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(54) Composite foam molded article, process for production thereof, and foamable powder composition

Verbundschuamstoffgegenstand, Verfahren zu seiner Herstellung und schäumbare Pulverzusammensetzung

Objet composite moulé en mousse, procédé pour sa fabrication et composition moussable à base de poudre

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Description

The present invention relates to an integrally formed composite foam molded article comprising a nonfoam layer formed from a thermoplastic elastomer powder composition and a foamed layer formed from a foammable powder composition, a process for production thereof, and a foammable powder composition.

In recent years, there has been a demand for covering materials for, for example, the interior of automobiles, which are light in weight and have an excellent soft and high quality feeling and to which have been given complicated patterns such as a leather grain pattern or stitch pattern.

As a method for producing a cushiony covering material, there is known a method of forming a covering material from a vinyl chloride based resin composition by a powder molding method, then filling and causing to foam a urethane material in the same way as in conventional vacuum molded articles so as to produce a covering material with a layer of urethane bonded to it.

Further, there has been proposed a method for simultaneously integrally forming a nonfoam layer comprised of a vinyl chloride based resin and a foamed layer comprised of a vinyl chloride based resin by a powder molding method.

In these methods, however, while it is possible to impart complicated patterns and the resultant covering material is soft in touch, there are disadvantages inherent to polyvinyl chloride, that is, an insufficiently light weight and the production of acidic substances upon incineration during disposal of cars. This causes, for example, atmospheric pollution and acid rain, making the resin inferior in "cleanness". A sufficiently satisfactory covering material has not been obtained.

The present invention seeks to eliminate the above-mentioned disadvantages of the prior art and to provide a composite foam molded article which is superior in cleanliness, light in weight, soft in touch and which can be given complicated patterns.

The present invention provides a molded composite article comprising (I) a nonfoam layer and (II) a foamed layer, said article being obtainable by conducting powder molding of (A) a thermoplastic elastomer powder composition to form the nonfoam layer (I) and subsequently conducting powder molding of a foammable composition comprising (B) 100 parts by weight of a thermoplastic synthetic resin powder, (C) 2 to 11 parts by weight of a heat decomposable foaming agent, and optionally (D) 0.1 to 8 parts by weight of a liquid coating agent to form the foamed layer (II) on the nonfoam layer (I); (A) said thermoplastic elastomer powder composition comprising an ethylene-α-olefin copolymer rubber and a polyolefin resin, which composition may be partially cross-linked and has a complex dynamic viscosity $\eta^*(1)$ at 250°C and a frequency of 1 radian/sec of not more than $1.5 \times 10^4$ Pas ($1.5 \times 10^5$ poise) and having a Newtonian viscosity index $n$, calculated by the following formula using the above-mentioned complex dynamic viscosity $\eta^*(1)$ and the complex dynamic viscosity $\eta^*(100)$ at a frequency of 100 radian/sec, of not more than 0.67:

$$n = \frac{\log \eta^*(1) - \log \eta^*(100)}{2}$$

The present invention also provides a process for producing a composite molded article as defined above which comprises conducting powder molding of the thermoplastic powder (A) to form the nonfoam layer (I) and subsequently conducting powder molding of the foammable composition to form the foamed layer (II) on the nonfoam layer (I).

The present invention additionally provides a foammable powder composition comprising 2 to 11 parts by weight of a heat decomposing foaming agent (C), optionally 0.1 to 8 parts by weight of a liquid coating agent (D) and 100 parts by weight of a thermoplastic elastomer powder (B); wherein (B), (C) and (D) are as defined above.

The present invention will be better understood from the description set forth below with reference to the accompanying drawings, wherein:

Fig. 1 is a plane view of a powder feed box;
Fig. 2 is an elevation view of the powder feed box;
Fig. 3 is a side view of the powder feed box;
Fig. 4 is a plane view of a mold;
Fig. 5 is an elevation view of the mold;
Fig. 6 is a side view of the mold; and
Fig. 7 is a schematic sectional view of the process for manufacturing a sintered sheet.

In view of the above-mentioned situation prior to the date of this invention, the present inventors engaged in earnest studies on a method of powder molding to produce a cushiony covering material which is superior in cleanliness, light in weight, soft in touch, and which can be given complicated patterns and found that by using a specific thermoplastic elastomer powder as a nonfoam layer starting material, the above-mentioned object can be achieved.

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The present invention will be further explained in detail below.

The present invention is characterized by the use, as the nonfoam layer starting material, of a thermoplastic elastomer powder composition comprising an ethylene-α-olefin copolymer rubber and a polyolefin resin or a partially cross-linked thermoplastic elastomer powder composition obtained by dynamically cross-linking a mixture of an ethylene-α-olefin copolymer rubber and a polyolefin resin in the presence of a cross-linking agent. Examples of the ethylene-α-olefin copolymer rubber are ethylene-propylene copolymer rubber, ethylene-propylene-nonconjugated diene copolymer rubber, and other rubber having olefins as main constituents. Examples of the nonconjugated diene are dicyclopentadiene, ethylidenenorbornene, 1,4-hexadiene, cyclooctadiene, methylenenorbornene. Among these, ethylene-propylene-ethylidenenorbornene rubber (hereinafter referred to as EPDM) is preferred. When EPDM is used, an elastomer powder superior in, for example, heat resistance and tensile properties may be obtained.

The Mooney viscosity of the ethylene-α-olefin copolymer rubber, i.e., the Mooney viscosity measured at 100°C according to ASTM D-927-57T (ML_1+4 100°C), is preferably from 130 to 350, more preferably 200 to 300.

It is also preferable to use an oil-extended olefin copolymer rubber comprising of ethylene-α-olefin copolymer rubber and a mineral oil based softening agent, such as a paraffinic process oil. In this case, not only does the melt flowability rise, but also the softness of the molded article is improved. The content of the mineral oil softening agent is preferably 30 to 120 parts per 100 parts by weight of ethylene-α-olefin copolymer rubber.

The polyolefin resin usable in the present invention is preferably polypropylene, a copolymer of propylene and ethylene, or a copolymer of propylene and an α-olefin other than propylene. In particular, when a copolymer resin of propylene and butene is used, it is possible to reduce the hardness of the molded article.

When the melt flow rate (MFR, measured according to JIS K-2210 at 230°C under a load of 2.16 kg) of the polyolefin resin is less than 20 g/10 min, it becomes difficult for the particles of powder to melt-adhere to each other during the powder molding and the strength of the molded article is decreased, so usually a resin having a MFR of 20 g/10 min or more is used. Preferably, the MFR is 50 g/10 min or more.

The thermoplastic elastomer composition usable in the present invention comprises an ethylene-α-olefin copolymer rubber and a polyolefin resin. The composition may be partially cross-linked by dynamic cross-linking the composition. The ratio of the ethylene-α-olefin copolymer rubber to the olefin resin is preferably 5 : 95 to 80 : 20 by weight.

In producing the partially cross-linked composition, an organic peroxide is usually used as a cross-linking agent. Examples of the organic peroxides usable in the present invention are dialkyl peroxides. Further, it is preferable to perform the dynamic cross-linking using a very small amount of an organic peroxide in the presence of a cross-linking agent such as a bismaleimide compound. In this case, the ethylene-α-olefin copolymer rubber is suitably cross-linked to have heat resistance and, simultaneously, a high flowability. The cross-linking agent is preferably used in an amount of not more than 1.5 parts by weight, more preferably not more than 0.6 part by weight, per 100 parts by weight of the composition of the ethylene-α-olefin copolymer rubber and the polyolefin resin. The organic peroxide is preferably used in an amount of not more than 0.2 parts by weight, more preferably not more than 0.1 parts by weight, and most preferably not more than 0.07 parts by weight.

A single-screw kneading extruder, a twin-screw kneading extruder or other continuous kneading extruders are suitably used as the apparatus used for the dynamic cross-linking. When a twin-screw kneading extruder is used, if the extrusion cross-linking is performed at a shear rate of less than 10³ sec⁻¹, the dispersed particle size of the ethylene-α-olefin copolymer rubber becomes large and it becomes difficult to realize the viscosity conditions of the present invention, so it is preferable to perform continuous extrusion cross-linking at a shear rate of 10³ sec⁻¹ or more.

