

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
23 December 2004 (23.12.2004)

PCT

(10) International Publication Number
WO 2004/111145 A1

(51) International Patent Classification⁷: **C09G 1/02**,
C09K 3/14

Aza Horogo, Narumicho, Midori-ku, Nagoya-shi, Aichi
4580801 (JP).

(21) International Application Number:
PCT/JP2004/008581

(74) Agents: **AOKI, Atsushi** et al.; A. Aoki, Ishida & As-
sociates, Toranomom 37 Mori Bldg., 5-1, Toranomom
3-chome, Minato-ku, Tokyo 1058423 (JP).

(22) International Filing Date: 11 June 2004 (11.06.2004)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
2003-169395 13 June 2003 (13.06.2003) JP
60/480,736 24 June 2003 (24.06.2003) US

(81) Designated States (*unless otherwise indicated, for every
kind of national protection available*): AE, AG, AL, AM,
AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN,
CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI,
GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, KE, KG,
KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG,
MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH,
PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN,
TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(71) Applicants (*for all designated States except US*): **SHOWA
DENKO K.K.** [JP/JP]; 13-9, Shiba Daimon 1-chome, Mi-
nato-ku, Tokyo 1058518 (JP). **YAMAGUCHI SEIKEN
KOGYO K.K.** [JP/JP]; 153, Aza Horogo, Narumicho, Mi-
dori-ku, Nagoya-shi, Aichi 4580801 (JP).

(72) Inventors; and

(75) Inventors/Applicants (*for US only*): **MIYATA, Nori-
hiko** [JP/JP]; c/o Shiojiri Plant, Showa Denko K.K., 1,
Oaza Soga, Shiojiri-shi, Nagano 3996461 (JP). **ANDO,
Junichiro** [JP/JP]; c/o YAMAGUCHI SEIKEN KO-
GYO K.K., 153, Aza Horogo, Narumicho, Midori-ku,
Nagoya-shi, Aichi 4580801 (JP). **KUMITA, Tetsuro**
[JP/JP]; c/o YAMAGUCHI SEIKEN KOGYO K.K., 153,

(84) Designated States (*unless otherwise indicated, for every
kind of regional protection available*): ARIPO (BW, GH,
GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM,
ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),
European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI,
FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI,
SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ,
GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report

*For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.*

(54) Title: POLISHING COMPOSITION AND POLISHING METHOD

(57) Abstract: A polishing composition characterized by comprising water, abrasive grains, a polishing accelerator, and auxiliary abrasive grains, wherein the auxiliary abrasive grains assume a finely divided crystal powder having a ratio of a primary particle diameter of auxiliary abrasive grains to that of abrasive grains of 1/2 to 1/1,000. The polishing composition having the aforementioned constitution attains high polishing rate and provides high-quality mirror-finished surface without forming surface defects. Thus, the composition is remarkably useful.

WO 2004/111145 A1

DESCRIPTION

POLISHING COMPOSITION AND POLISHING METHOD

5 Cross Reference to Related Application

This application is an application filed under 35 U.S.C. 111(a) claiming benefit, pursuant to 35 U.S.C. §119(e)(1), of the filing date of the U.S. Provisional Application No.60/480,736 filed on June 24, 2003,
10 pursuant to 35 U.S.C. §111(b).

Technical Field

The present invention relates to a polishing composition for use in precise polish-finishing of metal,
15 plastic, glass, or a similar material and to a polishing method. More particularly, the invention relates to a polishing composition and a polishing method for a magnetic disk which is installed in a hard disk drive of a computer.

20

Background Art

The recording density of a magnetic disk has been increased by reducing the gap between the magnetic disk and a magnetic head in a hard disk drive (i.e., the
25 flying height). In recent years, in order to cope with trends of a drastic increase in magnetic recording density and a drastic decrease in diameter, there has been continuous demand for a magnetic disk having a high-quality finished surface. In order to meet such demand,
30 a variety of technical developments have been attained.

Recently, as the recording density has progressively increased from current 40 GB to 60 to 80 GB, rigorous requirements have been imposed on polishing agents. Such requirements are diversified and include a high polishing
35 rate, a reduction in surface roughness, a lack of surface defects (micro-pits, micro-protrusions, and micro-scratches), a reduction in waviness generally and

locally, prevention of cut-off at the edge surface, prevention of adhesion of abrasive grains on a disk surface, prevention of staining of a disk surface, and excellent washability.

5 Regarding the aforementioned polishing composition, there has been conventionally proposed a variety of polishing compositions for enhancing polishing rate and providing a high-quality disk surface.

10 For example, in order to maintain a high polishing rate (one of the most important characteristics during polishing) and attain a high-quality polished surface which is resistant to polishing-related scratches and surface defects such as scratches, pits, and protrusions, aluminum nitride disclosed in Japanese Patent Application
15 Laid-Open (*kokai*) No. 62-25187 and a variety of inorganic acids and salts thereof have been proposed as polishing accelerators serving as additives for a polishing composition. There have been proposed a variety of etchants based on organic acids such as gluconic acid,
20 lactic acid (both disclosed in Japanese Patent Application Laid-Open (*kokai*) No. 2-84485), and organic acids disclosed in subsequent publications, the etchants being effective for reducing surface roughness of a polished surface so as to meet a demand for improved
25 surface precision. Furthermore, as the aforementioned polishing compositions effective for attaining, at high efficiency, a high-quality polished surface without surface defects, there have been proposed a polishing composition containing boehmite alumina sol or colloidal alumina as disclosed in Japanese Patent Application Laid-
30 Open (*kokai*) No. 1-188264. Furthermore, a chelate compound (Japanese Patent Application Laid-Open (*kokai*) No. 11-92749) has been proposed as a polishing accelerator. Boehmite sol and colloidal alumina also
35 have functions of surface modification agents. Prevention of dub-off is a type of surface modification, and Japanese Patent Application Laid-Open (*kokai*) No.

2002-167575 discloses hydroxy polymers such as polyoxyethylene polyoxypropylene alkyl ethers as a dub-off preventing agents.

Meanwhile, use of alumina, titania, ceria, zirconia, and silica, of various crystal forms, as abrasive grains has been proposed. Among them, α -alumina is predominantly employed as abrasive grains. In Japanese Patent Application Laid-Open (*kokai*) No. 2002-30273, a combination of α -alumina, intermediate alumina, and a dub-off preventing agent is proposed.

