

FIBER FOR ARTIFICIAL HAIR, AND HAIR ACCESSORY FORMED FROM SAME

Technical Field

[0001]

The present invention relates to a fiber for artificial hair and a fiber bundle for artificial hair having an excellent styling property and a soft and smooth texture similar to those of human hair; a hair accessory and an artificial hair product formed therefrom; and a polyvinyl chloride-based resin fiber forming the fiber for artificial hair and the fiber bundle for artificial hair.

Background Art

[0002]

As a synthetic fiber for artificial hair which is commercially available, there are many materials such as polyvinyl chloride-based resin fibers, polyester-based resin fibers, and modacrylic resin fibers. These synthetic fibers each have superior properties derived from the material, and they have been used in a headdress product in a field in which they excel depending on the properties of each fiber. Recently, combined fibers are used to fabricate one headdress product, harmonizing and utilizing various excellent properties. The resulting commodities, which consequently have value relatively similar to those of human hair products, have been placed on the market. They show the following properties. For example, the polyvinyl chloride-based resin fiber has soft texture similar to that of human hair, can be easily processed into any style, and rarely gets tangled. The

polyester-based resin fiber has strong resilience, resulting in good feel of elasticity when a commodity is worn and moved, and has good use durability because of its high morphological stability. In addition, the modacrylic resin fiber is light and has high voluminousness, and can impart a natural style utilizing roughness on its surface. On the other hand, however, when fibers formed from different materials are combined to be used, it is difficult to fully utilize the properties of each fiber, and thus so far the commercial value, which is comparable with that of human hair products, cannot be obtained in headdress products made of synthetic fibers.

[0003]

The biggest problem when the fibers formed from different materials are combined to be used is that an optimum processing temperature varies depending on the material. In order to increase the commercial value of the headdress product, it is necessary to improve the three qualities of appearance, texture, and styling property without impairing any of them. In order to realize this, it is important to heat the fibers at an optimum temperature when a curl shape is imparted, in addition to appropriately select a forming ratio of fibers and a fiber-treating agent. Specifically, when a curl shape is imparted at an optimum temperature, elasticity and shape holding power is improved, whereby a feeling of pulsation and use durability as a hair commodity can be improved. Further, specific fiber-treating agents are compatible with a fiber surface by being heated at a high temperature, whereby smooth moisturizing feel (moisture texture) similar to that of human hair can be exhibited. On the other hand, however, when it is heated at a temperature extremely higher than an optimum temperature

of a material, fusion occurs between fibers to lose softness, and the fiber is bent due to heat-shrinkage, resulting in bad texture with rough feel. When it is heated at an extremely lower temperature, the shape cannot be kept sufficiently, thus resulting in reduced styling property. The quality as a commodity is more greatly reduced in the problems caused at a relatively high temperature, and thus when fibers formed from different materials are combined, curls are generally imparted at an optimum processing temperature of a material with the lowest heat-resistance.

[0004]

In particular, the polyvinyl chloride-based resin has a low heat-resistance, and the quality is remarkably reduced with increase of a temperature, and thus a temperature at which a curl shape is imparted is limited to 80 to 90°C. For this reason, when it is particularly mixed with a high heat-resistant fiber such as a polyester-based resin fiber, curls are imparted at a processing temperature lower than an optimum temperature of the polyester-based resin fiber, and thus strong curls, which are originally imparted from the polyester-based resin fiber, cannot be utilized. In addition, original improvement effects of texture by the fiber-treating agent cannot be sufficiently exhibited. The polyvinyl chloride-based resin fiber, however, has very outstanding properties as a fiber for hair in soft and smooth texture similar to that of human hair, styling property of a curl shape, and a cost performance, and thus it is difficult to ignore the fiber in this field, and the conventional technique cannot reach a fully satisfactory level in an overall quality.

[0005]

Specifically, for example, Patent Documents 1 and 2 describe examples in which a polyester-based resin fiber and a halogen-containing resin fiber, or a modacrylic resin fiber, and a polyvinyl chloride-based resin fiber are mixed, and curls are imparted by heating them at a temperature of 100°C or higher. These techniques succeed at exhibition of the quality as a commodity superior to conventional produces by mixing different materials and utilizing the properties. However, because the properties of the polyvinyl chloride-based resin fiber are not sufficiently utilized, there are rooms to improve the texture, and the resulting products do not reach a level in which the quality as a commodity comparative with human hair products is imparted.

[0006]

For the purpose of solving the problems described above, some attempts about the polyvinyl chloride-based resin fiber have further been performed, but sufficient effects have not yet been obtained.

[0007]

For example, Patent Document 3 describes a method for calculating conditions to impart curls, but an effect of suppressing occurrence of fiber bending is insufficient only by simply decreasing a shrinkage percentage and the texture is not considered, for example, the fiber becomes hard in high-temperature conditions, and thus sufficient qualities cannot be obtained as a commodity for hair.

[0008]

In addition, Patent Document 4 describes examples in which a chlorinated polyvinyl chloride resin having a high chlorine content is

admixed in order to improve a heat-resistance of a polyvinyl chloride-based resin fiber, but sufficient texture as a commodity for hair cannot be obtained only by decreasing a shrinkage percentage.

[0009]

In addition, in all of Patent Documents, studies to sufficiently obtain effects of a fiber-treating agent are not performed, and a smooth and moisturizing texture, which is required for hair products, does not reach a sufficient level.

Citation List

Patent Literatures

[0010]

Patent Document 1: JP-A No. 2002-227019

Patent Document 2: WO 2005/082184

Patent Document 3: JP-A No. 2003-293213

Patent Document 4: JP-A No. 4491414

Summary of Invention

Technical Problem

[0011]

The present invention aims at providing a fiber for artificial hair and an artificial hair product having an excellent styling property, and soft and smooth texture similar to that of human hair.

Solution to Problem

[0012]

In order to solve the problems described above, the present inventors have repeated painstaking studies. As a result, they have found when the polyvinyl chloride-based resin fiber is improved to reduce a shrinkage stress, mixed with a fiber having an excellent heat-resistance and an excellent rigidity as needed, and processed at a selected temperature at which a curl shape is imparted and shrinkage percentage and with a selected fiber-treating agent, then headress products in which the above-mentioned problems are solved can be produced, and have achieved the present invention. Principles of the present invention will be explained below.

[0013]

When the polyvinyl chloride-based resin fiber is processed at a temperature higher than a glass transition temperature of 90°C, the fiber is bent due to shrinkage, thus resulting in a bad texture of rough feel, because, as described above, the polyvinyl chloride-based resin, its main component, has a low softening temperature. The bending of this fiber occurs by the following principle. First, in a step in which a curl shape is imparted, fiber bundles are wound spirally or concentrically around a cylindrical pipe, the resulting pipe is heated for a pre-determined time while that shape is maintained, whereby the fiber bundles memorize the wound shape, and then the fiber bundles are taken out from the pipe after cooling it to finish the step. At this time, if fibers having quite different shrinkages are mixed, a fiber having a large shrinkage pulls a fiber having a small shrinkage to cause a deflection in the fiber having a small shrinkage percentage, and the deflection becomes fiber bending in a condition of a high temperature, which

results in deteriorated texture. It has been found that when an angle of bending is less than 170° , humans feel the texture of rough feel. In addition, it has also been found that the polyvinyl chloride-based resin fiber easily cause a fiber bending with an angle of less than 170° to other fibers such as a modacrylic resin fiber or a polyester-based resin fiber, and furthermore softness is lost due to fusion between the fibers and thus the degree of deterioration of the texture is extremely large.

[0014]

As a result of the present inventors' repeated painstaking studies, it has been found that when a fiber having a higher shrinkage percentage has a lower shrinkage stress, a fiber having a lower shrinkage percentage takes a rule of a support, and thus it is less likely to cause a deflection. In addition, it has also been found that when the fiber having a lower shrinkage percentage has a high rigidity, the shrinkage of the fiber having a higher shrinkage percentage can be suppressed, and it is less likely to cause the fiber bending. Applying that principle, when the shrinkage stress of the polyvinyl chloride-based resin fiber, which easily causes the fiber bending, is reduced, and, for example, a polyester-based resin fiber whose rigidity is higher and whose shrinkage is lower than those of the polyvinyl chloride-based resin fiber, is mixed with it as needed, imparting of a curl shape is succeeded even at a temperature higher than 90°C which has been conventionally used, without increase of the fiber bending.

[0015]

The effect of increasing the temperature at which the curl shape is imparted influences on the texture by a fiber-treating agent, and the

compatibility with the fiber-treating agent on the fiber surface is improved by heating at a high temperature. In particular, it has been found that when an amino-modified silicone compound is used, softness of the fiber and an effect of increasing a moisturizing feel can be obtained, compared with a case in which a curl shape is imparted at a temperature of 90°C or less. Furthermore, it has been found that because an effect of suppressing fusion between fibers of the polyvinyl chloride-based resin fiber can be obtained from an amino-modified silicone compound, it is possible to ensure the softness of the fiber which has conventionally reduced by being heated at a high temperature, and thus excellent texture comprehensively similar to that of human hair can be obtained.

[0016]

Thus, the present invention has the following gist.

[0017]

One of characteristics of the present invention is a polyvinyl chloride-based resin fiber which has a shrinkage stress of 70 $\mu\text{N/dtex}$ or less at 130°C.

[0018]

Another characteristic of the present invention is a polyvinyl chloride-based resin fiber for artificial hair which has a shrinkage stress of 70 $\mu\text{N/dtex}$ or less at 130°C.