The thermoplastic elastomer in the present invention has a complex dynamic viscosity \( \eta''(1) \) measured at 250°C and a frequency of 1 radian/sec of not more than 1.5 × 10⁴ Pas (1.5 × 10⁵ poise), preferably not more than 1.0 × 10⁴ Pas (1.0 × 10⁵ poise).

When the complex dynamic viscosity is more than 1.5 × 10⁴ Pas (1.5 × 10⁵ poise), the elastomer powder no longer flows in a molten state on the surface of the mold and molding becomes impossible by a powder molding method with an extremely low shear rate during processing, e.g., 1 sec⁻¹ or less.

Further, the Newtonian viscosity index \( n \) calculated by the following formula using the complex dynamic viscosity \( \eta''(1) \) measured at 250°C and a frequency of 1 radian/sec and a complex dynamic viscosity \( \eta''(100) \) measured at a frequency of 100 radians/sec is not more than 0.67, preferably not more than 0.60:

\[
\eta''(1) = (\log \eta''(1) - \log \eta''(100)) / 2
\]

When the Newtonian viscosity index \( n \) is more than 0.67, even assuming the complex dynamic viscosity \( \eta''(1) \) measured at a frequency of 1 radian/sec is not more than 1.5 × 10⁴ Pas (1.5 × 10⁵ poise), the frequency dependence of the complex dynamic viscosity becomes larger and, with molding methods with an extremely low shaping pressure during molding of less than 1 kg/cm² such as in powder molding, the heat-fusion of molten elastomer powder particles becomes incomplete and only a molded article with poor mechanical properties can be obtained.

The thermoplastic elastomer composition usable in the present invention may be used by blending therewith not
more than 50 parts by weight of a non-cross-linked ethylene-\(\alpha\)-olefin copolymer rubber or ethylene-\(\alpha\)-olefin copolymer resin, based upon 100 parts by weight of the elastomer, so as to further improve the flexibility of the molded article. The \(\alpha\)-olefins for example the propylene and butene, may be used alone or together. In particular, an ethylene-propylene copolymer rubber having an ethylene content of 40 to 90 percent by weight, preferably 70 to 85 percent by weight, and having an ML\(_{1+4}\) at 100°C of 50 or less is preferable.

The thermoplastic elastomer powder used in the present invention is usually manufactured by pulverizing the above-mentioned thermoplastic elastomer composition at a low temperature of not more than the glass transition temperature. For example, a freeze pulverization method using liquid nitrogen is suitably used. The powder may be obtained by mechanically pulverizing elastomer composition pellets, which are cooled to -70°C or lower, preferably -90°C or lower, using a ball mill or other impact type pulverizer. When pulverized at a temperature of higher than -70°C, the particles of the pulverized elastomer powder become rougher and the powder moldability becomes lower, and therefore this is not desirable. To prevent the polymer temperature from increasing to or above the glass transition temperature during the pulverization operation, a method which generates little heat and has a high pulverization efficiency is preferable. Further, it is preferable that the pulverization apparatus itself be cooled by outside cooling.

The resultant elastomer powder is preferably pulverized to a degree such that 95% or more of the total weight can pass through a 32 mesh sieve of a Tyler standard sieve. When the 32 mesh sieve blocking rate exceeds 5%, this can become one factor causing unevenness of thickness during the pulverizing and molding. Uneven thickness causes unevenness in the flexibility of the molded article and for example leads to a susceptibility to crease upon bending. This detracts from the commercial value of the molded article.

When performing powder molding using the thermoplastic elastomer powder composition used in the present invention, sometimes the adhesion to the inside surface of the mold is strong when detaching the molded article from the mold. When the molded article is removed by force from the mold, creases or whitening may occur. To prevent this, it is possible to coat the inside surface of the mold before the molding by spraying on a conventional mold release agent, for example dimethyl polysiloxane.

For continuous production of a large number of articles, however, the mold release agent must be coated each time several articles are molded, which leads to a rise in the molding costs. In such a case, it is possible to improve the mold material, but it is also possible to preinsert a methyl polysiloxane compound as an internally added mold release agent in the powder composition.

In this case, the use of a methyl polysiloxane compound having a viscosity at 25°C of not less than 20 \(\times\) 10\(^{-6}\) m\(^2\)/s (20 centistokes) is suitable. The preferred range of the viscosity is 50 \(\times\) 10\(^{-6}\) to 5000 \(\times\) 10\(^{-6}\) m\(^2\)/s (50 to 5000 centistokes). When the viscosity becomes too large, the effect as a mold release agent is reduced.

The content of the mold release agent should be not more than 2 parts by weight per 100 parts by weight of the powder composition. When the content is more than 2 parts by weight, there is a danger that the heat fusion among elastomer powder particles will be obstructed and only a molded article with inferior mechanical properties will be obtained. Further, there is a danger of bleeding of the mold release agent at the surface of the mold and contamination of the mold.

When the internally added mold release agent is included, the agent may be added either before or after the powdering.

The powder composition usable in the present invention may, for example, contain in necessary amounts a phenol type, sulfite type, phenylalkane type, phosphite type, amine type, or amide type stabilizer or other known heat resistance stabilizer, anti-aging agent, weather resistance stabilizer, anti-static agent, metal soap, wax, or other lubricant or coloring pigment. These additives may be added either before or after the powdering.

Next, the foamed composition used in the foamed layer will be explained.

Preferred thermoplastic synthetic resin powders usable in the foamed composition are a thermoplastic elastomer, polyethylene resin or polypropylene resin powder.

The thermoplastic elastomeric may include, for example, a thermoplastic elastomer comprising of an elastomer composition of the same ethylene-\(\alpha\)-olefin copolymer rubber as used in the above-mentioned nonfoam layer and a polyolefin resin, a thermoplastic elastomer comprised of a partially cross-linked composition of an ethylene-\(\alpha\)-olefin copolymer rubber and polyolefin resin, and also styrene type, urethane type, polyester type, polyvinyl chloride type, and other thermoplastic elastomers.

The thermoplastic elastomer generally has a complex dynamic viscosity \(\eta'(1')\) measured at a temperature of 250°C and a frequency of 1 radian/sec of not more than 1.5 \(\times\) 10\(^6\) Pas (1.5 \(\times\) 10\(^5\) poise), preferably not more than 1.0 \(\times\) 10\(^6\) Pas (1.0 \(\times\) 10\(^5\) poise), and a Newtonian viscosity index, \(n\), calculated by the following formula using the complex dynamic viscosity \(\eta'(1')\) measured at 250°C and a frequency of 1 radian/sec and the complex dynamic viscosity \(\eta'(100)\) measured at a frequency of 100 radians/sec, of not more than 0.67, preferably not more than 0.60:

\[
\eta = \frac{(\log \eta'(1') - \log \eta'(100))}{2}
\]
Examples of the polyethylene resin are high density polyethylene, low density polyethylene, linear low density polyethylene, ethylene-vinyl acetate copolymer, ethylene-methacrylic acid copolymer, ethylene-acrylic ester-maleic anhydride terpolymer, ethylene-glycidyl methacrylate copolymer, ethylene-glycidyl methacrylate-methacrylate terpolymer, ethylene-glycidyl methacrylate-vinyl acetate terpolymer, ethylene-α-olefin copolymer, modified polyolefin, chlorinated polyethylene, and other thermoplastic synthetic resins mainly composed of ethylene.

Examples of the propylene resin are propylene homopolymer, propylene-ethylene random copolymer, propylene-ethylene, block copolymer, propylene-butenes random copolymer and propylene-ethylene-butenes terpolymer.

Examples of the thermoplastic synthetic resin powder are, in addition to the above, polyvinyl chloride, polyvinyl chloride-vinyl acetate copolymer, chlorinated polyvinyl chloride, polyvinyl chloride-ethylene-vinyl acetate copolymer, polyvinyl chloride-urethane copolymer, acrylonitrile-butadiene-styrene copolymer, methyl methacrylate-butadiene-styrene copolymer, styrene-butadiene-styrene block copolymer, acrylonitrile-styrene copolymer, and other vinyl based resin powders.

The powders of the polyethylene type resins, polypropylene type resins, vinyl type resins, etc., preferably have a melt flow rate (MFR, measured according to JIS K-7210 at 190°C or 230°C under a load of 2.16 kg) of not less than 3 g/10 min and have a particle size such that not less than 95 percent of the total weight passes through a 32 mesh sieve of a Tyler standard sieve. Two or more types of the thermoplastic synthetic resin powder may be used together.

