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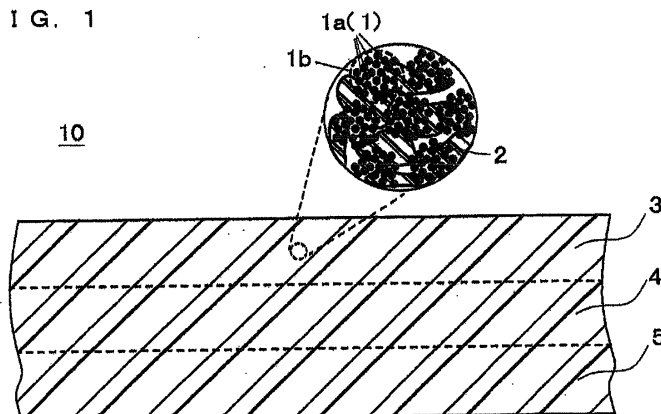
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(54) **RIGID SHEET AND PROCESS FOR MANUFACTURING RIGID SHEET**

(57) Provided is a hard sheet including a non-woven fabric of ultrafine fibers and elastic polymer added into the non-woven fabric. JIS-D hardness of the sheet is 45 degrees or more. $R\%$ thereof calculated by $R(\%) = (D \text{ hardness maximum} - D \text{ hardness minimum}) / D \text{ hardness average} \times 100$ is 0 to 20%, when a sectional surface of the sheet extending in the thickness direction thereof is evenly divided into three parts corresponding to a first

outer layer, an intermediate layer, and a second outer layer in order from any one surface side of the sheet; JIS-D hardness measurements are made at six points being three arbitrary points each on the first outer layer and on the intermediate layer; and then the JIS-D hardnesses obtained are used for the calculation. In the sheet, the total content of ions capable of changing the pH of water is $400 \mu\text{g}/\text{cm}^3$ or less.

FIG. 1



Description

[Technical Field]

[0001] The present invention relates to a hard sheet favorably used as a polishing pad, specifically, as a polishing layer of a polishing pad for polishing semiconductor wafers, semiconductor devices, silicon wafers, hard disks, glass substrates, optical products, various metals, or the like.

[Background Art]

[0002] Integrated circuits formed on semiconductor wafers are highly integrated and have multilayer wiring. Such semiconductor wafers require a high degree of planarity.

[0003] Chemical mechanical polishing (CMP) has been known as a polishing method for polishing semiconductor wafers. CMP is a method wherein the surface of a member to be polished is polished with a polishing pad, while a polishing slurry (hereafter also simply referred to as slurry) containing abrasive grains is dropped to the surface.

[0004] Patent Literatures 1 to 4 listed below each disclose a polishing pad formed of a polymeric foam having a closed cell structure, which is for use in CMP. A polymeric foam is made by foam casting a curable-type two-component liquid polyurethane. A polishing pad made of a polymeric foam has greater rigidity compared to a polishing pad of a non-woven fabric type that will be described later; and is therefore preferably used for polishing semiconductor wafers which require a high degree of planarity.

[0005] A polishing pad made of a polymeric foam has high rigidity. Therefore, load is selectively applied to the protrusions on the member to be polished. As a result, a relatively high polishing rate is obtained. However, when there is an aggregate of abrasive grains on the surface to be polished, load is also selectively applied to the aggregate of abrasive grains. Therefore, scratches tend to occur easily on the surface to be polished. Particularly, in the case of polishing a member having copper wiring or a low-dielectric material having weak adherence at the interface, scratches or boundary separation tend to occur easily (e.g., see Non-Patent Literature 1). Moreover, in foam casting, the elastic polymer tends to foam unevenly easily; therefore, for the member to be polished, the planarity and the polishing rate during polishing tend to become uneven easily. Furthermore, since abrasive grains and polishing dust gradually clog the separate pores in the polymeric foam, the polishing rate gradually lowers.

[0006] Patent Literatures 5 to 14 listed below each disclose a non-woven-fabric-type polishing pad obtained by impregnating a non-woven fabric with porous polyurethane that has undergone wet coagulation. A non-woven-fabric-type polishing pad has excellent flexibility and tends to deform easily. Therefore, since load is unlikely to be selectively applied to the abrasive grains that are aggregated on the surface to be polished, scratches are unlikely to occur. However, due to the flexibility of the non-woven-fabric-type polishing pad, the polishing rate is low. Moreover, a non-woven-fabric-type polishing pad deforms in conformity with the surface shape of the member to be polished; therefore planarization performance, i.e., the ability to planarize the member to be polished, is low.

[0007] Moreover, Patent Literatures 15 to 18 listed below each disclose a polishing pad comprising a non-woven fabric of ultrafine fibers that is capable of high planarization performance. For example, Patent Literature 15 discloses a polishing pad as a sheet-like product comprising: a non-woven fabric formed by entanglement of ultrafine polyester fiber bundles with an average fineness of 0.0001 to 0.01 dtex; and an elastic polymer mainly composed of polyurethane included in the non-woven fabric via impregnation. This reference discloses that such polishing pad achieves a polishing work with higher precision than in the past.

[0008] In common polishing pads that have used a non-woven fabric comprising ultrafine fibers, there has been used a non-woven fabric obtained by needle punching short ultrafine fibers. Such non-woven fabric has had low apparent density, high porosity, and thus low rigidity. Therefore, due to such non-woven fabric deforming in conformity with the surface shape of the surface to be polished, planarization performance was low.

[0009] Patent Literature 19 discloses a polishing pad comprising: an entangled fiber body formed of a fiber bundle of individual ultrafine fibers; and an elastic polymer, wherein one part of the elastic polymer is present in the fiber bundle to bundle together the individual ultrafine fibers, and the volume percent of the part excluding the pores falls within the range of 55 to 95%.

[0010] Moreover, Patent Literature 20 discloses a polishing pad having a polishing layer and a base layer, wherein an intermediate layer with a water absorption of 1 % or less is interposed between the polishing layer and the base layer, and the difference between the D hardness of the polishing layer and the D hardness of the intermediate layer is 20 degrees or less.

[Prior Art]

[Patent Literatures]

5 **[0011]**

[Patent Literature 1] Japanese Laid-Open Patent Publication No. 2000-178374
 [Patent Literature 2] Japanese Laid-Open Patent Publication No. 2000-248034
 [Patent Literature 3] Japanese Laid-Open Patent Publication No. 2001-89548
 10 [Patent Literature 4] Japanese Laid-Open Patent Publication No. Hei 11-322878
 [Patent Literature 5] Japanese Laid-Open Patent Publication No. 2002-9026
 [Patent Literature 6] Japanese Laid-Open Patent Publication No. Hei 11-99479
 [Patent Literature 7] Japanese Laid-Open Patent Publication No. 2005-212055
 [Patent Literature 8] Japanese Laid-Open Patent Publication No. Hei 3-234475
 15 [Patent Literature 9] Japanese Laid-Open Patent Publication No. Hei 10-128674
 [Patent Literature 10] Japanese Laid-Open Patent Publication No. 2004-311731
 [Patent Literature 11] Japanese Laid-Open Patent Publication No. Hei 10-225864
 [Patent Literature 12] Japanese Unexamined Patent Publication No. 2005-518286
 [Patent Literature 13] Japanese Laid-Open Patent Publication No. 2003-201676
 20 [Patent Literature 14] Japanese Laid-Open Patent Publication No. 2005-334997
 [Patent Literature 15] Japanese Laid-Open Patent Publication No. 2007-54910
 [Patent Literature 16] Japanese Laid-Open Patent Publication No. 2003-170347
 [Patent Literature 17] Japanese Laid-Open Patent Publication No. 2004-130395
 [Patent Literature 18] Japanese Laid-Open Patent Publication No. 2002-172555
 25 [Patent Literature 19] Japanese Laid-Open Patent Publication No. 2008-207323
 [Patent Literature 20] Japanese Laid-Open Patent Publication No. 2011-200984

[Non-Patent Literature]

30 **[0012]** [Non-Patent Literature 1] "CMP No Saiensu (The Science of CMP)"; Science Forum Inc.; August 20, 1997; pp. 113-119

[Summary of Invention]

35 [Technical Problem]

[0013] An object of the present invention is to provide a polishing pad with a high polishing rate that is unlikely to change with time.

40 [Solution to Problem]

[0014] One aspect of the present invention relates to a hard sheet including:

45 a non-woven fabric of ultrafine fibers having a fineness of 0.0001 to 0.5 dtex; and
 an elastic polymer added into the non-woven fabric,
 the hard sheet having:

a JIS-D hardness of 45 degrees or more;
 a R% calculated by an equation of $R(\%) = (D \text{ hardness maximum} - D \text{ hardness minimum}) / D \text{ hardness average}$
 50 $\times 100$ of 0 to 20%, when a sectional surface of the hard sheet extending in a thickness direction of the hard
 sheet is evenly divided into three parts corresponding to a first outer layer, an intermediate layer, and a second
 outer layer in order from any one surface side; JIS-D hardness measurements are made at a total of six points
 being three arbitrary points on the first outer layer and three arbitrary points on the intermediate layer; and then
 the JIS-D hardnesses obtained at the six points are used for the calculation, and
 55 a total content of ions capable of causing a pH change in water, of 400 $\mu\text{g}/\text{cm}^3$ or less.

[0015] Moreover, another aspect of the present invention relates to a polishing pad including the foregoing hard sheet as a polishing layer.

[0016] Moreover, still another aspect of the present invention relates to a production method of hard sheet including:

- (1) a step of preparing an entangled fiber sheet including long fibers of ultrafine-fiber-forming fibers, the entangled fiber sheet being capable of forming a non-woven fabric with an apparent density of 0.35 g/cm³ or more including ultrafine fibers with a fineness of 0.5 dtex or less, by subjecting ultrafine-fiber-forming treatment;
- (2) a step of impregnating the entangled fiber sheet with a first emulsion including an elastic polymer and a gelling agent containing ions capable of causing a pH change in water, then allowing the first emulsion to gelate, and then solidifying the elastic polymer by heating and drying;
- (3) a step of forming a first composite body including the non-woven fabric and the elastic polymer by subjecting the ultrafine-fiber-forming fibers to ultrafine-fiber-forming treatment;
- (4) a step of forming a second composite body by impregnating the first composite body with a second emulsion including an elastic polymer and a gelling agent and then solidifying the elastic polymer by heating and drying, the second composite body having a difference in porosity between a first outer layer and an intermediate layer of 5% or less, when the second composite body formed is evenly divided into three parts in a thickness direction of the second composite body, the three parts corresponding to the first outer layer, the intermediate layer, and a second outer layer in order from any one surface side;
- (5) a step of water washing the second composite body such that a total content of the ions becomes 400 μg/cm³ or less to obtain a hard sheet; and
- (6) a step of hot pressing at least one selected from the first composite body, the second composite body, and the hard sheet, such that a surface hardness of the hard sheet becomes 45 degrees or more in JIS-D hardness.

[Advantageous Effects of Invention]

[0017] There is obtained a hard sheet for obtaining a polishing pad having a high polishing rate that is unlikely to change with time.

[Brief Description of Drawing]

[0018] Fig. 1 is schematic sectional illustration of one embodiment of a hard sheet.