[0019]

Another characteristic of the present invention is a fiber bundle for artificial hair including 20 to 100% by weight of a polyvinyl chloride-based resin fiber having a shrinkage stress of 70 $\mu\text{N/dtex}$ or less at 130°C and 0 to

80% by weight of a thermoplastic resin fiber having a composition including no polyvinyl chloride-based resin.

[0020]

Another characteristic of the present invention is a fiber bundle for artificial hair including 20 to 100% by weight of a polyvinyl chloride-based resin fiber having a shrinkage stress of 70 $\mu\text{N/dtex}$ or less at 130°C and 0 to 80% by weight of a thermoplastic resin fiber having a Young's modulus of 4 to 9 GPa, a shrinkage percentage of 10% or less at 130°C, and a composition including no polyvinyl chloride-based resin.

[0021]

Another characteristic of the present invention is a fiber bundle for artificial hair wherein the polyvinyl chloride-based resin fiber has a shrinkage percentage at 130°C which is not lower than a shrinkage percentage of the thermoplastic resin fiber at 130°C, and a difference between the shrinkage percentage at 130°C of the polyvinyl chloride-based resin fiber and the shrinkage percentage at 130°C of the thermoplastic resin fiber is 6% or less.

[0022]

Another characteristic of the present invention is a fiber bundle for artificial hair wherein the polyvinyl chloride-based resin fiber and the thermoplastic resin fiber includes an amino-modified silicone compound.

[0023]

Another characteristic of the present invention is a fiber bundle for artificial hair wherein the polyvinyl chloride-based resin fiber includes a polyalkylene oxide-based compound having a weight average molecular

weight of 2000 to 25000 in a content of 0.07 to 0.5 omf%.

[0024]

Another characteristic of the present invention is a fiber bundle for artificial hair wherein the polyvinyl chloride-based resin fiber includes a silicone-based compound in a content of 0 to 0.5 omf%.

[0025]

Another characteristic of the present invention is an artificial hair product obtained by processing a fiber bundle for artificial hair including 20 to 100% by weight of a polyvinyl chloride-based resin fiber having a shrinkage stress of 70 $\mu\text{N/dtex}$ or less at 130°C and 0 to 80% by weight of a thermoplastic resin fiber having a composition including no polyvinyl chloride-based resin.

Advantageous Effects of Invention

[0026]

According to the present invention, a fiber for artificial hair and an artificial hair product having an excellent styling property and a soft and smooth texture similar to that of human hair can be obtained.

Brief Description of the Drawing

[0027]

Fig. 1 is a diagram showing measurement results of a shrinkage stress of polyvinyl chloride-based resin fibers described in Preparation Examples 1-4 of the present invention wherein PVC-1 is a conventional product, and PVC-2 to PVC-4 are improved products of the present

invention.

Description of Embodiments

[0028]

The present invention will be explained in detail below.

[0029]

The fiber bundle for artificial hair of the present invention is characterized by including 20 to 100% by weight of a polyvinyl chloride-based resin fiber having a shrinkage stress of 70 $\mu\text{N/dtex}$ or less at 130°C, and 0 to 80% by weight of a thermoplastic resin fiber having a Young's modulus of 4 to 9 GPa, a shrinkage percentage of 10% or less at 130°C, and a composition including no polyvinyl chloride-based resin.

[0030]

The fiber bundle in the present invention refers to a bulk material of two or more monofilaments with each size being 20 to 100 dtex, which may be fixed in order not to break the bulk material of monofilaments or may not be fixed. Synthetic fibers for artificial hair are usually produced as bundles of continuous fiber having a length of several hundreds of meters, and the bundles are cut into an arbitrary length and they are made into a product by mixing the fibers and imparting a curl shape when they are processed into a commodity. The term "fiber bundle" in the present invention, however, is not particularly limited, and it shows, for example, a bundle of continuous fiber in the production, a cut fiber bundle in the commodity process, a fiber bundle in a product for hair, and the like, unless otherwise specified.

[0031]

The polyvinyl chloride-based resin fiber used in the present invention is a fiber including as a main component a polyvinyl chloride-based resin, and is characterized by having a small shrinkage stress. In general, the shrinkage stress has a tendency to become higher when the shrinkage percentage is high. Even if there is a potential shrinkage stress, however, it is possible to reduce a stress caused during shrinkage, whereby the occurrence of fiber bending can be suppressed. In order to reduce the shrinkage stress, a method in which a mild heat treatment is performed at a high temperature, for example, of 110°C or higher for a long period of time in a fiber production is effective, and the shrinkage stress can be reduced even if the same shrinkage percentage is maintained. The method for reducing the shrinkage stress, however, is not limited to this, but any method can be used. The polyvinyl chloride-based resin fiber generally has a shrinkage stress with a peak at about 130°C as shown in Fig. 1, and in the present invention a preferable value of the shrinkage stress is specifically 70 $\mu\text{N/dtex}$ or less, preferably 50 $\mu\text{N/dtex}$ or less, more preferably 40 $\mu\text{N/dtex}$ at 130°C. When the shrinkage stress is more than 70 $\mu\text{N/dtex}$, the effect by the thermoplastic resin fiber, which supports the polyvinyl chloride-based resin fiber and suppresses the shrinkage, is insufficient. This causes deflection and fiber bending in the polyvinyl chloride-based resin fiber, thus resulting in deteriorated texture.

[0032]

The polyvinyl chloride-based resin fiber used in the present invention can be preferably used as a polyvinyl chloride-based resin fiber for artificial hair.

[0033]

The polyvinyl chloride-based resin fiber used in the present invention has a component percentage of 20 to 100% by weight, preferably 30 to 75% by weight, more preferably 40 to 60% by weight in the fiber bundle for artificial hair. The component percentage is less than 20% by weight in the fiber bundles for artificial hair, the soft texture and the styling property, which are provided by the polyvinyl chloride-based resin fiber, are insufficient, and the satisfactory quality as a commodity cannot be obtained, i.e., the quality as a commodity tends to be deteriorated.

[0034]

As the polyvinyl chloride-based resin fiber used in the present invention, the polyvinyl chloride-based resin fiber having 0.07 to 0.5 omf% of a polyalkylene oxide-based compound with a weight average molecular weight of 2000 to 25000 and 0 to 0.5 omf% of a silicone-based compound, which are supported on its surface, can be preferably used in the state of a fiber bundle before processing into a commodity.

[0035]

The phrase "supported on a fiber surface" refers to a state in which a specific compound bonds to a surface layer of the fiber, and components which penetrate inside the fiber and cannot be removed therefrom are excluded. In the present invention, as a solvent which does not penetrate inside the polyvinyl chloride-based resin fiber, ethanol/cyclohexane = 50 wt%/50 wt% is used, and a weight of compounds which are extracted by immersing a fiber in this solvent is treated as a supported amount.

[0036]

In the method for reducing the shrinkage stress of the fiber described above, when the mild heat treatment is performed at a high temperature, the conventional polyvinyl chloride-based resin fiber for hair has a problem in which fusion occurs between the fibers, and thus the soft texture similar to that of human hair, which is provided by the starting material, cannot be obtained. This is caused by an insufficient performance of an oil solution usually used in a step in order to suppress fusion. For the polyvinyl chloride-based resin fiber, a mixed emulsion including a nonionic surfactant, a cationic surfactant, an oil component such as an ester oil, and the like, has been used as the oil solution in a step, but these oil solutions are all low molecular weight components having a weight average molecular weight of less than 1500. This is because the use of a component having a high molecular weight leads to a sticky texture and to difficulty in sufficiently washing out the oil solution when another oil solution is used in processing the commodity instead of the oil solution which has been used, causing a problem of insufficient texture in a final commodity. As a result of the present inventors' repeated studies, it has been found that when a fiber-treating agent component having a weight average molecular weight of less than 1500 is supported on a surface of the vinyl chloride resin fiber and then heated at 100°C or higher, the fiber-treating agent is gradually penetrated inside the fiber, and thus an amount of the agent remaining on the surface layer of the fiber is significantly decreased to reduce the effect of suppressing fusion, and furthermore, the oil component, which has been penetrated inside the fiber, exhibit a plasticizing effect, thus resulting in enhanced fusion between the fibers and increased shrinkage stress. As a

result of repeated studies, it has been found that when a polyalkylene oxide-based compound having a weight average molecular weight of 2000 to 25000 is used as the oil solution in a step, the oil solution is not penetrated inside the fiber, and even if it is kept at a high temperature of 120°C or higher, the effect of suppressing fusion can be sufficiently exhibited. The sticky feeling of the texture can be improved by controlling an adhering amount of the oil solution, and a comb-passing property and an effect of suppressing static electricity are good even in a small amount.