The heat decomposable foaming agent (C) usable in the foamy composition is not particularly limited so long as it decomposes upon the heating and melting step in powder molding and generates a gas. A general organic or inorganic chemical foaming agent may be used. Specific examples are azodicarbonamide, 2,2'-azobisisobutyronitrile, azohexahydrobenzonitrile, diazoaminobenzene, and other azo compounds, benzene sulfonohydrazide, benzene-1,3-sulfonylhdyrazide, diphenylsulfone-3,3'-disulfonohydrazide, diphenyl-oxide-4,4'-disulfonohydrazide, 4,4'-oxbis(benzene-sulfonylhdyrazide), paratoluensulfonohydrazide, and other sulfonohydrazide compounds. N,N'-dinitrosoptamethylenetetramine, N,N'-dinitroso-N,N'-dimethylureaphthalamide, and other nitroso compounds, terephthalazide, p-tetrahydrobenzamide, and other azide compounds, sodium bicarbonate, ammonium bicarbonate, ammonium carbonate, and other inorganic compounds. These compounds may be used alone or in combination. Among them, azodicarbonamide and 4,4'-oxbis(benzene-sulfonylhdyrazide) are preferably used.

The heat decomposable foaming agent usable in the present invention preferably has a decomposition temperature of 120 to 200°C, more preferably 120 to 180°C.

The heat decomposable foaming agent is mixed in an amount of 2 to 11 parts by weight, preferably 2 to 7 parts by weight, per 100 parts by weight of thermoplastic synthetic resin powder (B) for powder molding.

It is also possible to use a foaming accelerator or foaming coagent for the purpose of lowering the decomposition temperature of the heat decomposable foaming agent. Examples of the foaming accelerator or foaming coagent are zinc oxide, zinc nitrate, lead phthalate, lead carbonate, trichlorophosphate, trisacetic lead sulfate, and other inorganic salts, zinc fatty acid soap, lead fatty acid soap, cadmium fatty acid soap, and other metal soaps, borax, oxalic acid, succinic acid, adipic acid, and other acids, urea, biurea, ethanolamine, glucose and glycerol.

On the other hand, it is also possible to use a foaming suppressing agent for the purpose of raising the decomposition temperature of the heat decomposable foaming agent. Examples of the foaming suppressing agent are organic acids such as maleic acid, fumaric acid, phthalic acid, maleic anhydride, phthalic anhydride, halogenated organic acids such as stearoyl chloride, phthaloyl chloride, polyhydric alcohols such as hydroquinone, organic nitrogen-containing compounds such as fatty acid amine, amide, oxime, isocyanate, organic sulfur-containing compounds such as mercaptan, sulfides, phosphoric acid salts such as phosphite compounds, tin compounds such as dibutyl tin maleate, tin chloride, tin sulfate and hexachlorocyclopentadiene.

According to the present invention the stability of the foam cells can be improved by using a liquid coating agent (D), in addition to the above-mentioned heat decomposable foaming agent.

The liquid coating agent is preferably capable of curing at ordinary temperature to 220°C.

Examples of the liquid coating agent are polysiloxane, melamine type, urethane type, fluorine-containing type, and other heat curable coating agents capable of protecting surfaces of, for example, plastic, unsaturated polyesters, alkyds, oil-free alkyds, linear polyester resin, and other polyester resins, melamine resins, modified melamine resins, and other amine resins, novolak type, β-methylphlicloro type, cyclic fatty acid type, noncyclic fatty acid type, epoxylated fatty acid ester type, polyhydric carbonic acid ester type, aminoglycidyl type, chlorinated type, resorcin type, and other epoxy resins, oil-modified, moisture-curing block polyurethane resins of the single component type, catalyst-curing polyol-curing polyurethane resins of the double component type, and other polyurethane resins, and acrylic resins comprising as main monomers the organic solvate type, aqueous type, solvent-less type, and other polyacrylic acid esters and methacrylic acid esters. Of these liquid coating agents, polysiloxane, noncyclic fatty acid type and cyclic fatty acid type epoxy resins, and solvent-less acrylic resins such as methacrylic acid esters are preferably used, among which cyclic fatty acid type epoxy resins and solvent-less acrylic resins such as methacrylic acid esters which cure at from ordinary temperature to 150°C are particularly preferable.

The liquid coating agent preferably has a viscosity of about 0.05 to 50 Pas (50 to 50000 cps) at 25°C, but may also
be diluted with a solvent upon use. Further, the present invention may make use of an ordinary curing agent at the same time for the purpose of promoting the curing of the liquid coating agent.

An epoxy resin curing agent usable in the present invention may include, for example, diethylene triamine, triethylene tetramine, tetraethylene pentamine, 2,4,6-tris(dimethylaminomethyl)phenol, methaxylylene diamine, and other amine types, phthalic anhydride acid, hexahydrophthalic anhydride, methyladipic anhydride, pyromellitic anhydride, and other acid anhydrides, polyamide resin, and any mixtures thereof. Further, a curing agent for acrylic resins may include, for example, dicumyl peroxide, di-tert-butylperoxide, 2,5-dimethyl-2,5-di(tert-butylperoxide)hexane, benzyolperoxide, laurylperoxide and other organic peroxides and any mixtures thereof.

The liquid coating agent is mixed in an amount of 0.1 to 8 parts by weight, preferably 0.2 to 5 parts by weight, per 100 parts by weight of the powder molding thermoplastic synthetic resin powder. The curing agent used is preferably an amount of not more than 100 parts by weight in the case of acid anhydrides, and 3 parts by weight in the case of amines and peroxides, based upon 100 parts by weight of the liquid coating agent.

When the foamable compound is produced by mixing the above-mentioned compounds or agents, a heat decomposable foaming agent is usually mixed in the thermoplastic synthetic resin powder (B) and then the liquid coating agent is mixed therein.

The composite foam molded article of the present invention is integrally molded with a nonfoam layer formed from the thermoplastic elastomer powder composition (A) and a foamed layer formed from the thermoplastic synthetic resin powder (B), the heat decomposable foaming agent (C) and, optionally, the liquid coating agent (D). For the molding, the powder molding method is used.

The powder molding method usable in the present invention may include, for example, the fluidized method, the powder sintering method, the electrostatic coating method, the powder flame-spray method, the powder rotational molding method and the powder slush molding method (Japanese Unexamined Patent Publication (Kokai) No. 58-132507). It is particularly preferable to use the powder slush molding method.

When the powder slush molding method is used, for example, it is possible to produce a composite foam molded article by:

(1) affixing a container having an opening and holding the necessary amount of the thermoplastic elastomer powder (A) and a mold having an opening and heated to a sufficiently high temperature from the melting temperature of the powder so that their openings are aligned or else making them integral, affixing the former in the hollow portion in the mold and rotating and/or shaking the same so as to quickly supply the powder from the container in the different portions of the mold to deposit and melt there and discharging the excess powder to the inside of the container,

(2) affixing a container having an opening and holding the necessary amount of the foamy composition and the mold heated to a sufficiently high temperature from the melting temperature of the composition and having the nonfoam layer obtained in the above step (1) so that their openings are aligned or else making them integral, affixing the former in the hollow portion in the mold and rotating and/or shaking the same so as to quickly supply the foamy composition from the container to the different portions of the nonfoam layer to deposit and melt there and discharging the excess powder composition to the inside of the container,

(3) heating the molded article obtained in step (2) so as to cause foaming.

The system of heating the mold used in the powder molding method is not particularly limited. For example, the gas-fired furnace system, the hot medium oil circulation system, the hot medium oil or hot fluidized sand immersion system, or the high frequency induction heating system may be used. These heating sources may also be used to cause the powder composition to foam.

The molding temperature of the nonfoam layer of the present invention is preferably 160 to 300°C, more preferably 180 to 280°C. The molding time is not particularly limited and may be suitably selected in accordance with, for example, the size of the molded article or the thickness of the molded article. Further, the temperature for causing the foamed layer of the present invention to foam is usually 180 to 280°C, preferably 180 to 260°C. The foaming time is particularly limited and may be suitably selected in accordance with the thickness of the foamed layer and the foaming rate.

A composite foam molded article can be obtained as mentioned above. According to the present invention, it is possible to produce a composite foam molded article having an integral nonfoam layer given a complicated shape and a foam layer with uniform cells and a high foaming rate and further it is possible to obtain a composite foam molded article which is large in size and has a small residual strain.

