al., "The effect of Surface Energy of Boron Nitride Powders on Gross Melt Fracture Elimination," ANTEC (2001).
- Supplementary European Search Report for European Patent Application No. EP02756606 (Sep. 17, 2009) EP Appl. published as EP 1417093 A1.
- Supplementary Partial European Search Report for European Patent Application No. EP02756606 (Jun. 29, 2006) EP Appl. published as EP 1417093 A1.
- Written Opinion for International Patent Application No. PCT/US02/23396 (Jun. 3, 2003), PCT Appl. published as WO 03013845 A1.
- Written Opinion for International Patent Application No. PCT/US2004/026765 (Dec. 3, 2004) PCT Appl. published as WO 2005021428 A1.
- Yip et al., "Effect of Combining Boron Nitride with Fluoroelastomer on the Melt Fracture of HDPE in Extrusion Blow Molding," J. Vinyl & Additive Tech. 6(4):196-204 (2000).
- Yip et al., "The Effect of the Boron Nitride Type and Concentration of the Rheology and Processability of Molten Polymers," ANTEC 1999, Tech. Papers 45 New York (1999).
- Phone Call Report (Oct. 20, 1998), shipment information (Oct. 23, 1998) for XP-1115 and Experimental Product Analysis (Oct. 23, 1998).
- Quotation (Dec. 2, 1999), Request for Quotation Form for Item 1, Item 2, and Item 3 (Nov. 30, 1999), Experimental Product Analysis for XP1101 (Oct. 18, 1999) and Experimental Product Analysis for XP 1123 (Nov. 12, 1999).
- Quotation (Jun. 5, 1998) and Request for Quotation Form (May 15, 1998) with Phone Call Report (May 15, 1998), Experimental Product Analysis for XP1101 (May 8, 1998), and Experimental Product Analysis for XP1101 (May 26, 1998).
- Quotation (May 19, 1999) and Experimental Product Analysis for XP1104 (May 18, 1999).
- Tres BN Boron Nitride Powder, 2 pages, Carborundum Corporation, Amherst, NY (May 1998).
- Combat Boron Nitride Powders Specifications, Carborundum, p. 1-2 (1990).
- Machine Translation of Pub. No. EP 0 432 007 A1, published Jun. 1991, European Patent Office, obtained online at @ http://ep.espacenet.com/numberSearch?locale=en_EP (Downloaded Dec. 6, 2010), pp. 1-4.
- Derwent Abstract on East, London: Derwent Publications Ltd., AN1978-04412A, DE 2629960 A (Moscow Mendeleev Chem IN), abstract.
- Translation of First Office Action, Chinese Patent Application No. 02815595.5, 8 pages (Jun. 3, 2005).
- Translation of Second Office Action, Chinese Patent Application No. 02815595.5, 5 pages (Jan. 20, 2006).
- Translation of Third Office Action, Chinese Patent Application No. 02815595.5, 5 pages (May 26, 2006).
- Translation of First Office Action, Chinese Patent Application No. 200710004476.2, 8 pages (Aug. 22, 2008).
- Translation of Second Office Action, Chinese Patent Application No. 200710004476.2, 8 pages (Jun. 28, 2011).
- Notice of Requisition, Canadian Patent Application No. 2,455,794, 4 pages (Jan. 12, 2007).
- Notice of Requisition, Canadian Patent Application No. 2,455,794, 3 pages (Nov. 13, 2007).
- Notice of Requisition, Canadian Patent Application No. 2,455,794, 1 page (Jul. 13, 2009).
- Notice of Reasons for Rejection (Translation), Japanese Patent Application No. 2003-518818, 11 pages (Sep. 4, 2007).
- Notice of Reasons for Rejection (Translation), Japanese Patent Application No. 2003-518818, 12 pages (May 7, 2008).
- Notice of Reasons for Rejection (Translation), Japanese Patent Application No. 2003-5188186 pages (Jan. 6, 2009).
- Decision of Final Rejection (Translation), Japanese Patent Application No. 2003-518818, 6 pages (Aug. 11, 2009).
- Communication Pursuant to Article 94(3) EPC, European Patent Application No. 02756606.6, 4 pages (Jul. 5, 2010).
- Communication Pursuant to Article 94(3) EPC, European Patent Application No. 02756606.6, 6 pages (Dec. 7, 2010).
- Final Office Action, U.S. Appl. No. 12/542,424, 16 pages (Feb. 2, 2011).
- Non-Final Office Action, U.S. Appl. No. 12/542,424, 16 pages (Mar. 22, 2010).
- Non-Final Office Action, U.S. Appl. No. 12/542,424, 24 pages (Jan. 25, 2012).
- Japanese Unexamined Patent Application Publication No. JP 2001-122615 (May 8, 2001).
- Japanese Unexamined Patent Application Publication No. JP 11-269302 (Oct. 5, 1999).
- Japanese Unexamined Patent Application Publication No. JP 2000-63180 (Feb. 29, 2000).
- GE Advanced Ceramics, "PolarTherm Thermally Conductive Boron Nitride Fillers for Polymeric Materials," Brochure (1997).
- Alkoy et al., "Crystallization Behavior and Characterization of Turbostratic Boron Nitride," J. of European Ceramic Society 17(12):1415-1422 (1997).
- Hubacek et al., "Hypothetical Model of Turbostratic Layered Boron Nitride," J. Ceramic Soc. Japan 104(8):695-698 (1996).
- Hagio et al., "Microstructural Development With Crystallization of Hexagonal Boron Nitride," J. Mat. Sci. Lett. 16:795-798 (1997).
- Japanese Unexamined Patent Application Publication No. 2006-257392 (Sep. 28, 2006).
- Japanese Unexamined Patent Application Publication No. 2007-182369 (Jul. 19, 2007).
- Japanese Unexamined Patent Application Publication No. 2008-510878 (Apr. 10, 2008).
- NO 905289 (abstract only) (Jun. 10, 1991).
- Notification (translation) and Information Statement Japanese Patent Application No. 2009-282105, 9 pages (Jan. 17, 2012).
- MatSE 411, Processing of Ceramics, Penn State Undergraduate Course Notes, Glossary, Unit 1, p. 73 (2010).
- GE Advanced Ceramics, "PolarTherm Thermally Conductive Boron Nitride Fillers for Polymeric Materials," Brochure, 2 pages, Pub. No. 81501 (Sep. 2003).
- GE Advanced Ceramics Worldwide, PolarTherm Thermally Conductive Fillers, http://www.advceramics.com/geac/products/polartherm_fillers/, 4 pages (accessed Sep. 5, 2006).
- GE Advanced Materials, PolarTherm XLR Boron Nitride Filler PTX60, 1 page, Pub. 82530U Rev. 3 (Feb. 2005).
- GE Advanced Materials, PolarTherm XLR Boron Nitride Filler PTX25, 1 page, Pub. 82530V Rev. 3 (Mar. 2005).
- Partial European Search Report, European Patent Application No. 12175111.9, 5 pages (Sep. 17, 2012).
- Final Office Action, U.S. Appl. No. 12/542,424, USPTO, Alexandria, VA, USA, 13 pages (Nov. 1, 2012).
- Notice of Reasons for Rejection (Translation), Japanese Patent Application No. 2009-282105, 5 pages (Sep. 19, 2012).
- Notice of Reasons for Rejection (Translation), Japanese Patent Application No. 2008-286337, 5 pages (Jul. 17, 2012).
- Extended European Search Report for European Patent Application Serial No. 1217511.9 (Dec. 3, 2013).
- Examiner's Answer for U.S. Appl. No. 12/542,424 (Sep. 20, 2013).
- Notice of Reasons for Rejection (Translation), Japanese Patent Application No. 2008-286337 (Dec. 20, 2011).
- Communication for European Patent Application No. 02756606.6 (Dec. 2, 2013).
- Japanese Publication No. JP 2001-274300 (abstract) Oct. 2001, Patent abstracts of Japan.
- Office Action for U.S. Appl. No. 12/542,424 dated Jul. 22, 2014.