However, in the field of rapidly-developing computer hardware, there has been continuous and keen demand for a magnetic disk substrate having a higher quality finished surface so as to further increase the recording density. Therefore, it may be difficult to attain a generally evaluated polishing composition which would satisfy all of the aforementioned rigorous requirements in quality (e.g., rate, surface quality, and dub-off).

As mentioned above, in order to increase recording density, the following conditions must be met: excellent smoothness and flatness of a disk, low surface roughness, absence of pits, protrusions, scratches, waviness, and absence of dub-off generated at the periphery of the disk. In order to attain such high-quality finishing, a more excellent polishing composition is demanded.

In order to meet the demand, the present invention contemplates providing a polishing composition which attains a high polishing rate and provides a high-quality polished surface without surface defects.

30

Summary of the Invention

The gist of the present invention resides in a polishing composition which can attain the above object and which contains water, abrasive grains, finely divided crystal powder, and one or more polishing accelerators. Accordingly, the present invention provides the

35

following.

(1) A polishing composition characterized by comprising water, abrasive grains, a polishing accelerator, and auxiliary abrasive grains, wherein the auxiliary abrasive grains assume a finely divided crystal powder having a ratio of a primary particle diameter of the auxiliary abrasive grains to that of the abrasive grains of 1/2 to 1/1,000.

(2) The polishing composition as described in (1) above, wherein the auxiliary abrasive grains have a primary crystal size falling within a range of 0.005 μm to 0.07 μm .

(3) The polishing composition as described in (1) or (2) above, wherein the auxiliary abrasive grains have a mean secondary particle size falling within a range of 0.05 μm to 8 μm .

(4) The polishing composition, as described in any one of (1) to (3) above, wherein the auxiliary abrasive grains have a specific surface area (BET value) falling within a range of 20 to 250 m^2/g .

(5) The polishing composition as described in any one of (1) to (4) above, which contains the auxiliary abrasive grains in an amount falling within a range of 0.1 to 20 mass%.

(6) The polishing composition as described in any one of (1) to (5) above, wherein the auxiliary abrasive grains are finely divided crystal alumina formed through an ammonium alum method, an ammonium dawsonite method, an aluminum alkoxide method employing metallic aluminum serving as a starting material, or a spark discharge method; fumed alumina; and/or alumina formed from boehmite/pseudoboehmite/bayerite.

(7) The polishing composition, as described in any one of (1) to (6) above, wherein the abrasive grains are selected from the group consisting of alumina, silica, titania, zirconia, ceria, calcia, magnesia, manganese

oxide and iron oxide.

(8) The polishing composition, as described in (7) above, wherein the abrasive grains are α -alumina.

(9) The polishing composition, as described in (8) above, wherein the abrasive grains are gibbsite-type α -alumina having a specific surface area (BET value) of at least 6 m²/g to 15 m²/g.

(10) The polishing composition as described in any one of (1) to (9) above, wherein the abrasive grains and the auxiliary abrasive grains are of the same material.

(11) The polishing composition as described in any one of (1) to (10) above, wherein the abrasive grains have a mean primary crystal size falling within a range of 0.1 to 5 μ m.

(12) The polishing composition as described in any one of (1) to (11) above, wherein the abrasive grains have a mean secondary particle size falling within a range of 0.3 to 5 μ m.

(13) The polishing composition as described in any one of (1) to (12) above, which contains the abrasive grains in an amount falling within a range of 1 to 35 mass%.

(14) The polishing composition as described in any one of (1) to (13) above, wherein the polishing accelerator includes at least one species selected from among an organic acid, an inorganic acid salt, a combination of an organic acid and an organic acid salt, a combination of an organic acid and an inorganic acid salt, a sol product formed from an aluminum salt, and an organic phosphonic acid chelate compound.

(15) The polishing composition as described in any one of (1) to (14) above, which has a content of the polishing accelerator of the organic acid, the inorganic acid salt, the combination of an organic acid and an organic acid salt, or, the combination of an organic acid and an inorganic acid salt, falling within a range of

0.01 to 10 % by mass.

(16) The polishing composition as described in any one of (1) to (15) above, which has a content of the sol product formed from an aluminum salt or the organic phosphonic acid chelate compound, in a range of 0.01 to 5 % by mass.

(17) The polishing composition as described in any one of (1) to (16) above, which has a pH falling within a range of 2 to 6.

(18) The polishing composition as described in any one of (1) to (17) above, which further contains, as a surface modification agent, an inorganic acid containing a non-metallic element belonging to Group 5 or 6 of the periodic table or a hydroxyalkyl alkyl cellulose.

(19) The polishing composition as described in any one of (1) to (18) above, wherein the surface modification agent includes at least one species selected from among sulfamic acid, phosphoric acid, nitric acid, hydroxypropyl cellulose, hydroxypropyl methyl cellulose, hydroxyethyl methyl cellulose, and ethyl hydroxyethyl cellulose.

(20) A composition which forms the polishing composition as described in any one of (1) to (19) above, by dilution.

(21) A method for using the composition as described in (20) above as a composition for transportation or storage.

(22) A method for polishing a substrate, the method employing the composition as recited in any one of (1) to (20) above.

(23) A method for polishing, comprising preparing a composition having a concentration of ingredients thereof higher than that when used, diluting the concentration of the composition to form the composition as recited in any one of (1) to (19) above, and using the polishing composition for polishing.

(24) A method for producing a substrate, the method

employing a method as recited in (22) or (23) above.

Brief Description of the Drawings]

Fig. 1 is a schematic representation employed for
5 explanation of determination of the amount of dub-off, in
which reference marks stand for the followings:
S...Curve in the vicinity of the periphery of a disk,
which is drawn by use of a surfcorder
h...Perpendicular line which is in contact with the
10 circumferential end of a disk
A...Point on the curve which is 3,000 μm from
perpendicular line h
B...Point on the curve which is 2,000 μm from
perpendicular line h
15 C...Point on a straight line passing through points A and
B, which is 500 μm from perpendicular line h
k...Perpendicular line passing through point C
D...Point at which perpendicular line k and curve S cross
t...Length between point C and point D (the amount of
20 dub-off)

Modes for Carrying Out the Invention

The polishing composition of the present invention
comprises water, abrasive grains, a polishing
25 accelerator, and auxiliary abrasive grains, wherein the
auxiliary abrasive grains assume a finely divided crystal
powder having a ratio of a primary particle diameter of
auxiliary abrasive grains to that of abrasive grains of
1/2 to 1/1,000, preferably 2/5 to 1/100, more preferably
30 1/3 to 1/30. Thus, the auxiliary abrasive grains
remarkably promote the polishing performance of abrasive
grains included in a slurry-like polishing composition.

