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(54) **FEUILLE EN RESINE FLUOREE, SON PROCEDE DE
FABRICATION ET SON UTILISATION**

(54) **FLUORORESIN SHEET, PROCESS FOR PRODUCING THE
SAME, AND THE USE OF SAME**

(57) L'invention concerne une feuille en résine fluorée à base de pâte polyamide aromatique et dont une résine fluorée est un constituant essentiel, la résistance à la traction de cette feuille n'étant pas inférieure à 250 kg/cm^2 , ainsi qu'un procédé relatif à la fabrication de ladite feuille et, qui comprend les étapes suivantes: dispersion de la pâte polyamide aromatique et de la poudre de résine fluorée dans l'eau; adjonction à la dispersion d'un coagulant qui déstabilise la dispersion de la poudre de résine fluorée, en vue de déposer ladite poudre à la surface de la pâte polyamide aromatique; étape de fabrication du papier, suivie d'un séchage, afin d'obtenir un article sous forme de feuille; et compression dudit article à l'aide d'un rouleau, suivie d'un chauffage.

(57) Disclosed is a fluororesin sheet comprising an aromatic polyamide pulp and a fluororesin as an essential component, the tensile strength of the fluororesin sheet being not less than 250 Kg/cm^2 , a process for producing the fluororesin sheet which comprises dispersing the aromatic polyamide pulp and the fluororesin powder in water; adding a coagulating agent which destabilizes the dispersing of the fluororesin powder to the dispersion to deposit the fluororesin powder on the surface of the aromatic polyamide pulp; paper-making, followed by drying to obtain a sheet article; and compressing the sheet article using a roller, followed by heating.



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(21) International Application Number: PCT/EP96/03496 (22) International Filing Date: 5 August 1996 (05.08.96) (30) Priority Data: 7/198350 3 August 1995 (03.08.95) JP (71) Applicant (for all designated States except US): AKZO NOBEL N.V. [NL/NL]; Velperweg 76, NL-6824 BM Arnhem (NL). (72) Inventors; and (75) Inventors/Applicants (for US only): ASAGI, Kosaku [JP/JP]; 4-5-68, Ninomiya, Tsukuba Ibaraki 305 (JP). YAMABAYASHI, Toshiharu [JP/JP]; 2-13-1, Umezono, Tsukuba Ibaraki 305 (JP). (74) Agent: SCHALKWIJK, Pieter, Cornelis; Akzo Nobel N.V., Patent Dept. (Dept. APTA), P.O. Box 9300, NL-6800 SB Arnhem (NL).		(81) Designated States: CA, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: FLUORORESIN SHEET, PROCESS FOR PRODUCING THE SAME, AND THE USE OF SAME		
(57) Abstract <p>Disclosed is a fluororesin sheet comprising an aromatic polyamide pulp and a fluororesin as an essential component, the tensile strength of the fluororesin sheet being not less than 250 Kg/cm², a process for producing the fluororesin sheet which comprises dispersing the aromatic polyamide pulp and the fluororesin powder in water; adding a coagulating agent which destabilizes the dispersing of the fluororesin powder to the dispersion to deposit the fluororesin powder on the surface of the aromatic polyamide pulp; paper-making, followed by drying to obtain a sheet article; and compressing the sheet article using a roller, followed by heating.</p>		

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FLUORORESIN SHEET, PROCESS FOR PRODUCING THE SAME, AND
THE USE OF SAME

5 The present invention relates to a sheet which is useful for various
packings, bearings, thrust washers, etc., a process for producing the same,
and the use of same. More particularly, the invention relates to a
fluororesin sheet comprising an aromatic polyamide pulp and a fluororesin
as an essential component, the fluororesin sheet having excellent
10 mechanical characteristics, friction and wear characteristics, heat
resistance and chemical resistance, to a process for producing the same,
and to a sliding material comprising the fluororesin sheet.

Because of its excellent friction and wear characteristics, heat resistance
15 and chemical resistance, fluororesin is widely used as sliding material ^{such as} ~~for~~
various packings, bearings ^{and} ~~thrust washers, etc.~~. However, fluororesin alone
is liable to be deformed by external force, and the wear loss is high.
Therefore, various reinforcing fillers have been formulated to correct these
drawbacks.

20 For the above applications such as packing, thrust washer, etc., thin-sheet
sliding material is required. However, it tends to be difficult to melt the
fluororesin or dissolve it in a solvent. Therefore, it is impossible to use the
sheet forming processes such as casting, blow moulding, etc. which are
25 normally used in thermoplastic resins such as nylon ^{and} ~~polyethylene, etc.~~

Accordingly, what tends to be used is a so-called skiving process
comprising subjecting a cylindrical block to compression moulding and
heating and skiving the resulting sheet to obtain a thin sheet. However, this

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process gives inferior productivity and, therefore, an economical process for producing a sheet article is needed which also provides high productivity.

- 5 Characteristics such as hardness, wear performance, etc. can be improved by further adding fibrous fillers (e.g. glass fibre~~/etc~~) and particulate fillers (e.g. bronze powder~~/etc~~), but the mechanical performance (e.g. tensile strength~~/etc~~) cannot be improved because the fluoro-resin's adhesion is inferior to that of the filler.

10

In order to improve this, the present inventors have suggested a resin composition for sliding material in which use is made of a highly-fibrillated aromatic polyamide pulp in combination with fluoro-resin powder [Japanese Patent Kokai (laid-open) No. 5-117476]. Since the highly-fibrillated aromatic
15 polyamide pulp is used as a reinforcement in this composition, the fluoro-resin is reinforced by physical interlocking of the aromatic polyamide pulp, which gives a strong reinforcing effect. However, also in this case a sufficiently strong reinforcing effect is obtained only in the block state.

- 20 In addition, a sheet produced from this block according to the skiving process has high anisotropy, and it is difficult to obtain sufficient tensile strength in all directions of the sheet surface. Therefore, materials having a tensile strength of not less than $\sqrt{250 \text{ Kg/cm}^2}$ in all directions of the sheet surface have never been obtained. The reason for this is considered to be
25 that the fibres are mainly oriented in the direction perpendicular to the compressing direction at the time of press moulding of the block and scarcely in the compressing direction itself.