[Description of Embodiment]

[0019] An embodiment of a hard sheet according to the present invention will now be described in detail. Fig. 1 is a schematic sectional view of a hard sheet 10 of the present embodiment. In Fig. 1, the circled area schematically depicts an enlarged view of a portion of the sectional view.

[0020] As in Fig. 1, the hard sheet 10 includes: a non-woven fabric 1 being an entangled body of ultrafine fibers 1 a; and an elastic polymer 2 added into the non-woven fabric 1. The hard sheet 10 has a JIS-D hardness of 45 degrees or more; and has a R% calculated by the equation of $R(\%) = (D \text{ hardness maximum among six points} - D \text{ hardness minimum among six points}) / D \text{ hardness average of six points} \times 100$ of 0 to 20%, when the hard sheet 10 is evenly divided into three parts in the sheet thickness direction and the three parts correspond to a first outer layer 3, an intermediate layer 4, and a second outer layer 5 in order from the sheet surface side; JIS-D hardness measurements are made at a total of six points being three arbitrary points in the first outer layer 3 and at three arbitrary points in the intermediate layer 4; and then R% is calculated using the D hardnesses obtained at the six points. Moreover, the R% calculated by the above equation is preferably also 0 to 20%, when JIS-D hardness measurements are made at a total of six points being three arbitrary points in the second outer layer 5 and at three arbitrary points in the intermediate layer 4, and the D hardnesses obtained at the six points are used for the calculation. Furthermore, the total content of ions capable of causing a pH change in water, is 400 μg/cm³ or less.

[0021] In the hard sheet 10, regarding the ultrafine fibers 1 a which form the non-woven fabric 1, a plurality of the ultrafine fibers 1a form a fiber bundle 1 b. Moreover, the fiber bundles 1 b are bound together with the elastic polymer 2. Preferably, half or more of the fiber bundles 1 b are bound together with the elastic polymer 2. Furthermore, the ultrafine fibers 1a which form each of the fiber bundles 1 b are also bound together with the elastic polymer 2. Preferably, half or more of the ultrafine fibers 1a are bound together with the elastic polymer 2. Such composite body comprising the non-woven fabric 1 and the elastic polymer 2 corresponds to the hard sheet 10 that is closely-packed, with a small amount of pores and a high degree of hardness. Such hard sheet 10 has high rigidity due to the reinforcing effect by the fiber bundles 1b and the high packing rate (i.e., low porosity) of the hard sheet.

[0022] The hard sheet 10 comprises the non-woven fabric 1 of the ultrafine fibers which form the fiber bundles. The fiber bundles in the non-woven fabric that are present at the surface separate into individual fibers or become fibrillated during polishing. As a result, the ultrafine fibers with a high fiber density become exposed at the polishing surface. These

exposed ultrafine fibers come in contact with the member to be polished, over a wide area; and also can retain large amounts of slurry. Furthermore, since the exposed ultrafine fibers soften the surface of the polishing pad, selective load application to aggregates of abrasive grains is suppressed. As a result, occurrence of scratches is suppressed.

[0023] Moreover, the hard sheet 10 has a JIS-D hardness of 45 degrees or more; and is adjusted to be uniform in the thickness direction such that $R\%$ calculated by the equation of $R(\%) = (D \text{ hardness maximum} - D \text{ hardness minimum}) / D \text{ hardness average} \times 100$ by using the JIS-D hardnesses measured at a total of six points, i.e., three points in the first outer layer 3 and three points in the intermediate layer 2, is 0 to 20%. Moreover, preferably, the hard sheet 10 is adjusted to be uniform in the thickness direction such that $R\%$ calculated by using the JIS-D hardnesses measured at a total of six points, i.e., three points in the second outer layer 5 and three points in the intermediate layer 2, also becomes 0 to 20%. As such, by adjusting to obtain a uniform degree of hardness, a uniform degree of polishing becomes possible.

[0024] Furthermore, the hard sheet 10 is adjusted such that the total content of ions capable of causing a pH change in water becomes $400 \mu\text{g}/\text{cm}^3$ or less. In order for the elastic polymer to be uniformly added into the hard sheet in the thickness direction as described above, typically, a gelling agent is used. Ions in the hard sheet may change the pH of the slurry during polishing. When the pH of the slurry changes, the polishing rate tends to lower and abrasive grains tend to aggregate easily. In such case, by reducing ionizable compounds in the hard sheet by water washing or the like, lowering of the polishing rate caused by a pH change in the slurry can be suppressed. Note that the ions capable of causing a pH change in water correspond to all ions capable of changing the pH of water when dissolved therein.

[0025] As will be described in detail below, the hard sheet of the present embodiment is produced by adding an elastic polymer into a closely-packed non-woven fabric of the ultrafine fibers via impregnation, uniformly and in large proportions in the thickness direction. Moreover, in such production of the hard sheet, in order to add large proportions of the elastic polymer into the non-woven fabric via impregnation, an emulsion of elastic polymer containing a gelling agent is preferably used. Furthermore, production is made possible by water washing the non-woven fabric in the production process, such that the total content of ions in the gelling agent that are capable of causing a pH change in water becomes $400 \mu\text{g}/\text{cm}^3$ or less.

[0026] The components of the hard sheet of the present embodiment will now be described in further detail.

[0027] The non-woven fabric in the present embodiment is formed of ultrafine fibers, and the ultrafine fibers preferably form fiber bundles.

[0028] The ultrafine fibers has a fineness of 0.0001 to 0.5 dtex and preferably 0.001 to 0.01 dtex. When the fineness of the ultrafine fibers is less than 0.0001 dtex, the ultrafine fibers in the vicinity of the surface are unlikely to sufficiently separate into individual fibers during polishing, resulting in decrease in the amount of the slurry retained. When the fineness of the ultrafine fibers exceeds 0.5 dtex, the surface becomes too rough, thereby causing a lower polishing rate; and also, abrasive grains tend to aggregate easily on the surface of the ultrafine fibers.

[0029] The ultrafine fibers are preferably long fibers (filaments), and specifically, have an average fiber length of preferably 100 mm or more and further preferably 200 mm or more. The upper limit of the average fiber length is not particularly limited; and fibers with a length of, for example, several meters, several hundred meters, several kilometers, or a higher value may be included, if not cut during the entanglement process as will be described below. When the ultrafine fibers are long fibers, fiber density can be increased, and therefore, rigidity of the hard sheet is increased. Moreover, the long fibers are unlikely to become detached during polishing. Note that when the ultrafine fibers are short fibers, fiber density cannot be easily increased, and therefore, a high rigidity cannot be obtained for the hard sheet. Moreover, the short fibers tend to become detached easily during polishing.

[0030] Regarding the ultrafine fibers which form the non-woven fabric, it is preferable that a plurality thereof bundled together form a fiber bundle. The average sectional area of the fiber bundle present on a sectional surface of the hard sheet extending in the thickness direction thereof is preferably $80 \mu\text{m}^2$ or more, further preferably $100 \mu\text{m}^2$ or more, and particularly preferably $120 \mu\text{m}^2$ or more, in terms of obtaining a hard sheet with a particularly high rigidity.

[0031] Moreover, regarding the fiber bundles present on the sectional surface of the hard sheet extending in the thickness direction thereof, the proportion of the fiber bundles with a sectional area of $40 \mu\text{m}^2$ or more is preferably 25% or more, relative to a predetermined total number of the fiber bundles on the sectional surface of the hard sheet extending in the thickness direction thereof. When the hard sheet is used in polishing pads for silicon wafers, semiconductor wafers, and semiconductor devices which all require a particularly high degree of planarity, the proportion of the fiber bundles with a sectional area of $40 \mu\text{m}^2$ or more is preferably 40% or more, further preferably 50% or more, and particularly preferably 100%. When the proportion of the fiber bundles of $40 \mu\text{m}^2$ or more is too low, polishing rate tends to lower and planarization performance tends to degrade.

[0032] Moreover, in the hard sheet of the present embodiment, the bundle density of the fiber bundles per unit area of the sectional surface of the hard sheet extending in the thickness direction thereof is preferably 600 bundles/ mm^2 or more, and further preferably 1000 bundles/ mm^2 or more, and moreover, preferably 4000 bundles/ mm^2 or less and further preferably 3000 bundles/ mm^2 or less. In case of such bundle density, during polishing, the fiber bundles at the surface separate into individual fibers or become fibrillated, and ultrafine fibers become formed in large amounts, thereby increasing the amount of the slurry retained. Moreover, by such separation or fibrillation of the fiber bundles, the polishing

surface becomes soft and thus suppresses occurrence of scratches. When the bundle density is too low, the fiber density of the ultrafine fibers formed on the polishing surface lowers; and therefore, polishing rate tends to lower or planarization performance tends to degrade. Moreover, when the fiber bundle density is too high, the polishing surface becomes too closely-packed and tends to cause reduction in the amount of the slurry retained and in the polishing rate. Note that in the hard sheet of the present embodiment, variations in the fiber bundle density are preferably small in the thickness direction and the planar direction, in terms of improving polishing stability.

[0033] The ultrafine fibers are preferably formed of a thermoplastic resin with a glass transition temperature (T_g) of preferably 50°C or more and further preferably 60°C or more. When T_g of the thermoplastic resin is too low, during polishing, planarization performance tends to degrade due to insufficient rigidity, and also, polishing stability and polishing uniformity tend to lower due to lowering of rigidity with time. The upper limit of T_g is not particularly limited, and is preferably 300°C and further preferably 150°C, considering that production is industrial. Note that since the ultrafine fibers will be water-absorbable in the polishing process, T_g is still further preferably 50°C or more, when measured on the ultrafine fibers that remain wet after having undergone treatment with warm water at 50°C. Moreover, water absorption of the thermoplastic resin is preferably 4 mass% or less and further preferably 2 mass% or less. When water absorption exceeds 4 mass%, during polishing, the ultrafine fibers gradually absorb water in the slurry and thereby cause rigidity to lower with time. In such case, planarization performance tends to degrade easily with time, or, polishing rate and polishing uniformity tend to vary easily. Water absorption is preferably 0 to 2 mass%.

[0034] Specific examples of the thermoplastic resin include: aromatic polyester-based resins such as polyethylene terephthalate (PET, T_g : 77°C, water absorption: 1 mass%), isophthalic acid-modified polyethylene terephthalate (T_g : 67 to 77°C, water absorption: 1 mass%), sulfoisophthalic acid-modified polyethylene terephthalate (T_g : 67 to 77°C, water absorption: 1 to 4 mass%), polybutylene naphthalate (T_g : 85°C, water absorption: 1 mass%), and polyethylene naphthalate (T_g : 124°C, water absorption: 1 mass%); and semi-aromatic polyamide-based resins such as copolymerizable nylon comprising terephthalic acid, nonanediol, and methyl octanediol (T_g : 125 to 140°C, water absorption: 1 to 4 mass%). These may be used singly or in a combination of two or more. Among these, polyethylene terephthalate (PET), isophthalic acid-modified polyethylene terephthalate, polybutylene naphthalate, and polyethylene naphthalate are preferred, in terms of being capable of sufficiently maintaining rigidity, water resistance, and wear resistance. Particularly, PET and modified PET such as isophthalic acid-modified PET become crimped to a considerable degree in the wet heat treatment process as will be described below, wherein ultrafine fibers are formed from a sheet of entangled web comprising sea-island-type conjugated fibers; and are therefore preferred in terms of being capable of forming a closely-packed, highly-dense body of entangled fibers; of tending to easily increase rigidity of the hard sheet; of tending not to easily cause progressive change in the hard sheet due to moisture, during polishing; and the like.