[0037]

As the polyalkylene oxide-based compound used in the present invention, a polyalkylene oxide compound in which an alkylene oxide including ethylene oxide is addition polymerized to an organic compound having two active hydrogen groups can be preferably used. The organic compound including two active hydrogen groups may include, for example, ethylene glycol, propylene glycol, polyethylene glycol, polypropylene glycol, polytetramethylene glycol, 1,6-hexanediol, aniline, and the like. At least one compound selected from these compounds can be preferably used. The alkylene oxide including ethylene oxide is ethylene oxide or an alkylene oxide having 3 to 30 carbon atoms, and for example, propylene oxide, butylene oxide, styrene oxide, α -olefin epoxide, or glycidyl ethers can be used. At least one compound selected from these compounds can be preferably used. Of these, compounds whose number of carbon atoms is small are preferable in terms of the texture, but because it is necessary to have fluidity at room temperature for obtaining the effect of suppressing fusion, a copolymer of ethylene oxide and propylene oxide is preferable. The addition

polymerization of the alkylene oxide can be performed according to a known method, and either a random type or a block type may be performed. As for the molecular weight, the weight average molecular weight is enough from 2000 to 25000, preferably from 5000 to 20000, more preferably from 10000 to 18000. When the weight average molecular weight is less than 2000, the compound is penetrated inside the fiber on heating to reduce the effect of suppressing fusion, thus resulting in hard texture of the fiber; whereas when it is more than 25000, the deteriorated texture with sticky feel is obtained even if the adhering amount is controlled. In order to strike a balance between the good texture and the antistatic effect, the polyalkylene oxide compounds having different weight average molecular weights within the range described above may be mixed.

[0038]

An amount of the polyalkylene oxide-based compound used in the present invention supported on the fiber is enough from 0.07 to 0.5 omf%, preferably from 0.07 to 0.3 omf%, more preferably from 0.1 to 0.2 omf%. When the amount of the compound supported on the fiber is less than 0.07, the fiber becomes hard because of insufficient effect of suppressing fusion, and the comb-passing property or the effect of suppressing static electricity becomes insufficient. On the other hand, when the amount of the compound supported on the fiber is more than 0.5 omf%, deteriorated texture with sticky feel is obtained, and the fibers converge excessively to deteriorate the voluminousness.

[0039]

A silicone-based compound may be supported on the polyvinyl

chloride-based resin fiber used in the present invention, in addition to the polyalkylene oxide-based compound. A silicone-based compound having a specific viscosity does not penetrate inside the fiber, similar to the polyalkylene oxide-based compound, and a high effect of suppressing fusion can be obtained therefrom. Further, when an amino-modified silicone-based compound is used as the silicone-based compound, the good texture can be obtained by performing the heat treatment at a high temperature, as described above. In particular, because heating is performed in a tensile state in the mild heat treatment step, the fiber bending is not caused, and thus the heating can be performed at a temperature higher than a temperature at which a curl shape is imparted, whereby a higher effect of improving the texture can be obtained. However, the silicone-based compound cannot be used alone as the oil solution because of its large charging effect, it is necessary to use it together with the polyalkylene oxide-based compound.

[0040]

As the silicone-based compound used in the present invention, linear polydimethyl siloxanes which are in a liquid state at 23°C, or compounds generally called "silicone oils" in which an amino group, an epoxy group, a carboxyl group, a polyether group, or a thiol group is introduced into a side chain of the polydimethylsiloxane, and which have a methyl group or a hydroxyl group at the molecular ends can be preferably used. In addition, multiple silicone compounds may be mixed for the surface of the fiber, and a silsesquioxane having the functional group described above may be mixed within a range in which stability of an emulsion can be maintained. Of

these, polydimethylsiloxane, amino group-modified dimethylsiloxane, and epoxy-modified dimethylsiloxane are preferable, and amino-modified dimethylsiloxane and dimethylsiloxane are more preferable. The amino-modified dimethylsiloxane can be compatible with the surface of the fiber at a temperature relatively lower than that used in other silicone compounds, and thus the better texture can be obtained. When dimethylsiloxane is added in an arbitrary amount thereto, smoother texture can be obtained. A molecular weight of the silicone oil among the silicone compounds is generally often defined as a kinematic viscosity, and in the present invention, the kinematic viscosity thereof is preferably from 500 to 20000 mm²/s, more preferably from 1000 to 10000 mm²/s at 25°C. When the kinematic viscosity is less than 500 mm²/s, the amount penetrating inside the fiber is increased, and thus the effect of suppressing fusion becomes insufficient, thus the fiber becomes hard. When it is more than 20000 mm²/s, it is difficult to uniformly attach it on the surface of the fiber, and thus the sufficient effect of suppressing fusion and improving the texture cannot be obtained.

[0041]

An amount of the silicone compound used in the present invention supported on the fiber is enough from 0 to 0.5 omf%, preferably from 0.02 to 0.3 omf%, more preferably from 0.05 to 0.2 omf%. When the amount supported on the fiber is more than 0.5 omf%, static electricity is caused because of a large charging effect, and a problem in which monofilaments get tangled arises during processing the fiber.

[0042]

To the polyvinyl chloride-based resin fiber used in the present invention may be added an anti-static agent and a smoothing agent, in addition to the polyalkylene oxide-based compound and the silicone-based compound. However, an amount of oil components such as a mineral oil which penetrates into the fiber to exhibit a plasticizing effect and an ester oil is preferably small. Thus the adhering amount of the oil component is preferably 0.15 omf% or less, more preferably 0.07 omf% or less.

[0043]

A method for mixing or producing the polyvinyl chloride-based resin fiber used in the present invention is not particularly limited, and it can be produced in a conventionally known production method. In order to obtain a fineness or a cross-sectional shape of the fiber suitable for the fiber for hair, it is preferable to use production methods in that field. One example thereof will be explained below.

[0044]

The polyvinyl chloride-based resin fiber used in the present invention is the fiber including as a main component the polyvinyl chloride-based resin, and a known compounding agent used in a vinyl chloride composition may be added thereto according to its purpose, so long as the quality of the fiber such as transparency or spinning stability is not impaired. Specifically, for example, a heat-resistance improver such as a chlorinated vinyl chloride resin or an AS resin, a metal soap-based heat stabilizer, a stabilizing aid such as a β -diketone, phosphite, or polyol, a plasticizer, a ultra-violet absorber, an antioxidant, an anti-static agent, a filler, a flame retardant, a pigment, or the like, may be used. In some cases, a specific compounding

agent such as a foaming agent, a cross-linking agent, a tackifier, an agent of providing conductivity, and a perfume may be used.

[0045]

The polyvinyl chloride-based resin used in the polyvinyl chloride-based resin fiber used in the present invention may be a conventionally known homopolymer resin of vinyl chloride, conventionally known various copolymer resins thereof, or the like, which is not particularly limited. The copolymer resin may typically include copolymer resins of vinyl chloride and a vinyl ester such as a vinyl chloride-vinyl acetate copolymer resin and a vinyl chloride-vinyl propionate copolymer resin; copolymer resins of vinyl chloride and an acrylic ester such as a vinyl chloride-butyl acrylate copolymer resin and a vinyl chloride-2-ethylhexyl acrylate copolymer resin; copolymer resins of vinyl chloride and an olefin such as a vinyl chloride-ethylene copolymer resin and a vinyl chloride-propylene copolymer resin; vinyl chloride-acrylonitrile copolymer resins, and the like.

Preferable vinyl chloride resin may include the homopolymer resin of vinyl chloride. In the copolymer resin, a content of the comonomer is not particularly limited, and it can be decided depending on the molding processability into fiber, and the property of the fiber. When the copolymer resin has a low softening temperature, however, it is preferable to use it together with the homopolymer resin of vinyl chloride, because it results in reduced heat-resistance.

[0046]

The vinyl chloride resin used in the polyvinyl chloride-based resin

fiber used in the present invention has a viscosity-average polymerization degree of preferably 450 or more, in order to obtain sufficient strength and heat-resistance as the fiber. In order to perform a stable production of fiber under a suitable nozzle pressure, the polymerization degree is preferably 1800 or less. In order to attain the molding processability and the fiber properties, when the homopolymer resin of vinyl chloride is used, its viscosity-average polymerization degree is particularly preferably within a range of 650 to 1450. When the copolymer is used, its viscosity-average polymerization degree is particularly preferably within a range of 1000 to 1700, though it also depends on the content of the comonomer. The viscosity-average polymerization degree is obtained by solving 200 mg of a resin in 50 ml of a nitrobenzene, measuring a specific viscosity of the resulting polymer solution in a thermostatic chamber having a temperature of 30°C using a Ubbelohde viscometer, and performing calculation in accordance with JIS-K-6721.

[0047]

The vinyl chloride resin used in the polyvinyl chloride-based resin fiber used in the present invention can be produced by an emulsion polymerization, a bulk polymerization, a dispersion polymerization, or the like. A polymer produced by the dispersion polymerization is preferable, in consideration of an initial colorability of the fiber, and the like.

[0048]

A chlorinated vinyl chloride resin can also be used as the vinyl chloride resin in the polyvinyl chloride-based resin fiber used in the present invention. As the chlorinated vinyl chloride resin, a polymer obtained by

reacting chlorine with a vinyl chloride resin used as a starting material to increase its chlorine content to 58 to 72% is used. By using the chlorinated vinyl chloride resin, an effect of suppressing shrinkage of the fiber is exhibited, because the heat-resistance of the fiber is improved owing to the increase of the chlorine content by the chlorination. The chlorinated vinyl chloride resin preferably has a viscosity-average polymerization degree (a viscosity-average polymerization degree of the vinyl chloride resin which is the starting material) of 300 to 1100. When the viscosity-average polymerization degree is less than 300, the resulting fiber has a slightly high shrinkage percentage, because the effect of lowering a heat shrinkage percentage of the fiber is reduced. On the other hand, when the viscosity-average polymerization degree is more than 1100, a melt viscosity becomes high and a nozzle pressure becomes high on spinning, and thus it tends to be difficult to perform a safety operation. The chlorinated vinyl chloride resins having a viscosity-average polymerization degree of 500 to 900 are particularly preferable. When the chlorine content is less than 58%, the effect of reducing the heat shrinkage percentage of the fiber is reduced; whereas when it is more than 72%, the melt viscosity becomes high, and it tends undesirably to be difficult to perform a safety operation.

