

DESCRIPTION
FLUORORESIN SHEET

Technical Field

5 [0001]

The present invention relates to a fluororesin sheet.

Background Art

[0002]

10 Sheets obtained by filling a fluororesin with a filler and processing the resin into sheets have chemical resistance and heat resistance inherent in the fluororesin, and in addition, they have been imparted with functions and properties inherent in the filler or have been improved in creep resistance that
15 is a defect of the fluororesin. Therefore, they have been often used as sealing materials, etc.

[0003]

As such a sealing material, the present inventor has disclosed a process for producing a fluororesin sheet containing
20 a fluororesin, a filler and a processing aid in Japanese Patent Laid-Open Publication No. 2007-253519 (patent literature 1). As this filler, clay or the like has been mentioned. By this production process, a fluororesin sheet, which has high recovery properties and high gas tight properties compatible with each

other and which is suited to a gasket material, can be obtained.

[0004]

This fluororesin sheet, however, is liable to become a hard sheet having a low compressibility, and therefore, when this sheet is used for a gasket or the like, a high clamp pressure is necessary in order to obtain given sealing properties. Moreover, when the sheet is hard like this, its processability as in punching the sheet into a gasket with a desired shape is poor. The processability needs to be further improved.

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Citation List

Patent Literature

[0005]

Patent literature 1: Japanese Patent Laid-Open

15 Publication No. 2007-253519

Summary of Invention

Technical Problem

[0006]

20

The present invention has been made in the light of such problems as above, and it is an object of the present invention to provide a fluororesin sheet which has a high compressibility at a low clamp pressure, is inexpensive and has good processability.

Solution to Problem

[0007]

In order to solve the above problems, the present inventors
5 have earnestly studied, and as a result, they have found that
a sheet produced from a composition containing a fluoro-resin,
a filler (except perlite), perlite and a processing aid is
inexpensive, has a high compressibility, acquires sealing
properties equal to or higher than those of conventional products
10 at a low clamp pressure and has good punching processability
in punching the sheet into a gasket with a desired shape or the
like, and they have accomplished the present invention.

Specific constitution of the present invention is
described below.

15 The fluoro-resin sheet of the present invention is
characterized by being produced from a sheet-forming composition
containing (A) a fluoro-resin, (B) a filler (except perlite),
(C) perlite and (D) a processing aid.

[0008]

20 The amount of the perlite (C) in the composition is
preferably 4 to 20 parts by weight based on 100 parts by weight
of the total amount of the fluoro-resin (A), the filler (B) (except
perlite) and the perlite (C).

The "filler" referred to in the present application means

a filler other than perlite.

The amount of the processing aid (D) in the composition is 5 to 50 parts by weight based on 100 parts by weight of the total amount of the fluororesin (A), the filler (B) (except
5 perlite) and the perlite (C).

Advantageous Effects of Invention

[0009]

In the fluororesin sheet of the present invention, porous
10 perlite (C) and a filler (B) other than the perlite, such as clay, are used in combination, and the fluororesin sheet can be produced inexpensively.

By the present invention, a fluororesin sheet which is excellent in secondary processing such as punchability into a
15 shape of a gasket or the like, has a high compressibility at a low clamp pressure and exhibits good sealing properties even when it is used at a low clamp pressure can be obtained.

Description of Embodiments

20 [0010]

The present invention is described in more detail hereinafter.

<Fluororesin sheet>

The fluororesin sheet of the present invention is

characterized by being produced from a sheet-forming composition containing (A) a fluoro-resin, (B) a filler (except perlite), (C) perlite and (D) a processing aid.

[0011]

5 <(A) Fluoro-resin>

As the fluoro-resin (A), any of hitherto known fluoro-resins, such as polytetrafluoroethylene resin (PTFE), modified PTFE, polyvinylidene fluoride resin (PVDF), ethylene/tetrafluoroethylene copolymer resin (ETFE),
10 polychlorotrifluoroethylene resin (PCTFE), tetrafluoroethylene/hexafluoropropylene ethylene copolymer resin (FEP) and tetrafluoroethylene/perfluoroalkyl copolymer resin (PFA), can be preferably used. From the viewpoint of processability in extrusion molding, rolling, etc.,
15 polytetrafluoroethylene resin (PTFE) is preferable among them, and PTFE fine powder obtained by emulsion polymerization is particularly preferable. Since the PTFE fine powder has properties that it becomes fibrous when a shear force is applied, a composition and/or a sheet wherein the resin has been
20 intertwined with the filler (B) and the perlite (C) in the later-described process of stirring and mixing the components of the composition or forming of a sheet can be obtained, and therefore, a fluoro-resin sheet having more excellent sealing properties and mechanical strength can be obtained.