* cited by examiner

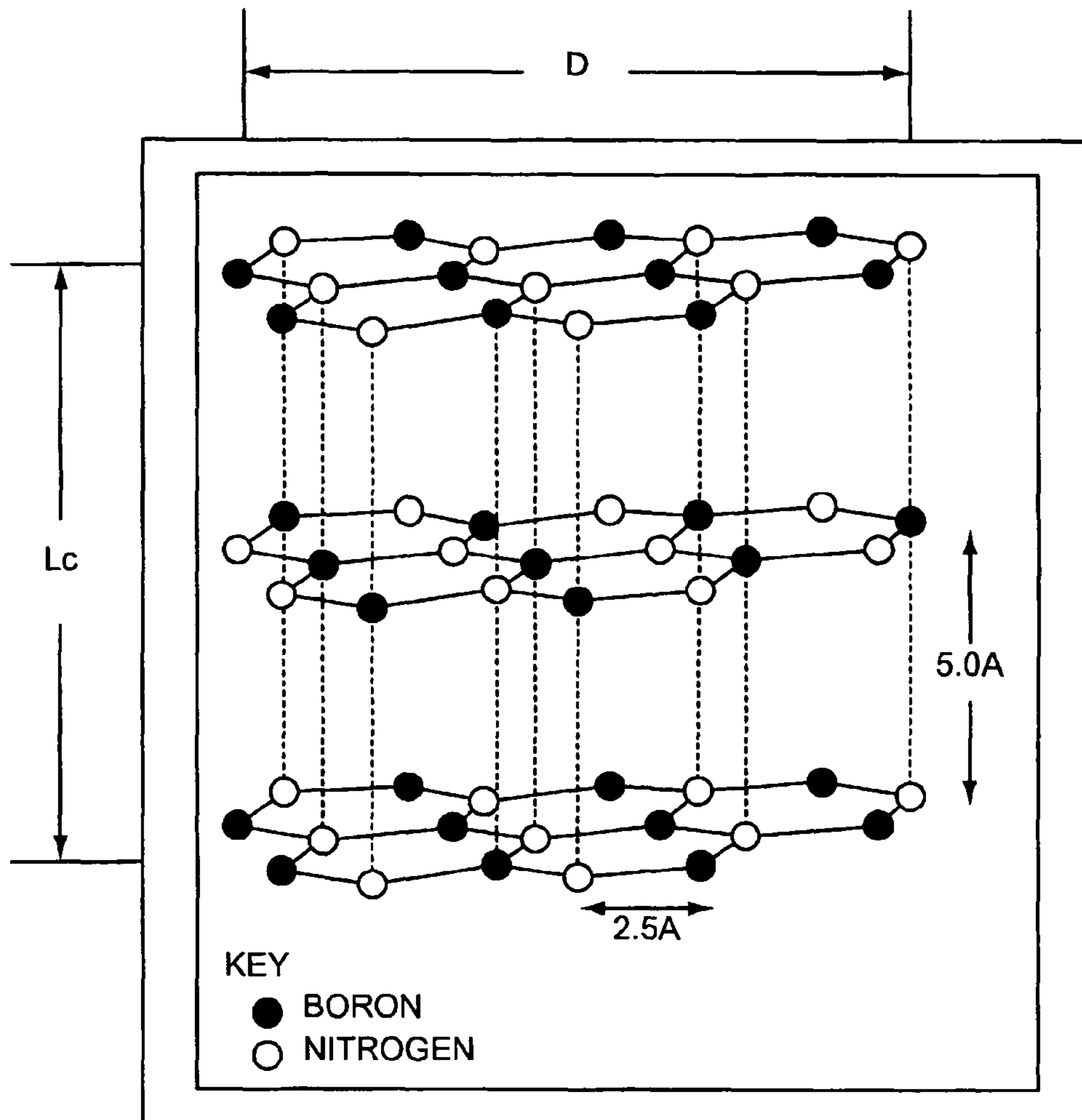
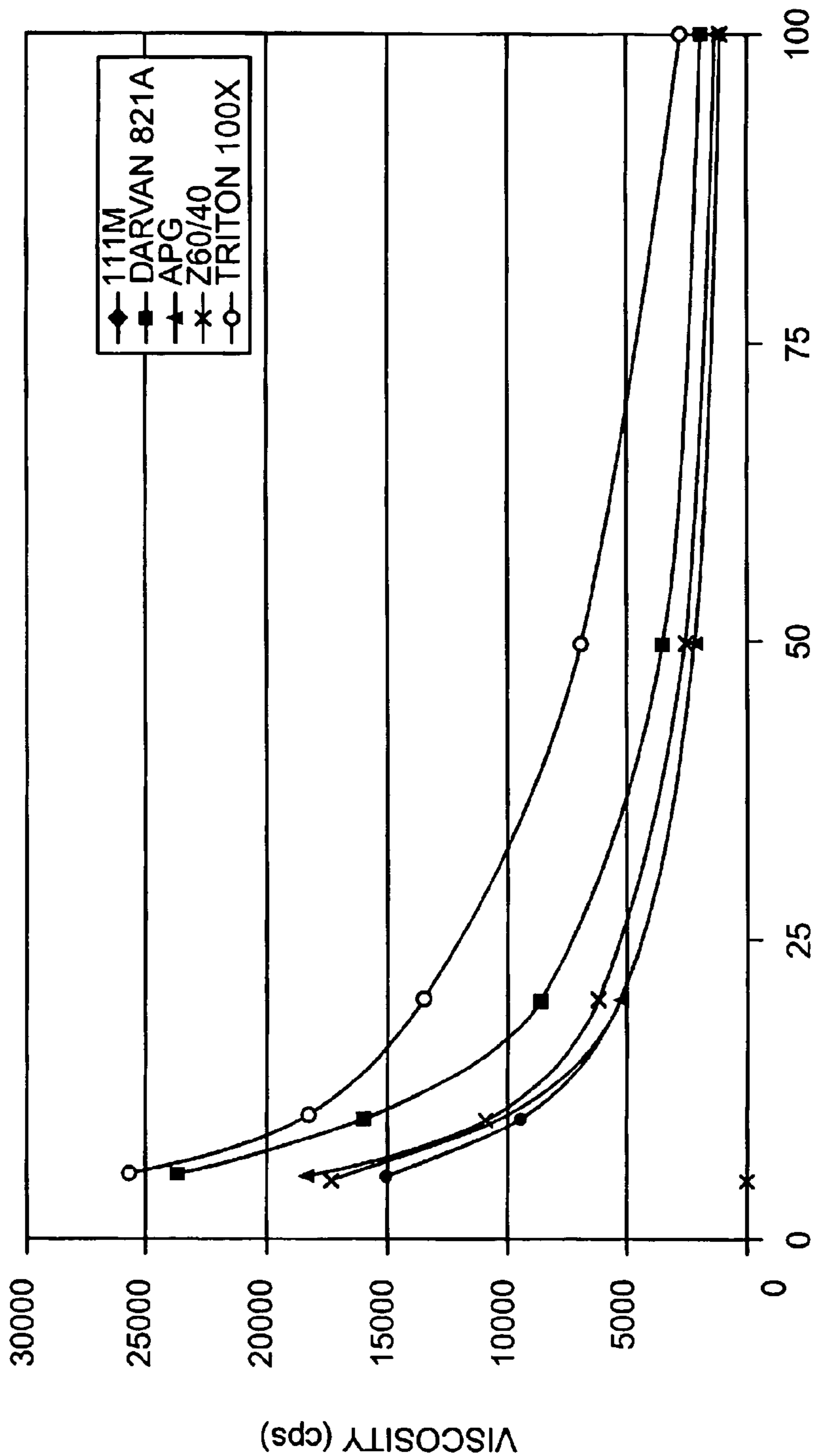