[0035] Moreover, to the extent of not adversely affecting the effects of the present invention, as necessary, the ultrafine fibers may contain ultrafine fibers formed of another thermoplastic resin. Examples of such thermoplastic resin for combined use include: aromatic polyesters, aliphatic polyesters, and copolymers thereof, such as polylactic acid, polybutylene terephthalate, polyhexamethylene terephthalate, polyethylene succinate, polybutylene succinate, polybutylene succinate adipate, and polyhydroxybutyrate-polyhydroxyvalerate copolymer; aliphatic nylons and copolymers thereof, such as nylon 6, nylon 66, nylon 10, nylon 11, and nylon 12; polyolefins such as polyethylene and polypropylene; modified polyvinyl alcohols containing 25 to 70 mol% of ethylene units; and elastomers such as polyurethane-based elastomer, nylon-based elastomer, and polyester-based elastomer.

[0036] The hard sheet includes an elastic polymer that is added into the non-woven fabric of the ultrafine fibers.

[0037] Specific examples of the elastic polymer include polyurethane, polyamide-based elastomers, (meth)acrylic ester-based elastomers, (meth)acrylic ester-styrene-based elastomers, (meth)acrylic ester-acrylonitrile-based elastomers, (meth)acrylic ester-olefin-based elastomers, (meth)acrylic ester-(hydrogenated) isoprene-based elastomers, (meth)acrylic ester-butadiene-based elastomers, styrene-butadiene-based elastomers, styrene-hydrogenated isoprene-based elastomers, acrylonitrile-butadiene-based elastomers, acrylonitrile-butadiene-styrene-based elastomers, vinyl acetate-based elastomers, (meth)acrylic ester-vinyl acetate-based elastomers, ethylene-vinyl acetate-based elastomers, ethylene-olefin-based elastomers, silicone-based elastomers, fluorine-based elastomers, and polyester-based elastomers.

[0038] The elastic polymer is preferably non-porous. Note that being non-porous means that there are substantially no pores (no closed cells) as those in porous or sponge-like elastic polymer. For example, it means that the elastic polymer is not of the kind having a plurality of closed cells as in an elastic polymer obtained by solidifying a solvent-based polyurethane.

[0039] When the elastic polymer is non-porous, high polishing stability is obtained, wearing is unlikely, and residues of the slurry and of the pad are unlikely to remain in the pores. Therefore, a high polishing rate can be maintained for long hours. Moreover, since the elastic polymer has high adhesion to the ultrafine fibers, the ultrafine fibers are unlikely to fall out. Furthermore, since a high degree of rigidity is obtained, planarization performance is excellent.

[0040] Water absorption of the elastic polymer is preferably 0.5 to 8 mass% and further preferably 1 to 6 mass%. When water absorption of the elastic polymer is too low, slurry wettability thereof lowers. As a result, polishing rate,

polishing uniformity, and polishing stability tend to lower and abrasive grains tend to aggregate easily. When water absorption of the elastic polymer is too high, rigidity of the hard sheet lowers with time during polishing and planarization performance degrades. Moreover, polishing rate and polishing uniformity becomes varied easily. Note that water absorption of the elastic polymer corresponds to water absorption when a film of the elastic polymer after drying treatment is immersed in water at room temperature for saturation and swelling. Note that when two or more kinds of elastic polymers are included, water absorption is theoretically calculated by multiplying water absorption of each kind of the elastic polymer by its mass fraction and then adding together the obtained values.

[0041] Water absorption of the elastic polymer can be adjusted by introducing a hydrophilic functional group or by adjusting the degree of crosslinkage. Examples of the hydrophilic functional group include a carboxyl group, a sulfonic acid group, and a polyalkylene glycol group with three or less carbon atoms. The hydrophilic group can be introduced by copolymerization of monomers having the hydrophilic group. For copolymerization, the proportion of the monomer units having the hydrophilic group is preferably 0.1 to 20 mass% and further preferably 0.5 to 10 mass%.

[0042] Regarding the elastic polymer, the storage elastic modulus at 150°C [E' (150°C, dry)] is preferably 0.1 to 100 MPa and further preferably 1 to 80 MPa. The storage elastic modulus of the elastic polymer can be adjusted by adjusting the degree of crosslinkage. Note that when two or more kinds of elastic polymers are included, the storage elastic modulus is theoretically calculated by multiplying the storage elastic modulus [E' (150°C, dry)] of each kind of the elastic polymer by its mass fraction and then adding together the obtained values.

[0043] Regarding the elastic polymer, one may be used singly or two or more may be used in a combination. Among those given in above, polyurethane is preferred in terms of having excellent ability to bind to the ultrafine fibers.

[0044] The ultrafine fibers that form the fiber bundles are preferably bundled together by the elastic polymer; and half or more of the ultrafine fibers are further preferably bundled together by the elastic polymer.

[0045] Moreover, the fiber bundles are preferably bound together by the elastic polymer present on the outer side of the fiber bundles; and half or more of these fiber bundles are further preferably bound together by the elastic polymer and are thus present in bulk form. By the fiber bundles being bound together, structural stability of the hard sheet improves and polishing stability thus improves. By bundling together the ultrafine fibers and also binding together the fiber bundles by the elastic polymer, the hard sheet with a uniform and high degree of hardness is obtained.

[0046] When the ultrafine fibers that form the fiber bundles are not bundled together, since the ultrafine fibers obtain flexibility, it becomes difficult to obtain excellent planarization performance. Moreover, the ultrafine fibers tend to fall out easily during polishing, and abrasive grains tend to aggregate on the ultrafine fibers that have fallen out, thereby easily causing scratches. To have the ultrafine fibers bundled together by the elastic polymer, means that the ultrafine fibers present in the fiber bundle adhere and bond to one another via the elastic polymer present in the fiber bundle.

[0047] The ratio between the non-woven fabric and the elastic polymer (non-woven fabric/elastic polymer) in the resin sheet is preferably 90/10 to 55/45 and further preferably 85/15 to 65/35, in mass ratio. When the ratio between the non-woven fabric and the elastic polymer falls within the above range, the rigidity of the hard sheet can be easily increased. Moreover, the density of the ultrafine fibers that are exposed at the surface of the hard sheet can be sufficiently increased. As a result, polishing stability, polishing rate, and planarization performance can be sufficiently improved.

[0048] The apparent density of the hard sheet is preferably 0.5 to 1.2 g/cm³ and further preferably 0.6 to 1.2 g/cm³, in terms of maintaining high rigidity.

[0049] The JIS-D hardness of the hard sheet of the present embodiment is 45 degrees or more; and the R% calculated by the equation of $R(\%) = (D \text{ hardness maximum} - D \text{ hardness minimum}) / D \text{ hardness average of six points} \times 100$ is 0 to 20%, when a sectional surface of the hard sheet extending in the thickness direction thereof is evenly divided into three parts corresponding to a first outer layer, an intermediate layer, and a second outer layer in order from any one surface side of the hard sheet, JIS-D hardness measurements are made at a total of six points, i.e., three arbitrary points on the first outer layer and three arbitrary points on the intermediate layer, and the D hardnesses obtained at the six points are used for the calculation. Moreover, the R% calculated by the above equation by using D-hardnesses measured at a total of six points, i.e., three arbitrary points on the second outer layer and three arbitrary points on the intermediate layer, is also preferably 0 to 20%.

[0050] The JIS-D hardness of the hard sheet is 45 degrees or more, preferably 45 to 75 degrees, and further preferably 50 to 70 degrees. By adjusting the hardness of the first outer layer to 45 degrees or more in JIS-D hardness, excellent planarization performance is obtained. When the JIS-D hardness is too high, scratches tend to occur easily. Note that regarding the hard sheet of the present embodiment, since the ultrafine fibers exposed at the sheet surface have high fiber density, despite the sheet being hard, the sheet surface is soft. Therefore, scratches are unlikely to occur.

[0051] The R% calculated by the above equation using the D-hardnesses measured at a total of six points, i.e., three arbitrary points on the first outer layer and three arbitrary points on the intermediate layer, is 0 to 20% and preferably 0 to 15%. When the R% of the first outer layer and the intermediate layer falls within the above range, when the hard sheet is used as a polishing pad, the change in the polishing rate at the first outer layer and the intermediate layer becomes small and a stable polishing performance is obtained. When the R% exceeds 20%, the change in the polishing rate thereat becomes large during polishing and a stable polishing performance is not obtained. Note that arbitrary points

for JIS-D hardness measurement mean that points for measurement on each of the layers are selected arbitrarily, and that regardless of the positions of the points measured uniformly, the R% obtained would be 0 to 20%. In such case, there will be no deviation in hardness, not only in the thickness direction but also in the width direction; and therefore, there will be a uniform polishing rate and thus a stable polishing performance in the planar direction as well. Similarly, the R% calculated by the above equation using D-hardnesses measured at a total of six points, i.e., three arbitrary points on the second outer layer and three arbitrary points on the intermediate layer, is preferably 0 to 20% and further preferably 0 to 15%.

[0052] In the hard sheet of the present embodiment, the total content of ions that cause a pH change in water is 400 $\mu\text{g}/\text{cm}^3$ or less. As will be described below, the hard sheet of the present embodiment is produced, for example, by impregnating a non-woven fabric with an emulsion of an elastic polymer and then solidifying the elastic polymer by heating and drying, thereby to add the elastic polymer into the non-woven fabric. In such process, water in the emulsion in the non-woven fabric via impregnation starts drying from the fabric surface. Therefore, as evaporation of the water progresses, there occurs migration of the emulsion from inside the non-woven fabric to the outer layer of the non-woven fabric. When migration occurs, the elastic polymer is unevenly distributed to the vicinity of the outer layer of the non-woven fabric, the amount of the elastic polymer in the vicinity of the intermediate layer becomes small, and voids tend to easily remain in the vicinity of the intermediate layer. Such migration is suppressed by adding a gelling agent into the emulsion, so that the emulsion would gelate before drying. The present inventors found that when ions included in the gelling agent that are capable of causing a pH change in water remain in predetermined amounts or more in the hard sheet, the polishing rate lowered during polishing.

[0053] In the hard sheet, the total content of the ions capable of causing a pH change in water is 400 $\mu\text{g}/\text{cm}^3$ or less, preferably 350 $\mu\text{g}/\text{cm}^3$ or less, and further preferably 100 $\mu\text{g}/\text{cm}^3$ or less. Moreover, the total content of the ions is preferably 0 $\mu\text{g}/\text{cm}^3$, but is preferably about 1 to 100 $\mu\text{g}/\text{cm}^3$ and further preferably about 10 to 50 $\mu\text{g}/\text{cm}^3$, in terms of efficiency in industrial water washing. When the total content of the ions capable of causing a pH change in water in the hard sheet exceeds 400 $\mu\text{g}/\text{cm}^3$, a pH change occurs in the slurry and the polishing rate lowers, and furthermore, abrasive grains tend to aggregate easily.

[0054] Note that the ions that causes a pH change in water correspond to all kinds of ions that change the pH of water when dissolved therein. Specifically, for example, there are ions included in a common gelling agent, such as sulfate ions, nitrate ions, carbonate ions, ammonium ions, sodium ions, calcium ions, and potassium ions.