[0012]

When PTFE is used as the fluororesin (A), the aforesaid fluororesins other than the PTFE may be contained in small amounts, for example, not more than 10% by weight (total amount of fluororesins: 100% by weight).

As the fluororesin (A), a fluororesin in the form of a powder may be used as it is, or a dispersion in which fluororesin fine particles are dispersed in water may be used.

[0013]

10 <(B) filler>

As the filler (B), a filler other than the below-described perlite, for example, a carbon-based filler, such as graphite, carbon black, expanded graphite, activated carbon or carbon nanotube, an inorganic filler, such as talc, mica, clay, calcium carbonate, magnesium oxide, silicon carbide, alumina or silica, a powder of a resin, such as PPS, or the like is used according to the use purpose. A fiber material having a fiber length of not more than 10 mm, which is composed of carbon fiber, aramid fiber, rock wool or the like, may be used as the filler (B).

20 [0014]

According to the present invention, a fluororesin sheet which has a low filling ratio of the fluororesin (A) and exhibits a high compressibility even if it has a high filling ratio of the filler (B) can be obtained. The weight ratio between the

fluororesin (A) and the filler (B) (except perlite) is preferably 1:0.1 to 3, more preferably 1:0.1 to 2.

When the filler (B) is contained in such an amount, a fluororesin sheet exhibiting properties of the filler
5 sufficiently can be obtained.

[0015]

<(C) Perlite>

The perlite (C) is a foam of a volcanic-based rock having a high silica content (SiO_2), and it is composed of silica (SiO_2 ,
10 70 to 80%), alumina (Al_2O_3 , 10 to 20%), and Na_2O and K_2O (total: 0 to 10%). Examples of the volcanic-based rocks include pearlstone, obsidian and pitchstone. In the present invention, any of foam of these rocks can be used, but pearlstone that is porous and has an excellent oil absorption ratio is particularly
15 preferable.

[0016]

Such perlite (C) is extremely lightweight, has excellent heat insulation properties, is inexpensive and is incombustible. On that account, a fluororesin sheet that is suitable for uses
20 at high temperatures and is inexpensive can be obtained.

Moreover, the perlite (C) is excellent also in liquid absorption properties, and therefore, it is considered that the perlite can absorb a processing aid (D) in the sheet-forming composition in the present invention. It is considered that

when the following process (I) is used for forming a sheet from the sheet-forming composition, a large number of pores in the perlite are impregnated with the processing aid (D) and keep it therein in the rolling step. It is also considered that by virtue of this, the pore structure of the perlite is rarely crushed in the rolling step, and when the processing aid (D) is vaporized in the subsequent drying step, voids (pores) are held in the perlite in the resulting sheet. Accordingly, it is considered that a fluororesin sheet having a particularly high compressibility and exhibiting proper sealing properties at a low clamp pressure can be obtained.

[0017]

The amount of the perlite (C) in the sheet-forming composition is preferably 4 to 20 parts by weight, more preferably 5 to 8 parts by weight, based on 100 parts by weight of the total amount ((A)+(B)+(C)) of the fluororesin (A), the filler (B) (except perlite) and the perlite (C).

Also in the resulting fluororesin sheet of the present invention, the amount of the perlite (C) based on 100 parts by weight of (A)+(B)+(C) is the same as above.

The mean particle diameter of the perlite (C) (measured by laser particle size distribution analyzer) is preferably not more than 150 μm , more preferably about 75 to 125 μm .

When the perlite (C) is contained in such an amount and

the mean particle diameter of the perlite (C) is in the above range, a fluororesin sheet having a high compressibility while maintaining high gas tight properties can be obtained.

When the amount of the perlite (C) in the sheet-forming
5 composition is 5 to 8 parts by weight based on 100 parts by weight of the total amount of the fluororesin (A), the filler (B) (except perlite) and the perlite (C), a fluororesin sheet having a particularly good balance of properties, such as low compressibility, high sealing properties, high tensile strength
10 and low stress relaxation properties, can be obtained, so that such an amount is preferable.

[0018]

<(D) Processing aid>

As the processing aids (D), hitherto publicly known
15 processing aids, such as petroleum-based hydrocarbon solvents, alcohols and water, can be used without any restriction.