FIG. 1



SHEAR RATE

FIG. 2

**HIGH SOLIDS HBN SLURRY, HBN PASTE,
SPHERICAL HBN POWDER, AND METHODS
OF MAKING AND USING THEM**

Matter enclosed in heavy brackets [] appears in the original patent but forms no part of this reissue specification; matter printed in italics indicates the additions made by reissue; a claim printed with strikethrough indicates that the claim was canceled, disclaimed, or held invalid by a prior post-patent action or proceeding.

More than one reissue application has been filed for reissuance of U.S. Pat. No. 6,645,612. U.S. Reissue application Ser. No. 12/542,424, filed Aug. 17, 2009, is co-pending with the present reissue application.

FIELD OF THE INVENTION

The present invention relates to a method for making a hexagonal boron nitride slurry, a method for making a hexagonal boron nitride paste, and a method for making a spherical hexagonal boron nitride powder. The present invention also relates to the resulting hexagonal boron nitride slurry, paste, and spherical hexagonal boron nitride powder, and the use of the spherical hexagonal boron nitride powder in a polymer blend and system including a heat source and a heat sink.

BACKGROUND OF THE INVENTION

Microelectronic devices, such as integrated circuit chips, are becoming smaller and more powerful. The current trend is to produce integrated chips which are steadily increasing in density and perform many more functions in a given period of time over predecessor chips. This results in an increase in the electrical current used by these integrated circuit chips. As a result, these integrated circuit chips generate more ohmic heat than the predecessor chips. Accordingly, heat management has become a primary concern in the development of electronic devices.

Typically, heat generating sources or devices, such as integrated circuit chips, are mated with heat sinks to remove heat which is generated during their operation. However, thermal contact resistance between the source or device and the heat sink limits the effective heat removing capability of the heat sink. During assembly, it is common to apply a layer of thermally conductive grease, typically a silicone grease, or a layer of a thermally conductive organic wax to aid in creating a low thermal resistance path between the opposed mating surfaces of the heat source and the heat sink. Other thermally conductive materials are based upon the use of a binder, preferably a resin binder, such as a silicone, a thermoplastic rubber, a urethane, an acrylic, or an epoxy, into which one or more thermally conductive fillers are distributed.

Typically, these fillers are one of two major types: thermally conductive, electrically insulative or thermally conductive, electrically conductive fillers. Aluminum oxide, magnesium oxide, zinc oxide, aluminum nitride, and boron nitride are the most often cited types of thermally conductive, electrically insulative fillers used in thermal products. Boron nitride, and, more specifically, hexagonal boron nitride (hBN) is especially useful in that it has excellent heat transfer characteristics and is relatively inexpensive.

For fillers, it is desirable to achieve as high a thermal conductivity (or as low a thermal resistant) as possible. In

order to achieve sufficient thermal conductivity with presently used fillers, such as hBN, it is desirable to employ high loadings of filler in the binder. However, because of the flaky (platelet) structure of hBN particles, achieving solids loading higher than 20 vol. % becomes difficult.

U.S. Pat. Nos. 5,898,009, 6,048,511, and European Patent No. EP 0 939 066 A1, all to Shaffer et al., teach an alternate methodology to further improve solids hBN loading. This involves: (a) cold pressing crushed hBN powder, (b) breaking the cold pressed compact into smaller pieces, and (c) screening the resulting pieces to achieve agglomerates in a desired size range. These agglomerates, however, are non-spherical (angular shape) with jagged short edges. This shape is not ideal for optimizing solids loading due, primarily, to the following reasons: (1) non-spherical shaped agglomerates do not slide against each other easily, thus raising the viscosity; and (2) non-spherical shaped agglomerates have higher surface area and hence absorb greater amounts of polymer on their surface which results in lower amounts of free available polymer, thus, once again raising the viscosity.

Thus, there is a need for thermally conductive filler materials which can be used at high loading levels to achieve sufficient thermal conductivity without increasing viscosity. The present invention is directed to overcoming this deficiency in the art.

SUMMARY OF THE INVENTION

The present invention relates to a method for making a hexagonal boron nitride slurry. The method involves mixing from about 0.5 wt. % to about 5 wt. % surfactant with about 30 wt. % to about 50 wt. % hexagonal boron nitride powder in a medium under conditions effective to produce a hexagonal boron nitride slurry.

The present invention also relates to a hexagonal boron nitride slurry including from about 0.5 wt. % to about 5 wt. % surfactant and about 30 wt. % to about 50 wt. % hexagonal boron nitride powder in a medium.

Another aspect of the present invention is a method for making spherical boron nitride powder which includes providing a hexagonal boron nitride slurry, spray drying the slurry under conditions effective to produce spherical boron nitride powder, including spherical agglomerates of boron nitride platelets, and sintering the spherical boron nitride powder.

Yet another aspect of the present invention relates to a spherical boron nitride powder including spherical agglomerates of boron nitride platelets.

The present invention also relates to a method for making a hexagonal boron nitride paste. This method involves providing a hexagonal boron nitride slurry and treating the slurry under conditions effective to produce a hexagonal boron nitride paste including from about 60 wt. % to about 80 wt. % solid hexagonal boron nitride.

Another aspect of the present invention relates to a hexagonal boron nitride paste including from about 60 wt. % to about 80 wt. % solid hexagonal boron nitride in a medium.

The present invention further relates to a polymer blend including a polymer and a powder phase including spherical agglomerates of hexagonal boron nitride platelets. The powder phase is distributed homogeneously within the polymer.

Another aspect of the present invention relates to a system including a heat source, a heat sink, and a thermally conductive material connecting the heat source to the heat sink, wherein the thermally conductive material includes a powder phase including spherical agglomerates of hexagonal boron nitride platelets.