[Production method of polishing pad]

[0055] A detailed description of an example of a hard sheet production method will now be given. A hard sheet can be produced, for example, by following steps given below.

(1) Step of preparing an entangled fiber sheet comprising long fibers of ultrafine-fiber-forming fibers

[0056] In the present step, an entangled fiber sheet of long fibers of ultrafine-fiber-forming fibers will be prepared. The entangled fiber sheet of long fibers of ultrafine-fiber-forming fibers can be produced, for example, as follows.

[0057] First, a web of long fibers formed of sea-island-type conjugated fibers comprising a water-soluble thermoplastic resin as the sea component and a water-insoluble thermoplastic resin as the island components, will be produced. Such sea-island-type conjugated fibers correspond to ultrafine-fiber-forming fibers capable of forming ultrafine fibers which comprise the resin of the island components, by dissolution of the sea component. Although the example described for the present embodiment uses the sea-island-type conjugated fibers as the ultrafine-fiber-forming fibers, in place of such sea-island-type conjugated fibers, well-known ultrafine-fiber-forming fibers such as multilayer-stack-section fibers may be used.

[0058] The water-soluble thermoplastic resin corresponds to a thermoplastic resin that can be removed by dissolution or decomposition by using water, an alkaline aqueous solution, an acidic aqueous solution, or the like. Specific examples of the water-soluble thermoplastic resin include: PVA-based resins such as polyvinyl alcohol (PVA) and PVA copolymers; modified polyesters containing polyethylene glycol and/or alkali metal salt of sulfonic acid as copolymerizable components; and polyethylene oxide. Among these, PVA-based resins are preferred.

[0059] When PVA-based resin included as the sea component in the sea-island-type conjugated fibers is dissolved therefrom, the ultrafine fibers, i.e., the island components, become crimped to a considerable degree. As a result, a non-woven fabric with a high fiber density is obtained. Moreover, when the PVA-based resin is dissolved from the sea-island-type conjugated fibers including the PVA-based resin, since the ultrafine fibers, i.e., the island components and an elastic polymer are neither decomposed nor dissolved, physical properties of the ultrafine fibers and the elastic polymer are unlikely to degrade.

[0060] For the PVA-based resin, an ethylene-modified PVA containing preferably 4 to 15 mol% and further preferably 6 to 13 mol% of ethylene units is preferred, in terms of improving the physical properties of the sea-island-type conjugated

fibers.

[0061] The viscosity-average degree of polymerization of the PVA-based resin is preferably 200 to 500, further preferably 230 to 470, and particularly preferably 250 to 450. Moreover, the melting point of the PVA-based resin is preferably 160 to 250°C, further preferably 175 to 224°C, and particularly preferably 180 to 220°C, in terms of excellent mechanical characteristics and excellent thermal stability, and thus, excellent melt spinning ability.

[0062] For the water-insoluble thermoplastic resin which forms the island components, a thermoplastic resin that cannot be removed by dissolution or decomposition by using water, an alkaline aqueous solution, an acidic aqueous solution, or the like; and that can undergo melt spinning, is used. As specific examples of the water-insoluble thermoplastic resin, the various resins capable of forming ultrafine fibers as given above, preferably thermoplastic resins with T_g of 50°C or more and water absorption of 4 mass% or less, are used.

[0063] Moreover, the water-insoluble thermoplastic resin may contain additives such as a catalytic agent, an anti-coloring agent, a heat resistance modifier, a flame retardant, a lubricant, a stain inhibitor, a fluorescent whitening agent, a delustering agent, a coloring agent, a gloss enhancer, an anti-static agent, an aroma modifier, a deodorizing agent, an anti-bacterial agent, a tick repellent, and inorganic particulates.

[0064] The sea-island-type conjugated fibers can be produced by a conjugate spinning method wherein the water-soluble thermoplastic resin and the water-insoluble thermoplastic resin having low compatibility with the water-soluble thermoplastic resin are each melt spun and then conjugated. Thereafter, the sea-island-type conjugated fibers, remaining in long fiber form, are preferably converted into a web.

[0065] The web of the long fibers of the sea-island-type conjugated fibers is obtained, for example, by a spunbonding method wherein the water-soluble thermoplastic resin and the water-insoluble thermoplastic resin are each melt spun and then conjugated, and the resultant is drawn and then deposited. Note that the long fibers correspond to continuous fibers that are produced without undergoing a cutting process as in production of short fibers. A detailed description will now be given of a production method of a web of long fibers of sea-island-type conjugated fibers, in one example.

[0066] First, the water-soluble thermoplastic resin and the water-insoluble thermoplastic resin are each melted and kneaded by separate extruders, and are then ejected at once from separate spinnerets, as molten resin strands. Then, the ejected strands are conjugated by a composite nozzle; and thereafter, the resultant is ejected from a nozzle opening of a spinning head, thereby to form a sea-island-type conjugated fiber.

[0067] The mass ratio between the water-soluble thermoplastic resin and the water-insoluble thermoplastic resin in the sea-island-type conjugated fibers is not particularly limited, and is preferably 5/95 to 50/50 and further preferably 10/90 to 40/60. It is favorable that the mass ratio between the water-soluble thermoplastic resin and the water-insoluble thermoplastic resin falls within the above range, in terms of obtaining a high-density non-woven fabric and securing excellent ultrafine fiber formability. Moreover, in conjugate melt spinning, the number of islands in the sea-island-type conjugated fibers is preferably 4 to 4000 islands/fiber and further preferably 10 to 1000 islands/fiber. Moreover, fineness of the sea-island-type conjugated fiber is not particularly limited, and is preferably about 0.5 to 3 dtex from an industrial perspective.

[0068] The sea-island-type conjugated fibers are cooled by using a cooling device; and then drawn by a high-speed air flow at a rate corresponding to a take-up speed of 1000 to 6000 m/min such that a target fineness is obtained, by using a suction device such as an air-jet nozzle. Thereafter, the conjugated fibers that have been drawn are deposited on top of a mobile capturing surface, thereby to form a web of long fibers. At that time, the deposited web of the long fibers may be partially pressure bonded as necessary.

[0069] Subsequently, plural sheets of the web are overlapped and entangled. Entanglement of the sheets of the web can be conducted by needle punching or high-pressure water jetting. As a typical example, an entanglement treatment by needle punching will be described in detail.

[0070] First, a silicone-based oiling agent such as an anti-needle-breakage oiling agent, an anti-static oiling agent, or an entanglement-enhancing oiling agent, or a mineral-oil-based oiling agent is added into the web. Then, the web is entangled by needle punching. The mass per unit area of the entangled web preferably falls within the range of 100 to 1500 g/m², in terms of excellent handling characteristics.

[0071] Subsequently, the entangled web of the long fibers is shrunk to increase fiber density. By shrinking the web of the long fibers, shrinking is allowed to a greater extent compared to when shrinking a web of short fibers. Shrinkage treatment is preferably conducted by a wet heat shrinkage treatment such as steam heating. Regarding steam heating conditions, for example, a condition of heating for 60 to 600 seconds at an ambient temperature of 60 to 130°C and at a relative humidity of preferably 75% or more and further preferably 90% or more, can be given.

[0072] The wet heat shrinkage treatment preferably causes the entangled web of the long fibers to shrink such that the area shrinkage becomes preferably 35% or more and further preferably 40% or more. By allowing such high degree of shrinkage, fiber density increases significantly. The upper limit of the area shrinkage is preferably about 80% or less, in terms of shrinkage limit and treatment efficiency. Note that the area shrinkage (%) is calculated by the following equation:

(Area of entangled web before shrinkage treatment – Area of entangled web after shrinkage treatment) /

Area of entangled web before shrinkage treatment × 100.

[0073] The entangled web that has undergone the wet heat shrinkage treatment as above may further be hot rolled or hot pressed, thereby to further increase fiber density. Regarding the change in mass per unit area of the entangled web before and after the wet heat shrinkage treatment, the mass per unit area thereafter compared to the mass per unit area thereof (mass ratio) is preferably 1.2 times or more and further preferably 1.5 times or more, and preferably 4 times or less and further preferably 3 times or less. As such, a web of long fibers of sea-island-type conjugated fibers (hereafter referred to as entangled fiber sheet) is obtained.

[0074] Such entangled fiber sheet becomes converted to a non-woven fabric with an apparent density of 0.35 to 0.90 g/cm³, due to the sea-island-type conjugated fibers subsequently forming ultrafine fibers.

[0075] Compared to an entangled web comprising short fibers, the entangled web comprising the long fibers shrinks to a more considerable extent by wet heating, due to formation of the ultrafine fibers. Therefore, the fiber density of the ultrafine fibers is of a higher degree. Subsequently, the water-soluble thermoplastic resin in the sea-island-type conjugated fibers is removed selectively, thereby to form a non-woven fabric comprising fiber bundles of the ultrafine fibers. At that time, voids are created at portions from which the water-soluble thermoplastic resin has been extracted by dissolution. By adding large proportions of elastic polymer into the voids, the ultrafine fibers that form the fiber bundles are bundled together, and also, the fiber bundles are bound together. As such, a hard sheet with high fiber density, low porosity, and high rigidity is obtained.

(2) Step of impregnating the entangled fiber sheet with a first emulsion comprising a gelling agent and an elastic polymer, the gelling agent containing ions that cause a pH change in water; allowing the first emulsion to gelate; and then solidifying the elastic polymer by heating and drying

[0076] In the present step, an elastic polymer is packed in the entangled fiber sheet, uniformly in the sheet thickness direction. Since an emulsion of elastic polymer is highly concentrated, low in viscosity, and excellent in permeability via impregnation, the entangled fiber sheet can be easily filled with large proportions of the emulsion. Moreover, by including a gelling agent in the emulsion of elastic polymer, it is possible to suppress migration of the emulsion which causes uneven distribution thereof in the sheet thickness direction when dried.

[0077] In contrast to when a conventional and typical solution of elastic polymer is used, when the emulsion of elastic polymer is used, a non-porous elastic polymer can be formed.

[0078] For the elastic polymer, elastic polymer capable of hydrogen bonding is preferable in terms of high adhesion to fibers. Elastic polymers capable of hydrogen bonding correspond to, for example, elastomers comprising a polymer capable of crystallization or aggregation by hydrogen bonding, as with polyurethanes, polyamide-based elastomers, polyvinyl alcohol-based elastomers, and the like.

[0079] A detailed description of when polyurethane is used as the elastic polymer will now be given in a typical example.

[0080] Examples of the polyurethane include various kinds thereof obtained by reacting polymeric polyol having an average molecular weight of 200 to 6000, organic polyisocyanate, and a chain-elongating agent, in a predetermined molar ratio.

