

Description

Title of Invention: HYDROGENATED BLOCK COPOLYMER CRUMB
AND PROCESS FOR PRODUCTION THEREOF

Technical Field

[0001]

The present invention relates to a hydrogenated block copolymer crumb, and a method for producing the same.

Background Art

[0002]

Since hydrogenated block copolymers which are hydrogenated substances of block copolymers composed of a vinyl aromatic hydrocarbon and a conjugated diene have properties excellent in impact resilience and low-temperature properties, the hydrogenated block copolymers are conventionally used as a modifying agent to improve impact resistance, low-temperature properties, processability and the like of thermoplastic resins.

Compositions of the hydrogenated block copolymer and a thermoplastic resin are broadly used in the fields of electric and electronic components, automobile components, various types of industrial components, daily commodities and the like.

Since particularly high-molecular weight hydrogenated block copolymers are excellent in mechanical properties besides the above-mentioned various properties, the copolymers are used as materials for various types of industrial components such as electric wire cables, and automobile components by combining the copolymers with a liquid softening agent such as an oil, a plasticizer, and a thermoplastic resin such as polypropylene.

[0003]

The above-mentioned high-molecular weight hydrogenated block copolymers are handled usually not in a form of pellets but in a form of porous dry crumbs in many cases in order to make good kneadability with an oil and the like at the time of compounding.

Many of methods of obtaining porous dry crumbs of such hydrogenated block copolymers have conventionally been proposed.

[0004]

For example, a method is known which obtains a polymer crumb having a moisture content of 1 mass % or lower by removing a solvent by steam stripping from a solution of a hydrogenated block copolymer obtained by a copolymerization step and a hydrogenation step, and thereafter dehydrating and drying the resultant by an extrusion dehydrator (for example, see Patent Documents 1 and 2).

[0005]

As methods of improving the oil absorption of a high-molecular weight hydrogenated block copolymer crumb, there are proposed a dehydration and drying method using an extrusion dehydrator in which the operational temperature of the extruder to dehydrate the hydrogenated block copolymer crumb, and the amount of slurry moisture before the crumb is placed in the extruder are regulated (for example, see Patent Document 3), and a method of subjecting the hydrogenated block copolymer crumb to a drying treatment under a specific temperature condition by using a hot air drying machine (for example, see Patent Document 4).

Prior Art Documents

Patent Document

[0006]

Patent Document 1: Japanese Patent Laid-Open No. 64-56713

Patent Document 2: Japanese Patent Laid-Open No. 2-189304

Patent Document 3: National Publication of International Patent Application No. 2002-542963

Patent Document 4: International Publication No.
WO99/55752

Summary of Invention

Problems To Be Solved By The Invention

[0007]

However, although the methods disclosed in Patent Documents 1 and 2 are preferable as a method of obtaining a low-molecular weight hydrogenated block copolymer crumb, a sufficient property cannot yet be acquired for the oil absorption at the time of compounding of a high-molecular weight hydrogenated block copolymer crumb.

Problems of the high-molecular weight hydrogenated block copolymer crumbs obtained by the methods disclosed in Patent Documents 3 and 4 are that the compounding processability is still instable, including that at the time of compounding with a thermoplastic resin, an oil and the like, the oil is not uniformly dispersed entirely in the crumb, and the crumb does not completely melt and consequently remains as unmelted polymers.

[0008]

Thus, it is an object of the present invention, in consideration of the above-mentioned problems in conventional technologies, to provide a hydrogenated block copolymer crumb having such an excellent compounding processability that in compounding with a thermoplastic resin, a process oil and the like, the oil is uniformly dispersed entirely in the crumb, and the amount of remaining unmelted polymers in the compound is suppressed, and a method for producing the hydrogenated block copolymer crumb.

Means For Solving The Problems

[0009]

As a result of exhaustive studies on a technique for acquiring such a stable compound processability that in a compound of a high-molecular weight hydrogenated block copolymer crumb with a thermoplastic resin, and a softening agent such as a process oil, the oil is uniformly dispersed entirely in the crumb, and the amount of remaining unmelted polymers is suppressed, the present inventor has found that a high-molecular weight hydrogenated block copolymer crumb comprising a vinyl aromatic hydrocarbon and a conjugated diene and having specific ranges of the specific surface area and the particle diameter distribution of the crumb, and a method for producing the hydrogenated block copolymer crumb comprising specific dehydration and drying steps, can solve the above-mentioned problems in conventional technologies, and this finding has led to the completion of the present invention.