$\tau_{25} \text{ MPa}$

In Japanese Patent Kokoku No. 4-36181 is disclosed a process of depositing a tetrafluoroethylene resin polymer (PTFE) on a fibre sheet to give a sheet. In this process, however, chopped fibres made simply by cutting up long fibres are used as reinforcing fibres instead of the pulp and, therefore, a special mixer is required for the dispersion. In addition, a mixed solution of water and isopropanol is used as a dispersant, so there is a drainage treatment problem and normal paper-making processes using only water as the dispersant cannot be applied.

In Japanese Patent Kohyo No. 6-511029 is disclosed a process for producing a composite material which comprises bringing a mat obtained from a fibre material into contact with an aqueous dispersant of a fluoropolymer to precipitate the fluoropolymer onto the mat.

On the other hand, if a cut fibre is used without first making a fibrous mat, a problem is incurred in that the rate of deposition of the fluororesin onto the cut fibre is too low.

As described above, there has never been a conventional technique for producing a sheet comprising an aromatic polyamide pulp as reinforcement and a fluororesin as matrix, with the sheet having sufficient tensile strength and the process having excellent productivity. Therefore, such a process is urgently needed.

An object of the present invention is to provide a sheet comprising an aromatic polyamide pulp and a fluororesin as an essential component, the

sheet having excellent mechanical characteristics and friction and wear characteristics, a process for producing the same, and the use thereof as a sliding material.

- 5 In other words, the present invention provides a fluororesin sheet comprising an aromatic polyamide pulp and a fluororesin as a main component, the tensile strength of the fluororesin sheet being not less than 25 MPa (250 Kg/cm^2).
- 10 The present invention also provides a process for producing a fluororesin sheet comprising an aromatic polyamide pulp and a fluororesin as a main component, which process comprises the steps of:
- (1) preparing a dispersion in which the aromatic polyamide pulp and the
15 fluororesin powder are dispersed in water;
 - (2) adding a coagulating agent (flocculant) to the dispersion to deposit the fluororesin powder on the surface of the aromatic polyamide pulp;
 - (3) subjecting the aromatic polyamide pulp on which the fluororesin has
20 been deposited to paper making, followed by drying to obtain a sheet article; and
 - (4) compressing the sheet article, followed by heating (sintering).

The present invention also provides a sliding material comprising a
25 fluororesin sheet comprising an aromatic polyamide pulp and a fluororesin as a main component, the tensile strength of the fluororesin sheet being not less than 250 Kg/cm^2

25 MPa

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The invention also provides a composite molded material which is a laminate of composite sheets as described above, the composite molded material having a tensile strength of not less than $\sqrt{2} 50 \text{ Kgf/cm}^2$.

5

Accordingly, the invention also pertains to a process for producing such a composite molded material, comprising making a sheet material as described above, and laminating a plurality of such sheet-like materials, followed by sintering. The present invention also provides a sliding material
10 of the above composite molded material.

The present invention will be explained in detail below.

The aromatic polyamide resin as the raw material of the aromatic
15 polyamide pulp to be used in the present invention is one in which at least 85 mole% of an amide bond is obtained from aromatic diamine and aromatic dicarboxylic acid components.

Examples thereof include polyparaphenylene terephthalamide, polymeta-
20 phenylene terephthalamide, polyparabenzamide, poly-4, 4' -diamino-benzanilide, polyparaphenylene-2, 6-naphthalic amide, copolyparaphenylene/4, 4'-(3,3' -dimethylbiphenylene) terephthalamide, copolyparaphenylene/2,5-pyridylene terephthalamide, polyorthophenylene phthalamide, polymetaphenylene phthalamide, polyparaphenylene
25 phthalamide, polyorthophenylene isophthalamide, polymetaphenylene isophthalamide, polyparaphenylene isophthalamide, polyorthophenylene terephthalamide, poly-1,5-naphthalene phthalamide, poly-4,4'-diphenylene

$T_{25} \text{ MPa}$

orthophthalamide, poly-4,4'-diphenylene isophthalamide, poly-1,4-naphthalene phthalamide, ^{and} poly-1,5-naphthalene isophthalamide ~~/etc/~~; and aromatic polyamides containing an alicyclic amine, represented by compounds obtained by substituting a part of the benzene ring of these

5 aromatic diamines with piperazine, 1,5-dimethyl piperazine, ^{and} 2,5-diethyl piperazine ~~/etc/~~; or copolymers of aromatic polyamides containing two phenyl groups, wherein aromatic diamines are bonded with ether bonds (e.g. 8,3' -oxydiphenylene diamine, 3,4-oxydiphenylene diamine ~~/etc/~~) and groups (e.g. -S-, SO₂-, -CO-, -NH- ~~/etc/~~), such as poly-8,8' -oxydiphenylene

10 terephthalamide/polyparaphenylene terephthalamide copolymer, ^{and} poly-3,4-oxydiphenylene terephthalamide/polyparaphenylene terephthalamide copolymer ~~/etc/~~.

The aromatic polyamide pulp to be used in the present invention can be

15 obtained by highly fibrillating the fibres of the above aromatic polyamide resin. A BET specific surface area is often used as an index of the fibrillation. The value of the BET surface area of the aromatic polyamide pulp which is suitable for the process of the present invention is 3 to 25 m²/g, preferably 5 to 20 m²/g, more preferably 9 to 16 m²/g.

20 When the value of the BET specific surface area of the pulp is too low, there is insufficient interlocking of the pulps and a sheet having high mechanical strength is not obtained. In addition, it becomes difficult to deposit fluororesin particles on the pulp. On the other hand, when the value of the specific surface area is too high, the freeness necessarily becomes

25 inferior and hence more time is required for paper-making, resulting in lower efficiency.

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Examples of the fluororesin to be used in the present invention include tetrafluoroethylene resin (hereinafter also referred to sometimes as PTFE), perfluoro-alkoxy resin (hereinafter also referred to sometimes as PFA), tetrafluoroethylene-hexafluoropropylene copolymer resin (hereinafter also referred to sometimes as FEP), tetrafluoroethylene-ethylene copolymer resin (hereinafter also referred to sometimes as ETFE), vinylidene fluoride resin (hereinafter also referred to sometimes as PVDF), *and* chlorotrifluoroethylene resin (hereinafter also referred to sometimes as PCTFE) ~~etc.~~. Among these, PTTE is particularly preferred in view of its heat resistance ^{*and*} ~~sliding characteristics~~ ~~etc.~~

The average particle size of the fluororesin powder is preferably 0.01 to 10 μm , more preferably 0.1 to 1 μm . When the particle size is too small, it becomes difficult to deposit particles on the fibre surface. On the other hand, when the particle size is too large, it becomes difficult to obtain a stable dispersion. In addition, it becomes difficult to disperse the resin uniformly in the sheet.