[0081] Specific examples of the polymeric polyol include: polyether-based polyols such as polyethylene glycol, polypropylene glycol, polytetramethylene glycol, and poly(methyl tetramethylene) glycol, and copolymers thereof; polyester-based polyols such as polybutylene adipate diol, polybutylene sebacate diol, polyhexamethylene adipate diol, poly(3-methyl-1,5-pentylene adipate) diol, poly(3-methyl-1,5-pentylene sebacate) diol, and polycaprolactone diol, and copolymers thereof; polycarbonate-based polyols such as polyhexamethylene carbonate diol, poly(3-methyl-1,5-pentylene carbonate) diol, polypentamethylene carbonate diol, and polytetramethylene carbonate diol, and copolymers thereof; and polyester carbonate polyols. Moreover, as necessary, these may be used in a combination with a polyfunctional alcohol such as a trifunctional alcohol, e.g., trimethylolpropane, or a tetrafunctional alcohol, e.g., pentaerythritol; or a short-chain alcohol such as ethylene glycol, propylene glycol, 1,4-butanediol, or 1,6-hexanediol. Such polymeric polyols may be used singly or in a combination of two or more. Particularly, amorphous polycarbonate-based polyol, alicyclic polycarbonate-based polyol, linear polycarbonate-based polyol, a mixture of any one of these polycarbonate-based polyols and polyether-based polyol, and polyester-based polyol are preferred in terms of obtaining a hard sheet that is excellent in durability characteristics such as hydrolysis resistance and oxidation resistance. Moreover, polyurethane having a polyalkylene glycol group with five carbon atoms or less and particularly three carbon atoms or less is preferred, in terms of water wettability becoming particularly favorable.

[0082] Specific examples of the organic polyisocyanate include: non-yellowing diisocyanates such as aliphatic or alicyclic diisocyanates, e.g., hexamethylene diisocyanate, isophorone diisocyanate, norbornene diisocyanate, and 4,4'-

dicyclohexylmethane diisocyanate; and aromatic diisocyanates such as 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate, 4,4'-diphenylmethane diisocyanate, and xylylene diisocyanate polyurethane. Moreover, as necessary, these may be used in a combination with a multifunctional isocyanate such as a trifunctional isocyanate or a tetrafunctional isocyanate. Such organic polyisocyanates may be used singly or in a combination of two or more. Among these, 4,4'-dicyclohexylmethane diisocyanate, 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate, 4,4'-diphenylmethane diisocyanate, and xylylene diisocyanate are preferred, in terms of high adhesion to fibers and of obtaining a hard sheet with a high degree of hardness.

[0083] Specific examples of the chain-elongating agent include: diamines such as hydrazine, ethylenediamine, propylenediamine, hexamethylenediamine, nonamethylenediamine, xylylenediamine, isophoronediamine, piperazine and derivatives thereof, adipic dihydrazide, and isophthalic dihydrazide; triamines such as diethylenetriamine; tetramines such as triethylenetetramine; diols such as ethylene glycol, propylene glycol, 1,4-butanediol, 1,6-hexanediol, 1,4-bis(β -hydroxyethoxy)benzene, and 1,4-cyclohexanediol; triols such as trimethylolpropane; pentanols such as pentaerythritol; and amino alcohols such as aminoethyl alcohol and aminopropyl alcohol. These may be used singly or in a combination of two or more. Among these, two or more from hydrazine, piperazine, hexamethylenediamine, isophoronediamine or a derivative thereof, and a triamine such as ethylenetriamine are preferably used in a combination, in terms of completing a curing reaction in a short time. Moreover, monoamines such as ethylamine, propylamine, or butylamine; monoamine compounds having a carboxyl group such as 4-aminobutanoic acid and 6-aminohexanoic acid; or monools such as methanol, ethanol, propanol, or butanol, may be used in a combination with the chain-elongating agent at the time of chain-elongation reaction.

[0084] Moreover, a compound such as a diol having a carboxyl group, or the like, such as 2,2-bis(hydroxymethyl)propionic acid, 2,2-bis(hydroxymethyl)butanoic acid, or 2,2-bis(hydroxymethyl)valeric acid, can be used in a combination with the polyurethane, thereby to introduce an ionic group such as a carboxyl group into the polyurethane skeleton. This can further improve water wettability.

[0085] Moreover, in order to control water absorption and storage elastic modulus of the polyurethane, a crosslinking agent having molecules that contain two or more of a functional group capable of reacting with a functional group included in monomer units that form polyurethane, or a self-crosslinking compound such as a polyisocyanate-based compound or a polyfunctional blocked isocyanate-based compound, is added, thereby to form a crosslinked structure.

[0086] Examples of the combination of the functional group with monomer units and the functional group in the crosslinking agent, include: a carboxyl group and an oxazoline group; a carboxyl group and a carbodiimide group; a carboxyl group and an epoxy group; a carboxyl group and a cyclocarbonate group; a carboxyl group and an aziridine group; and a carbonyl group and a hydrazine or hydrazide derivative. Among these, a combination of monomer units having a carboxyl group and a crosslinking agent having an oxazoline group, a carbodiimide group, or an epoxy group; a combination of monomer units having a hydroxyl group or an amino group and a crosslinking agent having a blocked isocyanate group; and a combination of monomer units having a carbonyl group and a hydrazine or hydrazide derivative, are particularly preferred in terms of allowing easy formation of crosslinks as well as excellent rigidity and wear resistance of the hard sheet. Note that the crosslinked structure is preferably formed in the heat treatment process conducted after the polyurethane is added into the entangled fiber sheet, in terms of being able to maintain stability of the emulsion of elastic polymer. Among the above, a carbodiimide group and/or an oxazoline group that allow excellent crosslinking performance and pot life of the emulsion, and that are problem-free in regard to safety, are particularly preferred. Examples of the crosslinking agent having a carbodiimide group include water-dispersion carbodiimide-based compounds such as "CARBODILITE E-01", "CARBODILITE E-02", and "CARBODILITE V-02" all available from Nisshibo Industries, Inc. Moreover, examples of the crosslinking agent having an oxazoline group include water-dispersion oxazoline-based compounds such as "EPOCROS K-2010E", "EPOCROS K-2020E", and "EPOCROS WS-500" all available from Nippon Shokubai Co., Ltd. Regarding the amount of the crosslinking agent added into the polyurethane, effective components of the crosslinking agent relative to the polyurethane is preferably 1 to 20 mass%, further preferably 1.5 to 1 mass%, and still further preferably 2 to 10 mass%.

[0087] Moreover, in terms of increasing adhesion to the ultrafine fibers so as to increase rigidity of the fiber bundles, the content of the components of the polymeric polyol in the polyurethane is preferably 65 mass% or less and further preferably 60 mass% or less. Moreover, the content thereof in the polyurethane is preferably 40 mass% or more and further preferably 45 mass% or more, in terms of being able to suppress occurrence of scratches due to imparting of moderate elasticity.

[0088] The method for preparing an emulsion of the polyurethane is not particularly limited and a known method can be used. Specifically, for example, a method for imparting an ability of self-emulsification in water to the polyurethane, by using monomers having a hydrophilic group such as a carboxyl group, a sulfone group, or a hydroxyl group, as copolymerizable components; or a method for emulsifying the polyurethane by adding a surfactant thereto, can be given. An elastic polymer that include monomeric units having a hydrophilic group as copolymerizable components have excellent water wettability and therefore can retain large amounts of slurry.

[0089] Specific examples of the surfactant used for emulsification include: anionic surfactants such as sodium lauryl

sulfate, ammonium lauryl sulfate, polyoxyethylene tridecyl ether sodium acetate, sodium dodecylbenzenesulfonate, sodium alkylidiphenyletherdisulfonate, and sodium dioctylsulfosuccinate; and non-ionic surfactants such as polyoxyethylene nonylphenyl ether, polyoxyethylene octylphenyl ether, polyoxyethylene lauryl ether, polyoxyethylene stearyl ether, and polyoxyethylene-polyoxypropylene block copolymer. Moreover, a surfactant having reactivity, i.e., a reactive surfactant may be used. Moreover, by arbitrarily selecting the clouding point of the surfactant, a thermosensitive gelation ability also can be imparted to the emulsion.

[0090] The solidifying concentration of the emulsion is preferably 15 to 40 mass% and further preferably 25 to 35 mass%, in terms of being able to pack the entangled fiber sheet with the elastic polymer, highly and uniformly in the sheet thickness direction. Moreover, the particle size of the emulsion is preferably 0.01 to 1 μm and further preferably 0.03 to 0.5 μm .

[0091] A first emulsion includes a gelling agent containing ions that cause a pH change in water. The gelling agent is used in order to allow gelation of the emulsion particles by heating, by causing change in the pH of the emulsion. The water in the emulsion included in the non-woven fabric via impregnation starts drying from the surface of the non-woven fabric. Therefore, as evaporation of the water progresses, migration of the emulsion from inside the non-woven fabric to the outer layer of the non-woven fabric tends to easily occur. When migration of the emulsion inside the non-woven fabric occurs, the elastic polymer is unevenly distributed to the vicinity of the outer layer of the non-woven fabric, the amount of the elastic polymer in the vicinity of the intermediate layer becomes small, and voids tend to easily remain in the vicinity of the intermediate layer. When voids remain in the vicinity of the intermediate layer, hardness at the intermediate layer lowers and also becomes non-uniform. Such migration is suppressed by adding the gelling agent into the emulsion, so that the emulsion would gelate before drying.

[0092] For the gelling agent, any kind can be used without particular limitation, as long as the gelling agent is a water-soluble salt capable of changing the pH of the emulsion to the extent that the emulsion particles would gelate by heating. Specific examples of the gelling agent include monovalent or bivalent inorganic salts such as sodium sulfate, ammonium sulfate, sodium carbonate, calcium chloride, calcium sulfate, calcium nitrate, zinc oxide, zinc chloride, magnesium chloride, potassium chloride, potassium carbonate, sodium nitrate, and lead nitrate.

[0093] The proportion of the gelling agent in the first emulsion is preferably 0.5 to 5 parts by mass and further preferably 0.6 to 4 parts by mass, relative to 100 parts by mass of the elastic polymer, in terms of being able to moderately impart a gelation ability.

[0094] The first emulsion may further contain a penetrating agent, an antifoam, a lubricant, a water repellant, an oil repellant, a viscous agent, an extender, a curing accelerator, an antioxidant, an ultraviolet absorber, a fluorescing agent, an antifungal agent, a foaming agent, a water-soluble polymeric compound such as polyvinyl alcohol or carboxymethyl cellulose, a dye, a pigment, inorganic particulates, or the like.

[0095] The method for impregnating the entangled fiber sheet with the first emulsion is not particularly limited, and for example, a method of dipping and nipping, knife coating, bar coating, or roll coating can be used.

[0096] Subsequently, after the entangled fiber sheet is impregnated with the first emulsion, heating is conducted to allow the first emulsion to gelate inside the entangled fiber sheet. Regarding heating conditions for such gelation, for example, a condition of holding heating for about 0.5 to 5 minutes at preferably 40 to 90°C and further preferably 50 to 80°C, is preferably used. Moreover, heating is preferably conducted with steam, in terms of being able to uniformly heat the inner layer, while also suppressing migration of the emulsion that is due to rapid evaporation of water from the outer layer.

[0097] Then, after the first emulsion gelates, heating and drying is conducted to solidify the elastic polymer.

[0098] For heating and drying, for example, a method for heating and drying in a dryer such as a hot-air dryer, or a method for heating and drying in the dryer after conducting infrared heating, can be given. Regarding heating and drying conditions, for example, a condition of heating in 2 to 10 minutes such that the maximum temperature becomes preferably 130 to 160°C and further preferably 135 to 150°C, can be given. By heating and drying, the water in the first emulsion evaporates, resulting in even aggregation of the elastic polymer. Therefore, the elastic polymer is able to be uniformly added into the entangled fiber sheet, also in the sheet thickness direction.