The conceivable mechanism of promoting polishing
caused by auxiliary abrasive grains may be as follows.
35 When the finely divided crystal abrasive grains serving
as auxiliary abrasive grains intervene between the

polishing surface and abrasive grains, the finely divided crystal abrasive grains interact with abrasive grains. For example, the kinetic energy of abrasive grains is transferred to the finely divided crystal abrasive grains via collision with abrasive grains or via pressing by abrasive grains. As a result, auxiliary abrasive grains exert mechanical energy directly to the polishing surface, thereby providing an edgy polishing action.

In the polishing composition of the present invention, the auxiliary abrasive grains preferably have a primary crystal size falling within a range of 0.005 μm to 0.07 μm .

In the polishing composition of the present invention, the auxiliary abrasive grains preferably have a mean secondary particle size falling within a range of 0.05 μm to 8 μm .

Thus, the auxiliary abrasive grains are sufficiently small in size with respect to the roughness of the polishing surface, and therefore, exert mechanical energy directly to the polishing surface, thereby providing an edgy polishing action.

In the polishing composition of the present invention, the auxiliary abrasive grains are preferably contained in the polishing composition in an amount falling within a range of 0.1 to 20 mass%. Within this range, the auxiliary abrasive grains are necessarily and sufficiently distributed on the polishing surface, and therefore, they exert mechanical energy directly to the polishing surface, thereby providing an edgy polishing action.

The abrasive grains employed in the polishing composition of the present invention are alumina, silica, titania, zirconia, ceria, calcia, magnesia, manganese oxide, iron oxide, or a similar compound. Among them, alumina is particularly preferable.

No particular limitation is imposed on the crystal

form (e.g., α , θ , or γ) of the alumina used in the composition. However, α -alumina is preferred as base abrasive grains from the viewpoint of high polishing rate. In addition, a dense crystal structure including
5 few pores and a smaller primary crystal size are preferred, so long as the powder possesses a polishing performance. The mean primary crystal size preferably falls within a range of 0.1 to 5 μm , particularly preferably 0.1 to 0.5 μm where both strength and density
10 are satisfied.

The mean size of secondary particles (which are formed by aggregating primary crystal particles) preferably falls within a range of 0.3 to 5.0 μm , more preferably 0.5 to 3 μm . The amount of secondary
15 particles preferably falls within a range of 1 to 35 mass%, more preferably 5 to 30 mass%.

The alumina used as the abrasive grains can be produced by firing, at an appropriate firing temperature, a finely divided powder of aluminum hydroxide (gibbsite
20 or bayerite) having a small mean particle size or firing at an appropriate firing temperature aluminum hydroxide providing a dense crystal structure having few pores after firing (e.g., boehmite or pseudo-boehmite).

Specifically, by virtue of a low crystal water
25 content, a fired product of boehmite-type aluminum hydroxide provides a more dense crystal structure as compared with a fired product of gibbsite-type aluminum hydroxide, thereby enhancing a polishing rate. From an economical aspect, gibbsite-type α -alumina having a
30 primary crystal size of 0.5 μm or less and a specific surface area (BET value) of at least 6 m^2/g to about 15 m^2/g is particularly preferred.

The primary crystal size can be calculated from an average value obtained through analysis of a scanning
35 electron microscope (SEM) photograph, and the mean second

particle size can be obtained through measurement by means of a laser Doppler diffraction scattering particle size analyzer (e.g., SHIMADZU SALD-2000J), a laser Doppler diffraction particle size analyzer (Microtrac UPA), or a similar apparatus.

The finely divided crystal powder as the auxiliary abrasive grains may be formed from a material identical to or different from that of the aforementioned abrasive grains. However, the same material is more preferred, with alumina being particularly preferred.

When alumina is employed as the auxiliary abrasive grains, no particular limitation is imposed on the crystal form (e.g., α , θ , χ). However, the alumina species which is readily crushed to form particles of a primary crystal size level is preferred for the purpose of regulating the surface roughness and surface quality in combination with the aforementioned base abrasives. The primary crystal size preferably falls within a range of 0.005 μm to 0.07 μm , particularly preferably 0.01 to 0.05 μm . The crystal form is preferably α , θ , κ , δ , and γ , with θ , δ , and γ being more particularly preferred. The specific surface area (BET value) is preferably 20 to 250 m^2/g , particularly preferably 60 to 100 m^2/g . The mean secondary particle size preferably falls within a range of 0.05 to 8 μm , more preferably 0.5 to 5 μm . The alumina content preferably falls within a range of 0.1 to 20 mass%, more preferably 0.5 to 10 mass%.

The primary crystal size D is calculated from particle density ρ and specific surface area S determined by use of a BET specific surface area meter (e.g., SHIMADZU FlowSorb II), in accordance with the following equation ($D [\mu\text{m}] = 6/(\rho [\text{g}/\text{cm}^3] \times S [\text{m}^2/\text{g}])$). The mean secondary particle size can be determined through measurement by means of the aforementioned laser Doppler diffraction scattering particle size analyzer (e.g.;

SHIMADZU SALD-2000J), a laser doppler diffraction particle size analyzer (Microtrac UPA), or a similar apparatus.

5 The auxiliary abrasive grains included in a slurry-like polishing composition promote polishing performance of abrasive grains. Specifically, it has been confirmed that, by incorporating finely divided crystal abrasive grains having a fine particle size to abrasive grains, the finely divided crystal abrasive grains act directly
10 on the polishing surface, thereby remarkably enhancing the polishing action. It has also been confirmed that the quality of the polished surface is not adversely affected.

The action of the finely divided crystal abrasive grains is conceived on the basis of the following facts.
15 Generally, abrasive grains act on a polishing surface by means of mechanical energy provided through agitation of the abrasive grains upon polishing a substrate. Therefore, a limitation is imposed on the reduction of
20 the diameter of the abrasive grains to a minute level. Thus, abrasive grains themselves must be relatively large in size with respect to the roughness of the polishing surface.

In contrast to abrasive grains, auxiliary abrasive grains have a remarkably small particle size. Therefore,
25 the auxiliary abrasive grains themselves have low kinetic energy, resulting in a small action force of polishing. However, by virtue of their small particle radius, the auxiliary abrasive grains are considered to provide an
30 edgy polishing action on the polishing surface.