The formulation proportion of aromatic polyamide pulp to fluororesin powder is appropriately selected according to the desired final product, and it is preferred that the weight ratio of aromatic polyamide pulp to fluororesin is within a range of 10:90 to 70:30.

In the first step of the production process of the present invention, a dispersion in which the above polyamide pulp and fluororesin powder are dispersed in water is prepared. The preparation process of the dispersion is

not specifically limited, for example, a process can be used which comprises preparing a dispersion by first dispersing fluoro-resin powder in water and then dispersing the fluoro-resin powder dispersion and an aromatic polyamide pulp in water, a process which comprises first
5 preparing a dispersion in which fluoro-resin powder is dispersed in water and then dispersing an aromatic polyamide pulp in the dispersion of the fluoro-resin powder in water, a process of dispersing fluoro-resin powder and an aromatic polyamide pulp in water ~~etc.~~ Hereinafter, a preferred process of preparing the dispersion will be specifically explained.

10

Fluoro-resin powder is stably dispersed in water containing an anionic, cationic or nonionic surfactant to prepare a fluoro-resin dispersion (hereinafter also referred to sometimes as a fluoro-resin dispersion or emulsion). It is also possible to prepare the same dispersion of the
15 fluoro-resin powder by subjecting a monomer as the raw material of the fluoro-resin to aqueous polymerization in the presence of one or more types of the above surfactants.

20

It is also possible to use a commercially available water dispersion of fluoro-resin powder. Examples of the water dispersion of fluoro-resin powder include fluoro-resin dispersions of fluoro-resin powders which are commercially available from Asahi Glass Co. , Ltd. and Daikin Kogyo Co. . Ltd.

25

Then, the dispersions of the fluoro-resin powder and the aromatic polyamide pulp are dispersed in water. As the dispersing process can be

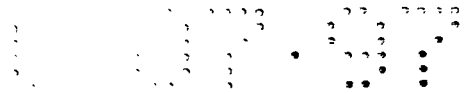
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used a process which has hitherto been used for wood pulp paper-making. For example, the dispersion can be prepared by using various pulpers, various beaters (e.g. Niagara beater~~/etc/~~) or various refiners (e.g. single disc refiner~~/etc/~~).

- 5 The concentration of aromatic polyamide pulp and fluoro-resin powder in the dispersion can be freely selected, but it is preferred to select the concentration as high as possible unless the fluidity of the dispersion reduces economical efficiency.
- 10 The formulation proportion of aromatic polyamide pulp to fluoro-resin powder in the dispersion is decided by the composition ratio of aromatic polyamide pulp to fluoro-resin of the final product, but is preferably within a range of 10:90 to 70:30 (weight ratio).
- 15 When the proportion of aromatic polyamide pulp is too small, a sufficient reinforcing effect cannot be obtained. On the other hand, when the proportion is too large, a sheet having sufficient mechanical strength and friction and wear characteristics cannot be obtained. Furthermore, fillers (e.g. graphite, bronze powder~~/etc/~~), additives or other components can be
- 20 added to the dispersion for the purpose of improving the performance of the sheet and imparting other characteristics, unless the homogeneity of the dispersion is reduced.

Then, a coagulating agent which destabilizes the dispersing of fluoro-resin

- 25 particles is added to this dispersion of aromatic polyamide pulp and fluoro-resin powder to deposit particles of the fluoro-resin powder on the



surface of the aromatic polyamide pulp. The kind and amount of coagulating agent to be added is decided by the kind of the surfactant used for dispersing the fluoro-resin powder and the specific surface area of the aromatic polyamide pulp.

5

When the fluoro-resin powder is stabilized by the anionic surfactant, coagulating agents (e.g. strong acid, strong electrolyte~~/etc/~~) or polymer coagulating agents (e.g. polyacrylamide, sodium polyacrylate~~/etc/~~) can be used and, furthermore, these polymer coagulating agents can be used in combination with strong acid or strong electrolyte.

10

When the particles of the fluoro-resin are stabilized by the cationic surfactant, coagulating agents (e.g. base, strong electrolyte~~/etc/~~) or polymer coagulating agents (e.g. polyacrylamide, polymethacrylate~~/etc/~~) can be used and, furthermore, these polymer coagulating agents can be used in combination with base or strong electrolyte.

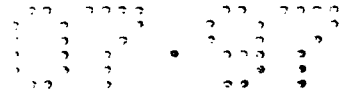
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When the particles of the fluoro-resin are stabilized by the nonionic surfactant, coagulating agents (e.g. strong electrolyte~~/etc/~~) or polymer coagulating agents (e.g. polyacrylamide~~/etc/~~) can be used and, furthermore, these polymer coagulating agents can be used in combination with strong electrolyte.

20

In addition, it is particularly preferred to use tannic acid in combination with an electrolyte containing a polyhydric metal ion (e.g. aluminum sulfate~~/etc/~~) as the coagulating agent irrespective of the kind of surfactant used. At this

25



time, it is effective for depositing substantially 100% of the fluoro-resin powder on the aromatic polyamide pulp to adjust the pH of the system within a range of 3.5 to 6.0 by adding an alkaline component (e.g. potassium hydroxide, ammonia ~~(etc)~~).

5

In the present invention, it is particularly important to select an optimum combination of aromatic polyamide pulp, fluoro-resin dispersion, and coagulating agent, paying attention to the following:

- 10 • The fluoro-resin powder in the dispersion should be deposited on the surface of the aromatic polyamide pulp as much as possible, preferably substantially 100%. This is important in view of getting effective use out of an expensive fluoro-resin raw material. In the case of a fluoro-resin which is scarcely deposited (100%) flowing into
15 the drainage at the time of paper-making, the corresponding drainage treatment is required, significantly reducing economical efficiency. From this viewpoint, the term "substantially 100 %" used herein should be understood to mean that the amount of fluoro-resin flowing into the drainage at the time of paper-making should be
20 reduced to the level where no drainage treatment is required.
- The destabilized fluoro-resin powder deposited on the surface of the aromatic polyamide pulp should be uniformly deposited on the surface of the aromatic polyamide pulp without forming a large floc.

25

- The dispersion after depositing of the fluoro-resin powder should have suitable freeness. This can be evaluated by measuring the freeness of the dispersion in accordance with the method described hereinafter.