The hexagonal boron nitride slurry of the present invention allows high solids loading while keeping low viscosity. In addition, the slurry can be used to produce high yields of hexagonal boron nitride powder and paste. The spherical shape of the hBN agglomerates of the present invention reduces inter-agglomerate friction, thus allowing higher solids loading in a polymer and, accordingly, higher thermal conductivity. In addition, spherical shaped hBN agglomerates have the lowest surface area possible, which reduces the amount of adsorbed polymer on the agglomerate surfaces, thus freeing up more polymer to improve flowability/reduce viscosity. Moreover, in the spherical hBN powder of the present invention, the distribution of hBN platelets in the spherical agglomerates is random (as compared to aligned flakes in pressed agglomerates of the prior art). Thus, spherical hBN filled polymer in accordance with the present invention should show more isotropic thermal conductivity and higher thermal conductivity through the thickness of the polymer.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a graphic showing the structure of boron nitride, where many of these units make up a BN platelet.

FIG. 2 is a graph showing the rheological properties of a 50% solids BN slurry with various surfactants.

DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to a method for making a hexagonal boron nitride slurry. The method involves mixing from about 0.5 wt. % to about 5 wt. % surfactant with about 30 wt. % to about 50 wt. % hexagonal boron nitride powder in a medium under conditions effective to produce a hexagonal boron nitride slurry.

As used herein, a slurry is a thin mixture or suspension of a liquid (i.e., aqueous or non-aqueous medium) and insoluble matter.

Hexagonal boron nitride is an inert, lubricious ceramic material having a platey hexagonal crystalline structure (similar to that of graphite) ("hBN"). The well-known anisotropic nature of hBN can be easily explained by referring to FIG. 1, which shows hexagons of an hBN particle. The diameter of the hBN particle platelet is the dimension shown as D in FIG. 1, and is referred to as the a-direction. BN is covalently bonded in the plane of the a-direction. The particle thickness is the dimension shown as Lc, which is perpendicular to diameter and is referred to as the c-direction. Stacked BN hexagons (i.e., in the c-direction) are held together only by Van der Waals forces, which are relatively weak. When a shearing force greater than the weak Van der Waals force is imparted across of the planes of BN hexagons, the weak Van der Waals force is overcome and the planes slide relative to each other. The relative ease with which these planes of BN slide against each other may be one of the reasons for the high lubricity of hBN.

Preferably, the hBN is a powder having a highly ordered hexagonal structure. Such powders have a crystallization index (Hubacek, "Hypothetical Model of Turbostratic Layered Boron Nitride," J. Cer. Soc. of Japan, 104:695-98 (1996), which is hereby incorporated by reference in its entirety) of at least 0.12 (quantification of highly hexagonal hBN) and, preferably, greater than 0.15. Preferably, the hBN powder has a crystallinity of about 0.20 to about 0.55, most preferably, from about 0.30 to about 0.55.

Typically, this starting powder is produced by a "high fire" treatment of a raw, essentially turbostratic (amorphous) boron

nitride powder (see Hagio et al., "Microstructural Development with Crystallization of Hexagonal Boron Nitride," J. Mat. Sci. Lett. 16:795-798 (1997), which is hereby incorporated by reference in its entirety) to produce what is conventionally referred to as "high purity hexagonal boron nitride." In a preferred embodiment, a fine turbostratic BN powder having a crystallization index of less than 0.12 is heat treated in nitrogen at about 1400 to 2300° C. for about 0.5-12 hours. This heat treatment typically acts to produce a more crystalline hBN platelets, as the fine, <1 μm crystallites, of turbostratic powder platelets become more ordered (crystallized) and larger (>1 micron) during the heat treatment.

Preferably, the particles of the hBN starting material have an average particle-platelet size of from about 2 μm to about 20 μm, more preferably between about 2 μm and 12 μm, and most preferably, between about 4 μm and about 12 μm. As used herein, "particle size" or "diameter" of the hBN particle platelet is the dimension shown as D in FIG. 1. This is typically measured by scanning electron microscopy and laser scattering techniques using, e.g., a Leeds & Northrup Microtrac X100 (Clearwater, Fla.).

In another embodiment, the hBN starting material has an oxygen content of from about 0 wt. % to about 1.0 wt. %, preferably, from about 0 wt. % to about 0.5 wt. %. The use of hBN starting material with a low oxygen content produces boron nitride powders with a higher tap density. Higher tap density powders have many advantages as fillers in thermal management applications including: higher thermal conductivity, higher powder loading in a polymer; stronger agglomerates of hBN platelets (leading to improved metal adhesion in polymer BN composites); and lower porosity within the agglomerates (which results in less infiltration of polymer resin or liquid into the agglomerate).

Preferably, the hBN slurry of the present invention includes from about 40 wt. % to about 50 wt. % hexagonal boron nitride powder.

In yet another embodiment, the hBN starting material has a surface area of from about 5 m²/g to about 30 m²/g, and more preferably, about 7 m²/g to about 20 m²/g.

The hBN slurry of the present invention may include an aqueous or non-aqueous medium. Suitable non-aqueous medium include isopropyl alcohol, methanol, and ethanol.

The hexagonal boron nitride slurry of the present invention is a "high solids" hBN slurry which, in one embodiment, includes from about 30 wt. % to about 50 wt. % hexagonal boron nitride solids loading. In another embodiment, the high solids hexagonal boron nitride slurry of the present invention includes from about 40 wt. % to about 50 wt. % hexagonal boron nitride solids loading.

Suitable surfactants for the above method of the present invention include polycarboxylic acids (e.g., Rhodamine 111M™ available from Rhodia, Inc., Cranbury, N.J.), silanes (e.g., Z-6040 Silane™ available from Dow Chemical, Midland Mich.), and organometallic compounds (e.g., APG™ available from Cavedon Chemical Co., Woonsocket, R.I.).

The hBN slurry of the present invention may include additives, such as binders and sintering additives. Suitable binders include polyethylene glycol, polyvinyl alcohol, glycerol, and latex. When the hBN slurry of the present invention is used to produce hBN powder, the slurry may contain sintering additives which include, but are not limited to, yttria, CaO, MgO, CeB₆, and boron.

The present invention also relates to a hexagonal boron nitride slurry including from about 0.5 wt. % to about 5 wt. % surfactant and about 30 wt. % to about 50 wt. % hexagonal boron nitride powder in a medium.

The hBN slurry of the present invention achieves high solids loading while keeping low viscosity. In particular, solids loading of from about 30 wt. % to about 50 wt. % is achieved in the high solids hBN slurry of the present invention. Although not wishing to be bound by theory, it is believed that because of the flaky, non-wettable nature of hBN, the use of from about 0.5 wt. % to about 5 wt. % surfactant in the slurry of the present invention allows such high solids loading. This is in contrast to prior art methods which used about 0.1 wt. % to about 0.5 wt. % surfactant to achieve a BN solids loading of from about 20 wt. % to about 25 wt. %.

The high solids hBN slurry of the present invention may be used to produce high yields of hexagonal boron nitride powder and paste, as described in detail below.

Another aspect of the present invention relates to a method for making spherical boron nitride powder which includes providing a hexagonal boron nitride slurry, spray drying the slurry under conditions effective to produce spherical boron nitride powder including spherical agglomerates of boron nitride platelets, and sintering the spherical boron nitride powder.