[0019]

Examples of commercial products of the petroleum-based hydrocarbon solvents include Isopar C (hydrocarbon-based
20 organic solvent, fractional distillation temperature: 97 to 104°C), Isopar G (hydrocarbon-based organic solvent, fractional distillation temperature: 158 to 175°C) and Isopar M (hydrocarbon-based organic solvent, fractional distillation temperature: 218 to 253°C) (all manufactured by Exxon Mobil

Corporation), and Cactus Solvent R5N (manufactured by Japan Energy Corporation) as an industrial solvent having advantages, such as non normal hexane, low benzene and low aromatic solvent.

[0020]

5 When the following process (I) is used for preparing a fluororesin sheet, the amount of the processing aid (D) has only to be such an amount that an appropriate amount of the processing aid is present after the rolling step, and specifically, the amount of the processing aid (D) in the sheet-forming composition
10 is preferably 5 to 50 parts by weight, more preferably 10 to 40 parts by weight, based on 100 parts by weight of the total amount of the fluororesin (A), the filler (B) (except perlite) and the perlite (C). When the processing aid (D) is used in such an amount, the raw materials can be easily homogeneously
15 mixed and dispersed after blending, and besides, the resulting composition is excellent in processability into a sheet. When the following process (I) is used for preparing a fluororesin sheet, the fluororesin can be sufficiently swollen in the initial stage of the later-described rolling step. Moreover, all the
20 processing aid does not vaporize before the later-described calcining step, and a sheet containing an appropriate amount of the processing aid after rolling can be obtained.

[0021]

The sheet-forming composition consists essentially of the

fluororesin (A), the filler (B), the perlite (C) and the processing aid (D).

[0022]

For preparing the sheet-forming composition containing
5 these components, these components have only to be added to the container at once or plural times by portions in an arbitrary order, then stirred and mixed.

[0023]

Although the method to stir and mix the components is not
10 specifically restricted, the fluororesin (A), the filler (B), the perlite (C) and the processing aid (D) are blended in such amounts as correspond to the composition of the fluororesin sheet to be produced, and they are stirred and mixed in an arbitrary order. When the stirring efficiency is poor, it is possible
15 that the processing aid is added in a large amount and after completion of stirring an excess processing aid is removed by filtration.

[0024]

As the temperature in the stirring and mixing of the
20 components, a temperature that is lower than the roll temperature in the rolling step is preferable in order that the processing aid will not vaporize.

[0025]

[Process for producing fluororesin sheet]

The process for producing a fluororesin sheet of the present invention is not specifically restricted as long as a fluororesin sheet can be formed from the above-mentioned sheet-forming composition, and hitherto known processes are employable. A process comprising subjecting the sheet-forming composition to preforming, rolling the resulting preform at a roll temperature of 40 to 80°C, then drying the preform and calcining it (also referred to as a "process (I)" hereinafter) is preferable.

10 This process (I) is described below in detail.

[0026]

<Process (I)>

The process (I) includes a preforming step, a rolling step, a drying step and a calcining step in this order.

15 [0027]

<Preforming step>

In the preforming step, the sheet-forming composition is extruded to produce a preform (extrudate).

20 The shape of the preform is not specifically restricted, but when efficiency of the subsequent sheet formation, homogeneity of sheet properties, etc. are taken into consideration, the preform preferably has a shape of a rod or a ribbon.

[0028]

In the production process of the present invention, the preforming step is preferably carried out at a temperature lower than the roll temperature in the rolling step so that the processing aid will not vaporize.

5 [0029]

<Rolling step>

In the rolling step subsequent to the preforming step, the preform is allowed to pass between rolling mill rolls such as twin rolls to roll and form it into a sheet.

10 In the production process of the present invention, the rolling step is carried out at a roll temperature of 40 to 80°C.

When the roll temperature is in the above range, the hardness of the fluororesin (A) is lowered a little, and the fluororesin sheet is apt to be densified. Moreover, all the
15 processing aid (D) does not completely vaporize.

[0030]

If the rolling step is carried out at a temperature lower than 40°C, the processing aid tends to rarely vaporize. On the other hand, if the rolling is carried out at a temperature higher
20 than 80°C, the processing aid (D) excessively vaporizes, and a filler-containing fluororesin sheet having a high compressibility tends to be unable to be formed. Further, since the processing aid (D) excessively vaporizes, the amount of the processing aid remaining at the beginning of the rolling step

is small. Therefore, it tends to become impossible to sufficiently swell the fluororesin (A) and make it fibrous, and the resulting fluororesin sheet tends to have poor strength. Furthermore, because of abrupt vaporization of the processing aid (D) in the composition, a bulge phenomenon occurs, and the gas tight properties of the fluororesin sheet tend to be lowered.