5

From these viewpoints, as described above, suitable aromatic polyamide pulp has a BET specific surface area of preferably 3 to 25 m²/g, more preferably 5 to 20 m²/g, most preferably 9 to 16 m²/g. Suitable fluoro-resin powder has an average particle size of 0.01 to 10 μm, more preferably 0.1 to 1 μm.

10

In addition, the dispersion of fluoro-resin powder stabilized with anionic surfactant is more easily destabilized than when it is stabilized with nonionic surfactant. Therefore, the amount of coagulating agent required for the deposition of the fluoro-resin powder tends to be reduced. However, a large amount of floc is liable to form, and it becomes difficult to obtain a uniform sheet.

15

By contrast, a dispersion stabilized with nonionic surfactant is not easily destabilized, but fine fluoro-resin powder is deposited on the surface of the aromatic polyamide pulp to obtain a uniform sheet. Therefore, it is preferred to use the nonionic dispersion as the raw material in the present invention.

20

To destabilize dispersing of the fluoro-resin powder, a process using a condensate of an aromatic polyhydroxy carboxylic acid and a glycol in combination with a polyvalent metal salt, and particularly tannic acid in combination with aluminium sulfate, is effective for the nonionic dispersion

25

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This combination is most preferred because) and is also effective for the anionic dispersion, ^{is required} in a smaller amount than when the other coagulating agent is used, ~~and it is most preferred.~~

After the dispersion destabilized with the coagulating agent was subjected
 5 to paper-making using a conventional method, the resultant product was
 optionally ~~dehydrated and~~ dried to obtain a sheet article. The term "paper
 making" used herein broadly indicates any known method of making a
 sheet-like material from a liquid containing a pulp in dispersed state. In the
 process of the present invention paper-making can be performed by
 10 applying a fourdrinier or a cylinder-type paper-making machine.

In order to produce a fluoro-resin sheet according to the present invention,
 the sheet-like material is pressurized (compressed) to form a dense
 structure and thereafter, or simultaneously, it is heated (in fact, sintered) to
 15 a temperature of at least the melting point or the softening point of the
 fluoro-resin. When using PTFE having a melting point of 320 °C as the
 fluoro-resin, the sheet according to the invention is obtained by sintering at
 a temperature of from 300 °C to 450 °C, and preferably 350 °C to 400 °C.
 The sintering is preferably conducted in a nitrogen atmosphere. The sheet
 20 can be compressed using a press machine or the like, but for the sake of
 high productivity, it is preferred to use rolls. The pressure is preferably of
 from $\sqrt{(300 \text{ to } 1500 \text{ Kg/cm}^2)}$ (preferably reached by gradually increasing the
 pressure from a normal pressure to the predetermined pressure in about 2
 minutes).

25 $\sqrt{29.4 \text{ to } 147 \text{ MPa}}$

In the same manner as with a conventional moulded article of fluoro-resin, the sheet obtained by pressurizing at room temperature can be calcined in an oven at a temperature above the melting point of the fluoro-resin according to a batch method. In addition, the sheet obtained by
5 compressing at a temperature below the melting point of the fluoro-resin can also be heated by being passed through a heat roller at a temperature above the melting point of the fluoro-resin.

The sheet article, after drying, can be simultaneously compressed and
10 heated by being passed directly through the heat roller at a temperature above the melting point of the fluoro-resin. This process is particularly preferred because of its high productivity and economical efficiency.

A preferred embodiment of step (4) of the present invention, i.e. the step of
15 compressing the sheet article followed by heating, includes the step of compressing the sheet article at a temperature below the melting point of the fluoro-resin (320°C in the case of PTFE) using a roller, and then heating the sheet article at a temperature above the melting point of the fluoro-resin using an oven or a heat roller; compressing the sheet article at a
20 temperature below the fluoro-resin using a roller, and then heating and compressing simultaneously, at a temperature above the melting point of the fluoro-resin; or compressing and heating simultaneously by compressing the sheet article at a temperature above the melting point of the fluoro-resin using a roller.

According to the process of the present invention, a fluororesin sheet comprising aromatic polyamide pulp and fluororesin as the main component can be produced, with the tensile strength of the sheet being not less than $\sqrt{250 \text{ Kg/cm}^2}$ when measured in any direction, in accordance with a conventional paper-making process.

In addition, the process of the present invention is an excellent process for industrial use because substantially 100% of the fluororesin powder can be deposited on the aromatic polyamide pulp.

The fluororesin sheet of the present invention is particularly useful as a sliding material because of its excellent mechanical characteristics and friction and wear characteristics.

The following Examples further illustrate the present invention in detail, but are not to be construed as limiting the scope thereof.

The measurement of the values of various physical properties in the Examples was conducted in accordance with the evaluation method described hereinafter.

Evaluation method of physical properties:

1. Freeness
- 1.1 Freeness of aromatic polyamide pulp

$\sqrt{25 \text{ MPa}}$

The freeness of the aromatic polyamide pulp was measured according to a Canadian standard type method described in JIS P8121, "Freeness Testing Method of Pulp."

1.2. Freeness of aromatic polyamide pulp/fluororesin dispersion

5 The freeness of the aromatic polyamide pulp/fluororesin dispersion after of the destabilizing fluororesin particles was measured as follows.

- 10 (1) A dispersion to the amount containing 1.2 g of aromatic polyamide pulp was taken from the dispersion.
- (2) The dispersion was diluted to make 1 l, using a measuring cylinder.
- 15 (3) The freeness was measured in accordance with a Canadian standard type method described in JIS P8121.

20 When the value of this freeness is 200 to 600 ml, more preferably 300 to 500 ml, paper-making can be suitably carried out.

2. COD of filtrate at the time of paper-making

The COD was measured by using a KMnO_4 method at 100°C, in accordance with JIS K 0102.17.

25

3. Deposition rate of fluororesin

The deposition rate of the fluororesin on the surface of the aromatic polyamide pulp was calculated from the following equation, assuming that the total amount of aromatic polyamide pulp charged remained in the sheet.

5

Deposition rate of fluororesin [%]

$$- \{ (\text{Dry weight of sheet} - \text{Charge amount of aromatic polyamide pulp}) / (\text{Charge amount of fluororesin}) \} \times 100$$

10

4. Tensile strength of sheet-shaped sliding material.

The tensile strength of the sheet-shaped sliding material was measured under the condition of a gauge length of 40 mm and a stress rate of $\sqrt{100}$ mm /minute) using a JIS No. 3 dumbbell-shaped specimen.