Therefore, the action may be as follows. When the finely divided crystal abrasive grains serving as auxiliary abrasive grains intervene between the polishing surface and abrasive grains, the finely divided crystal
35 abrasive grains interact with the abrasive grains. For example, the kinetic energy of abrasive grains is transferred to the finely divided crystal abrasive grains

via collision with abrasive grains or via pressing by abrasive grains. As a result, auxiliary abrasive grains exert mechanical energy directly to the polishing surface, thereby providing edgy polishing action. The auxiliary abrasive grains support the action of abrasive grains when the auxiliary abrasive grains intervene between the polishing surface and abrasive grains.

Among micro-ridges and micro-troughs present in the polishing surface, the micro-ridges receive the brunt of polishing action of the auxiliary abrasive grains, while the auxiliary abrasive grains are buried in the micro-troughs to cover the polishing surface. Thus, excessive polishing of the micro-troughs is prevented.

According to the polishing composition of the present invention, a surface of an aluminum magnetic disk substrate which is plated with, for example, Ni-P can be polished at a remarkably increased polishing rate, and a high-quality polished surface; i.e., a surface having no surface defects and having high surface precision and reduced dub-off and waviness, can be obtained.

Examples of particularly preferred finely divided alumina crystal powder employed in the present invention include ammonium alum method alumina products such as UA series (product of Showa Denko K. K., BaikaloX CR series), ammonium dawsonite method alumina products such as TM series (product of Taimei Chemicals Co., Ltd.), alumina products obtained through an aluminum alkoxide method starting from aluminum such as AKP series (product of Sumitomo Chemical Co., Ltd.), spark discharge method alumina products such as alumina of R, RA, RG, RK grades (product of Iwatani Kagaku), fumed alumina products such as UFA series (product of Showa Denko K. K.) and products of Nippon Aerosil Co., Ltd.; and derived alumina products obtained through firing boehmite-type or bayerite-type aluminum hydroxide such as products of Sasol, products of Alcoa Kasei Ltd., and versal alumina (product of UOP).

The polishing accelerator employed in the polishing

composition of the present invention may be an organic acid or an inorganic acid salt.

The organic acid may preferably be at least one species selected from the group consisting of malonic acid, succinic acid, adipic acid, lactic acid, malic acid, citric acid, glycine, aspartic acid, tartaric acid, gluconic acid, heptogluconic acid, iminodiacetic acid, and fumaric acid. The inorganic acid salt may preferably be at least one species selected from the group consisting of sodium sulfate, magnesium sulfate, nickel sulfate, aluminum sulfate, ammonium sulfate, nickel nitrate, aluminum nitrate, ammonium nitrate, ferric nitrate, aluminum chloride, and nickel sulfamate. The organic acid content or the inorganic acid salt content preferably falls within a range of 0.01 to 10 mass%. When the content is too small, the effect of the polishing accelerator decreases, whereas the content is excessively large, the viscosity of the composition may increase to much or pits and protrusions may be generated, thereby deteriorating the quality of the polished surface. An excessively large content may also adversely affect the quality of polishing liquid, for example, aggregation of alumina particles.

The aforementioned polishing accelerator may be a combination of an organic acid and an organic acid salt or a combination of an organic acid and an inorganic acid salt.

As mentioned above, the organic acid may be at least one species selected from the group consisting of malonic acid, succinic acid, adipic acid, lactic acid, malic acid, citric acid, glycine, aspartic acid, tartaric acid, gluconic acid, heptogluconic acid, iminodiacetic acid, and fumaric acid. The organic acid salt may be at least one species selected from the group consisting a potassium salt, a sodium salt, or an ammonium salt of the aforementioned organic acids. Also as mentioned above, the inorganic acid salt may be at least one species

selected from the group consisting of sodium sulfate, magnesium sulfate, nickel sulfate, aluminum sulfate, ammonium sulfate, nickel nitrate, aluminum nitrate, ammonium nitrate, ferric nitrate, aluminum chloride, and nickel sulfamate. In any of combinations of an organic acid with an organic acid salt and/or an inorganic acid salt, the total amount thereof preferably falls within a range of 0.01 to 10 mass% based on the entire polishing composition. Among these components, the organic acid is particularly preferably be incorporated in an amount at least 0.003 mass%. In the case where a combination type polishing accelerator is used, when the polishing aid content is less than 0.01 mass%, the effect of the polishing accelerator is poor, whereas when the content is in excess of 10 mass%, the quality of a polishing solution may be adversely affected, for example, an excessive increase in the viscosity of the solution or of aggregation of alumina particles, and the quality of the polished surface may be deteriorated through generation of pits and protrusions, which are disadvantageous. Notably, when an organic acid and an organic acid salt are used in combination, a combination of the same acid species may attain more excellent polishing characteristics.

The aforementioned polishing accelerator may be a sol product derived from an aluminum salt described in Japanese Patent Application Laid-Open (*kokai*) No. 2002-20732. Specifically, the sol product is produced through high shear agitation of an aqueous solution containing any one hydrate or anhydrate of aluminum salts, for example, inorganic acid aluminum salts such as aluminum sulfate, aluminum chloride, aluminum nitrate, aluminum phosphate, and aluminum borate; and organic acid aluminum salts such as aluminum acetate, aluminum lactate, and aluminum stearate, with one species selected from the group consisting of sodium hydroxide, potassium hydroxide, ammonia, organic amine compounds such as an

alkyl amine (e.g., monomethylamine) and an alkanolamine (e.g., triethanolamine), aminocarboxylic acids such as glycine, amine chelate compounds such as iminodiacetic acid, aminocarboxylic acid chelate compounds such as
5 ethylenediaminetetraacetic acid, aminophosphonic acid chelate compounds such as diethylenetriaminepentamethylenephosphonic acid and aminotrismethylenephosphonic acid. The sol product is formed in a chain mechanism by mixing an aluminum salt
10 with a substance (e.g., ammonia or amine) which readily releases a hydroxyl group upon reaction with water, a compound having a terminal hydroxyl group, or a compound having a hydroxyl group such as sodium hydroxide or potassium hydroxide.

15 The amount of the sol product derived from an aluminum salt preferably falls within a range of 0.01 to 5 mass% based on the entire polishing composition. When the amount is too small, the effect of the sol product is poor, whereas when the amount is excessively large,
20 gelation may occur and surface defects such as pits and protrusions may be generated. More preferably, the amount falls within a range of 0.05 to 2 mass%.