(3) Step of subjecting the ultrafine-fiber-forming fibers to an ultrafine-fiber-forming treatment, thereby to form a first composite body comprising a non-woven fiber of the ultrafine fibers and the elastic polymer included therein

[0099] The sea-island-type conjugated fibers included in the entangled fiber sheet into which the elastic polymer has been added via impregnation, are subjected to an ultrafine-fiber-forming treatment, thereby to form a first composite body comprising a non-woven fabric of the ultrafine fibers and the elastic polymer included therein.

[0100] The present step involves forming ultrafine fibers by an ultrafine-fiber-forming treatment whereby the water-soluble thermoplastic resin is removed from the sea-island-type conjugated fibers which comprise the water-soluble thermoplastic resin as the island components and the water-insoluble thermoplastic resin as the sea component.

[0101] The ultrafine-fiber-forming treatment is a treatment whereby the entangled fiber sheet comprising the sea-island-type conjugated fibers undergoes hot water heat treatment by using water, alkaline aqueous solution, acidic aqueous solution, or the like, thereby to remove the water-soluble thermoplastic resin forming the sea component, by dissolution or decomposition.

[0102] To give a specific example of a method preferably used for hot water heat treatment, at the first stage, the entangled fiber sheet is immersed in hot water at 65 to 90°C for 5 to 300 seconds; and then, at the second stage, the entangled fiber sheet is immersed in hot water at 85 to 100°C for 100 to 600 seconds. Moreover, in order to improve dissolution efficiency, as necessary, a treatment such as nipping with rollers, high-pressure water jetting, ultrasonication, showering, stirring, rubbing, or the like may be conducted.

[0103] By subjecting the entangled fiber sheet to hot water heat treatment, the water-soluble thermoplastic resin dissolves from the sea-island-type conjugated fibers, resulting in formation of ultrafine fibers. Note that when formed, the ultrafine fibers become crimped to a considerable degree. Such crimping causes the ultrafine fibers to have a higher fiber density. Moreover, due to the removal of the water-soluble thermoplastic resin from the sea-island-type conjugated fibers, voids are created at portions where the water-soluble thermoplastic resin had been present. These voids are packed with the elastic polymer by a subsequent process. Moreover, by subjecting the entangled fiber sheet to hot water heat treatment, the gelling agent included in the sheet is also removed by dissolution in hot water. As such, a first composite body is formed.

(4) Step of forming a second composite body by impregnating the first composite body with a second emulsion comprising a gelling agent and an elastic polymer; allowing the second emulsion to gelate; and then solidifying the elastic polymer by heating and drying

[0104] As described above, in the first composite body formed by removal of the water-soluble thermoplastic resin from the sea-island-type conjugated fibers, voids are created at portions where the water-soluble thermoplastic resin had been present. In order to obtain the hard sheet of the present embodiment having a uniform and high degree of hardness, the voids in the first composite body are packed with the elastic polymer, thereby to bind the ultrafine fibers together.

[0105] By packing the voids created by removal of the water-soluble thermoplastic resin, with the elastic polymer, the ultrafine fibers are bundled together and the porosity of the hard sheet can thus be lowered. When the ultrafine fibers form fiber bundles, the emulsion tends to permeate easily due to capillary action.

[0106] A second emulsion is selected from those listed for the first emulsion. Note that the second emulsion and the first emulsion may have the same composition or different compositions.

[0107] In the present step, it is preferable that the second emulsion is added and undergoes gelation, such that when the second composite body formed is evenly divided into three parts in the thickness direction thereof and the three parts correspond to a first outer layer, an intermediate layer, and a second outer layer in order from any one surface side thereof, the difference in porosity between the first outer layer and the intermediate layer is preferably 5% or less and further preferably 3% or less. By adjusting as such, a hard sheet with a uniform and high degree of hardness is obtained.

[0108] Note that the difference in porosity between the first outer layer and the intermediate layer is calculated by the following equation:

$$\text{Difference in porosity between first outer layer and intermediate layer (\%)} = \text{Absolute value (Porosity of}$$

$$\text{intermediate layer (\%)} - \text{Porosity of first outer layer (\%)).}$$

[0109] The porosity of each of the layers is obtained as follows. An image of a sectional surface of the second composite body extending in the thickness direction thereof, magnified 30X, is taken by a scanning electron microscope. Then, by using an image analysis software Popimaging (available from Digital being kids.Co), the image obtained is binarized by dynamic thresholding to determine the void portions. Then, a circle is inscribed in each of the void portions; and the total area of the inscribed circles is referred to as the total amount of voids in all of the layers in total. Then, by using the image, 1/3 of the second composite body in the thickness direction, from one surface, is determined as the first outer layer; 1/3 thereof in the thickness direction, from the other surface, is determined as the second outer layer; and the remaining layer is determined as the intermediate layer; and the total area of the inscribed circles is obtained for each of the layers and referred to as the amount of the voids in each of the layers. Then, porosity of each of the layers is obtained by the following equation:

Porosity of each layer = Amount of voids in each layer / Amount of voids in layers in total $\times$ 100 (%).

[0110] Regarding the method for impregnating the first composite body with the second emulsion and the methods for gelation and for heating and drying of the second emulsion, those similar to the method for impregnating the first composite body with the first emulsion and the methods for gelation and for heating and drying of the first emulsion, are used. As such, a second composite body is formed.

(5) Step of water washing such that the total content of ions that cause a pH change in the second composite body becomes $400 \mu\text{g}/\text{cm}^3$ or less

[0111] As described above, the hard sheet of the present embodiment used the emulsion containing the gelling agent, in order to suppress migration of the emulsion to the outer layer at the time of adding the elastic polymer into the non-woven fabric. The present inventors found that when considerable amounts of ions that had been in the gelling agent remained in the hard sheet obtained, the polishing rate lowered at the time of polishing. Moreover, they found that by conducting water washing and making the remaining amount of the ions $400 \mu\text{g}/\text{cm}^3$ or less, lowering of the polishing rate was able to be suppressed.

[0112] The process of water washing is such that the total content of the ions that cause a pH change in water included in the hard sheet becomes $400 \mu\text{g}/\text{cm}^3$ or less, preferably $350 \mu\text{g}/\text{cm}^3$ or less, and further preferably $100 \mu\text{g}/\text{cm}^3$ or less. As the water washing method, for example, heated water washing treatment is preferable in terms of excellent water washing efficiency. Regarding specific conditions, for example, a condition of immersing the second composite body in hot water at 80°C or more, can be given. In detail, for example, at the first stage, the second composite body is immersed in hot water at 65 to 90°C for 5 to 300 seconds; and then, at the second stage, the second composite body is immersed in hot water at 85 to 100°C for 100 to 600 seconds. Moreover, in order to improve water washing efficiency, as necessary, a treatment such as nipping with rollers, high-pressure water jetting, ultrasonication, showering, stirring, rubbing, or the like may be conducted.

(6) Step of hot pressing at least one selected from the first composite body, the second composite body, and the hard sheet, in order to make the surface hardness of the hard sheet 45 degrees or more in JIS-D hardness

[0113] The voids present in the hard sheet lower the degree of hardness as well as hardness uniformity of the sheet. In the present step, the first composite body, the second composite body, and/or the hard sheet as described above are hot pressed to reduce the number of voids. By reducing the number of voids as such, the apparent density of the hard sheet increases, the degree of hardness as well as hardness uniformity increases, and the rigidity thus increases. Regarding hot pressing conditions, a preferable condition is of pressing at a linear pressure of 30 to $100 \text{ kg}/\text{cm}$ by using metal rollers heated to, for example, 160 to 180°C as the temperature not allowing decomposition of the ultrafine fibers and the elastic polymer.

[0114] By following the steps as above, the hard sheet of the present embodiment is obtained. The hard sheet of the present embodiment is preferably used as a polishing layer of a polishing pad. Specifically, the hard sheet can be processed as desired as necessary to form a polishing layer. For example, the hard sheet is subjected to a napping treatment by using sandpaper, card clothing, diamond, or the like, or to a brushing by reverse sealing, hot press treatment, or emboss processing. Moreover, grooves in a grid pattern, a concentric pattern, a spiral pattern, or the like, or holes may be formed on the surface of the hard sheet.

[0115] Moreover, as necessary, an elastic layer such as that of a knitted fabric, a woven fabric, a non-woven fabric, an elastic resin film, or an elastic sponge-like body, may be stacked on the hard sheet serving as the polishing layer. Examples of such elastic film and such elastic sponge-like body include: non-woven fabrics impregnated with a kind of polyurethane currently widely used (e.g., "SUBA400" (available from Nitta Haas Incorporated)); rubbers such as natural rubber, nitrile rubber, polybutadiene rubber, and silicone rubber; thermoplastic elastomers such as polyester-based thermoplastic elastomer, polyamide-based thermoplastic elastomer, and fluorine-based thermoplastic elastomer; foamed plastic; and polyurethane. By stacking the elastic layer as such, local planarity of the surface to be polished (local planarity of wafer) can also be improved. Note that regarding the polishing pad, in addition to the kind comprising the polishing layer and the elastic layer directly joined to each other by fusion bonding or the like, there are also the kind comprising such two layers adhering to each other via an adhesive, a double-sided adhesive tape, or the like; and furthermore, the kind comprising such two layers with another layer further interposed therebetween.

[0116] The polishing pad which uses the hard sheet of the present embodiment can be used for chemical mechanical polishing (CMP) wherein the surface to be polished and the polishing pad are brought in contact with each other under pressure at a certain rate for a certain amount of time, via a slurry, by using a known CMP equipment. The slurry contains,

for example, a liquid medium such as water, oil, or the like; an abrading agent such as silica, aluminum oxide, cerium oxide, zirconium oxide, silicon carbide or the like; and a component such as a base, an acid, a surfactant, or the like. Moreover, in conducting CMP, as necessary, a lubricant, a coolant, or the like may be used in a combination with the slurry.

[0117] The product for polishing is not particularly limited and examples include crystal, silicon, glass, optical substrates, electronic circuit boards, multilayer wiring boards, and hard disks. Particularly, for polishing, silicon wafers and semiconductor wafers are preferred. Specific examples of semiconductor wafers include those having on the surface, for example, an insulating film of silicon oxide, silicon fluoride oxide, organic polymer, or the like; a film comprising metal for wiring material such as copper, aluminum, tungsten, or the like; or a barrier film of metal such as tantalum, titanium, tantalum nitride, titanium nitride, or the like.

[Examples]

[0118] The present invention will now specifically described by way of Examples. The following Examples, however, are not to be construed as limiting in any way the scope of the present invention.

[0119] First, evaluation methods used for the present Examples will be described on the whole as follows.

[Apparent density of hard sheet]

[0120] The value obtained by dividing the mass per unit area (g/cm^2) of the hard sheet by the thickness (cm) thereof was referred to as the apparent density (g/cm^3). Moreover, apparent density measurements were made at ten arbitrary points in the hard sheet, and the arithmetic average of the obtained values was calculated as the apparent density. Note that the thickness was measured with an applied load of $240 \text{ gf}/\text{cm}^2$ in compliance with JISL1096.

[0121] [JIS-D hardness measurements of surface, first outer layer, and intermediate layer of hard sheet, and calculation of R%]

[0122] D hardness measurements were made on the surface, the first outer layer, and the intermediate layer of the hard sheet in compliance with JIS K 7311. Specifically, for the D hardness of the surface of the hard sheet, eight hard sheets each with a thickness of about 1.25 mm were overlapped and D hardness measurements were made at three points at regular intervals in the width direction; and the average of the obtained values was referred to as the D hardness of the surface of the hard sheet.