[0031]

In the production process of the present invention, a step of further rolling the rolled sheet prepared by the above rolling step may be included, that is, it is possible to repeat the rolling step plural times (e.g., 3 to 50 times). In order that an appropriate amount of the processing aid may be left in the sheet after the rolling step, it is preferable to properly control the number of rolling times. When the rolling step is repeated, the distance between rolls is narrowed every time the rolling is repeated.

[0032]

In the sheet formation by rolling the preform using twin rolls, for example, the distance between rolls is set to 0.5 to 20 mm, and the preform is rolled at a roll surface moving rate (sheet extrusion rate) of 5 to 50 mm/sec.

[0033]

<Drying step>

In the drying step, the rolled sheet is allowed to stand

at ordinary temperature or heated at a temperature lower than the melting point of the fluororesin to remove the processing aid.

[0034]

5 <Calcining step>

In the calcining step, the sheet given after the drying step is heated at a temperature not lower than the melting point of the fluororesin to sinter the sheet. When it is taken into consideration that the whole sheet needs to be uniformly calcined and in the case of an excessively high temperature a fluorine-based harmful gas is generated, a suitable heating temperature is, for example, 340 to 370°C though it varies a little depending upon the type of the fluororesin.

[0035]

15 [Fluororesin sheet]

The fluororesin sheet is not specifically restricted provided that the sheet is produced from the sheet-forming composition. The fluororesin sheet is preferably a sheet produced by the above process (I). This fluororesin sheet is inexpensive and has a high compressibility. Specifically, the compressibility is preferably not less than 7%, more preferably not less than 8%, and its upper limit may be 15%. The leakage (gastight properties, contact pressure against specimen of $\phi 48\text{mm} \times \phi 67\text{mm} \times 1.5\text{mm}$ (thickness): 19.6 MPa, nitrogen gas internal

pressure: 0.98 MPa) is preferably not more than 7.0×10^{-3} Pa·m³/s, more preferably not more than 2.0×10^{-4} Pa·m³/s, and its lower limit may be 1.0×10^{-5} Pa·m³/s.

[0036]

5 Such a fluororesin sheet of the present invention can be used for a gasket, and a gasket made of the fluororesin sheet of the present invention can be used at high temperatures (e.g., above 200°C) over a long period of time. From the fluororesin sheet, a gasket having high sealing properties can be obtained
10 even at a low clamp pressure.

 The gasket can be easily produced by cutting out (punching) an article of a desired shape from the fluororesin sheet of the present invention. The filler-containing fluororesin sheet of the present invention has ease of cutting (punching) and high
15 handling properties.

[0037]

Examples

 The production process of the present invention is further
20 described with reference to the following examples, but it should be construed that the present invention is in no way limited to those examples.

[0038]

<Test method>

From a sheet having a thickness of 1.5 mm, a specimen was prepared, and gas tight properties were measured in the following manner.

[0039]

5 Leakage (gas tight properties)

A punched gasket specimen having a size of $\phi 48\text{mm} \times \phi 67\text{mm}$ was set between steel flanges (each flange: $\phi 100\text{mm} \times 50\text{mm}$ (height), surface roughness $R_{\text{max}} = 12 \mu\text{m}$), and a load was applied to the specimen by a compression tester so that the contact pressure might become 19.6 MPa (200 kgf/cm²G). Through a through-hole for pressure injection provided at the flange, a nitrogen gas internal pressure of 0.98 MPa (1.0 kgf/cm²G) was applied to the gasket inner diameter side, thereafter the pressure injection pipe was sealed, and the specimen was kept for 1 hour. A change in pressure before and after keeping of the specimen was read out by a pressure sensor, and from the pressure drop, a leakage was determined.

[0040]

Stress relaxation

20 Stress relaxation ratios at 100°C and 200°C were measured on the basis of ASTM F38 B method.

[0041]

Compressibility

Compressibility was measured on the basis of ASTM F36.

Tensile strength

Tensile strength was measured on the basis of JIS R3453.

[0042]

[Example 1]

5 In a kneader, 17.1 kg of PTFE (CD-1, manufactured by Asahi Glass Co., Ltd.), 9.6 kg of finely powdered clay (XN-D325, manufactured by Anhui Snow Satisfied Non-Metallic Materials Co., Ltd.), 1.7 kg of perlite (mean particle diameter: 100 μ m, manufactured by Qingdao Yuzhou Chemical Co., Ltd.) and 7.5 kg
10 of a hydrocarbon-based organic solvent (Isopar G, Exxon Mobil Corporation) were mixed at room temperature for 15 minutes. Thereafter, the mixture was allowed to stand at room temperature (25°C) for 16 hours to age the mixture, whereby a sheet-forming composition was prepared.