In addition, it is possible to provide a composite foam molded article which is light in weight and superior in cleanliness.

The composite foam molded article of the present invention has the superior properties mentioned above, so can be used in various fields. For example, in the automobile field, it is suitable for the interior covering material for the instrument panel, console box, armrests, headrests, door trims, rear panel, pillar trims, sun visors, trunkroom trims,
trunk lid trims, airbag holding box, seat buckles, head liners, glove compartments, steering wheel covers, and ceiling material, interior molded articles such as kicking plate, change lever boot and ceiling material, and external components of an automobile such as the spoiler, side mold, number plate housing, mirror housing, air dam skirt, and mud guard.

Further, in the field of household electrical appliances and office automation equipment, it is suitable, for example, for the covering materials and housings of television sets, video cassette recorders, washing machines, dryers, vacuum cleaners, coolers, air-conditioners, remote control unit cases, microwave ovens, toasters, coffee makers, vacuum bottles, thermos bottles, dish washers, electric shavers, hair dryers, microphones, headphones, beauty equipment, compact disk and cassette storage boxes, personal computers, typewriters, video equipment, telephones, copiers, facsimile machines and telex machines.

In the sporting goods field, it is suitable, for example, for decorative parts of sports shoes, rackets for various type of ball games, grips for sports equipment and accessories, saddle coverings and handle grips for bicycles, motor bicycles and tricycles.

In the construction and housing fields, it is suitable, for example, for covering materials for, for example, furniture, tables and chairs, covering materials for, for example, doors, gates and fences, decorative wall materials, decorative ceiling materials, curtain wall covering materials, indoor floor materials for kitchens, bathrooms, and toilets, outdoor floor materials for, for example, verandas, terraces, balconies and carports, welcome mats, table cloths, coasters, ashtrays, and other articles.

In the field of industrial parts, it is suitable, for example, for grips of power tools, hoses and their covering materials, and packing materials.

In addition to the above, it is suitable, for example, for covering materials of attache cases, cases, files, memo books, albums, stationery, camera bodies, and dolls and other toys, watchbands and other molded articles, and picture frames and their covering materials.

Examples

The present invention will be explained in more detail in the following Examples.

In the Examples and the Comparative Examples, the outer appearances of the covering side and foam side of the composite foam molded articles, the thicknesses of the composite foam molded articles, the states of the cells of the foamed layers, and the foaming rates of the foamed layers were evaluated as follows:

Outer Appearance of Covering Side of Composite Foam Molded Article

The covering layer was inspected visually and evaluated in the following way:

- Good: The melt-fusion was good and no pinholes were observed.
- Poor: The melt-fusion was poor and pinholes were observed.

Outer Appearance of Foam Side of Composite Foam Molded Article

The foam layer was observed visually and evaluated in the following way:

- Good: There was no unevenness of thickness and the foaming was uniform.
- Fair: There was unevenness of thickness, but the foaming was substantially uniform.
- Poor: There was major unevenness of thickness and the foaming was not uniform.
- Very poor: There was almost no foaming.

Thickness of Composite Foam Molded Article

The thicknesses of the nonfoam layer and the foam layer were measured by a dial gauge made by Toyo Seiki Seisakusho.

State of Cells of Foam Layer

The cross-section of the foamed article was visually inspected and evaluated in the following way:

- Good: The cells were uniform.
- Fair: The cells were somewhat nonuniform.
- Poor: The cells were nonuniform.
Foaming Rate of Foam Layer

The foaming rate was calculated by the following formula:

\[
\text{Foaming rate} = \frac{\text{Density of nonfoamed layer}}{\text{Density of foamed layer}}
\]

Note that the density of the foamed layer was measured in water using a densimeter made by Toyo Seiki Seisakusho (Densimeter H).

The decomposition temperature of the heat decomposable foaming agent was measured as follows.

A sample was placed in a capillary tube and heated at a heating rate of 2°C/min by a melting point determination apparatus (Model MP manufactured by Yanagimoto Seisakusho). The temperature at which the foaming was started was determined as a decomposition temperature.

Further, the dynamic viscoelasticity of the thermoplastic elastomer composition was measured as follows.

The dynamic viscoelasticities at 250°C at a vibration frequencies of 1 radian/sec and 100 radian/sec were measured by using a Dynamic Analyzer Model RDS-7700 manufactured by Rheometrics Co. The measurement was conducted in the parallel plate mode under the conditions of an applied strain of 5% and the complex dynamic viscosities \( n''(1) \) and \( n''(100) \) were calculated.

Example 1

40 parts by weight of oil-extended EPDM (ML-1,4 = 100°C = 53) comprising 100 parts by weight of EPDM (ML-1,4 = 100°C = 242, propylene content of 28% by weight, iodine value of 12), and added thereto, 100 parts by weight of a mineral oil softening agent (made by Idemitsu Kosan Co., Ltd., registered trademark Diana Process PW-380) was kneaded with 60 parts by weight of propylene-ethylene random copolymer resin (ethylene content of 5% by weight, MFR of 85 g/10 min), and 0.4 part by weight of a cross-linking coagent (made by Sumitomo Chemical Co., Ltd., registered trademark Sumifine BM -bismaleimide compound) for 10 minutes by a Banbury mixer to make a pellet-shaped masterbatch for cross-linking by an extrusion machine.

0.04 parts by weight of organic peroxide (made by Sakken Chemical Co., Ltd., registered trademark Sanperox APO (2,5-dimethyl-2,5-dil-(butylperoxy) hexane)) was added to 100 parts by weight of the masterbatch. Dynamic cross-linking was performed at 220°C using a twin-screw kneader (made by Japan Steel Works, Ltd., registered trademark TEX-44) to obtain elastomer composition pellets. The pellets were cooled to -100°C using liquid nitrogen, then were pulverized while frozen to obtain a thermoplastic elastomer powder for powder molding having a complex dynamic viscosity \( n''(1) \) of 310 Pas (3.1 x 10^5 poise) and a Newtonian viscosity index \( n \) of 0.24.

99% by weight of the powder passed through a 32 mesh sieve of a Tyler standard screen scale sieve.

An embossed nickel plate mold (30 cm x 30 cm) was heated in a 300°C Geer oven. When the surface temperature of the mold became 220°C, the above-mentioned powder molding thermoplastic elastomer powder was sprinkled therein for 5 seconds. The excess powder was removed, then immediately a thermoplastic elastomer powder composition for powder molding comprised of 100 parts by weight of the same powder molding thermoplastic elastomer as the above mixed with 5 parts by weight of a heat decomposable foaming agent, azo compound Cellmic CAP-500 (made by Sankyo Chemical Co., Ltd. main component: azodicarbonamide, decomposition temperature 150°C) was sprinkled for 20 seconds. The excess powder composition was removed.

The mold was then placed in a Geer oven having an atmospheric temperature of 220°C and was heated for 60 seconds to foam the composition.

Next, the mold was taken out from the Geer oven and cooled by water, then the composite foam molded article was removed from the mold.

The results of evaluation of the resultant composite foam molded article are shown in Table 1.

Example 2

Except for using 60 parts by weight of propylene-butenone random copolymer resin (butene content of 24% by weight and MFR of 90 g/10 min) and using 40 parts by weight of the oil-extended EPDM in Example 1, the same conditions as in Example 1 were followed to obtain a powder molding thermoplastic elastomer powder having a complex dynamic viscosity \( n''(1) \) of 690 Pas (6.9 x 10^5 poise) and a Newtonian viscosity index \( n \) of 0.39.

99% by weight of the powder passed through a 32 mesh sieve of a Tyler standard sieve.

5 parts by weight of the same heat decomposable foaming agent as in Example 1 was mixed with 100 parts by weight of the same powder as this powder to obtain a foameable thermoplastic elastomer powder composition.

Thereafter, a composite foam molded article was produced under the same conditions as Example 1. The results of the evaluation of the composite foam molded article are shown in Table 1.
Example 3

Except for using 50 parts by weight of propylene-ethylene random copolymer resin (ethylene content of 3% by weight and MFR of 60 g/10 min) and using 50 parts by weight, instead of 40 parts by weight, of the oil-extended EPDM in Example 1, the same conditions as in Example 1 were followed to obtain a powder molding thermoplastic elastomer powder having a complex dynamic viscosity $\eta^*(1)$ of 3400 Pas (3.4 x $10^4$ poise) and a Newtonian viscosity index $n$ of 0.59.