15

5. Friction and wear performances of sheet-shaped sliding material

The friction and wear test of the sheet-shaped sliding material was conducted by using the following test method and condition.

20

Testing machine: ring-on-disc vertical type frictional wear testing machine (manufactured by Takachiho Seiki Co., Ltd.)

Specimen: disc-shaped

Opposite material: S55C ring-shaped

Pressure: $\sqrt{6}$ Kg/cm²

25

Rate: $\sqrt{40}$ m/minute)

Testing time: 4 hours

$\Gamma 0.6$ MPa

$F 0.67$ m/s

$\Gamma^0 1.67$ mm/s

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6. Critical PV value of sheet-shaped sliding material

The critical PV value of the sheet-shaped sliding material was determined by using the following testing method and condition.

Testing machine: ring-on-disc vertical type frictional wear testing

5 machine (manufactured by Takachiho Seiki C., Ltd.)

Specimen: disc-shaped

Opposite material: S55C, ring-shaped

Rate: $\sqrt{150}$ m/minute (constant)

10 The pressure was increased at intervals of $\sqrt{0.5 \text{ MPa}}$ $\sqrt{5 \text{ Kg/cm}^2}$ ~~5~~ 5, 10, 15, 20, and 25 Kg/cm^2 ~~(etc.)~~, and the test was conducted at each respective pressure for 10 minutes, to determine the critical PV value where a friction coefficient changes rapidly or a sheet is fractured.

15 **Example 1 and Comparative Example 1**

An aromatic para-polyamide pulp, Twaron 1094 (provided by Nippon Aramid Co., Ltd., BET specific surface area: $13.5 \text{ m}^2/\text{g}$, freeness: 100 ml) (1.0g; ~~(dry weight)~~) and a nonionic dispersion of PTFE, Fluon Dispersion AD¹ (manufactured by Asahi Glass Co., Ltd., average particle size of PTFE:

20 $0.25 \sqrt{\mu\text{m}}$ ~~2.5~~, solids content: 60 % by weight) (6.67 g; ~~(solids content: 4.0 g)~~) were weighed and dispersed in deionized water to give 400 g of dispersion.

A coagulating agent (flocculant) described in Table 1 was added to the dispersion so that a desired concentration was obtained, followed by stirring for 10 minutes. At that time, ammonia water was added to the dispersion to adjust the pH to 3.5 to 4.5 in Example 1. Thereafter, the dispersion was filtered off using a No. 1 filter paper, and the filtered product was dried to obtain a sheet article. Then, the sheet article was weighed to

$\sqrt{2.5 \text{ m/s}}$

F (e.g. 0.5, 1, 1.5, 2, and 2.5 MPa)

determine the deposition rate of the fluoro-resin powder. The results are shown in Table 1.

Table 1.

	Flocculant		Concentration of aluminum sulfate (ppm)	Fluoro-resin Deposition rate (%)
	Item	Concentration (ppm)		
Example 1	Tannic acid	600	400	100
Comparative Example 1	None	-	2000	5

5 Examples 2 to 5

An aromatic para-polyamide pulp, Twaron 1094 (provided by Nippon Aramid Co., Ltd. BET specific surface area: 13.5 m²/g, freeness: 100 ml) (1.0g/(dry weight)) and an anionic dispersion of PTFE Fluon Dispersion AD2 (manufactured by Asahi Glass Co., Ltd., average particle size of PTFE: 0.17 μ m solids content: 55 % by weight) (7.27 g/solids content: 4.0 g) were weighed and dispersed in deionized water to give 400 g of dispersion. A coagulating agent described in Table 2 was added to the dispersion so that a desired concentration was obtained, followed by stirring for 10 minutes. Thereafter, the dispersion was filtered off using a No. 1 filter paper, and the filtered product was dried to obtain a sheet article. Then, the sheet article was weighed to determine the deposition rate of the fluoro-resin powder. The results are shown in Table 2. Sumifloc is a polymer coagulating agent manufactured by Sumitomo Chemical Industries Co., Ltd.

Table 2

	Flocculant		Concentration of aluminum sulfate (ppm)	Fluororesin Deposition rate (%)
	Item	Concentration (ppm)		
Example 2	Tannic acid	60	40	100
Example 3	Sumifloc FN-10H	250	40	89
Example 4	Sumifloc FC-145	250	-	89
Example 5	Sumifloc FC-145	250	40	89

Example 6

5 After Twaron 1094 (absolute dry weight: 15.9 g) and Fluon Dispersion AD1 (83.3 g, solid^s content: 50 g) were dispersed in 2 l of deionized water, an aqueous 10 % (by weight) solution of a special oil-water separating agent Glazine CF (2 g) [manufactured by Matsumoto Yushi Co., Ltd., component: tannic acid (60 parts by weight)/aluminium sulfate (40 parts by weight)] was

10 added to adjust the concentration of tannic acid and aluminium sulfate in the system to 600 ppm and 400 ppm, respectively. The pH of the mixture was adjusted by adding calcium hydroxide powder (200 mg), followed by stirring for 10 minutes to deposit the fluororesin powder on the surface of the aromatic polyamide pulp.

15

Then, the paper-making of the dispersion was performed on a wire cloth of 250 mm square by using a rectangular sheet machine (manufactured by

Kumagaya Riki Co., Ltd.), followed by dehydration and further drying to obtain a sheet article. The COD of the filtrate at the time of paper-making was 14 ppm. The deposition rate of the fluororesin powder was 100 %.

- 5 The sheet article was pressurized at room temperature at a linear pressure of $\sqrt{100 \text{ Kg/cm}}$ using a roller, and then calcined in an oven at 380°C under a nitrogen atmosphere for one hour. A sheet having a composition ratio of aromatic polyamide pulp to fluororesin of 24:76 (weight ratio) and a thickness of 0.55 mm was obtained.

10

The tensile strength of this sheet was $\sqrt{420 \text{ Kg/cm}^2}$. The friction and wear performances of this sheet were measured. The result was a dynamic friction coefficient of 0.18 and a wear rate of $\sqrt{2 \times 10^{-5} \text{ mm/Kgf/cm}^2 \text{ Km}}$. In addition, the critical PV value was $\sqrt{3500 \text{ Kg/cm}^2 \text{ m/minute}}$.