The aforementioned polishing accelerator may be a organic phosphonic acid chelate compound described in
25 Japanese Patent Application Laid-Open (*kokai*) No. 2001-131535. Specifically, the chelate compound is at least one species selected from the group consisting of diethylenetriaminepentamethylenephosphonic acid, phosphonobutanetricarboxylic acid, phosphonohydroxyacetic
30 acid, hydroxyethyldimethylphosphonic acid, aminotrismethylenephosphonic acid, hydroxyethanediphosphonic acid, ethylenediaminetetramethylenephosphonic acid, hexamethylenediaminetetramethylenephosphonic acid, and
35 salts thereof.

The amount of the organic phosphonic acid chelate compound preferably falls within a range of 0.01 to 5

mass% based on the entire polishing composition. When the amount is too small, the effect of polishing rate enhancement is decreases, whereas when the amount is excessively large, surface defects such as pits and protrusions may be generated. More preferably, the amount falls within a range of 0.05 to 2 mass%.

The polishing composition of the present invention may further contain as a surface modification agent an inorganic acid containing a non-metallic element belonging to Group 5 or 6 in the periodic table. Examples of the inorganic acid containing a non-metallic element belonging to Group 5 or 6 in the periodic table include sulfamic acid, phosphoric acid, and nitric acid. Through addition of such an inorganic acid in an appropriate amount, generation of pits and protrusion is prevented, thereby enhancing the surface quality. The amount of the inorganic acid preferably falls within a range of 0.01 to 5 mass% based on the entire polishing composition. Both a too small amount and an excessive amount may decrease in the effect of the inorganic acid. An excessive amount may reduce polishing rate. More preferably, the amount falls within a range of 0.05 to 2 mass%.

As a surface modification agent (dub-off preventing agent), a hydroxyalkyl alkyl cellulose (hereinafter referred to as HRRC), for example, as disclosed in Pamphlet of WO 01/23485, may be used. Specific examples thereof include hydroxypropyl cellulose (HPC), hydroxypropyl methyl cellulose (HPMC), hydroxyethyl methyl cellulose (HEMC), and ethyl hydroxyethyl cellulose (EHEC). The amount of the HRRC preferably falls within a range of 0.001 to 2 mass% based on the entire polishing composition. When the amount is too small, the effect of reducing dub-off is poor, whereas when the amount is excessively large, the polishing rate may decrease. More preferably, the amount falls within a range of 0.01 to 1.0 mass%.

In addition to the aforementioned additives, the polishing composition of the present invention may further contain, in accordance with needs, alumina sol, a surfactant, a detergent, an anticorrosive agent, an antiseptic agent, a pH-regulator, a thickener, other cellulose species, or a surface modification agent.

Notably, the aforementioned concentrations of components constituting the polishing composition of the present invention are concentrations suitable for polishing a substrate. Thus, in an alternative way, the polishing composition of the present invention is prepared at component concentrations higher than the aforementioned concentrations, and upon use, diluted so as the concentrations to fall within the aforementioned ranges.

This concentrated composition may be used as a composition for transportation or storage.

The polishing composition of the present invention preferably has a pH of 2 to 6.

The present invention also encompasses a method for polishing a substrate by use of the aforementioned polishing composition and a substrate polished by use of the aforementioned polishing composition.

Examples

The present invention will next be described, in detail, by way of examples, which should not be construed as limiting the invention. Any modification to the examples performed without deviating from the spirit of the invention described above and below falls within the technical scope of the present invention.

Each polishing composition was prepared in the following manner, and the composition was evaluated in terms of polishing performance.

<Preparation of polishing compositions>

Aluminum hydroxide was heated at about 1,200°C in a firing furnace under atmospheric conditions, to thereby

form α -alumina. Separately, a commercial alumina serving as a starting material was pulverized and classified in a wet manner, to thereby form an alumina base material sample having a mean secondary particle size of 0.7 μm . In addition, finely divided alumina crystal powder was prepared by calcining at an appropriate temperature high-purity alumina or aluminum hydroxide. A sol product derived from an aluminum salt was prepared by high shearing agitating the aluminum salt with aqueous ammonia. In accordance with the compositional proportions shown in Tables 1 to 3, polishing composition samples were prepared by sequentially weighing, adding, and mixing the following components: water, alumina, finely divided alumina crystal powder, a polishing accelerator such as an organic acid or an organic acid salt, a sol product derived from an aluminum salt, a chelating agent, an inorganic acid containing an element of Group 5 or 6 in the periodic table, and a cellulose-based surface modification agent dissolved in water. These samples were subjected to a polishing test.

Polishing conditions, polishing characteristics, and the evaluation method are as follows.

(Polishing Conditions)

An electroless-NiP-plated aluminum disk (size: 3.5 inch) was employed as a workpiece to be polished. A polishing test and evaluation of the disk were carried out under the following conditions.

Polishing test conditions

Polishing test machine; 9B double-sided polishing machine (product of System Seiko K.K.)

Polishing pad; H9900S

Rate of rotation of surface plates; upper surface plate 28 rpm, lower surface plate 45 rpm

Feed rate of slurry; 100 mL/min

Polishing time; 5 minutes

Operation pressure; 80 g/cm²

(Evaluation of disk)

Polishing rate; Calculated by difference in weight
before and after polishing the disk

5 Quality of polished surface; Surface defects (pits,
protrusions, and scratches) on the side and backside
of each disk were observed crosswise under a
microscope (product of Nikon, differential
interference type, $\times 100$). Rating "good" was
10 assigned when no defects were observed ("A": the
total number of defects is 0, "B": the total number
of defects is 1 to 5), and rating "bad (C)" was
assigned when the total number of defects was six or
more for both sides of five disks.

15 Surface roughness: Tencor P-12

Amount of dub-off: Determined by use of a surfcorder
(model: SE-30D, product of Kosaka Kenkyujo). With
reference to Fig. 1, determination of the amount of
dub-off will be described. Curve S is drawn by use
20 of a surfcorder in the vicinity of the periphery of
a polished hard disk surface, and perpendicular line
h is provided at the outermost portion of the curve
S. A point on the curve which is 3,000 μm from
perpendicular line h toward the center of the disk
25 is represented by A, and a point on the curve which
is 2,000 μm from perpendicular line h toward the
center of the disk is represented by B. C
represents a point on a straight line passing
through points A and B, and is 500 μm from
30 perpendicular line h. Perpendicular line k passing
through point C is provided. D represents a point
at which perpendicular line k and curve S cross.
Length t between point C and point D was regarded as
the amount of dub-off.