15 This composition was extruded by an extruder with a die of 300 mm $\times$ 20 mm at room temperature (25°C) to prepare a preform.

[0043]

 This preform was rolled by twin rolls under the conditions of a roll diameter of 700 mm, a roll distance of 20 mm, a rolling
20 rate of 6 m/min and a roll temperature of 70°C. Immediately after the rolling, the resulting sheet was rolled again under the conditions of a roll distance of 10 mm, and further, while the roll distance was narrowed gradually to 8 mm, 6 mm, 4 mm, 2 mm and 1.5 mm, rolling was carried out 5 times in the same

manner as above to obtain a sheet having a thickness of 1.5 mm.

[0044]

This sheet was allowed to stand at room temperature (25°C) for 24 hours to remove the processing aid, and thereafter, the
5 sheet was calcined in an electric furnace at 350°C for 3 hours to obtain a fluororesin sheet.

This fluororesin sheet had a leakage (gas tight properties) of 2.1×10^{-5} (also described as 2.1E-05) Pa·m³/s and a compressibility of 9%.

10 [0045]

[Example 2]

A fluororesin sheet was produced in the same manner as in Example 1, except that the formulation of the sheet-forming composition used in Example 1 was changed as shown in the following
15 Table 1 and the roll temperature was changed to 80 °C.

[0046]

This fluororesin sheet had a leakage (gas tight properties) of 1.1×10^{-4} Pa·m³/s and a compressibility of 10%.

[0047]

20 [Example 3]

A fluororesin sheet was produced in the same manner as in Example 1, except that the sheet-forming composition used in Example 1 was changed as shown in Table 1 and the composition was extruded by an extruder with a ring die having an outer diameter

of 300 mm and an inner diameter of 260 mm at room temperature (25°C) to prepare a preform.

[0048]

This fluororesin sheet had a leakage (gas tight properties) of 6.2×10^{-4} Pa·m³/s and a compressibility of 9%.

[0049]

[Example 4]

A fluororesin sheet was produced in the same manner as in Example 3, except that the sheet-forming composition used in Example 3 was changed as shown in Table 1.

[0050]

This fluororesin sheet had a leakage (gas tight properties) of 5.3×10^{-4} Pa·m³/s and a compressibility of 10%.

[0051]

15 [Comparative Example 1]

A fluororesin sheet was produced in the same manner as in Example 1, except that the sheet-forming composition used in Example 1 was changed as shown in Table 1.

[0052]

20 This fluororesin sheet had a leakage (gas tight properties) of 1.1×10^{-4} Pa·m³/s and a compressibility of 6%.

[0053]

[Comparative Example 2]

A fluororesin sheet was produced in the same manner as

in Example 1, except that the sheet-forming composition used in Example 1 was changed as shown in Table 1.

[0054]

This fluororesin sheet had a leakage (gas tight properties)

5 of 1.1×10^{-4} Pa·m³/s and a compressibility of 4%.

[0055]

[Table 1]

Items	Unit	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Comp. Ex. 1	Comp. Ex. 2
CD-1	kg	17.1	17.1	15.6	15.6	13.3	17.1
XN-D325	kg	9.6	9.1	9.4	7.7	15	11.3
Perlite (mean particle diameter: 100 μ m)	kg	1.7	2.27	3.4	5.1	0	0
Isopar G	kg	7.5	9.4	8	9.4	8.6	7.5
Seal test, non-application of paste	Pa·m ³ /S	2.10E-05	1.1E-04	6.20E-04	5.3E-04	1.1E-04	1.1E-04
Compressibility	%	9	10	9	10	6	4
Tensile strength	MPa	18	15.6	13	10	17.7	15.6
Stress relaxation 100°C	%	28	33	34	30	29	37
Stress relaxation 200°C	%	46	55	51	50	48	66

CLAIMS

1. A fluororesin sheet produced from a sheet-forming composition containing (A) a fluororesin, (B) a filler (except perlite), (C) perlite and (D) a processing aid.

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2. The fluororesin sheet as claimed in claim 1, wherein the amount of the perlite (C) in the composition is 4 to 20 parts by weight based on 100 parts by weight of the total amount of the fluororesin (A), the filler (B) (except perlite) and the perlite (C).

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3. The fluororesin sheet as claimed in claim 1, wherein the amount of the processing aid (D) in the composition is 5 to 50 parts by weight based on 100 parts by weight of the total amount of the fluororesin (A), the filler (B) (except perlite) and the perlite (C).