That is, the present invention is as follows.

[0010]

[1]

A hydrogenated block copolymer crumb comprising a hydrogenated substance of a block copolymer of a vinyl aromatic hydrocarbon and a conjugated diene,

wherein the crumb satisfies the following (1) to (4):

- (1) a main peak molecular weight is 200,000 to 600,000;
- (2) a moisture content is 1 mass % or lower;
- (3) a specific surface area is 0.3 to 1.0 m²/g; and
- (4) components passing through a sieve having an aperture of 3.35 mm, and not passing through a sieve having an aperture of 0.425 mm account for 80 mass % or more of the entire crumb.

[2]

A method for producing the hydrogenated block copolymer crumb according to above [1], comprising the following <step 1> to <step 3>:

<step 1>: a step of subjecting an aqueous slurry containing a hydrogenated block copolymer crumb to a dehydration treatment to thereby obtain a crumb wherein the crumb has a moisture content of higher than 60 mass % and 80 mass % or lower, and crumb components not passing through a sieve having an aperture of 3.35 mm account for 60 mass % or more of the entire crumb;

<step 2>: a step of subjecting the crumb obtained in the <Step 1> to a dehydration treatment and a drying treatment to thereby obtain a crumb having a moisture content of 3 to 30 mass %; and

<step 3>: a step of subjecting the crumb obtained in the <Step 2> to a drying treatment to thereby obtain a crumb having a moisture content of 1 mass% or lower.

[3]

The method for producing the hydrogenated block copolymer crumb according to above [2], wherein an apparatus outlet port temperature in the drying treatment in the <Step 2> is made 135 to 175°C (inclusive).
[4]

The method for producing the hydrogenated block copolymer crumb according to above [2] or [3], comprising:

using an extrusion type drying machine having a dehydration treatment unit and a drying treatment unit wherein the dehydration treatment unit and the drying treatment unit are communicated, in the <Step 2>;

carrying out the dehydration treatment by the dehydration treatment unit; and

carrying out the drying treatment by the drying treatment unit.

[5]

The method for producing the hydrogenated block copolymer crumb according to above [4], wherein an outlet port temperature of the dehydration treatment unit is 120°C or lower, and an outlet port temperature of the drying treatment unit is 135 to 175°C.

Advantageous Effects of Invention

[0011]

The present invention can provide a hydrogenated block copolymer crumb having such an excellent

compounding processability that an oil is uniformly dispersed entirely in the crumb, the oil absorption (oil holding power) is good, and unmelted polymers are reduced.

Brief Description of Drawings

[0012]

[Figure 1] Figure 1 shows a cross-sectional photograph of a sheet having an unmelted polymer.

Mode For Carrying Out The Invention

[0013]

Hereinafter, an embodiment according to the present invention (hereinafter, referred to as the present embodiment) will be described.

It is noted that the present invention is not limited to the following embodiment.

In the present description, a term having "nearly" attached thereto indicates a meaning of the term excluding the "nearly" in the range of the general technical knowledge of those skilled in the art, and includes also a meaning itself excluding "nearly."

[0014]

[Hydrogenated block copolymer crumb]

A hydrogenated block copolymer crumb according to the present embodiment is a crumb comprising a hydrogenated substance of a block copolymer of a vinyl

aromatic hydrocarbon and a conjugated diene, and satisfies the following (1) to (4):

- (1) the main peak molecular weight is 200,000 to 600,000;
- (2) the moisture content is 1 mass % or lower;
- (3) the specific surface area is 0.3 to 1.0 m²/g; and
- (4) the components passing through a sieve having an aperture of 3.35 mm, and not passing through a sieve having an aperture of 0.425 mm account for 80 mass % or more of the entire crumb.

[0015]

The hydrogenated block copolymer crumb according to the present embodiment is prepared by adding hydrogen to a block copolymer comprising a vinyl aromatic hydrocarbon and a conjugated diene as described above; and as shown in the above (1), the main peak molecular weight is 200,000 or higher from the viewpoint of the mechanical strength and the impact resistance in the case of being made into a predetermined polymer composition, and is 600,000 or lower from the viewpoint of the processability and the compatibility with polymer substances such as a thermoplastic resin.

The main peak molecular weight is preferably 230,000 to 500,000, and more preferably 250,000 to 450,000.

The molecular weight of the main peak of a hydrogenated block copolymer is measured by GPC (gel permeation chromatography), and can be measured using a calibration curve determined from the measurement of

commercially available standard polystyrenes.