35 Tables 1 and 2 show polishing test scores of the
samples of the Examples of the present invention, and

Table 3 shows polishing test scores of the samples of the Comparative Examples.

Table 1 (1/2)

Ex.	Alumina / Finely divided alumina crystals			Polishing accelerator					
	Type	Primary crystal size μm	Amount mass%	Organic acid		Organic acid salt / Inorganic acid salt		Al sulfate sol	Chelate mass%
				Type	mass %	Type	mass %		
1	A-1 / UAY	0.2 / 0.01	6.0 / 1.0	Citric acid	0.5	Ammonium citrate	0.5	0.5	NTMP 0.5
2	A-2 / UAY	0.2 / 0.03	6.0 / 1.0	Citric acid	0.5	Ammonium citrate	0.5	0.5	HEDP 0.5
3	A-1 / UAY	0.2 / 0.07	6.0 / 1.0	Citric acid	0.5	Ammonium citrate	0.5	0.5	NTMP 0.5
4	A-1 / CRY	0.2 / 0.03	6.0 / 1.0	Citric acid	0.5	Ammonium citrate	0.5	0.5	NTMP 0.5
5	A-1 / UFAY	0.2 / 0.03	6.0 / 1.0	Citric acid	0.5	Ammonium citrate	0.5	0.5	NTMP 0.5
6	A-1 / AKPY	0.2 / 0.03	6.0 / 1.0	Citric acid	0.5	Ammonium citrate	0.5	0.5	NTMP 0.5
7	A-1 / RGY	0.2 / 0.05	6.0 / 1.0	Citric acid	0.5	Ammonium citrate	0.5	0.5	NTMP 0.5

Table 1 (2/2)

Ex.	Surface modification		Evaluation of polishing			
	Inorganic acid	HRRC	Polishing rate	Surface defect	Surface roughness	Dub-off
	mass%	mass%	$\mu\text{m}/\text{min}$	Rank	$\text{\AA}$	nm
1	Phosphoric acid 0.1	HPMC 0.05	0.97	A	9.3	80
2	Phosphoric acid 0.1	HPMC 0.05	1.08	A	9.7	70
3	Phosphoric acid 0.1	HPMC 0.05	0.94	A	9.4	80
4	Phosphoric acid 0.1	HPMC 0.05	0.96	A	9.5	70
5	Phosphoric acid 0.1	HPMC 0.05	1.08	A	9.2	80
6	Phosphoric acid 0.1	HPMC 0.05	1.05	A	9.3	80
7	Phosphoric acid 0.1	HPMC 0.05	1.07	A	9.2	80

Table 2 (1/2)

Ex.	Alumina / Finely divided alumina crystals			Polishing accelerator						
	Type	Primary crystal size	Amount	Organic acid		Organic acid salt / Inorganic acid salt		Al sulfate sol	Chelate	
		μm	mass%	Type	mass %	Type	mass %	mass%	mass%	
8	A-1 / A-2γ	0.2 / 0.05	6.0 / 1.0	Malic acid	0.5	Sodium malate	0.5	0.5	NTMP 0.5	
9	A-1 / A-2θ	0.2 / 0.07	6.0 / 1.0	Citric acid	0.5	Ammonium citrate	0.5	0.5	NTMP 0.5	
10	A-1 / UAY	0.2 / 0.01	6.0 / 1.0	-	-	-	-	-	PBTC 1.0	
11	A-1 / UAY	0.2 / 0.01	6.0 / 1.0	Citric acid	0.5	Ammonium citrate	0.5	-	-	
12	A-1 / UAY	0.2 / 0.01	6.0 / 1.0	Citric acid	0.5	Ammonium citrate	0.5	0.5	-	
13	A-1 / UAY	0.2 / 0.01	6.0 / 1.0	Citric acid	0.5	Ammonium citrate	0.5	0.5	PBTC 0.5	

Table 2 (2/2)

Ex.	Surface modification		Evaluation of polishing			
	Inorganic acid	HRRC	Polishing rate	Surface defect	Surface roughness	Dub-off
	mass%	mass%	$\mu\text{m}/\text{min}$	Rank	$\text{\AA}$	nm
8	Phosphoric acid 0.1	HPMC 0.05	1.06	A	9.4	80
9	Sulfamic acid 0.2	HPC 0.05	1.03	A	9.2	80
10	-	-	1.08	B	9.3	140
11	-	-	1.07	B	9.5	150
12	-	-	1.11	B	9.4	150
13	-	-	1.08	B	9.2	140

In Tables 1 and 2, A-1 represents gibbsite-derived α -alumina, and A-2 represents boehmite-derived α -alumina. $UA\gamma$ and $UA\alpha$ represent γ -alumina and α -alumina, respectively, produced through the ammonium alum method (products of Showa Denko K. K.). $CR\gamma$ represents γ -alumina produced through the same method (product of Baikowski). UFA represents fumed γ -alumina (product of Showa Denko K. K.). $AKP\gamma$ represents γ -alumina produced through the aluminum alkoxide method (product of Sumitomo Chemical Co., Ltd.). $RG\gamma$ represents γ -alumina produced through the spark discharge method (Iwatani Kagaku). $A-2\gamma$ represents γ -alumina produced by firing boehmite, and A-10 represents θ -alumina produced by firing gibbsite.

Table 3 (1/2)

Comp. Ex.	Alumina / Coarse alumina crystals			Polishing accelerator					
	Type	Primary crystal size μm	Amount mass%	Organic acid		Organic acid salt / Inorganic acid salt		Al sulfate sol	Chelate
				Type	mass%	Type	mass%		
1	A-1	0.2	7.0	Citric acid	0.5	Ammonium citrate	0.5	0.5	NTMP 0.5
2	A-2	0.2	7.0	Citric acid	0.5	Ammonium citrate	0.5	0.5	HEDP 0.5
3	A-3	3.0	7.0	Citric acid	0.5	Ammonium citrate	0.5	0.5	NTMP 0.5
4	A-1 / A-3	0.2 / 3.0	6.0 / 1.0	Citric acid	0.5	Ammonium citrate	0.5	0.5	NTMP 0.5
5	A-1	0.2	7.0	-	-	-	-	-	PBTC 1.0
6	A-1	0.2	7.0	Citric acid	0.5	Ammonium citrate	0.5	-	-
7	A-1	0.2	7.0	Citric acid	0.5	Ammonium citrate	0.5	0.5	-
8	A-1	0.2	7.0	Citric acid	0.5	Ammonium citrate	0.5	0.5	PBTC 0.5