99% by weight of the powder passed through a 32 mesh sieve of a Tyler standard sieve.

5 parts by weight of the same heat decomposable foaming agent as in Example 1 was mixed with 100 parts by weight of the same powder to obtain a foamable thermoplastic elastomer powder composition.

Thereafter, a composite foam molded article was produced under the same conditions as Example 1. The results of the evaluation of the composite foam molded article are shown in Table 1.

Comparative Example 1

Except for using 50 parts by weight of propylene-ethylene random copolymer resin (ethylene content of 3% by weight and MFR of 10 g/10 min) and using 50 parts by weight, instead of 40 parts by weight, of the oil-extended EPDM in Example 1, the same conditions as in Example 1 were followed to obtain a powder molding thermoplastic elastomer powder having a complex dynamic viscosity $\eta^*(1)$ of 2.3 x $10^4$ Pas (2.3 x $10^5$ poise) and a Newtonian viscosity index $n$ of 0.76.

99% by weight of the powder passed through a 32 mesh sieve of a Tyler standard sieve.

Thereafter, a composite foam molded article was produced under the same conditions as Example 1. The results of the evaluation of the composite foam molded article are shown in Table 1.

Comparative Example 2

60 parts by weight of EPDM (ML1+4100°C of 86, propylene content of 50% by weight, iodine value of 8), 20 parts by weight of EPM (ML1+4100°C of 143, propylene content of 53% by weight), and 20 parts by weight of homopolypropylene (MFR of 10 g/10 min) were mixed in Banbury mixer. 0.28 parts by weight of Sanpex ABO was added per 100 parts by weight, then the mixture was dynamically cross-linked by a twin-screw mixer to obtain elastomer composition pellets.

These pellets were pulverized in the same way as in Example 1, whereby a thermoplastic elastomer powder having a complex dynamic viscosity $\eta^*(1)$ of 5.7 x $10^4$ Pas (5.7 x $10^5$ poise) and a Newtonian viscosity index $n$ of 0.79 was obtained.

99% by weight of the powder passed through a 32 mesh sieve of a Tyler standard sieve.

A composite foam molded article was produced under the same conditions as in Example 1. The results of evaluation are shown in Table 1.

Comparative Example 3

52 parts by weight of oil-extended EPDM (ML1+4100°C of 78) comprising 100 parts of EPDM (ML1+4100°C of 145, propylene content of 36% by weight, iodine value of 10), and added thereto, 40 parts by weight of a mineral oil softening agent (Diana Process PW-380) was kneaded with 27 parts by weight of homopolypropylene (MFR of 20 g/10 min), 21 parts by weight of propylene-propylene random copolymer (butene content of 24%, MFR of 4 g/10 min), and 0.2 parts by weight of a cross-linking agent (Sumifine® BM) by Banbury mixer. 0.23 parts by weight of an organic peroxide (made by Sanken Chemical Co., Ltd., Sanpex TO-1,3) was added per 100 parts by weight of this, then the mixture was dynamically cross-linked by a twin-screw mixer to obtain elastomer composition pellets.

These were pulverized in the same way as in Example 1, whereby a thermoplastic elastomer powder having a complex dynamic viscosity $\eta^*(1)$ of 1.9 x $10^4$ Pas (1.9 x $10^5$ poise) and a Newtonian viscosity index $n$ of 0.83 was obtained.

99% by weight of the powder passed through a 32 mesh sieve of a Tyler standard sieve.

A composite foam molded article was produced under the same conditions as in Example 1. The results of evaluation are shown in Table 1.

Example 4

Except for using 5 parts by weight of Cellmic S (made by Sankyo Chemical Co., Ltd., 4,4'-oxybis (benzenesulfonyl-hydrazide)) instead of the heat decomposable foaming agent Cellmic CAP-500 in Example 1, Example 1 was followed to obtain a composite foam molded article. The results of evaluation are shown in Table 1.
Comparative Example 4

Except for using 1.5 parts by weight of the heat decomposable foaming agent Cellmic CAP-500 in Example 1, Example 1 was followed to obtain a composite foam molded article. The results of evaluation are shown in Table 1.

Example 5

Except for using 3 parts by weight of the heat decomposable foaming agent Cellmic CAP-500 in Example 1, Example 1 was followed to obtain a composite foam molded article. The results of evaluation are shown in Table 1.

Example 6

Except for using 10 parts by weight of the heat decomposable foaming agent Cellmic CAP-500 in Example 1, Example 1 was followed to obtain a composite foam molded article. The results of evaluation are shown in Table 1.

Comparative Example 5

Except for using 12 parts by weight of the heat decomposable foaming agent Cellmic CAP-500 in Example 1, Example 1 was followed to obtain a composite foam molded article. The results of evaluation are shown in Table 1.

Example 7

Except for the use, as the foam thermoplastic elastomer powder composition in Example 2, of a composition obtained by 5 parts by weight of the same heat decomposable foaming agent as used in Example 2, 0.5 parts by weight of liquid coating agent (made by Dainippon Ink & Chemicals, Inc., registered trademark Monocizer TD-1500, trimethylolpropane-methacrylate) diluted by 20 ml of ethyl acetate, and 0.005 parts by weight of dicumylperoxide (made by Sanke Chemical Co., Ltd., registered trademark Sanperox DC-98) diluted by 10 ml of methylketone, based upon 100 parts by weight of the powder molding thermoplastic elastomer powder obtained in the same way as in Example 2, the same procedure as in Example 2 as followed to produce a composite foam molded article. The results of the evaluation are shown in Table 1.

Example 8

Except for the use, as the foam thermoplastic elastomer powder composition in Example 2, of a composition obtained by mixing 5 parts by weight of the same heat decomposable foaming agent as used in Example 2, 0.5 parts by weight of liquid coating agent (made by Sumikin Chemical Co. Ltd., registered trademark Sumiexy ELA115, cyclic aliphatic epoxy resin polymerized from epsilon-chlorohydrine and bisphenol A), and 0.005 parts by weight of a curing agent, triethylene tetramine, based upon 100 parts by weight of the powder molding thermoplastic elastomer powder obtained in the same way as in Example 2, the same procedure as in Example 2 as followed to produce a composite foam molded article. The results of the evaluation are shown in Table 1.

Comparative Example 6

Except for the use of 10 parts by weight of the liquid coating agent and 1 part by weight of the curing agent in Example 8, the same procedure as in Example 8 was followed to produce a composite foam molded article. The results of the evaluation are shown in Table 1.

Example 9

A powder produced in the same way as Example 2 was used as the powder molding thermoplastic elastomer powder.

An embossed nickel plate mold (30 cm x 30 cm) was heated in a 300°C Geer oven. When the surface temperature of the mold became 250°C, the powder molding thermoplastic elastomer powder was sprinkled on it for 5 seconds. The excess powder was removed, then immediately a foamyable polyethylene resin powder composition obtained by mixing 3 parts by weight of a heat decomposable foaming agent, azodicarbonamide (made by Sankyo Chemical Co., Ltd., Cellmic CAP-250, decomposition temperature of 145°C) in 100 parts by weight of a straight chain low density polyethylene resin powder (made by Sumitomo Seika, FLO-THENE F-13142-N, MFR of 10 g/10 min, average particle size of 80±10 mesh) was sprinkled for 20 seconds. The excess powder composition was removed. The mold was then placed
in a Geer oven having an atmospheric temperature of 200°C and was heated for 70 seconds to foam the composition. Next, the mold was taken out from the Geer oven and cooled by water, then the composite foam molded article was removed from the mold. The results of evaluation are shown in Table 1.

Example 10

Except for using a foarmable ethylene-vinyl acetate copolymer resin powder composition comprised of 3 parts by weight of the heat decomposable foaming agent azodicarbonamide (made by Sankyo Chemical Co., Ltd., Cellmic CAP-250, decomposition temperature of 145°C) mixed with 100 parts by weight of ethylene-vinyl acetate copolymer resin powder (made by Sumitomo Seika Co., Ltd., Flowbanc H4001N, vinyl acetate content of 20% by weight, MFR of 20 g/10 min, average particle size of 55±5 mesh) instead of the foarmable thermoplastic elastomer powder composition in Example 1 and foaming in a 200°C Geer oven for 60 seconds, the same procedure was followed as in Example 1 to produce a composite foam molded article. The results of the evaluation are shown in Table 1.