15

Comparative Example 2

- The dynamic friction coefficient and the wear coefficient of a PTFE sheet which was not reinforced with the aromatic polyamide pulp, measured in the same manner as in Example 6, were 0.26 and $\sqrt{4000 \times 10^{-5} \text{ mm/Kgf/cm}^2 \cdot \text{Km}}$, respectively. In addition, the critical PV value was $\sqrt{1000 \text{ Kg/cm}^2 \text{ m/minute}}$.

20

Example 7

- After Twaron 1094 (absolute dry weight: 13.7 g) and Fluon Dispersion AD2 (58.1 g, solids content: 32 g) were dispersed in 2 l of deionized water, an aqueous 1 % (by weight) solution of a special oil-water separating agent Glazine CF (0.2 g) [manufactured by Matsumoto Yushi Co., Ltd.,

25

$\Gamma 10 \text{ MPa}$	$\Gamma 2.04 \cdot 10^{-3} \text{ m}^2 / \text{MPa}$	$\angle 4.08 \text{ m}^2 / \text{MPa}$
$F 42 \text{ MPa}$	$F 5.83 \text{ MPa} \cdot \text{m/s}$	$\angle 1.67 \text{ MPa} \cdot \text{m/s}$

component: tannic acid (60 parts by weight)/aluminium sulfate (40 parts by weight)] was added to adjust the concentration of tannic acid and aluminium sulfate in the system to 600 ppm and 400 ppm, respectively. The mixture was stirred for 10 minutes to deposit the fluoro-resin powder on the surface of the aromatic polyamide pulp. A dispersion to the amount containing 1.2g of pulp was taken from the dispersion and, after diluting to make 1 l, the freeness was measured. It was 350 ml.

Then, the paper-making of the remaining dispersion after dispersing (containing 12.5 g of pulp) was performed on a wire cloth of 250 mm square by using a rectangular sheet machine (manufactured by Kumagaya Riki Co., Ltd.) followed by dehydration and further drying to obtain a sheet article.

The COD of the filtrate at this time was 15 ppm. The deposition rate of the fluoro-resin powder was 100 %.

The sheet article was compressed at a linear pressure of $\sqrt{(100 \text{ Kg/cm}^2)}$ at room temperature using a roller, and then calcined in an oven at 380°C under a nitrogen atmosphere for one hour. A sheet having a composition ratio of aromatic polyamide pulp to fluoro-resin of 32:68 (weight ratio) and a thickness of 0.39 mm was obtained. The tensile strength of this sheet was 27 MPa (270 Kg/cm^2).

Comparative Example 3

After milled glass fibers MFB (weight: 12.5 g) (manufactured by Asahi Glass Co., Ltd., average fibre length: 200 μm) and Fluoro dispersion AD1

110 MPa

(83.3 g, solids content: 50 g) were dispersed in 2 l of deionized water, an aqueous 10 % (by weight) solution of a special oil-water separating agent Glazine CF (2g) [manufactured by Matsumoto Yushi Co., Ltd., component: tannic acid (60 parts by weight)/aluminium sulfate (40 parts by weight)] was added to adjust the concentration of tannic acid and aluminium sulfate in the system to 600 ppm and 400 ppm, respectively. The pH of the mixture was adjusted by adding calcium hydroxide powder (200 mg), followed by stirring for 10 minutes to deposit the fluororesin powder. Paper-making was performed on a wire cloth of 250 mm square by using a rectangular sheet machine (manufactured by Kumagaya Riki Co., Ltd.), followed by ~~dehydration and further~~ drying to obtain a sheet article. The weight of the sheet was 17.1 g and only 9% of charge amount of fluororesin powder remained in the sheet article. In addition, the mechanical strength of the resulting sheet was too low to allow its handling.

15

Comparative Example 4

After p-aramid fibers MFB(13.7 g, average fiber length: 3 mm) and Fluon Dispersion AD1 (53.3 g, solid content: 32 g) were dispersed in 2 liter of deionized water, an aqueous solution (20 g) containing 6% by weight of tannic acid and 4% by weight of aluminum sulfate was added to adjust the concentration of tannic acid and aluminum sulfate in the system to 450 ppm and 300 ppm, respectively. The pH of the mixture was adjusted by adding an aqueous 1% ammonia solution (7.5 g), followed by stirring for 10 minutes as it is to deposit the fluororesin powder. The sheet-making of the dispersion was conducted on a wire cloth of 250 mm square by using a

25

rectangular sheet machine (manufactured by Kumagaya Riki Co.,Ltd.), followed by dehydration and further drying to obtain a sheet-like material.

The weight of the sheet was 135 g and PTFE in the amount of 3.5% of the charge amount was merely remained in the sheet-like material. The tensile strength of a sheet obtained by pressurizing and sintering the sheet-like material according to the same manner as that described in Example 6 was 2.6 MPa (27 Kgf/cm²)

Comparative Example 5

After Twaron 1094 (absolute dry weight: 12.5 g) and PTFE particles [Fluon G163 (trade name) manufactured by Asahi Glass Co., Ltd., average particle size: $0.25 \mu\text{m}$] (37.5 g) were dispersed in 2 liter of an aqueous 0.8% lauryl trimethylammonium chloride solution, an aqueous solution (15 g) containing 6% by weight of tannic acid and 4% by weight of aluminum sulfate was added to adjust the concentration of tannic acid and aluminum sulfate in the system to 450 ppm and 300 ppm, respectively. The pH of the mixture was adjusted by adding an aqueous 1% ammonia solution (3.75 g), followed by stirring for 10 minutes as it is to deposit the fluororesin on the aromatic polyamide pulp. The sheet-making of the dispersion was conducted on a wire cloth of 250 mm square by using a rectangular sheet machine (manufactured by Kumagaya Rike Co.,Ltd.), followed by ~~dehydration and further~~ drying to obtain an sheet-like material. The sheet-like material was pressurized at room temperature at a linear pressure of 18.5 MPa (189 Kgf/cm^2) using a roll, and then sintered in an oven at 380 °C under a nitrogen atmosphere for one hour to obtain a sheet-like sliding material having a composition ratio of the aromatic polyamide pulp to fluororesin of

24:76 (weight ratio) and a thickness of 0.50 mm. The tensile strength of this sheet-like sliding material was $\sqrt{66 \text{ Kg/cm}^2}$.

Comparative Example 6

- 5 In order to compare with the sheet of Example 6, various physical properties of a commercially available PTEE sheet containing bronze powder and Nitoflon 900B containing bronze powder (manufactured by Nitto Denko Co., Ltd.) were evaluated. As a result, the following results were obtained.