Table 3 (2/2)

Comp. Ex.	Surface modification		Evaluation of polishing			
	Inorganic acid	HRRC	Polishing rate	Surface defect	Surface roughness	Dub-off
	mass%	mass%	$\mu\text{m}/\text{min}$	Rank	$\text{\AA}$	nm
1	Phosphoric acid 0.1	HPMC 0.05	0.74	B	9.9	110
2	Phosphoric acid 0.1	HPMC 0.05	0.85	B	9.8	110
3	Phosphoric acid 0.1	HPMC 0.05	0.66	B	9.9	110
4	Phosphoric acid 0.1	HPMC 0.05	0.63	B	12.3	110
5	-	-	0.68	C	10.2	180
6	-	-	0.73	C	10.0	190
7	-	-	0.76	C	10.5	180
8	-	-	0.79	C	10.0	190

In Table 3, similar to Tables 1 and 2, A-1 and A-3 represent gibbsite-derived α -alumina. A-2 represents boehmite-derived α -alumina.

5 The above Tables 1 and 2 show test results of
Examples 1 to 13, which polishing compositions fall
within the scope of the present invention. As is clear
from the Tables, all these samples provide polished
surfaces of excellent surface morphology in terms of
surface defects, surface roughness, dub-off, etc., and
10 provide a remarkably enhanced polishing rate. In
contrast, as shown in Table 3, all the samples of
Comparative Examples 1 to 8, containing no finely divided
crystal powder, exhibit a poor polishing rate and an
inferior surface morphology.

15 In Comparative Example 4, containing a powder having
a large crystal grain size, the polishing rate is reduced
compared with a similar sample containing no crystal
powder.

20 Industrial Applicability

The polishing composition of the present invention,
having the aforementioned constitution, attains high
polishing rate and provides a high-quality mirror-
finished surface without forming surface defects. Thus,
25 the composition is remarkably useful.

CLAIMS

1. A polishing composition characterized by comprising water, abrasive grains, a polishing accelerator, and auxiliary abrasive grains, wherein the
5 auxiliary abrasive grains assume a finely divided crystal powder having a ratio of a primary particle diameter of auxiliary abrasive grains to that of abrasive grains of 1/2 to 1/1,000.

2. The polishing composition, according to claim
10 1, wherein the auxiliary abrasive grains have a primary crystal size falling within a range of 0.005 μm to 0.07 μm .

3. The polishing composition, according to claim 1
15 or 2, wherein the auxiliary abrasive grains have a mean secondary particle size falling within a range of 0.05 μm to 8 μm .

4. The polishing composition, according to any one
of claims 1 to 3, wherein the auxiliary abrasive grains have a specific surface area (BET value) falling within a
20 range of 20 to 250 m^2/g .

5. The polishing composition, according to any one
of claims 1 to 4, which contains the are auxiliary
abrasive grains in an amount falling within a range of
0.1 to 20 mass%.

25 6. The polishing composition, according to any one
of claims 1 to 5, wherein the auxiliary abrasive grains are finely divided crystal alumina formed through an ammonium alum method, an ammonium dawsonite method, an aluminum alkoxide method employing metallic aluminum
30 serving as a starting material, or a spark discharge method; fumed alumina; and/or alumina formed from boehmite/pseudoboehmite/bayerite.

7. The polishing composition, according to any one
of claims 1 to 6, wherein the abrasive grains are
35 selected from the group consisting of alumina, silica, titania, zirconia, ceria, calcia, magnesia, manganese

oxide and iron oxide.

8. The polishing composition, according to claim 7, wherein the abrasive grains are α -alumina.

5 9. The polishing composition, according to claim 8, wherein the abrasive grains are gibbsite-type α -alumina having a specific surface area (BET value) of at least 6 m²/g to 15 m²/g.

10 10. The polishing composition according to any one of claims 1 to 9, wherein the abrasive grains and the auxiliary abrasive grains are of the same material.

11. The polishing composition, according to any one of claims 1 to 10, wherein the abrasive grains have a mean primary crystal size falling within a range of 0.1 to 5 μ m.

15 12. The polishing composition, according to any one of claims 1 to 11, wherein the abrasive grains have a mean secondary particle size falling within a range of 0.3 to 5 μ m.

20 13. The polishing composition, according to any one of claims 1 to 12, which contains the abrasive grains in an amount falling within a range of 1 to 35 mass%.

25 14. The polishing composition, according to any one of claims 1 to 13, wherein the polishing accelerator includes at least one species selected from among an organic acid, an inorganic acid salt, a combination of an organic acid and an inorganic acid salt, a combination of an organic acid and an inorganic acid salt, a sol product formed from an aluminum salt, and an organic phosphonic acid chelate compound.

30 15. The polishing composition, according to any one of claims 1 to 14, which has a content of the polishing accelerator of the organic acid, the inorganic acid salt, the combination of an organic acid and an organic acid salt, or, the combination of an organic acid and an inorganic acid salt, in a range of 0.01 to 10 % by mass.

35 16. The polishing composition, according to any one

of claims 1 to 15, which has a content of the sol product formed from an aluminum salt or the organic phosphonic acid chelate compound, in a range of 0.01 to 5 % by mass.

17. The polishing composition, according to any one
5 of claims 1 to 16, which has a pH falling within a range of 2 to 6.

18. The polishing composition, according to any one
of claims 1 to 17, which further contains, as a surface
modification agent, an inorganic acid containing a non-
10 metallic element belonging to Group 5 or Group 6 of the
periodic table or a hydroxyalkyl alkyl cellulose.

19. The polishing composition, according to any one
of claims 1 to 18, wherein the surface modification agent
includes at least one species selected from among
15 sulfamic acid, phosphoric acid, nitric acid,
hydroxypropyl cellulose, hydroxypropyl methyl cellulose,
hydroxyethyl methyl cellulose, and ethyl hydroxyethyl
cellulose.