[0049]

The chlorinated vinyl chloride resin is preferably used as it is mixed with a vinyl chloride resin rather than used alone, in terms of yarn breakage on the spinning and coloration of the yarn due to heat. It is preferable to mix the chlorinated vinyl chloride resin in a content of 0 to 40% by weight based on 100 to 60% by weight of the vinyl chloride resin, and more

preferably the chlorinated vinyl chloride resin is mixed in a content of 10 to 30% by weight based on 90 to 70% by weight of the vinyl chloride resin. When the content of the chlorinated vinyl chloride resin is more than 40% by weight, yarn breakage easily occurs on the spinning.

[0050]

As a stabilizer used for the polyvinyl chloride-based resin fiber used in the present invention, known stabilizers may be used, and of these at least one heat stabilizer selected from tin-based heat stabilizers, Ca-Zn-based heat stabilizers, hydrotalcite-based heat stabilizers, epoxy-based heat stabilizers, and β -diketone-based heat stabilizers are preferable. It is preferable to use the heat stabilizer in an amount of 0.2 to 5 parts by weight, more preferably 1 to 3 parts by weight. When the amount is less than 0.2 part by weight, effects as the heat stabilizer are poor. When it is more than 5 parts by weight, the heat stability cannot be greatly improved, and thus it is economically disadvantageous.

[0051]

As thermal decomposition of the resin on spinning is prevented by the addition of the heat stabilizer, effects in which a color tone of the fiber is not deteriorated and the spinning can be stably performed (long-run spinning property) are exhibited. The long-run spinning property refers to a property in which a continuous operation can be stably performed over several days without stopping the spinning step and fibers can be produced. When a resin composition having a low long-run spinning property is used, the yarn breakage starts to occur or a die pressure starts to elevate in a relatively short time after starting the operation due to, for example,

plate-out, and thus it is necessary to exchange breaker plates or nozzles before restart the operation, i.e., a productivity is low. The deterioration of the color tone of the fiber, described above, is about an initial coloration of the fiber on the spinning.

[0052]

In the heat stabilizers, the tin-based stabilizer may include mercaptotin-based heat stabilizers such as dimethyl tin mercapto, dimethyl tin mercaptide, dibutyl tin mercapto, dioctyl tin mercapto, dioctyl tin mercaptopolymers, and dioctyl tin mercaptoacetate; tin maleate-based heat stabilizers such as dimethyl tin maleate, dibutyl tin maleate, dioctyl tin maleate, and dioctyl tin maleate polymers; and tin laurate-based heat stabilizers such as dimethyl tin laurate, dibutyl tin laurate, and dioctyl tin laurate. The Ca-Zn-based heat stabilizer may include zinc stearate, calcium stearate, zinc 12-hydroxystearate, calcium 12-hydroxystearate, and the like. The hydrotalcite-based heat stabilizer may include ALCAMIZER manufactured by Kyowa Chemical Industry Co., Ltd. The epoxy-based heat stabilizer may include, for example, epoxidized soybean oil and epoxidized linseed oil. The β -diketone-based heat stabilizer may include, for example, stearylbenzoylmethane (SBM), dibenzoylmethane (DBM), and the like.

[0053]

As a lubricant used for the polyvinyl chloride-based resin fiber used in the present invention, conventionally known lubricants can be used. In particular, at least one lubricant selected from the group consisting of metal soap-based lubricants, polyethylene-based lubricants, higher fatty acid-based lubricants, ester-based lubricants, and higher alcohol-based

lubricants is preferable. The lubricant is effective for controlling a molten state of the composition, and a bonded state of the composition and a metal face of screws, cylinders, or dies in an extruder. The lubricant is preferably used in an amount of 0.2 to 5 parts by weight based on 100 parts by weight of the vinyl chloride resin. The lubricant is more preferably used in an amount of 1 to 4 parts by weight. When the amount is less than 0.2 part by weight, the productivity is reduced because a die pressure is increased and an ejection amount is reduced on spinning. Moreover, the yarn breakage and the increase of the nozzle pressure tend to happen more easily, thus resulting in difficulty in stable production. When it is more than 5 parts by weight, the ejection amount is reduced and the yarn breakage frequently occurs, and thus it is difficult to perform stable production as in the case in which the amount is less than 0.2 part by weight, and the fiber tends not to be clear, so that such an amount is not preferable.

[0054]

The metal soap-based lubricant may include, for example, metal soaps such as stearate, laurate, palmitate, and oleate of Na, Mg, Al, Ca, and Ba. The higher fatty acid-based lubricant may include, for example, saturated fatty acids such as stearic acid, palmitic acid, myristic acid, lauric acid, and capric acid; unsaturated fatty acids such as oleic acid; and their mixtures. The higher alcohol-based lubricant may include stearyl alcohol, palmityl alcohol, myristyl alcohol, lauryl alcohol, oleyl alcohol, and the like. The ester-based lubricant may include ester-based lubricants including an alcohol and a fatty acid; pentaerythritol-based lubricants such as monoester, diesters, triesters, tetraesters, or mixtures thereof of a higher fatty acid with

pentaerythritol or dipentaerythritol; montanoic acid wax-based lubricants such as esters of montanoic acid with a higher alcohol including a stearyl alcohol, palmityl alcohol, myristyl alcohol, lauryl alcohol, or oleyl alcohol.

[0055]

When the polyvinyl chloride-based resin fiber used in the present invention is produced, for example, a processing aid, a matting agent, a filler, a plasticizer, an ultraviolet absorber, an anti-oxidant, an anti-static agent, a flame retardant, and a pigment may be used according to the purpose.

[0056]

Of these, it may be added with an ethylene-vinyl acetate (EVA)-based resin, for example, PES-250 manufactured by Nippon Unicar Company Limited, and the like, for obtaining the soft texture, and an acrylic resin, for example, PA-20 manufactured by KANEKA CORPORATION, and the like, for further improving extrusion processability.

[0057]

The polyvinyl chloride-based resin fiber used in the present invention can be produced by a known melt-spinning method in a fiber formation step. For example, the vinyl chloride-based resin, the chlorinated vinyl chloride-based resin, the heat stabilizer, and the lubricant are mixed in a pre-determined ratio; the mixture is stirred in a Henschel mixer, or the like; the resulting mixture is filled in an extruder; the resin is extruded under conditions providing good spinning properties at a cylinder temperature of 150 to 190°C and a nozzle temperature of 180±15°C, thereby performing melt-spinning to obtain unstretched yarns.

[0058]

A conventionally known extruder can be used for spinning the unstretched yarns. For example, it is possible to use a single screw extruder, a counter-rotating twin screw extruder, or a conical twin screw extruder. It is particularly preferable to use a single screw extruder with an aperture size of about 35 to 85 mm ϕ , or a conical extruder with an aperture size of about 35 to 50 mm ϕ . A hole shape of the nozzle used then is made to be similar to a final cross-sectional shape, while considering and controlling the shape and size, which are slightly changed depending on the die swell and the stretching on spinning. The shape of the nozzle hole is not particularly limited, and can be selected from round-shape, flat oval-shape, eye-glass-shape, cocoon-shape, star-shape, C-shape, H-shape, T-shape, Y-shape, cross-shape, pentagon-shape, hexagon-shape, and octagon-shape. It is desirable not to remarkably increase the rigidity, and of these the flat oval-shape, the eye-glass-shape, and the cocoon-shape are preferable, and the eye-glass-shape and the cocoon-shape are more preferable.

[0059]

The extruded filaments are subjected to heat-treatment for about 0.5 to 1.5 seconds in a heat-spinning tube (at a 200 to 300°C atmosphere, and under conditions providing good spinning property) provided directly under the nozzle, and then the resulting unstretched yarns are sent through a take-in roll to a stretching process. Next, the unstretched yarns are stretched about two to four times between the take-in roll and a stretching roll through a hot-air circulation chamber in which the temperature has been adjusted to 100 to 130°C.

[0060]

Next, the yarns are stretched between two pairs of circular cone rolls arranged in the hot-air circulation chamber in which the temperature has been adjusted to 110 to 150°C, a relaxation treatment is continuously performed at about 20 to 50%, and multifilaments are wound, whereby the fiber of the present invention is produced. At this time, a high heat-treatment temperature is desirable to reduce the shrinkage stress, it is preferably from 120 to 145°C, more preferably from 130 to 140°C. When the heat-treatment temperature is lower than 110°C, the shrinkage stress cannot be sufficiently reduced at 130°C, thus resulting in occurrence of fiber bending to deteriorate the quality as a commodity; whereas when it is higher than 150°C, the fusion between the fibers cannot be suppressed even if the polyalkylene oxide compound is supported, and thus the texture becomes hard.

[0061]

In order to reduce a strain in the molecule, it is desirable to set the relaxation speed as slow as possible, and it is preferable to set it at a relaxation rate of 10%/minute or less, more preferably at a relaxation rate of 8%/minute or less. When the relaxation speed is set at a relaxation rate of more than 10%/minute, the strain in the fiber cannot be sufficiently removed, and thus the fiber bending easily occurs due to fiber shrinkage, thus resulting in deteriorated texture. The time for the mild heat treatment is preferably from 2 to 60 minutes, more preferably from 4 to 20 minutes. When the time for the heat treatment is shorter than 2 minutes, it is difficult to make the shrinkage percentages of the multifilaments uniform; whereas when it is longer than 60 minutes, the fusion between the fibers cannot be

sufficiently suppressed even if the polyalkylene oxide compound is supported, and thus the texture becomes hard.