10

Tensile strength: $\sqrt{200 \text{ Kg/cm}^2}$
 Critical PV value: $\sqrt{2000 \text{ Kg/cm}^2\text{m/minute}}$
 Compression creep: 5.3 %
 Composite molded material

- 15 Evaluation method of physical properties

1. Bending test

Shape of specimen: 60 x 13 x 2.5 mm

Span: 40 mm

Crosshead speed: $\sqrt{1 \text{ mm/minute}}$

- 20 Three-point bending

2. Frictional wear performances of molded material

The frictional wear test of the molded material was conducted under the following condition.

- 25 Testing machine: ring-on-disc vertical type frictional wear testing machine
 (manufactured by Takachiho Seiki Co., Ltd.)

Γ 6.5 MPa

F^0 0.0167 mm/s

F 19.6 MPa

Γ^0 3.34 MPa.m/s

AMENDED SHEET

Specimen: disc-shaped

Opposite material: S55C, ring-shaped

Pressure: $\sqrt{6 \text{ Kgf/cm}^2}$

Rate: $\sqrt{40 \text{ m/minute}}$, $PV = \sqrt{240}$

5 Testing time: 24 hours

3. Tensile strength

the same as that in case of the sheet

Example 8

- 10 After an aromatic para-polyamide pulp, Twaron 1094 (manufactured by Nippon Aramid Co., Ltd., BET specific surface area: $13.5 \text{ m}^2/\text{g}$, freeness: 100ml)
- (15.0 g (absolute dry weight)) and Fluon Dispersion AD1 (manufactured by Asahi Glass Co., Ltd., average particle size of PTFE: $0.25 \mu\text{m}$, solid
- 15 content: 60% by weight) (74.8 g) were dispersed in 2 liter of deionized water, an aqueous solution (15 g) containing 6% by weight of tannic acid and 4 % by weight of aluminum sulfate was added to adjust the concentration of tannic acid and aluminum sulfate in the system to 145 ppm and 300 ppm, respectively. The pH of the mixture was adjusted by
- 20 adding an aqueous 1% ammonia solution (7.5 g), followed by stirring for 10 minutes as it is to deposit the fluoro-resin on the surface of the aromatic polyamide pulp. The sheet-making of the dispersion was conducted on a wire cloth of 250 mm square by using a rectangular sheet machine (manufactured by Kumagaya Riki Co., Ltd.), followed by ~~dehydration and~~
- 25 ~~further~~ drying to obtain a sheet-like material.

$\sqrt{0.59 \text{ MPa}}$

$\sqrt{0.67 \text{ m/s}}$

$\sqrt{0.4 \text{ MPa} \cdot \text{m/s}}$

After cutting the resultant sheet-like material into pieces of 85 x 75 mm, six pieces thereof were laminated. The height of a sheet obtained by laminating six pieces was about 6 mm. The laminated sheet was set in a die having an inner diameter of 85 x 75 mm and then pressed by pressing at room temperature (surface pressure: 1000 kgf/cm^2) pressing time: 10 minutes) to obtain a preform. This preform was sintered by maintaining in nitrogen at 380°C for one hour to obtain a composite molded material having a composition ratio (weight basis) of the aromatic polyamide pulp to fluororesin of $1/25:75$ and having a size of 85 x 75 x 2.5 mm (thickness), wherein the aromatic polyamide pulp and fluororesin are uniformly dispersed.

The evaluation for using the resulting composite molded material as the sliding material was conducted. The tensile strength, the bending strength and the bending modulus of the composite molded material (sliding material) were 420 Kg/cm^2 , 6.26 kgf/mm^2 , and 261 kgf/mm^2 , respectively. A delamination between laminated sheets was not observed in the specimen after the bending test. The wear coefficient and frictional coefficient were 1×10^{-5} and 0.14, respectively. As a result, it has been found that the composite molded material has good frictional wear properties as the sliding material.

Example 9

After cutting a sheet-like material obtained according to the same manner as that described in Example 8 into pieces of 85 x 75 mm, six pieces thereof were laminated. The height of a sheet obtained by laminating six

$\Gamma 98.1 \text{ MPa}$

$F 46.2 \text{ MPa}, 61.4 \text{ MPa}, \text{ and } 2.56 \text{ GPa}$

AMENDED SHEET

pieces was about 6 mm. The laminated sheet was set in a die having an inner diameter of 85 x 75 mm and then pressed by pressing at room temperature (surface pressure (500 kgf/cm^2) , pressing time: 10 minutes) to obtain a preform. This preform was sintered by maintaining in nitrogen at

5 380 °C for one hour to obtain a composite molded material having a composition ratio (weight basis) of the aromatic polyamide pulp to fluororesin of 25:75 and having a size of 85 x 75 x 2.5 mm (thickness), wherein the aromatic polyamide pulp and fluororesin are uniformly dispersed.

10

The bending strength and bending modulus of the composite molded material (sliding material) were (5.29 kgf/mm^2) and $(218 \text{ (kgf/mm}^2))$ respectively. A delamination between laminated sheets was not observed in the specimen after the bending test. The wear coefficient and frictional

15 coefficient were 1×10^{-5} and 0.18, respectively. As a result, it has been found that the composite molded material has good frictional wear characteristics as the sliding material.

Comparative Example 7

20 A molded material of an aromatic polyamide pulp and PTFE was produced as follows.

(i) A composition (60 g) of a pulp ^{was} prepared by ^{ried} drying Twaron 1094 (15 g) and PTFE [Fluon G163 (trade name), manufactured by Asahi Glass Co., Ltd., average particle size: 25 μm] ^{and} (45 g) ^{was} stirred (stirring ^rate: 2000

25 rpm, stirring time: 2 minutes) using a 5 liter vertical type high-speed super mixer (manufactured by Kawata Co.) to obtain a uniform mixture.

$T_{49} \text{ MPa}$

$F_{51.9} \text{ MPa}$

$\rho_{2.14} \text{ GPa}$

- (ii) The mixture (30 g) was charged in a die having an inner diameter of 85 x 75 mm and then pressed by pressing at room temperature (surface pressure: 1000 kgf/cm^2 , pressing time: 10 minutes) to obtain a preform. The height of the mixture after charging in the die was about 20 mm.
- 5 (iii) The preform was maintained at 380 °C under a normal pressure to obtain a molded material.