As used herein, an agglomerate is a collection of boron nitride platelets bonded together. A non-agglomerated boron nitride platelet comprises one or more crystallites.

In one embodiment, the spherical agglomerates of boron nitride platelets have an average agglomerate size or diameter of from about 10 microns to about 500 microns.

In another embodiment, the majority of boron nitride agglomerates have an average diameter of from about 30 microns to about 150 microns.

The hexagonal boron nitride slurry is preferably a high solids hexagonal boron nitride slurry in accordance with the present invention.

Techniques for spray drying are known in the art and are described in, for example, James S. Reed, *Introduction to the Principles of Ceramic Processing*, John Wiley & Sons, Inc. (1988), which is hereby incorporated by reference in its entirety.

Preferably, the sintering is carried out at a temperature of at least about 1800° C. for about 1 to about 4 hours, more preferably, for about 2 to about 3 hours. Further, the sintering is preferably carried out at from about 1800° C. to about 2400° C., more preferably, from about 2000° C. to 2400° C., most preferably, from about 2000° C. to about 2100° C. Suitable atmospheres for sintering include inert gas, nitrogen, and argon. In one embodiment, the sintering is carried out in a vacuum. In another embodiment, the sintering is carried out under conditions of at least 1 atmosphere of pressure.

The resulting powder tap density preferably ranges from about 0.4 g/cc to about 0.7 g/cc.

In accordance with the present invention, the sintering step improves the thermal diffusivity and, thus, thermal conductivity of the resulting boron nitride powder and hardens and strengthens the boron nitride powder. Although not wishing to be bound by theory, it is believed that during sintering, individual grains of boron nitride grow into each other to form an interconnected network. The interconnectivity of the resulting sintered body results in increased thermal diffusivity and increased thermal conductivity.

In one embodiment, the spherical boron nitride powder is classified under conditions effective to obtain a desired agglomerate size distribution. As used herein, an agglomerate size distribution is the range of agglomerates from the smallest agglomerate present to the largest agglomerate present, as defined by characteristic diameter of the agglomerates, wherein the agglomerates span the range. Suitable methods

for classification include screening, air classifying, and elutriation, (see Chem. Eng. Handbook, Perry & Chilton, 5th Ed., McGraw-Hill (1973), which is hereby incorporated by reference in its entirety). As such classification methods are well known in the art, they will only be discussed briefly herein.

Screening is the separation of a mixture of various sized solid particles/agglomerates into two or more portions by means of a screening surface. The screening surface has openings through which the smaller particles/agglomerates will flow, while the larger particles/agglomerates remain on top. This process can be repeated for both the coarse and small particle/agglomerate size streams, as many times as necessary, through varying screen openings to obtain a classification of particles/agglomerates into a desired particle/agglomerate size range.

Air classifiers rely upon air drag and particle inertia, which depends upon particle/agglomerate size, to facilitate the separation of fine particles/agglomerates from coarse particles/agglomerates.

One design for elutriation is a vertical gravity type elutriator, where fluid flowing up through a column carries fine particles/agglomerates smaller than a critical size. The critical size is determined by the settling velocity of the particle/agglomerate in the fluid.

A desired agglomerate range or agglomerate size distribution (ASD) is determined by the intended use of the spherical boron nitride powder. For example, for compliant interface pads, where the polymer is a low durometer silicone rubber, the desired ASD is such that the coarsest agglomerate diameter is smaller than the thickness of the interface pad. For situations in which flexibility of a polymer including the spherical boron nitride is important, large agglomerates, e.g., above 150 microns, are reduced in concentration or removed entirely, as the use of smaller agglomerates improves flexibility of the resulting polymer blend. In addition, a plurality of agglomerate size ranges may be combined in the spherical boron nitride powder to achieve the desired flexibility and thermal conductivity, as smaller agglomerates will fit within the interstitial spaces of the larger agglomerates.

Preferably, the ASD is 30 to 125 microns (more preferably 74 to 125 microns, most preferably 74 to 105 microns), or 20 to 74 microns (more preferably 38 to 74 microns, most preferably 38 to 53 microns), or 10 to 38 microns (more preferably 20 to 38 microns).

The present invention also relates to a spherical boron nitride powder including spherical agglomerates of boron nitride platelets.

The spherical boron nitride powder of the present invention can be used as a filler for thermal management applications, e.g., in composites, polymers, and fluids, as described below. The spherical boron nitride powder can also be used in hot pressing, due to the improved packing density and uniform fill characteristics of the powder. Moreover, the resulting spherical boron nitride powder can be used as precursor feed stock material in the conversion of hexagonal boron nitride to cubic boron nitride. In the conversion of high purity hexagonal boron nitride to cubic boron nitride, the compacted form of boron nitride is subjected to extremely high pressures and temperatures within the stable region of the cubic boron nitride phase diagram. The density of the boron nitride pellets is significant to the economics of the cubic boron nitride conversion process.

Another aspect of the present invention is a method for making a hexagonal boron nitride paste. This method involves providing a hexagonal boron nitride slurry and treating the slurry under conditions effective to produce a hexago-

nal boron nitride paste including from about 60 wt. % to about 80 wt. % solid hexagonal boron nitride.

As used herein, as paste is a semisolid preparation.

The hexagonal boron nitride slurry is preferably a high solids hexagonal boron nitride slurry in accordance with the present invention.

In one embodiment, treating comprises placing the slurry in a plaster slip cast mold. The plaster mold will absorb water from the slurry to produce a hexagonal boron nitride paste according to the present invention. Knowing the porosity of the mold, e.g., from about 1 to about 5 μm , the solids content of the hexagonal boron nitride paste can be controlled by the casting time.

In another embodiment, treating comprises vacuum filtration of the slurry until the desired amount of liquid is removed from the slurry to produce a hexagonal boron nitride paste according to the present invention.

Yet another aspect of the present invention relates to a hexagonal boron nitride paste including from about 60 wt. % to about 80 wt. % solid hexagonal boron nitride in a medium.

The hBN paste of the present invention may include an aqueous or non-aqueous medium. Suitable non-aqueous medium include isopropyl alcohol, methanol, and ethanol.

Preferably, the hexagonal boron nitride paste includes from about 65 wt. % to about 75 wt. % solid hexagonal boron nitride.

The hexagonal boron nitride paste of the present invention can be used to form solids of varying shapes, e.g., by an extrusion process. Such solids can then be used, for example, as a filler in thermal management applications.

The present invention further relates to a polymer blend including a polymer and a powder phase including spherical agglomerates of hexagonal boron nitride platelets. The powder phase is distributed homogeneously within the polymer.

Suitable polymer systems may include melt-processable polymers, polyesters, phenolics, silicone polymers (e.g., silicone rubbers), acrylics, waxes, thermoplastic polymers, low molecular weight fluids, and epoxy molding compounds.

In one embodiment, the polymer blend comprises from about 30 wt. % to about 80 wt. % spherical boron nitride powder. However, the loading of the spherical boron nitride powder into the polymer blend is determined by the desired flexibility and thermal conductivity of the resulting blend. For example, lower loading of the spherical hBN powder, such as 30 wt. % to 50 wt. %, is desirable for high flexibility applications, but results in lower thermal conductivity. Thus, loading at from about 50 wt. % to about 80 wt. % is desirable in high thermal conductivity/low flexibility applications.