[0123] Moreover, for the D hardness of the first outer layer, a hard sheet with a thickness of about 1.25 mm was abraded starting from the second outer layer side, thereby obtaining a 0.40 mm-thick sheet for the first outer layer.

[0124] Then, 25 sheets of the sheet for the first outer layer thus obtained were overlapped and hardness measurements were made at three points at regular intervals in the width direction; and the average of the obtained values was referred to as the JIS-D hardness of the first outer layer. Furthermore, for the D-hardness of the intermediate layer, a hard sheet was abraded starting from the first outer layer side and the second outer layer side, evenly, thereby obtaining a 0.40 mm-thick sheet for the intermediate layer. Then, 25 sheets of the sheet for the intermediate layer thus obtained were overlapped and hardness measurements were made at three points at regular intervals in the width direction; and the average of the obtained values was referred to as the hardness of the intermediate layer. Thereafter, by using the values of the JIS-D hardnesses obtained at the total of six points being the three points in the first outer layer and the three points in the second outer layer, R(%) was obtained from the following equation:

$$R(\%) = (D \text{ hardness maximum} - D \text{ hardness minimum}) / D \text{ hardness average} \times 100.$$

[Total content of ions capable of causing pH change in water]

[0125] A piece of the hard sheet cut into a rectangle and 10 mL of water were put in a screw-cap test tube. Then, the screw-cap test tube was heated at 90°C for 2 hours with a block heater, thereby to extract water-soluble substances in the hard sheet by hot water extraction. Then, ion components in the liquid extract were detected by ion chromatography (ICS-1600). The total content of sulfate ions and ammonium ions, i.e., ions capable of causing a pH change in water, was measured and then converted to the amount of the ions included per unit volume of the hard sheet.

[Polishing rate]

[0126] The hard sheet was cut into a 51 cm-diameter circle, and a grid pattern of 1.0 mm-wide, 0.5 mm-deep grooves spaced 15.0 mm apart from one another was created on the surface, thereby to produce a polishing pad. Then, after an adhesive tape was attached to the back surface of the polishing pad, the back surface was attached to a CMP

polishing machine ("PPO-60S" available from Nomura Machine Tool Works, Ltd.). Next, under the conditions of a platen rotation of 70 rotations/min, a head rotation of 69 rotations/min, and a polishing pressure of 40 g/cm², a 4-inch diameter synthetic quartz was polished for 3 hours, while a slurry (SHOROX-31 available from Showa Denko K.K.) was fed thereto at a rate of 100 ml/min. Then, thickness measurements were made at 25 arbitrary points within the surface of the polished synthetic quartz; and then, the average of polished-off thicknesses at those points was divided by the polishing time, thereby to obtain the polishing rate (nm/min).

[0127] Note that polishing rate measurements were made on the first outer layer of a hard sheet about 1.25 mm thick, and also on a hard sheet 0.70 mm thick with the intermediate layer exposed.

[Example 1]

[0128] Water-soluble PVA was used as a sea component, and isophthalic acid-modified PET with a degree of modification of 6 mol% was used as island components. The water-soluble PVA and the isophthalic acid-modified PET were ejected from a spinneret for conjugate melt spinning (number of islands: 25 islands/fiber) at 260°C, such that the water-soluble PVA and the isophthalic acid-modified PET would be 25/75 (mass ratio). Then, the ejector pressure was adjusted so that the spinning rate would be 3700 m/min, long fibers with a fineness of 3 dtex were captured on a net, and a web with a mass per unit area of 35 g/m² was obtained.

[0129] Sixteen layers of the web were overlapped by cross lapping to produce overlapped webs with a total mass per unit area of 480 g/m². Then, an anti-needle-breakage oiling agent was sprayed to the overlapped webs. Then, a 42 count needle with 1 barb and a 42 count needle with 6 barbs were used to treat the overlapped webs by needle punching at 3150 punches/cm², thereby to obtain an entangled web. The entangled web had a mass per unit area of 770 g/m² and a delamination strength of 9.6 kg/2.5 cm. The area shrinkage due to the needle punching treatment was 25.8%.

[0130] Subsequently, the entangled web was treated with steam for 70 seconds under the conditions of 110°C and 23.5% RH. The area shrinkage at that time was 44%. Then, the entangled web was dried in an oven at 90 to 110°C and then hot pressed at 115°C, thereby to obtain an entangled fiber sheet with a mass per unit area of 1312 g/m², an apparent density of 0.544 g/cm³, and a thickness of 2.41 mm.

[0131] Subsequently, the entangled fiber sheet was impregnated with a polyurethane emulsion serving as a first emulsion. Note that the polyurethane was a non-yellowing polyurethane including: a polyol component being a mixture of polycarbonate-based polyol and polyalkylene glycol with 2 to 3 carbon numbers in a molar ratio of 99.8 : 0.2; and 1.5 mass% of carboxyl group-containing monomers. Moreover, the polyurethane was a non-porous polyurethane capable of forming a crosslinked structure by heat treatment. The first emulsion was prepared so as to contain 4.6 parts by mass of a carbodiimide-based crosslinking agent and 1.8 parts by mass of ammonium sulfate as a gelling agent, both relative to 100 parts by mass of the polyurethane; and also so that the solidifying content in the polyurethane would be 20%.

[0132] The entangled fiber sheet impregnated with the first emulsion was heated at 90°C in a 30% RH atmosphere to allow the first emulsion to gelate; and this was followed by drying treatment at 150°C. Then, the entangled fiber sheet was hot pressed at 140°C, thereby to adjust the mass per unit area to 1403 g/m², the apparent density to 0.716 g/cm³, and the thickness to 1.96 mm.

[0133] Subsequently, nipping treatment and high-pressure water jetting treatment were used to immerse the entangled fiber sheet with the polyurethane added therein in hot water at 95°C for 10 minutes, thereby to dissolve and thus remove the water-soluble PVA, thereby to convert ultrafine fibers with a fineness of 0.09 dtex; and this was followed by drying. As such, a first composite body with a mass per unit area of 1009 g/m², an apparent density of 0.538 g/cm³, and a thickness of 1.87 mm was obtained.

[0134] Subsequently, the first composite body was impregnated with a polyurethane emulsion (solid content: 30 mass%) serving as a second emulsion. Note that the polyurethane was of the same kind as the one used for the previous impregnation. The second emulsion was prepared so as to contain 4.6 parts by mass of a carbodiimide-based crosslinking agent and 1.0 part by mass of ammonium sulfate, both relative to 100 parts by mass of the polyurethane; and also so that the solidifying content in the polyurethane would be 30%.

[0135] The first composite body impregnated with the second emulsion was heated at 90°C in a 60% RH atmosphere, to allow the second emulsion to gelate; and this was followed by drying treatment at 150°C. As such, a second composite body with a mass per unit area of 1245 g/m², an apparent density of 0.748 g/cm³, and a thickness of 1.66 mm was obtained. The difference in porosity between the first outer layer and the intermediate layer in the second composite body was 1.8%.

[0136] Subsequently, nipping treatment and high-pressure water jetting treatment were used to water wash the second composite body by immersion in hot water at 95°C for 10 minutes. This was followed by drying at 180°C. Then, the second composite body was hot pressed under the conditions of a linear pressure of 100 kg/cm and 160°C, thereby to obtain an intermediary body for a hard sheet, with a mass per unit area of 1212 g/m², an apparent density of 0.795 g/cm², and a thickness of 1.53 mm.

[0137] The outer layer on both sides of the intermediary body for a hard sheet was abraded with a #100 paper to

reduce the outer layer thicknesses by 0.15 mm each, thereby finishing to obtain a hard sheet with a mass per unit area of 994 g/m², an apparent density of 0.788 g/cm³, and a thickness of 1.26 mm. JIS-D hardness of the hard sheet was 52 degrees. R% of the JIS-D hardness was 11.3%. In the hard sheet, the total content of sulfate ions and ammonium ions, i.e., ions capable of causing a pH change, was 26.9 µg/cm³.

[0138] The evaluation results are shown in Table 1.

[Table 1]

Example No.		1	2	3	Comp Ex. 1	Comp Ex. 2	Comp Ex. 3	Comp Ex. 4
D hardness		52	53	51	53	55	50	50
R (%)		11.3	6.6	19.6	14.6	30.2	19.6	19.6
Total ion content (μg/cm ³)		26.9	28.0	300	939	9.6	404	504
Initial polishing rate at first layer (nm/min)		128	129	125	93	133	122	121
Polishing rate in percentage at intermediate layer / first layer (%)	After 0.5 hrs	89.3	100	96.1	89	89.6	91.6	92.1
	After 3 hrs	97.7	96.9	88.8	93	88.7	82.8	81.8
	After 5 hrs	99.2	-	85.3	-	--	76.4	77.0
	Average	95.4	98.5	90.1	91.0	89.2	83.6	83.6

[Example 2]

[0139] Except that the first composite body before addition of the second emulsion was hot pressed under the conditions of a linear pressure of 100 kg/cm and 160°C, a hard sheet was produced as in Example 1 and then evaluated. Note that the hard sheet obtained had a mass per unit area of 996 g/m², an apparent density of 0.808 g/cm³, and a thickness of 1.23 mm. The results are shown in Table 1.

[Example 3]

[0140] Except that the second composite body was water washed to a lesser degree, a hard sheet was produced as in Example 1 and then evaluated. In the hard sheet, the total content of sulfate ions and ammonium ions, i.e., ions capable of causing a pH change, was 300 µg/cm³. The results are shown in Table 1.

[Comparative Example 1]

[0141] Except that the second composite body was not water washed instead of being water washed by immersion in hot water at 95°C for 10 minutes, a hard sheet was produced as in Example 1 and then evaluated. The results are shown in Table 1.

[Comparative Example 2]

[0142] Except that the first composite body was further hot pressed under the conditions of a linear pressure of 100 kg/cm and 160°C; and that the first composite body was impregnated with an emulsion with a similar composition as the second emulsion but not including the gelling agent, instead of being impregnated with the second emulsion including the gelling agent, a hard sheet was produced as in Example 1 and then evaluated. Note that the hard sheet obtained had a mass per unit area of 969 g/m², an apparent density of 0.817 g/cm³, and a thickness of 1.19 mm. The results are shown in Table 1.

[Comparative Example 3]

[0143] Except that the second composite body was water washed to a lesser degree, a hard sheet was produced as in Example 1 and then evaluated. In the hard sheet, the total content of sulfate ions and ammonium ions, i.e., ions

capable of causing a pH change, was $404 \mu\text{g}/\text{cm}^3$. The results are shown in Table 1.

[Comparative Example 4]

[0144] Except that the second composite body was water washed to a lesser degree, a hard sheet was produced as in Example 1 and then evaluated. In the hard sheet, the total content of sulfate ions and ammonium ions, i.e., ions capable of causing a pH change, was $504 \mu\text{g}/\text{cm}^3$. The results are shown in Table 1.