The tensile strength, the bending strength and the bending modulus of the resuting molded material were 190 Kgf/cm^2 , 3.49 kgf/mm^2 , and 134
 10 kgf/mm^2 respectively. The wear coefficient and frictional coefficient of the molded material were 6.0×10^{-5} and 0.14, respectively.

Comparative Example 8

After an aromatic para-polyamide pulp, Twaron 1094 (12.5 g. absolute dry
 15 weight) and PTFE [Fluon G163 (trade name), manufactured by Asahi Glass Co., Ltd., average particle size: $25 \mu\text{m}$] (37.5 g) were dispersed in 2 liter of deionized water, the mixture was stirred for 10 minutes as it is to obtain a dispersion of PTEF and an aromatic polyamide pulp. The sheet-making of the dispersion was conducted on a wire cloth of 250 mm square by using a
 20 rectangular sheet machine (manufactured by Kumagaya Rike Co.,Ltd.), followed by ~~dehydration and further~~ drying to obtain a sheet-like material. This operation was repeated twice to obtain two pieces of sheets. After cutting the resultant sheet into pieces of 85 x 75 mm, seven pieces thereof were laminated. The height of a sheet obtained by laminating seven pieces
 25 was about 9 mm. The laminated sheet was set in a die having an inner

$\Gamma 98.1 \text{ MPa}$
 $F 18.6 \text{ MPa}, 34.2 \text{ MPa}, \text{ and } 1.3 \text{ GPa}$

diameter of 85 x 75 mm and then pressed at room temperature (surface pressure: 1000 kgf/cm^2 , pressing time: 10 minutes) to obtain a preform.

This preform was sintered by maintaining in nitrogen at 380 °C for one hour.

- 5 However, an uniform and good molded material was not obtained because the aromatic polyamide pulp was not satisfactorily dispersed in PTFE.

According to the process of the present invention, a sheet can be obtained
10 where an aromatic polyamide pulp is uniformly dispersed in a fluoro-resin, the sheet having excellent mechanical characteristics and an excellent friction and wear performance. A conventional paper-making process can be used for the process of the present invention, and the aromatic polyamide pulp can be uniformly dispersed in the fluoro-resin by using a
15 simple device and operation. Therefore, it is industrially useful. In addition, the sheet of the present invention shows excellent characteristics when used as a sliding material.

20 $T_{93.1} \text{ MPa}$

Claims

1. A fluoro-resin sheet comprising an aromatic polyamide pulp and a fluoro-resin as a main component, the tensile strength of the fluoro-resin sheet being not less than 25 MPa (250 kg/cm²), measured under the condition of a gauge length of 40 mm and a stress rate of 1.67 mm/s, using a JIS No. 3 dumbbell-shaped specimen.
2. The fluoro-resin sheet of claim 1, which is obtained by subjecting an aqueous dispersion comprising an aromatic polyamide pulp component and a fluoro-resin component to paper making.
3. A process for producing a fluoro-resin sheet comprising an aromatic polyamide pulp and a fluoro-resin as a main component, which process comprises the steps of:
 - (1) preparing a dispersion in which the aromatic polyamide pulp and the fluoro-resin powder are dispersed in water;
 - (2) adding a coagulating agent selected from an acid, an electrolyte, a polymer, and a polymer in combination with an acid or an electrolyte, when the fluoro-resin powder is stabilized by an anionic surfactant; or
selected from a base, an electrolyte, a polymer, and a polymer in combination with a base or an electrolyte, when the fluoro-resin powder is stabilized by a cationic surfactant; or
selected from an electrolyte, a polymer, and a combination thereof, when the fluoro-resin powder is stabilized by a non-ionic surfactant;
 - (3) subjecting the aromatic polyamide pulp on which the fluoro-resin has been deposited to a paper making process, followed by drying to obtain a sheet article; and

- (4) compressing the sheet article, followed by heating to a temperature of at least the melting point or the softening point of the fluororesin.
4. The process for producing a fluororesin sheet according to claim 3 wherein the aromatic polyamide pulp used in the above step (1) is an aromatic polyamide pulp having a BET specific surface area of 3 to 25 m²/g and the fluororesin powder is fluororesin powder having an average particle size of 0.01 to 10µm.
5. The process for producing a fluororesin sheet according to claim 3 or 4, wherein step (4) of claim 4 is a step of compressing the sheet article using a roller at a temperature below the melting point of the fluororesin, followed by heating at a temperature above the melting point of the fluororesin.
6. The process for producing a fluororesin sheet of claim 3, wherein the coagulating agent is tannic acid in combination with an electrolyte containing a polyhydric metal ion.
7. A sliding material comprising the fluororesin sheet of claim 1.
8. A composite molded material having a tensile strength of not less than 25 MPa (250 kgf/cm²), which is a laminate of the fluororesin sheet of claim 1.
9. A process for producing a composite molded material of claim 8, comprising the steps of
- (1) preparing a dispersion in which the aromatic polyamide pulp and the fluororesin powder are dispersed in water;
 - (2) adding a coagulating agent to the dispersion to deposit the fluororesin powder on the surface of the aromatic polyamide pulp,

the coagulating agent being selected from an acid, an electrolyte, a polymer, and a polymer in combination with an acid or an electrolyte, when the fluororesin powder is stabilized by an anionic surfactant; or

selected from a base, an electrolyte, a polymer, and a polymer in combination with a base or an electrolyte, when the fluororesin powder is stabilized by a cationic surfactant; or

selected from an electrolyte, a polymer, and a combination thereof, when the fluororesin powder is stabilized by a non-ionic surfactant;

- (3) subjecting the aromatic polyamide pulp on which the fluororesin has been deposited to a paper making process, followed by drying to obtain a sheet-like material; and
- (4) laminating a plurality of the sheet-like materials, followed by heating at a temperature above the melting point of the fluororesin.

- 10. A process according to claim 9, wherein the aromatic polyamide pulp used in the above step (1) is an aromatic polyamide pulp having a BET specific surface area of 3 to 25 m²/g and the fluororesin powder is fluororesin powder having an average particle size of 0.01 to 10µm.
- 11. A process according to claim 9, wherein step (4) is conducted by first cutting a plurality of sheet-like materials into pieces having a predetermined shape, and then laminating and further compressing to prepare a preform which thereafter is heated at a temperature above the melting point of the fluororesin.
- 12. A sliding material comprising the composite molded material of claim 8.