[0062]

In order to control the shrinkage percentage, the fiber may be further stretched within a range of 0.1 to 4%, after the mild heat treatment.

Furthermore, in order to melt the slight fusion between the fibers, nip rolls and bended parts may be introduced into the step after the mild heat treatment.

[0063]

The monofilament forming the fiber for artificial hair of the present invention has a fineness of preferably 20 to 100 dtex, similar to usual fiber for artificial hair, and more preferably 40 to 90 dtex. When the fineness is thinner than 20 dtex, the curls become too weak after the commodity process, and thus the styling property is remarkably deteriorated. When it is thicker than 100 dtex, the rigidity of the fiber becomes high, and thus the texture becomes hard.

[0064]

The thermoplastic resin fiber used in the present invention is characterized by having a Young's modulus of 4 to 9 GPa, a shrinkage percentage of 10% or less at 130°C, and a composition including no polyvinyl chloride-based resin, and characterized in that it is included in a component percentage of 0 to 80% by weight in the fiber bundle for artificial hair.

[0065]

In the present invention, the thermoplastic resin fiber has a role to suppress the shrinkage of the polyvinyl chloride-based resin fiber, thereby

preventing the deterioration of the texture, and thus it is necessary to have rigidity to absorb the shrinkage stress. The rigidity can be shown using the Young's modulus as an indicator. In the present invention, it is necessary for the thermoplastic resin fiber to have a Young's modulus of 4 to 9 GPa, and it is preferably from 4.5 to 8 GPa, more preferably from 5 to 7 GPa. When the Young's modulus is less than 4 GPa, the effect of suppressing the shrinkage of the polyvinyl chloride-based resin fiber cannot be sufficiently obtained, and the texture is deteriorated due to the occurrence of the fiber bending. When the Young's modulus is more than 9 GPa, the texture and the styling property are deteriorated because of too strong resilience as the fiber for hair.

[0066]

It is necessary for the thermoplastic resin fiber not to be softened and deformed at a temperature at which the curl shape is imparted, and the shrinkage percentage at 130°C can be used as its indicator. When the shrinkage percentage is measured in the present invention, a fiber bundle having a total fineness of 15000 to 25000 dtex obtained by combining monofilaments is used, the measurement is performed 20 times, and an average thereof is used. At this time, a large fluctuation range in the shrinkage percentage even in the same fibers results in the fiber bending. When fibers having a difference in shrinkage percentage of 2% or more from the average shrinkage percentage are included in a content of 30% or more in the same fibers, it is preferable not to use such fibers, because the good texture may not be maintained. It is necessary for the thermoplastic resin fiber used in the present invention to have a shrinkage percentage of 10% or

less at 130°C, and it is preferably 4% or less, more preferably 1% or less. When the shrinkage percentage is more than 10% at 130°C, the effect of suppressing the shrinkage of the polyvinyl chloride-based resin fiber cannot be sufficiently obtained, and the fiber bending occurs to deteriorate the texture.

[0067]

The thermoplastic resin fiber used in the present invention is included in a component percentage of 0 to 80% by weight, preferably 25 to 70% by weight, more preferably 40 to 60% by weight, in the fiber bundle for artificial hair. When the component percentage in the fiber bundle for artificial hair is more than 80% by weight, the soft texture and styling property, which is provided by the polyvinyl chloride-based resin fiber, cannot be sufficiently obtained, and thus the quality as a commodity is deteriorated.

[0068]

The ingredients of the thermoplastic resin fiber used in the present invention are not particularly limited so long as they are thermoplastic resins excluding polyvinyl chloride-based resins. When the polyvinyl chloride-based resin fiber is used, it is possible to increase the rigidity by adding, for example, an inorganic substance thereto, but there is a property in which the fiber bending becomes sharp if deflection occurs, and thus it is difficult to prevent the deterioration of the texture, as described above. The ingredient for the thermoplastic resin fiber may specifically include, for example, acrylonitrile-based resins, modacrylic resins, polyolefin-based resins, polyester-based resins, polyamide-based resins, polyimide-based

resins, polyether-imide-based resins, polyamide-imide-based resins, polyoxymethylene-based resins, polyether-ketone-based resins, polycarbonate-based resins, polysulfone-based resins, polyether-sulfone-based resins, polyphenylene-ether-based resins, polyphenylene-sulfide-based fibers, Teflon® resins, and the like. Of these, the acrylonitrile resins, the modacrylic resins, the polyester-based resins, the polyamide-based resins, the polycarbonate-based resins, the polyether-sulfone-based resins, and the polyphenylene-sulfide-based resins are preferably used, because they can be naturally mixed as the fiber for hair, and the modacrylic resin and the polyester-based resins are more preferably used. Several kinds of these ingredients may be mixed, and further a composite fiber having a multi-layer structure such as a core-sheath structure may be used.

[0069]

The thermoplastic resin fiber used in the present invention has an LOI value of preferably 25 or more. The product for hair is required to have flame retardance in terms of its intended purpose, and a certain level of the flame retardance can be obtained by mixing a large amount of a polyvinyl chloride-based resin fiber having a fire extinguishing performance. The present invention is characterized by providing the fiber bundle for artificial hair, which is suitable for supporting the flammable amino-modified silicone compound on the fiber bundle, and it is desirable that the fiber bundle for artificial hair has high-level of flame retardance. For this reason, it is desirable that the thermoplastic resin fiber itself has also flame retardance, and the LOI value is used as its indicator.

[0070]

The thermoplastic resin fiber used in the present invention has an LOI value of preferably 25 or more, more preferably 27 or more. When the LOI value is less than 25, the fiber bundle cannot have sufficient flame retardance, and thus has a possibility of ignition and the spread of the fire. An LOI value of 25 or more may be obtained by a method in which a flame retardant resin such as a modacrylic resin or a polyphenylene sulfide-based resin is used, and a method in which various flame retardants are added to the resin. The flame retardants, which can be used for the thermoplastic resin fiber in the present invention, are not particularly limited as far as they do not impair the gloss and the hue, and specifically, for example, phosphorus-based flame retardants, bromine-containing polymers, and chlorine-containing polymers can be used. If necessary, a flame retardant promoter such as an antimony compound may be suitably used.

[0071]

In the thermoplastic resin fiber used in the present invention, multiple different kinds of fibers may be mixed, as long as they have the Young's modulus, the shrinkage percentage, and the LOI value which satisfy the conditions described above. For example, for the purpose of improvement of the appearance or the functionality such as the texture or the voluminousness of the fiber bundle for artificial hair, a fiber having a small specific gravity or a fiber whose surface is uneven, such as an acrylic synthetic fiber described in WO 2005/082184, may be used.

[0072]

In the present invention, when the fiber bundles obtained by mixing

the polyvinyl chloride-based resin fiber with the thermoplastic resin fiber are processed into a commodity for hair, the curl shape can be imparted at 95 to 130°C by supporting the amino-modified silicone compound on the surface of the fiber bundle.

[0073]

The amino-modified silicone compound used in the present invention has a role to exhibit the smooth moisturizing feel similar to that of human hair. When a conventional oil solution including no silicone compound is used for the polyvinyl chloride-based resin fiber, the resulting one has the problem in which fusion between the fibers occurs if heated at 95°C or higher, thus resulting in hard texture of the product for hair. The amino-modified silicone compound has a role to suppress the fusion.

[0074]

The amino-modified silicone compound used in the present invention is an oily compound in which imino group or amino group are at side chains of a linear polydimethyl siloxane, which is liquid at 23°C. The compound bonds to the fiber in the state of a monomolecular film more effectively than dimethyl silicone compounds usually used due to the adsorption of the amino groups to the fiber surface, and it reduces a surface energy of the fiber to reduce a frictional resistance, thus resulting in the acquisition of the good moisture texture with the smooth moisturizing feel, which is preferred in human hair. When the number of amino groups in the silicone compound is too many, however, the surface tension of the oil is increased to decrease the effect of reducing the frictional resistance, and the compound runs down from the surface of the fiber by sweat or rain due to the increased

hydrophilicity; as a result, the use durability is deteriorated. It is necessary, accordingly, to select the optimum number of the amino groups. An appropriate amine equivalent of the amino-modified silicone compound in the present invention is from 1000 to 20000 g/mol, preferably from 1250 to 10000 g/mol, more preferably from 1500 to 5000 g/mol. When the amine equivalent is less than 1000 g/mol, the texture and the use durability are deteriorated because of too many amino groups; whereas when the amine equivalent is more than 20000 g/mol, the adsorption amount to the fiber is reduced, and thus the texture is also deteriorated. Any of a methyl group, a hydroxyl group, and an amino group is attached to the molecular ends of the amino-modified silicone compound without problems, and an amino-modified silsesquioxane may be added within a range in which the mixture can keep a liquid state.

[0075]

In the present invention, the curl shape can be imparted at 95 to 130°C by the combination of the polyvinyl chloride-based resin fiber with the thermoplastic resin fiber, and the adsorption of the amino-modified silicone compound into the surface of the fiber can be optimized by heating it at such a high temperature. This can further improve the smoothness and the resistance of omission from the fiber surface, compared to a conventional case in which heating is performed at 90°C, thus resulting in the improved texture and use durability. The amino-modified silicone having a low molecular weight, however, penetrates inside the fiber, and thus the original improvement effect is reduced. It is necessary, accordingly, to select an optimum molecular weight. In general, the molecular weight of the silicone

oil among the silicone compounds is often defined in a kinematic viscosity. The amino-modified silicone compound in the present invention has a kinematic viscosity of preferably 500 to 20000 mm²/s, more preferably 1000 to 10000 mm²/s at 25°C. When the kinematic viscosity is less than 500 mm²/s, the penetration amount into the inside of the fiber is too much, and thus the effect of improving the texture becomes insufficient; whereas when it is more than 10000 mm²/s, it is difficult to perform the uniform adhesion on the surface of the fiber, and thus the effect of improving the texture is deteriorated.