The thermal conductivity of the resulting polymer blend is determined by loading, dispersion, and other factors. In one embodiment, the polymer blend has a thermal conductivity of from about 1 W/mK to about 15 W/mK.

Because of the spherical shape of the hBN agglomerates in the polymer blends of the present invention, inter-agglomerate friction is reduced, thus allowing higher solids loading and, accordingly, higher thermal conductivity.

In addition, spherical shaped hBN agglomerates have the lowest surface area possible, which reduces the amount of adsorbed polymer on the agglomerate surfaces, thus freeing up more polymer to improve flowability/reduce viscosity.

Typically, hBN powder for loading into polymers has been produced by a pressing process (see, e.g., U.S. Pat. Nos. 5,898,009, 6,048,511, and European Patent No. EP 0 939 066 A1 all to Shaffer et al., which are hereby incorporated by reference in their entirety), which produces hBN powder including non-spherical agglomerates of aligned hBN platelets. However, in the spherical hBN powder of the present

invention, the distribution of hBN platelets is random (as compared to aligned flakes in pressed agglomerates). Thus, spherical hBN filled polymer film in accordance with the present invention should show more isotropic thermal conductivity and higher thermal conductivity through the thickness of the polymer.

Another aspect of the present invention relates to a system including a heat source, a heat sink, and a thermally conductive material connecting the heat source to the heat sink, wherein the thermally conductive material includes a powder phase including spherical agglomerates of hexagonal boron nitride platelets.

As used herein, a heat sink is a body of matter, gaseous, liquid, or solid, that receives a heat transfer from its surrounding environment.

Suitable heat sources for the present invention include integrated circuit chips, power modules, transformers, and other electronic devices.

Suitable heat sinks in accordance with the present invention include finned aluminum, copper, beryllium, and diamond.

As used herein, a thermally conductive material may be a composite, polymer, or fluid. In one embodiment, the thermally conductive material is a polymer, such as a melt-processable polymer, a polyester, a phenolic, a silicone polymer (e.g., silicone rubbers), an acrylic, a wax, a thermoplastic polymer, a low molecular weight fluid, or an epoxy molding compound.

The thermally conductive material preferably includes from about 30 wt. % to about 80 wt. % spherical boron nitride powder and has a thermal conductivity of from about 1 W/mK to about 15 W/mK.

EXAMPLES

Example 1

Production of High BN Solids Loaded Slurry

A 50 wt. % solid loaded BN slurry was made using the mix composition as set forth in Table 1:

TABLE 1

Mix composition for 50 wt. % solid loaded BN slurry.			
Solids-50 wt. %		Liquids-50 wt. %	
XP1011 BN ¹	1400 g	85% DI water (pH 9)	1700 g
HPP 325 BN ²	500 g	10% IPA ⁴	200 g
Y ₂ O ₃ ³	100 g	5% 111 M ⁵ (surfactant)	100 g
		Opt. 4% glycerol	

¹Saint-Gobain Ceramics & Plastics, Amherst, NY

²Saint-Gobain Ceramics & Plastics, Amherst, NY

³Molycorp, Inc., Mountain Pass, CA

⁴Alfa Aesar, Ward Hill, MA

⁵Rhodamine 111 M, Rhodia, Inc., Cranbury, NJ

The correct amounts of powders and liquids set forth in Table 1 were measured out. The deionized (DI) water was then pH adjusted to 9-9.5. Surfactant was added to isopropyl alcohol (IPA) in a large "final mix" sized bucket (Nalgene Nunc, Rochester, N.Y.), approximately 10 L. The surfactant/IPA solution was agitated using air powered propeller mixer (Lightnin, Rochester, N.Y.). Powder was slowly added to the surfactant/IPA solution until the solution could no longer accept more powder. This was done to "coat" the majority of the BN powder with a thin layer of IPA, which wets the BN surface easier than DI water. pH balanced DI water was added

as needed maintain a mixable viscosity of slurry. Hand mixing with a spatula may be required to incorporate powder from container wall.

To ensure good mixing, the slurry was pumped through a high shear mill (Netzsch Mill, Netzsch, Inc., Exton, Pa.). Mill times determined "mixedness" and surface area. An auxiliary cooling unit (Chiller, Neslab Instruments, Portsmouth, N.H.) needed to be attached to mill to keep slurry temperature low enough to decrease the evaporation rate of IPA.

After all BN powder was added, the pH of the slurry was measured to be 8.5 and adjusted to 9 by the addition of NaOH. The slurry at this stage appeared quite viscous but exhibited good shear thinning.

The effect of slurry viscosity versus shear rate for several different surfactants was measured. The surfactant content, as shown in Table 1, was 5 wt. % of the of the total solids content. The results are shown in FIG. 2, where Rhodamine 111M™ (Rhodia, Inc., Cranbury, N.J.) proved most effective at reducing viscosity.

Subsequently, the slurry was transferred to a sealed container for use as needed.

Example 2

Mixing of Sintering Additives

The addition of sintering additives to BN powder was ideally done in a slurry form. This helped create a homogeneous blend of BN and sinter aid. If slurry blending was not possible or practical, a dry mixing method was used.

The technique used to make dry mixes depended on the amount of sample required. If the sample size was approximately less than 25 g, a mortar and pestle was used to mix the powders. The powder was mixed like this for 10 minutes then used as needed.

If larger amounts of powder were needed, a paint shaker was used to blend the powders. When using the paint shaker, $\frac{3}{8}$ " Si_3N_4 media was used in a Nalgene Nunc container (Rochester, N.Y.) to assist in blending powders. The amount of media used was approximately $\frac{1}{4}$ the height of the powder column in the Nalgene container. An appropriately sized container was used for each size batch. The paint shaker was set to run for 25 minutes and mixing began. After mixing, Si_3N_4 media was screened out and the powder was collected and pressed. If pressing was difficult, a few weight percent of low molecular weight polyethylene glycol was added in the mixing stage as a binder.

Example 3

Spray Drying of BN Slurry

The BN slurry of Example 1 was spray dried in order to produce a BN powder for die-fill applications. Spray drying also afforded the quickest way to produce a homogeneous, multi-component, pressureless sinter powder system. Although a 50 wt. % solids BN slurry seemed very highly loaded compared to other ceramic systems, it contained significant amounts of water. In order to evaporate all this water in the available residence time, [and] inlet and outlet temperatures had to be increased. Along with these changes, the flow rate of the slurry was slowed down and the revolutions per minute (rpm) of the atomizer increased. In addition, 4 wt. % glycerol was added into the slurry before spray drying if it was going to be used for dry pressing applications. During spray drying, the slurry was constantly mixed.

The inlet temperature was set to 235° C. which gave an outlet temperature of 85° C. The flow rate of the slurry was 60 ml/minute and the atomizer (Pentronix, Detroit, Mich.) was set at 12,500 rpm. These settings generally produced spherical BN powder in the size range of $-150 \mu\text{m}/+30 \mu\text{m}$. The lower end of the scale was quite variable depending on the dust collector damper setting. The powder collected had a moisture content of approximately 0.25-0.5%.