Example 11

Except for using a composition comprised of 2.5 parts by weight of the heat decomposable foaming agent azodicarbonamide (made by Sankyo Chemical Co., Ltd., Cellmic CAP-250, decomposition temperature of 145°C) mixed with 100 parts by weight of propylene-butene random copolymer resin powder (made by Sumitomo Chemical Co., Ltd., BH190G, butene content of 24% by weight, MFR of 79.1 g/10 min, average particle size of 133 μm) instead of the foam thermoplastic elastomer powder composition in Example 2, the same procedure was followed as in Example 2 to produce a composite foam molded article. The results of the evaluation are shown in Table 1.

Example 12

Except for using a composition comprised of 3 parts by weight of the heat decomposable foaming agent azodicarbonamide (made by Sankyo Chemical Co., Ltd., Cellmic CAP-250, decomposition temperature of 145°C) mixed with 100 parts by weight of ethylene-methyl methacrylate copolymer resin powder (made by Sumitomo Chemical Co., Ltd., Acryft WH501, methyl methacrylate content of 20% by weight, MFR of 70 g/10 min, average particle size of 160 μm) instead of the foarmable thermoplastic elastomer powder composition in Example 2, the same procedure was followed as in Example 2 to produce a composite foam molded article. The results of the evaluation are shown in Table 1.

Example 13

Except for using a composition comprised of 3 parts by weight of the heat decomposable foaming agent azodicarbonamide (made by Sankyo Chemical Co., Ltd., Cellmic CAP-250, decomposition temperature of 145°C) mixed with 100 parts by weight of ethylene-glycidyl methacrylate-vinyl acetate terpolymer resin powder (made by Sumitomo Chemical Co., Ltd., Bondfast 20B, glycidyl methacrylate content of 12% by weight, vinyl acetate content of 5% by weight, MFR of 20 g/10 min, average particle size of 324 μm) instead of the foarmable thermoplastic elastomer powder composition in Example 2, the same procedure was followed as in Example 2 to produce a composite foam molded article. The results of the evaluation are shown in Table 1.

Example 14

Except for using a composition comprised of 3 parts by weight of the heat decomposable foaming agent azodicarbonamide (made by Sankyo Chemical Co., Ltd., Cellmic CAP-250, decomposition temperature of 145°C) mixed with 100 parts by weight of ethylene-acrylic acid ester-anhydrous maleic acid terpolymer resin powder (made by Sumika Atochim Co., Ltd., Bondine HX8210, comonomer content of 9% by weight, MFR of 200 g/10 min, average particle size of 313 μm) instead of the foarmable thermoplastic elastomer powder composition in Example 2, the same procedure was followed as in Example 2 to produce a composite foam molded article. The results of the evaluation are shown in Table 1.

Comparative Example 7

Except for using a composition comprised of 3 parts by weight of the heat decomposable foaming agent azodicarbonamide (made by Sankyo Chemical Co., Ltd., Cellmic CAP-250, decomposition temperature of 145°C) mixed in with 100 parts by weight of polyurethane resin powder (pure product of resin obtained by causing a reaction of 50 parts by weight of polymeric MDI with an NCO content of 30.5% based upon 100 parts by weight of a mixture comprised of poly-
ols, mainly comprised of propylene oxide and ethylene oxide additions product of glycerol, water, triethanolamine, and triethylene diamine, particle size of about 300 μm, not melting at 190°C) instead of the foambale thermoplastic elastomer powder composition in Example 2, the same procedure was followed as in Example 2 to produce a composite foam molded article. The results of the evaluation are shown in Table 1.

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<th>No.</th>
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<th>Outer appearance of foam side of molded article</th>
<th>Thickness of nonfoam layer (mm)</th>
<th>Thickness of foam layer (mm)</th>
<th>State of cells of foam layer</th>
<th>Foaming ratio of foam layer</th>
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</table>

**Example 15**

A colourable thermoplastic elastomer powder (resin powder 5000 g) comprised of the thermoplastic elastomer powder obtained in the same way as in Example 2 mixed with 1.0 part by weight of a white pigment (made by Sumika Color Co., Ltd., White PV742) was fed into a 20 liter capacity supermixer and mixed for 10 minutes at 500 rpm to obtain 5050 g of a white powder molding thermoplastic elastomer powder composition (nonfoam layer use).

To the foambale thermoplastic elastomer powder composition obtained in the same way as in Example 2 was mixed 1.0 part by weight of a pigment (made by Sumika Color Co., Ltd., made of a mixture of 0.7 parts by weight White PV 742 and 0.3 parts by weight Black PV-817) to obtain 5300 g of a foambale thermoplastic elastomer powder composition coloured gray.

Two of the stainless steel rectangular containers (powder feed boxes) shown in Fig. 1 to Fig. 3 were prepared. To one container, 4000 g of the thermoplastic elastomer powder composition for the nonfoam layer was fed and to the other container, 4000 g of the foambale thermoplastic elastomer powder composition was fed. The rectangular contain-
ers have a rectangular opening 1 of 600 mm × 220 mm, and a depth of 210 mm, and were designed to be mounted to a single-screw rotating apparatus 3.

A nickel electrocast mold shown in Fig. 4 to Fig. 6 having an opening 4 of the same size as the opening 1 of the powder feed boxes shown in Fig. 1 was also prepared. The mold had a thickness of 3 mm and had a complicated shape with a rope pattern 5 and a leather grain pattern 6 on its inner surface. When the surface temperature of the mold reached 250°C, the heated mold was immediately positioned so that its opening 4 (600 mm × 220 mm) faced downward, was aligned with the opening 1 of the powder feed box filled with the thermoplastic elastomer powder composition for the nonfoam layer, the outer frame attached around the two openings was clamped tight, and the clip 2 was used to affix it to make the assembly an integral piece.

When the surface temperature of the mold became 220°C, the powder feed box filled with the thermoplastic elastomer powder composition for the nonfoam layer was immediately turned by 180° and the powder was brought into contact with the mold for 3 seconds to melt adhere it to the same. Immediately thereafter, the powder feed box was turned by 180° to return it to its original position and the excess powder adhering to the complicated shape portions was swept off into the powder feed box.

Immediately, the opening 4 of the mold forming the nonfoam layer as positioned to face downward, the opening 4 of the mold was aligned with the opening 1 of the powder feed box containing the foamy thermoplastic elastomer powder composition, an outer frame attached around the two openings was clamped closely, and the clip 2 was used to affix the same and make the assembly an integral piece. The surface temperature of the mold at this time was 189°C.

Immediately, the powder feed box containing the foamy thermoplastic elastomer powder composition was rotated by 180° and the powder composition was brought into contact with the mold for 15 seconds to melt-adhere it to the same. Then, the powder feed box was rotated by 180° to return it to its original position. The excess powder composition adhering to the complicated shape portion was swept off into the powder feed box.

With the opening 4 of the mold facing downward, the mold was detached from the powder feed box.

Next, the mold was post-heated for one minute in a heating furnace of 200°C, then immediately cooled by water, after which the molded article was removed from the mold.

The resultant composite foam molded article had a nonfoam layer of 120 g and a thickness of 0.7 mm and a foam layer of 110 g and a thickness of 3.3 mm, with a foam rate of 4.0. The nonfoam layer did not have any underfills or pinholes and faithfully reproduced the rope pattern and leather grain pattern. Further, the foam layer had uniform foam cells.

Example 16

In the apparatus shown in Fig. 7, the powder molding thermoplastic elastomer powder 5 obtained in the same way as in Example 1 was charged into the hopper 2. Further, a foamy thermoplastic elastomer powder composition 8 obtained by mixing 5 parts by weight of the heat decomposable foaming agent azodicarbonamide (made by Sankyo Chemical Co., Ltd., Celtic CAP-500, decomposition temperature of 150°C) in 100 parts by weight of the same powder molding thermoplastic elastomer powder was charged into the hopper 2.

The belt speed was adjusted to 1.75 m/min. The belt 1 used was a stainless steel one of a width of 30 cm and a thickness of 1 mm. The front sintering furnace 6 and the rear sintering furnace 6’ were set to 200°C. The surface temperature of the belt was 120°C. The thickness adjusting plate 3 was adjusted to form a 2 mm powder layer 4. The powder layer 4 was led into the sintering furnace 6 together with the progression of the belt and was sintered. The resultant sintered sheet was 0.7 mm in thickness and the surface was uniformly smooth.