[0076]

A method for supporting the amino-modified silicone compound used in the present invention on the fiber is not particularly limited, and there is, for example, a method in which an emulsion thereof using water as a vehicle is prepared, the fiber is immersed in the emulsion, and the amount thereof remaining on the fiber is controlled by centrifugal dehydration to support it on the surface of the fiber, or the like. When the emulsion is prepared using water as the vehicle, a solid concentration is controlled to 5 to 25% by using a surfactant, and the like, and the resulting emulsion is used after neutralization with acetic acid, or the like, as needed. At this time, an anti-static agent or a smoothing agent may be used together. A preferable component used together may include nonionic surfactants having a smoothing effect or an antistatic effect and functioning also as a surfactant in the emulsification.

[0077]

Before the fiber is immersed in the emulsion of the amino-modified

silicone compound, the fiber may be washed with a surfactant, in order to remove the extra fiber-treating agent adhering to the surfaces of the polyvinyl chloride-based resin fiber and the thermoplastic resin fiber therefrom.

[0078]

The amount of the amino-modified silicone compound used in the present invention supported on the fiber is enough from 0.05 to 0.8 omf%, preferably from 0.1 to 0.6 omf%, and more preferably from 0.2 to 0.4 omf%. When the support amount on the fiber is less than 0.05 omf%, the effect of improving the texture is small; whereas when it is more than 0.8 omf%, the fibers converge excessively to deteriorate the voluminousness, thus resulting in the deteriorated quality as a commodity.

[0079]

The fiber bundle for artificial hair of the present invention is characterized by imparting the curl shape at 95 to 130°C; by the relationship in which the shrinkage percentage of the polyvinyl chloride-based resin fiber is not lower than the shrinkage percentage of the thermoplastic resin fiber at that temperature; and by a difference in the shrinkage percentage between the polyvinyl chloride-based resin fiber and the thermoplastic resin fiber of 6% or less.

[0080]

A method of imparting the cure shape is not particularly limited and, for example, a method in which fiber bundles are wound spirally or concentrically around a cylindrical pipe, the resulting pipe is heated at a pre-determined temperature for a pre-determined time while that shape is

maintained, whereby the fiber bundles memorize the wound shape, and then the fiber bundles are removed from the pipe after cooling it can be employed. A bore diameter of the pipe used in this step can be arbitrarily selected depending on the style of the commodity. According to the present invention, the thermoplastic resin fiber bonds to the polyvinyl chloride-based resin fiber to form multiple fulcrums, and it supports the polyvinyl chloride-based resin fiber at the fulcrums to exhibit the effect of suppressing the shrinkage. For this reason, it is necessary to pressure-join the fiber bundle to the pipe so that the fibers bond to each other, and as such a method, a method in which the fiber bundle is wound around the pipe while the tension is kept in a state in which one end of the fiber bundle is fixed on the pipe, or a method in which the fiber bundle is wound around the pipe using a paper mat can be used. It can be applied to a straight style, in addition to the circular curl shape, and in such a case, it is necessary to use a method in which both ends are tied or the whole is placed between plates, in order to bond the fibers to each other.

[0081]

When the temperature at which the curl shape is imparted is set at a high temperature, the effect of improving the styling property and the effect of improving the texture of the amino-modified silicone are increased, but when the temperature is too high, the polyvinyl chloride-based resin fiber is molten by heat, thus resulting in the hard texture. For this reason, it is necessary to set the temperature within a range of 95 to 130°C, considering the balance between both, and the temperature is preferably from 100°C to 120°C, more preferably from 105°C to 115°C. When the temperature at

which the curl shape is imparted is lower than 95°C, the effect of improving the texture is not sufficient, and the styling property may be sometimes further deteriorated, compared to a case of using the polyvinyl chloride-based resin fiber alone, because the temperature is lower than the lowest temperature at which the thermoplastic resin fiber is processed. When the temperature at which the curl shape is imparted is higher than 130°C, it is difficult to suppress the fusion between the fibers only by the fiber-treating agent, because the temperature is remarkably higher than the softening temperature of the polyvinyl chloride-based resin fiber, and thus the texture becomes hard, resulting in the deteriorated quality as a commodity.

[0082]

When the difference in the shrinkage between the polyvinyl chloride-based resin fiber and the thermoplastic resin fiber is large even in the temperature range described above, the deflection is caused in the thermoplastic resin fiber to reduce the adhesion power between the fibers, thereby causing the fiber bending on the polyvinyl chloride-based resin fiber, thus resulting in the deteriorated texture. For that reason, it is necessary that the difference in the shrinkage percentage between the polyvinyl chloride-based resin fiber and the thermoplastic resin fiber is 6% or less at the temperature at which the curls are imparted, the difference is preferably 4% or less, more preferably 3% or less. When the difference in the shrinkage between the polyvinyl chloride-based resin fiber and the thermoplastic resin fiber is more than 6%, the deflection is caused in the thermoplastic resin fiber to reduce the adhesion power between the fibers,

thereby causing the fiber bending on the polyvinyl chloride-based resin fiber, thus resulting in the deteriorated texture. The thermoplastic resin fiber may be formed from multiple fibers having multiple compositions, but it is necessary that the fiber having any composition satisfies the relationship in the shrinkage percentage described above.

Examples

[0083]

Specific embodiments of the present invention will be explained in more detail showing Examples, but the present invention is not limited to these Examples.

[0084]

(Experimental Example 1) Shrinkage Percentage

A fiber bundle having a total fineness of 18000 ± 3000 dtex was formed by selecting monofilaments of one material from fiber bundles before or after mixing fibers and combining them. The resulting fiber bundle was cut into a length of 40 cm, marks were put at positions of 5 cm from both ends, heating was performed in a drying condition at a pre-determined temperature for 30 minutes while the one end was fixed, and cooling was performed at room temperature. After cooling, a length between the marks on the fiber bundle was measured, and a shrinkage percentage was obtained as a percentage thereof based on the original length of 30 cm. The measurement was repeated total of 20 times, and an average value thereof was defined as a shrinkage percentage of a sample. The length between the marks can be shortened depending on the length which can be sampled,

because a sample may sometimes have a length of shorter than 40 cm in an actual product for hair.

[0085]

(Experimental Example 2) Support Amount of Oil Solution

A fiber was taken out from a fiber bundle and a weight of the fiber was measured, it was then immersed in a mixed solvent of ethanol/cyclohexane = 50%/50% for 20 minutes and taken out from the mixed solvent. The mixed solvent was then vaporized by being heated at 120°C, and a weight of the residue of compounds, which were not vaporized, was measured. A support amount on the fiber was obtained from the measured value using the following equation: $\text{Weight of residue of compounds} / (\text{Weight of fiber} - \text{weight of residue of compounds}) \times 100 = \text{Support amount of compounds on fiber surface (omf\%)}$

[0086]

(Experimental Example 3) Young's Modulus

Using a Tensilon Universal Tester (RTC-1210A), manufactured by A & D Company, Limited, a Young's modulus value was obtained from a stress-strain curve at a tension speed of 20 cm/minute, and an average value thereof in N=20 was defined as a Young's modulus of a sample.

[0087]

(Experimental Example 4) Shrinkage Stress

Using an SSC 5200 H thermal analyzer TMA/SSI50C, manufactured by SEICO Electronics Industrial Co., Ltd, a heat shrinkage stress of a fiber was measured. Ten monofilaments having a length of 10 mm were taken, a load of 336.2 mN was applied to the filaments, and a shrinkage stress was

measured at a rate of temperature rise of 5 °C/minute at a range of 30 to 240°C. A shrinkage stress value at 130°C was divided by the number of the monofilaments of the sample, 10, to obtain a shrinkage stress per monofilament, and the obtained value was divided by a fineness of the monofilament to obtain a shrinkage stress ($\mu\text{N/dtex}$) per unit fineness.

[0088]

(Experimental Example 5) Limiting Oxygen Index (LOI)

After 16 cm/0.25 g filaments were weighed, both ends thereof were lightly collected with a double-sided tape, and it was put between twisting frames and twisted. After the filaments were fully twisted, the sample was folded in half at the center, and two bundles were twisted together. One end was fastened with a cellophane tape to make the full length 7 cm. It was dried at 105°C for 60 minutes, and in a desiccator for further 30 minutes or more. The dried sample was controlled so that it has a pre-determined oxygen concentration, it was ignited from the upper part using an igniter, which had been narrowed down to 8 to 12 mm, after 40 seconds, and after the ignition, the igniter was separated. An oxygen concentration was examined at the time when the sample burned 5 cm or more, or for 3 minutes or more. The test was repeated three times in the same conditions, whereby a limiting oxygen index was obtained.