The slurry example outlined above required about 70 minutes to put through the spray dryer under these conditions. The powder yield was about 80% after screening out coarse particles, accounting for wall material, and material collected in the cyclone.

All of the conditions above are only valid for the spray dryer used in the present Example. Minor changes would be needed for work in any other system, which is expected. Larger dryers would allow more flexibility in particle size distribution and higher production rates.

The effect of wt. % boron nitride solids slurry loading on spray dried properties was then tested, as shown in Table 2.

TABLE 2

Effect of wt. % BN solids slurry loading on spray dried properties.

Powder	Solids (wt. %)	LPD (g/cc)	Tap Density (g/cc)	Flow (sec)	Sizing (mm)
A	25	0.462	0.55	55.7	-150/+75
B	25	0.492	0.586	57.4	-75
C	25	n/a	0.541		-45
D	50	0.533	0.62	54	-75
E	50	0.574	0.652	43.2	-150
XP	n/a	0.44	0.562	75.3	-105/+74

Powders B and D, which were screened to the same size, showed that as solids loading increased, the density of the resulting spray dried powder increased.

Example 4

Production of BN Clay-Like Paste by the Slip Cast Method

Slurry from Example 1 was poured into a plaster slip cast mold. Pressure was applied and the set-up left to cast on the order of 12 hours. Because the molds were "blinded" so quickly, casting stopped and no more moisture was removed from the slip. The resultant material was a thick pasty material. The solids content was 76%.

Example 5

Production of BN Clay-Like Paste by the Vacuum Filtration Method

Slurry from Example 1 was poured into a Buchner Funnel with filter paper. A vacuum was pulled on the slurry from below. The water from the system flowed into a graduated flask. When the desired amount of water was removed from the slurry, the vacuum was removed. The BN paste sample, which had a solids content of 74%, was collected and sealed in an airtight bag for later use.

Although preferred embodiments have been depicted and described herein, it will be apparent to those skilled in the relevant art that various modifications, additions, substitutions and the like can be made without departing from the

11

spirit of the invention and these are therefore considered to be within the scope of the invention as defined in the following claims.

What is claimed:

1. A method for making spherical boron nitride powder comprising:

providing a hexagonal boron nitride slurry;
spray drying the slurry under conditions effective to produce spherical boron nitride powder comprising spherical agglomerates of boron nitride platelets; and
sintering the spherical boron nitride powder.

2. The method according to claim 1, wherein the hexagonal boron nitride slurry comprises from about 30 wt. % to about 50 wt. % hexagonal boron nitride powder.

3. The method according to claim 1, wherein the spherical boron nitride powder has a tap density of about 0.4 g/cc to about 0.7 g/cc.

4. The method according to claim 1, wherein the sintering is carried out at a temperature of from about 1800° C. to about 2400° C.

5. The method according to claim 1, wherein the spherical agglomerates of boron nitride platelets have an average agglomerate diameter of from about 10 microns to about 500 microns.

6. The method according to claim 5, wherein the majority of boron nitride agglomerates have an average diameter of from about 30 microns to about 150 microns.

7. The method according to claim 1 further comprising; classifying the spherical boron nitride powder under conditions effective to obtain a desired agglomerate size distribution.

8. The method according to claim 7, wherein the classifying is selected from the group consisting of screening, air classifying, and elutriation.

9. A spherical boron nitride powder comprising *sintered* spherical agglomerates of boron nitride platelets *having an average agglomerate diameter of from about 10 microns to about 500 microns.*

10. The spherical boron nitride powder according to claim 9, wherein the spherical boron nitride powder has a tap density of about 0.4 g/cc to about 0.7 g/cc.

11. The spherical boron nitride powder according to claim 9, wherein the spherical agglomerates of boron nitride platelets have an average agglomerate diameter of from about [10] 150 microns to about 500 microns.

[12. The spherical boron nitride powder according to claim 11, wherein the majority of boron nitride agglomerates have an average diameter of from about 30 microns to about 150 microns.]

[13. A method for making a hexagonal boron nitride paste comprising:

providing a hexagonal boron nitride slurry and treating the slurry under conditions effective to produce a hexagonal boron nitride paste comprising from about 60 wt. % to about 80 wt. % solid hexagonal boron nitride.]

[14. The method according to claim 13, wherein the hexagonal boron nitride slurry comprises from about 30 wt. % to about 50 wt. % hexagonal boron nitride solids loading.]

[15. The method according to claim 13, wherein said treating comprises placing the slurry in a plaster mold.]

[16. The method according to claim 13, wherein said treating comprises vacuum filtration.]

[17. A hexagonal boron nitride paste comprising from about 60 wt. % to about 80 wt. % solid hexagonal boron nitride in a medium.]

[18. The hexagonal boron nitride paste according to claim 17, wherein the medium is an aqueous medium.]

12

[19. The hexagonal boron nitride paste according to claim 18, wherein the medium is a non-aqueous medium selected from the group consisting of isopropyl alcohol, methanol, and ethanol.]

[20. A polymer blend comprising:
a polymer, and

a powder phase comprising spherical agglomerates of hexagonal boron nitride platelets, wherein the powder phase is distributed homogeneously within the polymer.]

[21. The polymer blend according to claim 20, wherein the powder phase has a tap density of about 0.4 g/cc to about 0.7 g/cc.]

[22. The polymer blend according to claim 20, wherein the polymer is selected from the group consisting of melt-processable polymers, polyesters, phenolics, silicone polymers, acrylics, waxes, thermoplastic polymers, low molecular weight fluids, and epoxy molding compounds.]

[23. The polymer blend according to claim 20, wherein the polymer blend comprises from about 30 wt. % to about 80 wt. % spherical boron nitride powder.]

[24. The polymer blend according to claim 20, wherein the polymer blend has a thermal conductivity of from about 1 W/mK to about 15 W/mK.]

[25. The polymer blend according to claim 20, wherein the spherical agglomerates of hexagonal boron nitride platelets have an average agglomerate diameter of from about 10 microns to about 500 microns.]

[26. The polymer blend according to claim 25, wherein the majority of spherical agglomerates have an average diameter of from about 30 microns to about 150 microns.]

[27. A system comprising:

a heat source;

a heat sink; and

a thermally conductive material connecting the heat source to the heat sink, wherein the thermally conductive material comprises a powder phase comprising spherical agglomerates of hexagonal boron nitride platelets.]

[28. The system according to claim 27, wherein the powder phase has a tap density of about 0.4 g/cc to about 0.7 g/cc.]

[29. The system according to claim 27, wherein the heat source is an integrated circuit chip, power module or transformer.]

[30. The system according to claim 27, wherein the heat sink is finned aluminum, copper, beryllium or diamond.]

[31. The system according to claim 27, wherein the thermally conductive material comprises from about 30 wt. % to about 80 wt. % spherical boron nitride powder.]

[32. The system according to claim 27, wherein the thermally conductive material has a thermal conductivity of from about 1 W/mK to about 15 W/mK.]

[33. The system according to claim 27, wherein the spherical agglomerates of hexagonal boron nitride platelets have an average agglomerate diameter of from about 10 microns to about 500 microns.]