Next, the above-mentioned foamy thermoplastic elastomer powder composition 8 was charged on the sintered sheet (nonfoam sheet layer) from the hopper 2 and was adjusted by a thickness adjusting plate 3’ to form the foamy powder composition layer 9. The layer comprised of the nonfoam sheet layer and the foamy powder composition layer 9 was passed through the rear sintering furnace 6’ set to 200°C.

The sintered sheet obtained above was an integral multilayer sintered sheet comprised of the nonfoam sheet layer and the foamed sheet layer. The multilayer sintered sheet had a thickness of the nonfoam sheet layer of 0.7 mm and a thickness of the foam sheet layer of 2.5 mm. The multilayer sintered sheet had a uniformly smooth surface and an excellent cushioning property.

Claims

1. A molded composite article comprising (1) a nonfoam layer and (II) a foamed layer, said article being obtainable by conducting powder molding of (A) a thermoplastic elastomer powder composition to form the nonfoam layer (I) and subsequently conducting powder molding of a foamy composition comprising (B) 100 parts by weight of a thermoplastic synthetic resin powder, (C) 2 to 11 parts by weight of a heat decomposable foaming agent, and optionally (D) 0.1 to 8 parts by weight of a liquid coating agent to form the foamed layer (II) on the nonfoam layer (I);
(A) said thermoplastic elastomer powder composition comprising an ethylene-α-olefin copolymer rubber and a polyolefin resin, which composition may be partially cross-linked and has a complex dynamic viscosity \( \eta^*'(1) \) at 250°C and a frequency of 1 radian/sec of not more than 1.5 \( \times \) 10⁴ Pas (1.5 \( \times \) 10⁵ poise) and having a Newtonian viscosity index \( n \), calculated by the following formula using the above-mentioned complex dynamic viscosity \( \eta^*'(1) \) and the complex dynamic viscosity \( \eta^*'(100) \) at a frequency of 100 radian/sec, of not more than 0.67:

\[
n = \frac{\log \eta^*'(1) - \log \eta^*'(100)}{2}
\]

2. A molded article according to claim 1, wherein the ethylene-α-olefin copolymer rubber is an ethylene-propylene-ethylene norbornene rubber.

3. A molded article according to claim 1 or 2, wherein the Mooney viscosity (ML₁₊₄100°C) of the ethylene-α-olefin copolymer rubber is 130 to 350.

4. A molded article according to claim 1, 2 or 3, wherein the ethylene-α-olefin copolymer rubber is an oil-extended olefin copolymer rubber.

5. A molded article according to any one of the preceding claims, wherein the polyolefin resin is polypropylene, a copolymer of propylene and ethylene, or a copolymer of propylene and butene.

6. A molded article according to any one of the preceding claims, wherein the weight ratio of the ethylene-α-olefin copolymer rubber and the olefin resin is 5:95 to 80:20.

7. A molded article according to any one of the preceding claims wherein the thermoplastic synthetic resin powder (B) comprises an ethylene-α-olefin copolymer rubber and a polyolefin resin, which composition may be partially cross-linked.

8. A molded article according to claim 7, wherein the thermoplastic elastomer powder (B) has a complex dynamic viscosity \( \eta^*'(1) \) of not more than 1.5 \( \times \) 10⁴ Pas (1.5 \( \times \) 10⁵ poise) and has a Newtonian viscosity index \( n \) of not more than 0.67.

9. A molded article according to any one of claims 1 to 6 wherein the thermoplastic synthetic resin powder (B) is a polyethylene resin powder.

10. A molded article according to claim 9, wherein the melt flow rate of the polyethylene resin powder, measured according to JIS K-7210, 190°C, 2.16 kg load, is 3 g/10 min or more.

11. A molded article according to any one of claims 1 to 6 wherein the thermoplastic synthetic resin powder (B) is a polypropylene resin powder.

12. A molded article according to claim 11, wherein the melt flow rate of the polypropylene resin powder, measured according to JIS K-7210, 230°C, 2.16 kg load, is 3 g/10 min or more.

13. A molded article according to any one of the preceding claims wherein the heat decomposable foaming agent (C) is used in an amount of 3 to 7 parts by weight, based upon 100 parts by weight of the thermoplastic synthetic resin powder (B).

14. A molded article according to any one of the preceding claims wherein the heat decomposable foaming agent (C) is an azo compound or a sulfonhydrazide compound.

15. A molded article according to any one of the preceding claims, wherein the liquid coating agent (D) is used in an amount of 0.2 to 5 parts by weight, based upon 100 parts by weight of the thermoplastic synthetic resin powder (B).

16. A molded article according to any one of the preceding claims, wherein the liquid coating agent (D) is polysiloxane, an epoxy resin, or an acrylic resin.

17. A process for producing a composite molded article as claimed in any one of the preceding claims which comprises conducting power molding of the thermoplastic elastomer powder composition (A) as defined in claim 1 to form the
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nonfoam layer (I) und subsequently conducting powder molding of the foamable composition to form the foamed layer (II) on the nonfoam layer (I).

18. A foamy powder composition comprising 2 to 11 parts by weight of a heat decomposing foaming agent (C), optionally 0.1 to 8 parts by weight of a liquid coating agent (D) and 100 parts by weight of a thermoplastic elastomer powder (B): wherein (B), (C) and (D) are as defined in any one of claims 7 to 12, 14 and 16.

Patentansprüche

1. Verbundformkörper aufweisend (I) eine Nichtschaum-Schicht und (II) eine geschäumte Schicht, wobei der Körper erhältlich ist durch Ausführen von Pulversintern von (A) einer Pulverzusammensetzung thermoplastischer Elastomere zur Ausbildung der Nichtschaum-Schicht (I) und nachfolgend Ausführen von Pulversintern einer schäumbaren Zusammensetzung, die (B) 100 Gewichtsteile eines Pulvers aus thermoplastischem synthetischem Harz, (C) 2 bis 11 Gewichtsteile eines wärmezersetzbaren Schaumbildners und, gewünschtenfalls, (D) 0,1 bis 8 Gewichtsteile eines flüssigen Beschichtungsmittels aufweist, zur Ausbildung der geschäumten Schicht (II) auf der Nichtschaum-Schicht (I);

(A) wobei die Pulverzusammensetzung aus thermoplastischem Elastomer einen Ethylen-α-Olefin-Copolymer-Kautschuk und ein Polyolefin-Harz aufweist, die Zusammensetzung teilweise vernetzt sein kann und eine komplexe dynamische Viskosität \( \eta''(1) \) bei 250°C und einer Frequenz von 1 Radiant/s von nicht mehr als 1,5 x 10^6 Pas (1,5 x 10^6 Poise) hat und einen Newtonschen Viskositätsindex \( n \), der nach der folgenden Formel unter Verwendung der oben angeführten komplexen dynamischen Viskosität \( \eta''(1) \) und der komplexen dynamischen Viskosität \( \eta''(100) \) bei einer Frequenz von 100 Radiant/s berechnet ist, von nicht mehr als 0,67 hat:

\[
n = (\log \eta''(1) - \log \eta''(100))/2.
\]


3. Formkörper nach Anspruch 1 oder 2, bei dem die Mooney-Viskosität (ML1+4100°C) des Ethylen-α-Olefin-Copolymer-Kautschuks 130 bis 350 beträgt.

4. Formkörper nach Anspruch 1, 2 oder 3, bei dem der Ethylen-α-Olefin-Copolymer-Kautschuk ein überstreckter Olefin-Copolymer-Kautschuk ist.

5. Formkörper nach einem der vorstehenden Ansprüche, bei dem das Polyolefin-Harz Polypropylen, ein Copolymer aus Propylen und Ethylen oder ein Copolymer aus Propylen und Buten ist.


7. Formkörper nach einem der vorstehenden Ansprüche, bei dem das Pulver aus thermoplastischem synthetischem Harz (B) einen Ethylen-α-Olefin-Copolymer-Kautschuk und ein Polyolefin-Harz aufweist, wobei die Zusammensetzung teilweise vernetzt sein kann.