[0089]

(Experimental Example 6) Quality as Commodity: Smoothness

A monofilament was pulled out and left at rest on a horizontal plate under no-load, and its shape was captured as a digital image. The number of fiber bendings having an angle of less than 170° was counted in 8 fibers

having a length of 20 cm per sample, and the number of fiber bendings per m was obtained. Also, as for a sample having multiple materials, the number of fiber bendings of each material was counted, and the number obtained was multiplied by a component percentage to obtain the number of fiber bendings as a fiber bundle. In addition to the number of fiber bendings, the fiber smoothness was evaluated according to the following five-grade evaluation based on evaluations by general technicians who engaged in evaluations of beauty product such as a wig, and the sample with 3 points or more was evaluated as acceptable.

5 point: 10 fiber bendings/m or less: Very good texture with no rough feel at all.

4 point: 10 fiber bendings/m or more and less than 20 fiber bendings/m: Good texture with no rough feel.

3 point: 20 fiber bendings/m or more and less than 50 fiber bendings/m: Texture having a level at which the sample is applicable as a commodity, though it has a slightly rough feel.

2 point: 50 fiber bendings/m or more and less than 100 fiber bendings/m: Texture having a level at which the sample is not applicable as a commodity because it has a rough feel.

1 point: 100 fiber bendings/m or more: Texture having a level at which the sample has a highly rough feel and it is not applicable as a commodity.

[0090]

(Experimental Example 7) Quality as Commodity: Softness

As for a fiber bundle for artificial hair, a five-grade appearance evaluation was performed based on repeatability of the soft texture similar

to that of human hair by general technicians who engaged in evaluations of beauty product such as a wig, and the sample with 3 points or more was evaluated as acceptable.

5 point: soft and good texture almost the same as human hair.

4 point: soft texture similar to that of human hair.

3 point: texture relatively similar to that of human hair, though the sample has a little hard feel.

2 point: texture of hard feel peculiar to a synthetic fiber.

1 point: texture which is apparently different from human hair with the sample having fusion between fibers in part.

[0091]

(Experimental Example 8) Quality as Commodity: Moisture

Feel/Moisturizing Feel

As for a fiber bundle for artificial hair, a five-grade appearance evaluation was performed based on whether or not the sample had the moisture feel or moisturizing feel similar to that of human hair by general technicians who engaged in evaluations of beauty product such as a wig, and the sample with 3 points or more was evaluated as acceptable.

5 point: Good texture having a level at which both moisture feel and moisturizing feel are similar to those of human hair.

4 point: Texture having a level at which both moisture feel and moisturizing feel are similar to those of human hair, though they are slightly insufficient.

3 point: Texture having a level at which either moisture feel or moisturizing feel is insufficient to some extent, but which is comparatively similar to that of human hair.

2 point: Texture having moisture feel and moisturizing feel which are apparently inferior to human hair.

1 point: Texture in which neither moisture feel nor moisturizing feel cannot be perceived.

[0092]

(Experimental Example 9) Quality as Commodity: Feel of Elasticity/Curl Shape Stability

A fiber bundle for artificial hair, to which a curl shape had been imparted, was hung for 60 hours, and a five-grade stability evaluation was performed based on whether or not the feel of elasticity and the curl shape could be maintained even after long time use by general technicians who engaged in evaluations of beauty product such as a wig, and the sample with 3 points or more was evaluated as acceptable.

5 point: Good state in which curls bound with pulsing feel and without uncomfortable feeling and the curl shape is hardly disheveled when the sample is moved.

4 point: State in which curls bound without uncomfortable feeling and the curl shape is not largely disheveled when the sample is moved.

3 point: State in which curls weakly bound and the curl shape is slightly disheveled when the sample is moved.

2 point: A state in which curls hang down and the curl shape is largely disheveled when the sample is moved.

1 point: State in which curls are elongated and largely disheveled after the sample is retained for 60 hours and before moved.

[0093]

(Experimental Example 10) Quality as Commodity: Voluminousness

As for the fiber bundle for artificial hair, a five-grade voluminousness evaluation was performed based on the appearance of the fiber bundle sample and the resiliency thereof when it was grasped tightly by general technicians who engaged in evaluations of beauty product such as a wig, and the sample with 3 points or more was evaluated as acceptable.

5 point: The sample has excellent bulkiness as well as excellent appearance and resiliency when it has the same weight with reference to a sample with 3 point.

4 point: The sample has slightly high bulkiness when it has the same weight with reference to a sample with 3 point.

3 point: Standard level

2 point: The sample has relatively inferior bulkiness with reference to a sample with 3 point.

1 point: The sample has apparently inferior bulkiness with reference to a sample with 3 point.

[0094]

(Experimental Example 11) Quality as Commodity: Overall Evaluation

The points of the five items, the smoothness, the softness, the moisture feel/moisturizing feel, the feel of elasticity/curl shape stability and the voluminousness, are added up. The sample with the total points of 21 or more is excellent; the sample with the total points of from 20 to 17 is good; the sample with the total points of from 16 to 14 is ordinary; and the sample with the total points of 13 or less is inferior, and when the sample is excellent or good, it was evaluated as acceptable.

[0095]

(Preparation Example 1) PVC-1

To 100 parts by weight of a polyvinyl chloride resin S 1001 (manufactured by Kaneka Corporation) were added 10 parts by weight of a chlorinated polyvinyl chloride resin H 438 (manufactured by Kaneka Corporation), 1 part by weight of a stabilizer, ALCAMIZER 1, which is a hydrotalcite heat stabilizer manufactured by Kyowa Chemical Industrial Co., Ltd., 0.5 part by weight of an ester-based lubricant, EW-100, manufactured by RIKEN VITAMIN Co., Ltd., 0.5 part by weight of a polyethylene wax-based lubricant, HW 400 P manufactured by Mitsui Chemicals, Inc., 0.4 part by weight of a β -diketone, 0.4 part by weight of a calcium soap-zinc soap, and 2 parts by weight of an epoxidized soybean oil, and the mixture was mixed and stirred in a Henschel mixer to produce a compound. In addition, a black pigment was added for controlling color. A nozzle with 120 holes each having a cross-sectional area of 0.1 mm² was attached to a 40 mm ϕ extruder. The holes were cocoon-shaped. The compound was extruded and melt-spun at a cylinder temperature of 140 to 190°C and a nozzle temperature of 180 $\pm$ 15°C under conditions providing good spinning property. The extruded filaments were subjected to heat-treatment for about 0.5 to 1.5 seconds in a heating spinning tube (at 200 to 400°C atmosphere and conditions providing good spinning property), which was provided directly under the nozzle, and they were subjected to spinning through first taking-up rolls. Just before the first taking-up rolls, an oil solution including a nonionic surfactant (a polyethylene oxide/polypropylene oxide copolymer with a molecular weight of about 800) and a cationic

surfactant (an ammonium sulfite-based compound with a molecular weight of about 800), and an ester oil (oleyl oleate with a molecular weight of about 500) was added to the fiber in an amount of 0.5 omf%. Next, between the first rolls and second stretching rolls, the yarns were passed through a hot-air circulation chamber having a temperature of 110°C, whereby the yarns were stretched about 3 times. Further, the yarns were stretched between two pairs of conical rolls provided in a chamber in which the temperature is controlled at 110°C, whereby about 35% of the mild heat treatment was performed for 2 minutes, and the multifilaments were taken up so that the monofilament therein had a fineness of about 77 to 81 dtex to produce a polyvinyl chloride-based resin fiber PVC-1.

[0096]

(Preparation Example 2) PVC-2

A polyvinyl chloride-based fiber PVC-2 was produced in the same manner as in Preparation Example 1 except that the components of the oil solution were changed to a polyethylene oxide/polypropylene oxide copolymer having a molecular weight of 10000, the addition amount of the oil solution was changed to 0.2 omf%, the temperature of the mild heat treatment was changed to 130°C, and the relaxation speed was controlled so that it took 4 minutes to perform a 35% relaxation.

[0097]

(Preparation Example 3) PVC-3

A polyvinyl chloride-based fiber PVC-3 was produced in the same manner as in Preparation Example 2 except that the relaxation speed was controlled so that it took 6 minutes to perform a 37% relaxation.

[0098]

(Preparation Example 4) PVC-4

A polyvinyl chloride-based fiber PVC-4 was produced in the same manner as in Preparation Example 2 except that the relaxation speed was controlled so that it took 8 minutes to perform a 39% relaxation.

[0099]

(Preparation Example 5) PVC-5

A polyvinyl chloride-based fiber PVC-5 was produced in the same manner as in Preparation Example 3 except that the components of the oil solution were changed to a nonionic surfactant (polyethylene oxide/polypropylene oxide copolymer with a molecular weight of 800), a cationic surfactant (ammonium sulfate-based compound with a molecular weight of about 800), and an ester oil (oleyl oleate with a molecular weight of about 500), and the addition amount of the oil solution was changed to 0.5 omf%.

[0100]

(Preparation Example 6) PVC-6

A polyvinyl chloride-based fiber PVC-6 was produced in the same manner as in Preparation Example 3 except that the components of the oil solution were changed to 75% by weight of a polyethylene oxide/polypropylene oxide copolymer with a molecular weight of 10000 and 25% by weight of amino-modified silicone oil with a kinematic viscosity of 1000 mm²/s, and the addition amount of the oil solution was changed to 0.2 omf%.

[0101]

(Preparation Example 7) TPR-1

An acrylic copolymer resin, which had been produced by copolymerization of 50% of acrylonitrile, 49% of vinyl chloride and 1% of styrene-sodium sulfonate, was dissolved in acetone to produce a 29% spinning stock solution. This spinning stock solution was subjected to spinning twist into a 20% aqueous acetone solution having a temperature of 20°C under conditions in which a nozzle draft was 1.6 using a dumbbell-shaped modified cross-section nozzle. From the obtained fibers were removed the solvent and they were stretched 1.5 times in a water-washing bath at 50°C, then they were dried with a dry hot air at 130°C, followed by dry heat stretching 2.5 times at 125°C and further relaxation heat treatment with dry hot air at 150°C. The thus obtained acrylic fiber had a monofilament fineness of 47 dtex, and had an almost horseshoe-shaped cross-sectional shape.