Specifically, the molecular weight can be measured by a method described in Examples described later.

[0016]

The hydrogenated block copolymer crumb according to the present embodiment has, as described in the above (2), a moisture content of 1 mass% or lower. Thereby, in the case where a thermoplastic resin composition is obtained by compounding with a predetermined thermoplastic resin, the appearance faults due to the occurrence of foams, silver streaks and the like can be prevented.

The hydrogenated block copolymer crumb according to the present embodiment has a moisture content of preferably 0.9 mass % or lower, and more preferably 0.8 mass % or lower.

[0017]

The hydrogenated block copolymer crumb according to the present embodiment has, as shown in the above (3), a specific surface area of 0.3 to 1.0 m²/g, preferably 0.35 to 0.8 m²/g, and more preferably 0.4 to 0.7 m²/g.

The hydrogenated block copolymer crumb according to the present embodiment has, as shown in the above (4), a crumb size in which the components passing through a sieve having an aperture of 3.35 mm, and not passing through a sieve having an aperture of 0.425 mm account for 80 mass % or more of the entire crumb, preferably 82 mass % or more thereof, and more preferably 85 mass % or

more thereof. Satisfaction of the requirements of the above (3) and (4) makes the oil absorption good, can suppress the oil absorption unevenness, can uniformly plasticize the compound at the time of manufacturing the compound, and can achieve the reduction of the number of unmelted polymers.

The moisture content, the specific surface area and the size of a hydrogenated block copolymer crumb can be determined by methods described in Examples described later.

[0018]

[Method for producing a hydrogenated block copolymer crumb]

First, a hydrogenated block copolymer is fabricated as described later, and thereafter subjected to predetermined treatments to thereby obtain a hydrogenated block copolymer crumb.

(Production step of a hydrogenated block copolymer)

A block copolymer of a vinyl aromatic hydrocarbon and a conjugated diene compound is obtained by a polymerization reaction, and thereafter subjected to a hydrogenation reaction to thereby obtain a hydrogenated block copolymer.

<Polymerization reaction>

The block copolymer can be manufactured by polymerizing a vinyl aromatic hydrocarbon and a

conjugated diene in a hydrocarbon solvent using an organolithium compound as a polymerization initiator.

Examples of the vinyl aromatic hydrocarbon may include styrene, α -methylstyrene, p-methylstyrene, 2-vinylnaphthalene and divinylbenzene.

Examples of the conjugated diene may include 1,3-butadiene, isoprene, 2,3-dimethyl-1,3-butadiene, 1,3-pentadiene and 1,3-heptadiene.

The content of the vinyl aromatic hydrocarbon of the block copolymer is preferably 90 mass % or lower, more preferably 60 mass % or lower, and still more preferably 40 mass % or lower, from the viewpoint of an improvement effect of the impact resilience.

[0019]

Examples of a method for producing the block copolymer may include methods described in Japanese Patent Publication Nos. 36-19286, 43-17979, 46-32415, 49-36957, 48-2423, 48-4106 and 51-49567, and Japanese Patent Laid-Open No. 59-166518.

Examples of the structure of the block copolymer may include ones represented by the general formulae $(A-B)_n$, $(A-B)_n-A$ and $B-(A-B)_n$.

A represents a polymer block containing a vinyl aromatic hydrocarbon as a main component; and B represents a polymer block containing a conjugated diene as a main component. The boundary between the A block and the B block does not necessarily need to be clearly

distinguished. n represents an integer of 1 or more, and preferably an integer of 1 to 5.

[0020]

In the above, the polymer block A containing a vinyl aromatic hydrocarbon as a main component indicates a copolymer block, of the vinyl aromatic hydrocarbon and a conjugated diene, containing 50 mass % or more of the vinyl aromatic hydrocarbon, preferably 70 mass % or more thereof, and/or a vinyl aromatic hydrocarbon homopolymer block.

The polymer block B containing a conjugated diene as a main component indicates a copolymer block, of the conjugated diene and a vinyl aromatic hydrocarbon, containing more than 50 mass % of the conjugated diene, preferably 60 mass % or more thereof, and/or a conjugated diene homopolymer block.

[0021]

In the case where the polymer block A and the polymer block B are copolymer blocks of a vinyl aromatic hydrocarbon and a conjugated diene, the vinyl aromatic hydrocarbon in the copolymer blocks may be uniformly distributed, or may be distributed in a tapered form.