20. A composition which forms the polishing
20 composition, as set forth in any one of claims 1 to 19,
by dilution.

21. A method for using the composition, as set
forth in claim 20, as a composition for transportation or
storage.

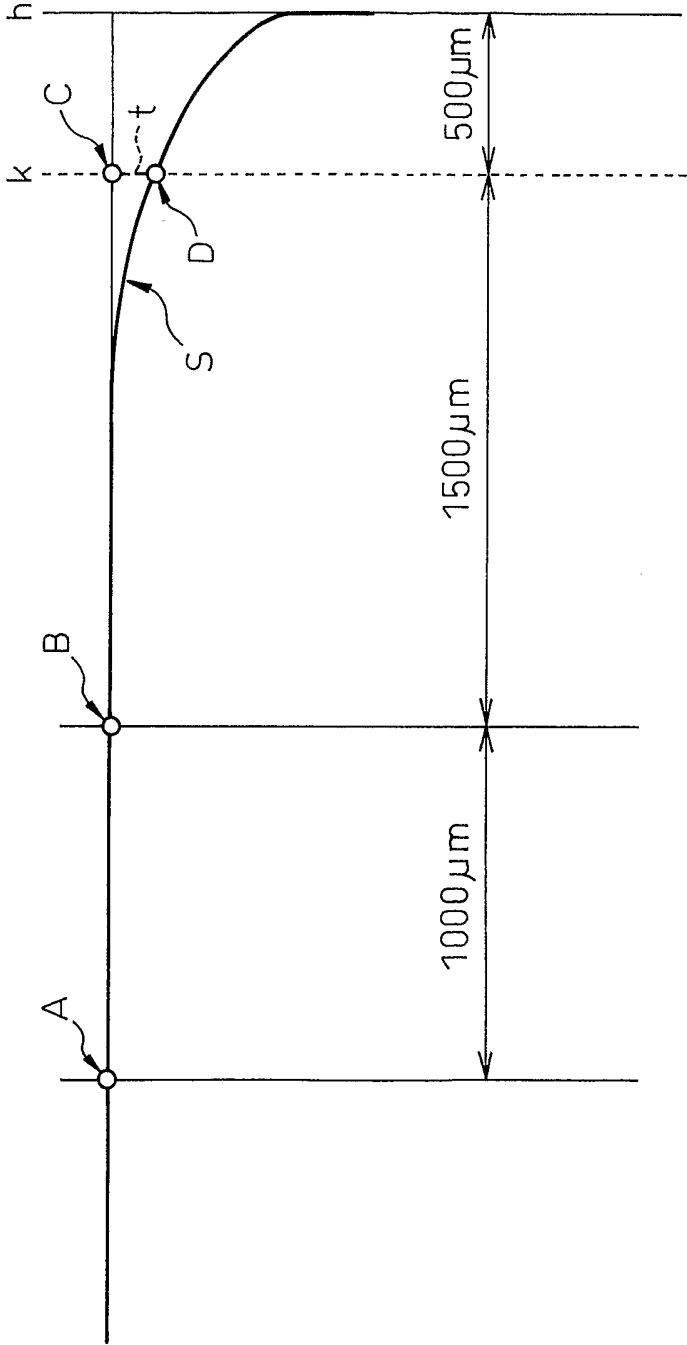
22. A method for polishing a substrate, the method
25 employing the composition as set forth in any one of
claims 1 to 20.

23. A method for polishing, comprising preparing a
composition having a concentration of ingredients thereof
30 higher than that when used, diluting the concentration of
the composition to form the composition as set forth in
any one of claims 1 to 19, and using the polishing
composition for polishing.

24. A method for producing a substrate, the method
35 employing a method as set forth in claim 22 or 23.

1/1

Fig. 1



INTERNATIONAL SEARCH REPORT

International Application No

JP2004/008581

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 7 C09G1/02 C09K3/14

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)
 IPC 7 C09G C09K

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

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

EPO-Internal, WPI Data, PAJ, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 98/23697 A (CABOT CORP) 4 June 1998 (1998-06-04) claims 1-5,7,10,14,35,36 page 8, line 10 - line 11 -----	1,3-7, 10,12, 14, 17-19, 22,24
X	US 6 270 393 B1 (KUBOTA TOSHIO ET AL) 7 August 2001 (2001-08-07) claim 1 examples ----- -/--	1,3,5-7, 10, 12-14, 22,24



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

° Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- * & * document member of the same patent family

Date of the actual completion of the international search

30 September 2004

Date of mailing of the international search report

07/10/2004

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
 NL - 2280 HV Rijswijk
 Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
 Fax: (+31-70) 340-3016

Authorized officer

Hillebrand, G

INTERNATIONAL SEARCH REPORT

International Application No

JP/JP2004/008581

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 03/020839 A (ANDO JUNICHIRO ; HONG GONG-HONG (JP); MIYATA NORIHIKO (JP); SHOWA DENK) 13 March 2003 (2003-03-13) claims 1-4 -----	1
A	WO 02/076902 A (YAMADA JIRO ; SHOWA DENKO KK (JP)) 3 October 2002 (2002-10-03) claims 1,4,6,9,10 -----	1
A	EP 0 811 665 A (CABOT CORP) 10 December 1997 (1997-12-10) claim 1 -----	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

JP2004/008581

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 9823697	A	04-06-1998	US 5958288 A	28-09-1999
			US 6015506 A	18-01-2000
			AT 214417 T	15-03-2002
			AU 5460898 A	22-06-1998
			AU 5464298 A	22-06-1998
			CN 1242729 A ,B	26-01-2000
			DE 69710993 D1	18-04-2002
			DE 69710993 T2	28-11-2002
			EP 0844290 A1	27-05-1998
			ES 2174192 T3	01-11-2002
			HK 1022661 A1	18-06-2004
			ID 23676 A	11-05-2000
			IL 130138 A	12-03-2003
			JP 10265766 A	06-10-1998
			TW 396201 B	01-07-2000
			TW 442364 B	23-06-2001
			WO 9823697 A1	04-06-1998
			WO 9823408 A1	04-06-1998
			US 5980775 A	09-11-1999
			US 6068787 A	30-05-2000
US 6270393	B1	07-08-2001	JP 2000109816 A	18-04-2000
			CN 1251380 A ,C	26-04-2000
			SG 84551 A1	20-11-2001
WO 03020839	A	13-03-2003	JP 2003147337 A	21-05-2003
			EP 1425357 A1	09-06-2004
			WO 03020839 A1	13-03-2003
WO 02076902	A	03-10-2002	JP 2002288821 A	04-10-2002
			WO 02076902 A1	03-10-2002
			US 2004166781 A1	26-08-2004
EP 0811665	A	10-12-1997	US 5858813 A	12-01-1999
			AU 2804897 A	05-12-1997
			EP 0811665 A2	10-12-1997
			ID 16901 A	20-11-1997
			IL 120753 A	06-12-2000
			JP 10044047 A	17-02-1998
			WO 9743087 A1	20-11-1997