[0102]

(Preparation Example 8) TPR-2

After 100 parts by weight of polyethylene terephthalate (BK-2180 manufactured by Mitsubishi Chemical Corporation), a bromine-based flame retardant (SR-T 20000 manufactured by Sakamoto Yakuhin Kogyo Co., Ltd.) and an antimony compound (SA-A manufactured by Nihon Seiko Co., Ltd.) were dried to a moisture content of 100 ppm or less, 2 parts of polyester pellets for coloration, PESM6100 BLACK (Dainichiseika Color & Chemicals Mfg. Co., Ltd., a carbon black content: 30%) was added thereto, and the mixture was dry-blended. The resulting mixture was put in a twin-screw extruder, melt-kneaded at 280°C, and formed into pellets, which were dried

to a moisture content of 100 ppm or less. Then, the molten polymer was discharged through spinning mouthpieces in a melt spinning machine at 280°C using an eye-glass-shaped nozzle. The resulting yarns were cooled in a water bath having a water temperature of 50°C, provided at a position of 30 mm below the mouthpieces, and they are wound at a speed of 100 m/minute to obtain unstretched yarns. The obtained unstretched yarns were stretched 4 times in a warm water bath having a temperature of 80°C, and they were wound at a speed of 100 m/minute using heat rolls heated to 200°C. The heat treatment was performed to obtain a polyester fiber (multifilament) having a monofilament fineness of about 65 dtex. The physical properties of the fibers obtained in Preparation Examples 1 to 8 were shown in Table 1.

[0103]

[Table 1]

	Polyvinyl chloride-based resin fiber (A)						Thermoplastic resin fiber (B)	
Name of fiber □	PVC-1	PVC-2	PVC-3	PVC-4	PVC-5	PVC-6	TPR-1	TPR-2
Fineness (dtex)	77	77	79	81	79	79	47	65
Addition amount of oil solution (omf%)	0.5	0.2	0.2	0.2	0.5	0.2	---	---
Amount of oil solution supported on fiber surface (omf%)	0.13	0.2	0.2	0.2	0.1	0.2	---	---
100°C shrinking percentage (%)	13.0	3.7	2.5	0.3	3.0	2.4	1.7	0.0
100°C shrinking percentage (%)	27.0	7.0	5.4	2.1	6.4	5.2	3.0	0.0
130°C shrinkage stress (μN/dtex)	111.9	47.2	42.9	31.8	43.3	41.8	96.8	0.0
Young's modulus (Gpa)	3.4	3.2	3.1	3.0	3.1	3.1	4.1	5.6
LOI	35	35	35	35	35	35	28	28

[0104]

(Examples 1 to 14 and Comparative Examples 1 to 6)

The polyvinyl chloride-based fibers (PVC-1 to PVC-6) and the thermoplastic resin fibers (TPR-1 and TPR-2) produced in Preparation Examples 1 to 8 were mixed in ratio shown in Table 2, which were subjected to hackling, thereby obtaining fiber bundles for artificial hair. An amino-modified silicone oil (BY 16203 manufactured by Dow Corning Toray Co., Ltd., with a kinematic viscosity of 2000 mm²/s and a functional group equivalent of 1900 g/mol), a poly ethylene oxide/polypropylene oxide copolymer with a molecular weight of 10000, and pure water were mixed in a weight ratio of 0.5:0.5:9, and the mixture was stirred in a homogenizer to obtain an emulsion. After that, the emulsion was neutralized by added with acetic acid thereto, thereby producing a fiber-treating agent. The fiber bundles from each of Examples 1 to 5 and 7 to 13, and Comparative Examples 2, 4, and 6 were immersed in this fiber-treating agent for 5 minutes, and then an excess amount of the fiber treating agent was removed therefrom by using an centrifugal dehydrator so that an amount of the agent supported on the fiber surface is 0.4 omf%. Then, the fiber bundles were separated into two fiber bundles, each bundle having a fineness of 1200,000 dtex. The fiber bundles, on which the fiber-treating agent was not supported, were also separated into two fiber bundles, each bundle having a fineness of 1200,000 dtex. Next, one of the fiber bundles were cut into a length of 35 cm, both ends thereof were tied with a string at a place of 5 cm from the end, and the bundle was heated at a temperature shown in Table 2 for one hour. The number of fiber bendings in the shrunk fiber bundle was counted. The remaining fiber bundle was then sewn using a sawing machine for wig to produce a hair extension having a length of 25 cm. This

was wound around a pipe having a diameter of 35 mm, and heat-set was performed in a convecting dryer at a temperature described in Table 2 for one hour to impart a curl shape. The hair extensions imparted with the curl shape were sewn on a net with 10 tiers at an interval of 1 cm to produce a commodity sample, and the quality as a commodity (the smoothness, the softness, the moisture feel/moisturizing feel, the feel of elasticity/curl shape stability, and the voluminousness) thereof was evaluated. The results are shown in Table 2.

[0105]

As apparent from Table 2, it was confirmed that the fibers for artificial hair of the present invention had excellent texture and styling property, and in particular, when they were combined with a fiber having a high rigidity, applied with a silicone oil solution, or imparted with curls at a high temperature, they had qualities which were considerably beyond those of conventional products.

[0106]

Reference Signs List

[0107]

- 1 Conventional PVC fiber PVC-1
- 2 PVC fiber of the present invention PVC-2
- 3 PVC fiber of the present invention PVC-3
- 4 PVC fiber of the present invention PVC-4

CLAIMS:

1. A polyvinyl chloride-based resin fiber which has a shrinkage stress of 70 $\mu\text{N/dtex}$ or less at 130°C.
2. The polyvinyl chloride-based resin fiber according to claim 1, wherein the shrinkage stress is 50 $\mu\text{N/dtex}$ or less at 130°C.
3. The polyvinyl chloride-based resin fiber according to claim 2, wherein the shrinkage stress is 40 $\mu\text{N/dtex}$ or less at 130°C.
4. The polyvinyl chloride-based resin fiber according to any one of claims 1 to 3, wherein the polyvinyl chloride-based resin fiber is a resin fiber including at least one resin selected from the group consisting of a homopolymer resin of vinyl chloride, a copolymer resin of vinyl chloride and a vinyl ester, a copolymer resin of vinyl chloride and an acrylic ester, a copolymer resin of vinyl chloride and an olefin, and a copolymer resin of a vinyl chloride-acrylonitrile.
5. The polyvinyl chloride-based resin fiber according to any one of claims 1 to 4, wherein the polyvinyl chloride-based resin fiber is a polyvinyl chloride-based resin fiber for artificial hair.
6. A fiber bundle for artificial hair comprising 20 to 100% by weight of the polyvinyl chloride-based resin fiber according to any one of claims 1 to 5, and

0 to 80% by weight of a thermoplastic resin fiber having a composition including no polyvinyl chloride-based resin.

7. The fiber bundle for artificial hair according to claim 6, wherein the thermoplastic resin fiber has a Young's modulus of 4 to 9 GPa.

8. The fiber bundle for artificial hair according to claim 6 or 7, wherein the thermoplastic resin fiber has a shrinkage percentage of 10% or less at 130°C.

9. The fiber bundle for artificial hair according to any one of claims 6 to 8, wherein the polyvinyl chloride-based resin fiber has a shrinkage percentage at 130°C, which is not lower than the shrinkage percentage at 130°C of the thermoplastic resin fiber.

10. The fiber bundle for artificial hair according to claim 9, wherein a difference between the shrinkage percentage at 130°C of the polyvinyl chloride-based resin fiber and the shrinkage percentage at 130°C of the thermoplastic resin fiber is 6% or less.

11. The fiber bundle for artificial hair according to any one of claims 6 to 10, wherein the thermoplastic resin fiber is a resin fiber including at least one resin selected from the group consisting of an acrylonitrile-based resin, a modacrylic resin, a polyolefin-based resin, a polyester-based resin, a polyamide-based resin, a polyimide-based resin, a polyether-imide-based resin, a polyamide-imide-based resin, a polyoxymethylene-based resin, a

polyether-ketone-based resin, a polycarbonate-based resin, a polysulfone-based resin, a polyether-sulfone-based resin, a polyphenylene-ether-based resin, a polyphenylene-sulfide-based fiber, and a Teflon[®] resin.

12. The fiber bundle for artificial hair according to any one of claims 6 to 11, wherein the polyvinyl chloride-based resin fiber and the thermoplastic resin fiber includes an amino-modified silicone compound.

13. The fiber bundle for artificial hair according to any one of claims 6 to 12, wherein the polyvinyl chloride-based resin fiber includes a polyalkylene oxide-based compound having a weight average molecular weight of 2000 to 25000 in a content of 0.07 to 0.5 omf%.

14. The fiber bundle for artificial hair according to any one of claims 6 to 13, wherein the polyvinyl chloride-based resin fiber includes a silicone-based compound in a content of 0 to 0.5 omf%.

15. An artificial hair product obtained by processing the fiber bundle for artificial hair according to any one of claims 6 to 14.

16. The artificial hair product according to claim 15, wherein the process is performed at a temperature of 95 to 130°C.