8. Formkörper nach Anspruch 7, bei dem das Pulver aus thermoplastischem Elastomer (B) eine komplexe dynamische Viskosität \( \eta''(1) \) von nicht mehr als 1,5 x 10^6 Pas (1,5 x 10^6 Poise) hat und einen Newtonschen Viskositätsindex \( n \) von nicht mehr als 0,67 hat.

9. Formkörper nach einem der Ansprüche 1 bis 6, bei dem das Pulver aus thermoplastischem synthetischem Harz (B) ein Polyethylenharz-Pulver ist.

10. Formkörper nach Anspruch 9, bei dem die Schmelzflußrate des Polyethylenharz-Pulvers, gemessen nach JIS K 7210, 190°C, 2,16 kg Kraft, 3 g/10 Min oder mehr beträgt.

11. Formkörper nach einem der Ansprüche 1 bis 6, bei dem das Pulver aus thermoplastischem synthetischem Harz (B) ein Polypropylenharz-Pulver ist.
Formkörper nach Anspruch 11, bei dem die Schmelzflußrate des Polypropylenharz-Pulvers, gemessen nach JIS K-7210, 230°C, 2,16 kg Kraft, 3 g/10 Min oder mehr beträgt.

Formkörper nach einem der vorstehenden Ansprüche, bei dem der wärmezerstörbare Schaumbildner (C) in einer Menge von 3 bis 7 Gewichtsteilen, auf der Basis von 100 Gewichtsteilen des Pulvers aus thermoplastischem synthetischem Harz (B), verwendet wird.

Formkörper nach einem der vorstehenden Ansprüche, bei dem der wärmezerstörbare Schaumbildner (C) eine Azo-Verbindung oder eine Sulfonhydrazid-Verbindung ist.

Formkörper nach einem der vorstehenden Ansprüche, bei dem das flüssige Beschichtungsmittel (D) in einer Menge von 0,2 bis 5 Gewichtsteilen, auf der Basis von 100 Gewichtsteilen des Pulvers aus thermoplastischem synthetischem Harz (B), verwendet wird.

Formkörper nach einem der vorstehenden Ansprüche, bei dem das flüssige Beschichtungsmittel (D) Polysiloxan, ein Epoxyharz oder ein Acrylharz ist.

Verfahren zur Herstellung eines Verbundformkörpers gemäß einem der vorstehenden Ansprüche, aufweisend das Ausführen von Pulversintern der Pulverzusammensetzung aus thermoplastischem Elastomer (A), wie sie in Anspruch 1 definiert ist, zur Ausbildung der Nichtschaum-Schicht (I) und nachfolgend das Ausführen von Pulversintern der schäumabaren Zusammensetzung zur Ausbildung der geschäumten Schicht (II) auf der Nichtschaum-Schicht (I).

Schäumbare Pulverzusammensetzung, aufweisend 2 bis 11 Gewichtsteile eines wärmezerstörbaren Schaumbildners (C), gewünschtenfalls 0,1 bis 8 Gewichtsteile eines flüssigen Beschichtungsmittels (D) und 100 Gewichtsteile eines Pulvers aus thermoplastischem Elastomer (B): wobei (B), (C) und (D) so sind, wie in einem der Ansprüche 7 bis 12, 14 und 16 definiert.

Revendications

1. Article composite moulé comprenant (I) une couche non expansée et (II) une couche expansée, lead article pouvant être obtenu en réalisant un moulage de poudre avec (A) une composition de poudre d’élastomère thermoplastique pour former la couche non expansée (I) et ensuite en réalisant un moulage de poudre avec une composition expansible comprenant (B) 100 parties en masse d’une poudre de résine de synthèse thermoplastique, (C) 2 à 11 parties en masse d’un agent d’expansion se décomposant à chaud et éventuellement (D) 0,1 à 8 parties en masse d’un agent d’enduction liquide pour former la couche expansée (II) sur la couche non expansée (I);

(A) ladite composition de poudre d’élastomère thermoplastique comprenant un caoutchouc copolymère éthylène-α-oléfine et une résine polyoléfinique, composition pouvant être partiellement réticulée et ayant une viscosité dynamique complexe $\eta*(1)$ à 250°C et à une fréquence de 1 radian/seconde ne dépassant pas $1,5 \times 10^4$ Pas ($1,5 \times 10^5$ poises) et ayant un indice de viscosité de Newton $n$, calculé par la formule suivante, en utilisant la viscosité dynamique complexe $\eta*(1)$ susdite et la viscosité dynamique complexe $\eta*(100)$ à la fréquence de 100 radians/seconde, ne dépassant pas 0,67 :

$$n = (\log \eta*(1) - \log \eta*(100))/2$$

2. Article moulé selon la revendication 1, dans lequel le caoutchouc copolymère éthylène-α-oléfine est un caoutchouc éthylène-propylène-éthylidène norbornène.

3. Article moulé selon la revendication 1 ou 2, dans lequel la viscosité de Mooney (ML1+4 100°C) du caoutchouc copolymère éthylène-α-oléfine se situe entre 130 et 350.

4. Article moulé selon la revendication 1, 2 ou 3, dans lequel le caoutchouc copolymère éthylène-α-oléfine est un caoutchouc copolymère oléfinique étendu à l’huile.

5. Article moulé selon une quelconque des revendications précédentes, dans lequel la résine polyoléfinique est du polypropylène, un copolymère du propylène et de l’éthylène ou un copolymère du propylène et du butène.

7. Article moulé selon une quelconque des revendications précédentes, dans lequel la poudre de résine de synthèse thermoplastique (B) comprend un caoutchouc copolymère éthylène - alpha-oléfine et une résine polyoléfinique, composition pouvant être partiellement réticulée.

8. Article moulé selon la revendication 7, dans lequel la poudre d'élastomère thermoplastique (B) a une viscosité dynamique complexe $\eta^*(1)$ ne dépassant pas $1,5 \times 10^4$ Pas ($1,5 \times 10^6$ poises) et a un indice de viscosité de Newton $n$ ne dépassant pas 0,67.

9. Article moulé selon une quelconque des revendications 1 à 6, dans lequel la poudre de résine de synthèse thermoplastique (B) est une poudre de résine polyéthylène.

10. Article moulé selon la revendication 9, dans lequel l'indice de fusion de la poudre de résine polyéthylène, mesuré selon JIS K-7210, 190°C, charge de 2,16 kg, est égal ou supérieur à 3 g/10 minutes

11. Article moulé selon une quelconque des revendications 1 à 6, dans lequel la poudre de résine de synthèse thermoplastique (B) est une poudre de résine polypropylène.

12. Article moulé selon la revendication 11, dans lequel l'indice de fusion de la poudre de résine polypropylène, mesuré selon JIS K-7210, 230°C, charge de 2,16 kg, est égal ou supérieur à 3 g/10 minutes

13. Article moulé selon une quelconque des revendications précédentes, dans lequel l'agent d'expansion se décomposant à chaud (C) est utilisé en une quantité de 3 à 7 parties en masse, par rapport à 100 parties en masse de poudre de résine de synthèse thermoplastique (B).

14. Article moulé selon une quelconque des revendications précédentes, dans lequel l'agent d'expansion se décomposant à chaud (C) est un composé azo ou un composé sulfonylehydrazide.

15. Article moulé selon une quelconque des revendications précédentes, dans lequel l'agent d'enduction liquide (D) est utilisé en une quantité de 0,2 à 5 parties en masse, par rapport à 100 parties en masse de poudre de résine de synthèse thermoplastique (B).

16. Article moulé selon une quelconque des revendications précédentes, dans lequel l'agent d'enduction liquide (D) est un polysiloxane, une résine époxy ou une résine acrylique.

17. Procédé de production d'un article moulé composite selon une quelconque des revendications précédentes comprenant la réalisation d'un moulage de poudre avec la composition de poudre d'élastomère thermoplastique (A) comme défini dans la revendication 1, pour former la couche non expansible (I) et ensuite la réalisation d'un moulage de poudre avec la composition expansible pour former la couche expansible (II) sur la couche non expansible (I).

18. Composition de poudre expansible comprenant 2 à 11 parties en masse d'un agent d'expansion se décomposant à chaud (C), éventuellement 0,1 à 8 parties en masse d'un agent d'enduction liquide (D) et 100 parties en masse d'une poudre d'élastomère thermoplastique (B) : dans laquelle (B), (C) et (D) sont tels que définis dans une quelconque des revendications 7 à 12, 14 et 16.
Fig. 1

Fig. 2
Fig. 3

Fig. 4