[34. The system according to claim 33, wherein the majority of spherical agglomerates have an average diameter of from about 30 microns to about 150 microns.]

[35. The system according to claim 27, wherein the thermally conductive material is a polymer.]

[36. The system according to claim 35, wherein the polymer is selected from the group consisting of melt-processable polymers, polyesters, phenolics, silicone polymers, acrylics, waxes, thermoplastic polymers, low molecular weight fluids, and epoxy molding compounds.]

37. A polymer blend comprising:
a polymer; and

a powder phase comprising sintered spherical agglomerates of boron nitride having an average diameter of from about 10 microns to about 500 microns.

38. The polymer blend according to claim 37, wherein the sintered spherical agglomerates of boron nitride have an average agglomerate diameter of from about 150 microns to about 500 microns.

39. The polymer blend according to claims 37 or 50 or 59, wherein the polymer is selected from the group consisting of melt-processable polymers, polyesters, phenolics, silicone polymers, acrylics, waxes, thermoplastic polymers, low molecular weight fluids, and epoxy molding compounds.

40. The polymer blend according to claims 37 or 50 or 59, wherein the polymer blend comprises from about 30 wt. % to about 80 wt. % of the powder phase.

41. The polymer blend according to claim 40, wherein the polymer blend comprises from about 50 wt. % to about 80 wt. % of the powder phase.

42. The polymer blend according to claims 37 or 50 or 59, wherein the polymer blend has a thermal conductivity of from about 1 W/mK to about 15 W/mK.

43. The method according to claim 2, wherein the hexagonal boron nitride slurry comprises from about 40 wt. % to about 50 wt. % hexagonal boron nitride powder.

44. A spherical boron nitride powder comprising sintered spherical agglomerates of boron nitride platelets, wherein the spherical agglomerates have been sintered at a temperature of at least about 1800° C.

45. The spherical boron nitride powder according to claim 44, wherein the spherical agglomerates have been sintered at a temperature of from about 2000° C. to about 2400° C.

46. The spherical boron nitride powder according to claim 44, wherein the spherical boron nitride powder has a tap density of about 0.4 g/cc to about 0.7 g/cc.

47. The spherical boron nitride powder according to claim 44, wherein the spherical agglomerates of boron nitride platelets have an average agglomerate diameter of from about 10 microns to about 500 microns.

48. The spherical boron nitride powder according to claim 47, wherein a majority of boron nitride agglomerates have an average diameter of from about 30 microns to about 150 microns.

49. The spherical boron nitride powder according to claim 44, wherein the spherical agglomerates of boron nitride platelets have an average agglomerate diameter of from about 150 microns to about 500 microns.

50. A polymer blend comprising:
a polymer; and

a powder phase comprising sintered spherical agglomerates of boron nitride, wherein the spherical agglomerates have been sintered at a temperature of at least about 1800° C.

51. The polymer blend according to claim 50, wherein the spherical agglomerates have been sintered at a temperature of from about 2000° C. to about 2400° C.

52. The polymer blend according to claim 50, wherein a majority of boron nitride agglomerates have an average agglomerate diameter of from about 10 microns to about 500 microns.

53. The polymer blend according to claim 52, wherein a majority of boron nitride agglomerates have an average diameter of from about 30 microns to about 150 microns.

54. The polymer blend according to claim 50, wherein the spherical agglomerates of boron nitride platelets have an average agglomerate diameter of from about 150 microns to about 500 microns.

55. A spherical boron nitride powder comprising sintered spherical agglomerates of boron nitride platelets having an average agglomerate diameter of from about 30 microns to about 125 microns.

56. A polymer blend comprising:
a polymer; and

a powder phase comprising sintered spherical agglomerates of boron nitride having an average diameter of from about 30 microns to about 125 microns.

57. A spherical boron nitride powder comprising sintered spherical agglomerates of hexagonal boron nitride platelets having a crystallization index of at least 0.12.

58. The spherical boron nitride powder according to claim 57, wherein the spherical boron nitride powder has a tap density of about 0.4 g/cc to about 0.7 g/cc.

59. A polymer blend comprising:
a polymer; and

a powder phase comprising sintered spherical agglomerates of boron nitride.

* * * * *

UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : RE45,923 E
APPLICATION NO. : 11/266751
DATED : March 15, 2016
INVENTOR(S) : Pujari et al.

Page 1 of 1

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

In the Specification

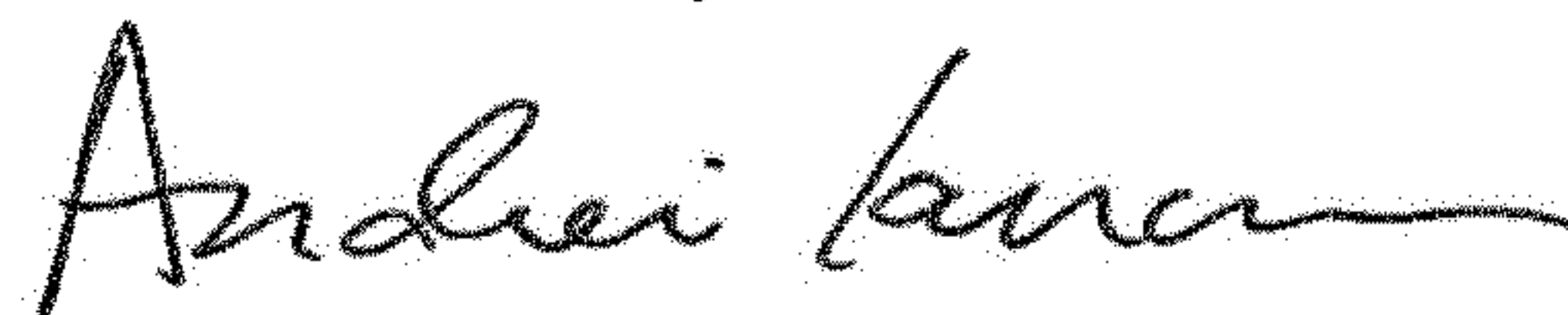
At Column 1, please replace the paragraph at Lines 14-17 (approx.) above the heading "FIELD OF THE INVENTION," with the following:

--CROSS-REFERENCE TO RELATED APPLICATIONS

NOTICE: More than one reissue application has been filed for the reissue of U.S.

Patent No. 6,645,612 B2. The reissue applications are U.S. Reissue Patent Application Serial No. 15/051,318, filed on February 23, 2016, now U.S. Reissue Patent No. RE47,635 E, issued October 8, 2019, which is a continuation reissue application of U.S. Reissue Patent Application Serial No. 11/266,751 (the present application), filed on November 3, 2005, now U.S. Reissue Patent No. RE45,923 E, issued March 15, 2018, which together with U.S. Reissue Patent Application Serial No. 12/542,424, filed on August 17, 2009, now U.S. Reissue Patent No. RE45,803 E, issued November 17, 2015, are each a reissue application of U.S. Patent Application Serial No. 09/923,994, filed on August 7, 2001, now U.S. Patent No. 6,645,612 B2, issued November 11, 2003.--

Signed and Sealed this
Twentieth Day of October, 2020



Andrei Iancu
Director of the United States Patent and Trademark Office