[0145] As showing the results in Table 1, the polishing pads according to the present invention which used the hard sheets obtained in Example 1, 2 and 3, respectively, wherein the JIS-D hardnesses were 45 degrees or more, the R%s were 0 to 20%, and the total contents of the ions capable of causing a pH change in water were $400 \mu\text{g}/\text{cm}^3$ or less, each exhibited a polishing rate at the first outer layer, i.e., the initial polishing rate, of 120 nm/min; and maintained 90% or more of the initial polishing rate based on the average thereof of until after five hours. In contrast, regarding the polishing pad which used the hard sheet of Comparative Example 1 wherein the gelling agent was added into the second emulsion and the second composite body was not sufficiently water washed, the polishing rate at the first outer layer was significantly low, being 93 nm/min. Moreover, regarding the hard sheet of Comparative Example 2, an effort was made to uniformly pack the hard sheet with the elastic polymer by hot pressing, instead of doing so by adding the gelling agent into the second emulsion. In the polishing pad with respect to Comparative Example 2, the total content of the ions was small but the R% was 30.2%, thus exhibiting non-uniformity. As a result, only 89% of the initial polishing rate based on the average thereof of until after five hours, was able to be maintained. Moreover, regarding Comparative Examples 3 and 4 wherein the total contents of the ions were $404 \mu\text{g}/\text{cm}^3$ and $504 \mu\text{g}/\text{cm}^3$, respectively, only about 84% of each of the initial polishing rates based on the averages thereof of until after five hours, were able to be maintained.

[Explanation of Reference Numerals]

[0146]

- 1 non-woven fabric
- 1a ultrafine fiber
- 1b fiber bundle
- 2 elastic polymer
- 3 first outer layer
- 4 intermediate layer
- 5 second outer layer

Claims

1. A hard sheet comprising:

a non-woven fabric of ultrafine fibers having a fineness of 0.0001 to 0.5 dtex; and
 an elastic polymer added into the non-woven fabric,
 the hard sheet having:
 a JIS-D hardness of 45 degrees or more;
 a R% calculated by an equation of $R(\%) = (D \text{ hardness maximum} - D \text{ hardness minimum}) / D \text{ hardness average} \times 100$ of 0 to 20%, when a sectional surface of the hard sheet extending in a thickness direction of the hard sheet is evenly divided into three parts corresponding to a first outer layer, an intermediate layer, and a second outer layer in order from any one surface side; JIS-D hardness measurements are made at a total of six points being three arbitrary points on the first outer layer and three arbitrary points on the intermediate layer; and then the JIS-D hardnesses obtained at the six points are used for the calculation; and
 a total content of ions capable of causing a pH change in water, of $400 \mu\text{g}/\text{cm}^3$ or less.

2. The hard sheet in accordance with claim 1, wherein the total content of the ions is 1 to $100 \mu\text{g}/\text{cm}^3$.

3. The hard sheet in accordance with claim 1, wherein the ultrafine fibers are long fibers and form fiber bundles.

4. The hard sheet in accordance with claim 3, wherein an apparent density of the non-woven fabric is 0.35 to $0.90 \text{ g}/\text{cm}^3$.

5. The hard sheet in accordance with claim 3, wherein, on the sectional surface of the hard sheet extending in the

thickness direction of the hard sheet, the ultrafine fibers forming the fiber bundles are, partially at least, bundled together by the elastic polymer.

6. The hard sheet in accordance with claim 5, wherein, on the sectional surface of the hard sheet extending in the thickness direction of the hard sheet, the fiber bundles are, partially at least, bound together by the elastic polymer.

7. The hard sheet in accordance with claim 3, wherein half or more of the ultrafine fibers forming the fiber bundles are bound together by the elastic polymer.

8. The hard sheet in accordance with claim 7, wherein on the sectional surface of the hard sheet extending in the thickness direction of the hard sheet, half or more of the fiber bundles are bound together by the elastic polymer.

9. The hard sheet in accordance with claim 1, wherein the elastic polymer is a non-porous elastic polymer.

10. The hard sheet in accordance with claim 1, wherein a mass ratio of the non-woven fabric to the elastic polymer (non-woven fabric/elastic polymer) is 90/10 to 55/45.

11. The hard sheet in accordance with claim 10, wherein an apparent density is 0.50 to 1.2 g/cm³.

12. The hard sheet in accordance with claim 1, wherein the second outer layer has a JIS-D hardness of 45 degrees or more, and the R% calculated by the equation of $R(\%) = (D \text{ hardness maximum} - D \text{ hardness minimum}) / D \text{ hardness average} \times 100$ is 0 to 20%, when JIS-D hardness measurements are made at a total of six points being three arbitrary points on the second outer layer and three arbitrary points on the intermediate layer, and then the JIS-D hardnesses obtained at the six points are used for the calculation.

13. A polishing pad comprising the hard sheet in accordance with any one of claims 1 to 12 as a polishing layer.

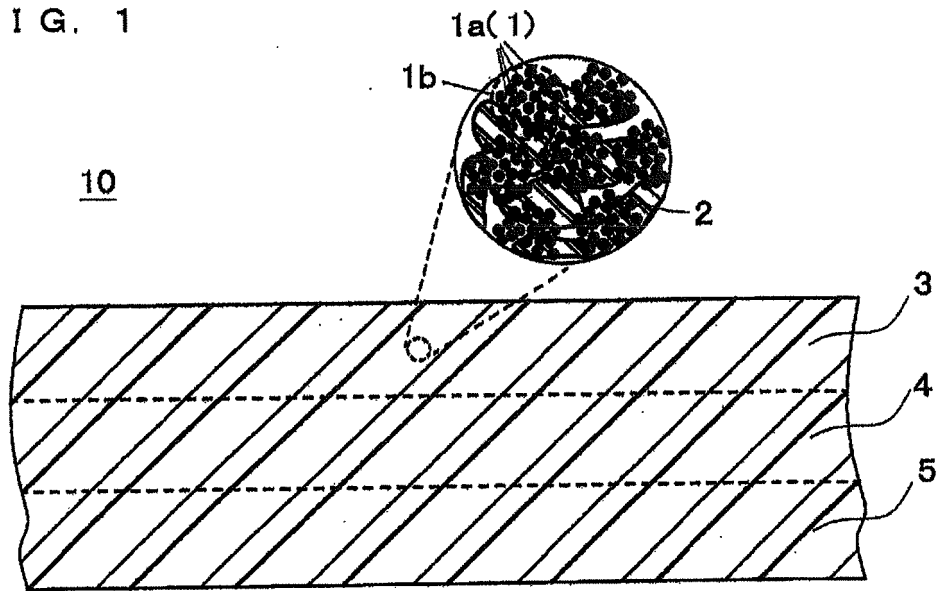
14. A production method of hard sheet comprising:

- (1) a step of preparing an entangled fiber sheet comprising long fibers of ultrafine-fiber-forming fibers, the entangled fiber sheet being capable of forming a non-woven fabric with an apparent density of 0.35 g/cm³ or more comprising ultrafine fibers with a fineness of 0.5 dtex or less, by subjecting ultrafine-fiber-forming treatment;
- (2) a step of impregnating the entangled fiber sheet with a first emulsion including an elastic polymer and a gelling agent containing ions capable of causing a pH change in water, then allowing the first emulsion to gelate, and then solidifying the elastic polymer by heating and drying;
- (3) a step of forming a first composite body comprising the non-woven fabric and the elastic polymer by subjecting the ultrafine-fiber-forming fibers to ultrafine-fiber-forming treatment;
- (4) a step of forming a second composite body by impregnating the first composite body with a second emulsion including an elastic polymer and a gelling agent and then solidifying the elastic polymer by heating and drying, the second composite body having a difference in porosity between a first outer layer and an intermediate layer of 5% or less, when the second composite body formed is evenly divided into three parts in a thickness direction of the second composite body, the three parts corresponding to the first outer layer, the intermediate layer, and a second outer layer in order from any one surface side;
- (5) a step of water washing the second composite body such that a total content of the ions becomes 400 μg/cm³ or less to obtain a hard sheet; and
- (6) a step of hot pressing at least one selected from the first composite body, the second composite body, and the hard sheet, such that a surface hardness of the hard sheet becomes 45 degrees or more in JIS-D hardness.

15. The production method of hard sheet in accordance with claim 14, wherein the total content of the ions is 1 to 100 μg/cm³.

16. The production method of hard sheet in accordance with claim 14, wherein the ultrafine-fiber-forming fibers are sea-island-type conjugated fibers comprising a water-soluble thermoplastic polyvinyl alcohol-based resin as a sea component and a water-insoluble thermoplastic resin as island components; and the ultrafine-fiber-forming treatment in the step (3) is a process whereby the water-soluble thermoplastic polyvinyl alcohol-based resin is dissolved in hot water and selectively removed.

FIG. 1



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2014/000616

A. CLASSIFICATION OF SUBJECT MATTER

D06N3/00(2006.01)i, B24B37/24(2012.01)i, C08J5/14(2006.01)i, D04H1/4382
(2012.01)i, H01L21/304(2006.01)i

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)

D06N1/00-7/06, C08J5/00-5/02, C08J5/12-5/22, H01L21/304, H01L21/463,
B24B3/00-3/60, B24B21/00-39/06

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

Jitsuyo Shinan Koho 1922-1996 Jitsuyo Shinan Toroku Koho 1996-2014
Kokai Jitsuyo Shinan Koho 1971-2014 Toroku Jitsuyo Shinan Koho 1994-2014

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

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2008-207323 A (Kuraray Co., Ltd.), 11 September 2008 (11.09.2008), entire text & US 2010/0087128 A1 & EP 2123400 A1 & WO 2008/093850 A1	1-16
A	JP 2010-058170 A (Kuraray Co., Ltd.), 18 March 2010 (18.03.2010), entire text (Family: none)	1-16
A	JP 2006-036909 A (Nicca Chemical Co., Ltd., Japan Vilene Co., Ltd.), 09 February 2006 (09.02.2006), entire text (Family: none)	1-16

☒ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

* Special categories of cited documents:

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Date of the actual completion of the international search
28 April, 2014 (28.04.14)

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Name and mailing address of the ISA/
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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2014/000616

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2007-054910 A (Toray Industries, Inc.), 08 March 2007 (08.03.2007), entire text (Family: none)	1-16
A	JP 2005-334997 A (Asahi Kasei Fibers Corp.), 08 December 2005 (08.12.2005), entire text (Family: none)	1-16
A	US 6130163 A (ProMOS Technologies Inc., Mosel Vitellic Inc., Infineon AG), 10 October 2000 (10.10.2000), entire text (Family: none)	1-16

Form PCT/ISA/210 (continuation of second sheet) (July 2009)

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- JP 2000178374 A [0011]
- JP 2000248034 A [0011]
- JP 2001089548 A [0011]
- JP HEI11322878 A [0011]
- JP 2002009026 A [0011]
- JP HEI1199479 A [0011]
- JP 2005212055 A [0011]
- JP HEI3234475 A [0011]
- JP HEI10128674 A [0011]
- JP 2004311731 A [0011]
- JP HEI10225864 A [0011]
- JP 2005518286 A [0011]
- JP 2003201676 A [0011]
- JP 2005334997 A [0011]
- JP 2007054910 A [0011]
- JP 2003170347 A [0011]
- JP 2004130395 A [0011]
- JP 2002172555 A [0011]
- JP 2008207323 A [0011]
- JP 2011200984 A [0011]

Non-patent literature cited in the description

- CMP No Saiensu. Science Forum Inc, 20 August 1997, 113-119 [0012]