In the copolymer block moiety, there may coexist a plurality of moieties in which the vinyl aromatic hydrocarbon is uniformly distributed and/or a plurality of moieties in which the vinyl aromatic hydrocarbon is distributed in a tapered form.

Further in the copolymer block moiety, there may coexist a plurality of moieties in which the contents of the vinyl aromatic hydrocarbon are different.

A block copolymer constituting a hydrogenated block copolymer crumb according to the present embodiment may be any mixture of the block copolymers represented by the above general formulae.

[0022]

The proportion (referred to as a block ratio of a vinyl aromatic hydrocarbon) of a vinyl aromatic hydrocarbon polymer block incorporated in a block copolymer before being hydrogenated with respect to the entire vinyl aromatic hydrocarbon in a hydrogenated block copolymer crumb according to the present embodiment is preferably 50 mass % or higher, and is recommended to be more preferably regulated at 70 to 98 mass %. Thereby, when a polymer composition is made by mixing the hydrogenated block copolymer crumb with predetermined materials, the favorably flexible rubbery polymer composition, and the polymer composition excellent in the balance of the impact resistance and the rigidity can be obtained.

It is noted that the block ratio of a vinyl aromatic hydrocarbon is determined from (a content of a vinyl aromatic hydrocarbon polymer block) / (a content of the entire vinyl aromatic hydrocarbon constituting a block copolymer) $\times$ 100.

The block ratio of a vinyl aromatic hydrocarbon is measured by a method of oxidatively decomposing a block copolymer by tertiary butyl peroxide using osmium tetroxide as a catalyst (the method described in I. M. Kolthoff, et al., J. Polym. Sci. 1, 429 (1946)).

[0023]

The microstructure (ratio of cis, trans and vinyl) of a conjugated dienic polymer incorporated in a block copolymer before being hydrogenated can be optionally changed by use of a polar compound and the like described later.

In the case of using 1,3-butadiene as a conjugated diene, the amount of the 1,2-vinyl bond of a block copolymer before being hydrogenated is preferably 10 to 80 %, and more preferably 25 to 75 %; and in the case of using isoprene or 1,3-butadiene and isoprene as conjugated dienes, the total amount of the 1,2-vinyl bond and the 3,4-vinyl bond is preferably 3 to 80 %, and more preferably 5 to 70 %.

The microstructure of a conjugated dienic polymer incorporated in a block copolymer can be determined by making a block copolymer before being hydrogenated into a carbon disulfide solution, measuring an infrared spectrum in the range of 600 to 1,000 cm^{-1} using a solution cell, and using the calculation expression of the Hampton method (styrene-butadiene copolymer) by absorbances at predetermined wave numbers.

[0024]

Examples of the hydrocarbon solvent usable in production of a block copolymer may include an aliphatic hydrocarbon solvent such as butane, pentane, hexane, isopentane, heptane, octane or isooctane; an alicyclic hydrocarbon solvent such as cyclopentane, methylcyclopentane, cyclohexane, methylcyclohexane or ethylcyclohexane; or an aromatic hydrocarbon solvent such as benzene, toluene, ethylbenzene or xylene.

These may be used singly, or may be used as a mixture of two or more.

[0025]

An organolithium compound used as a polymerization initiator in polymerization of a block copolymer is a compound in whose molecule one or more lithium atoms are bonded, and examples thereof may include ethyllithium, n-propyllithium, isopropyllithium, n-butyllithium, sec-butyllithium, tert-butyllithium, hexamethylene lithium, butadienyldilithium and isoprenyldilithium.

These may be used singly, or two or more thereof may be used.

The organolithium compound may be added fractionally in the course of the polymerization in production of a block copolymer.

[0026]

At the time of production of a block copolymer, a predetermined polar compound can be used for the purpose

of a regulation of the polymerization velocity, a change of the microstructure of a polymerized conjugated diene moiety, and others.

Examples of the polar compound may include ethers such as tetrahydrofuran, diethyl ether, dioxane, ethylene glycol dimethyl ether, ethylene glycol dibutyl ether, diethylene glycol dimethyl ether, diethylene glycol dibutyl ether, dimethoxybenzene and 2,2-bis(2-oxolanyl)propane; tertiary amine compounds such as tetramethylethylenediamine, dipiperidinoethane, trimethylamine, triethylamine, pyridine and quinuclidine; alkaline metal alkoxide compounds such as potassium t-amylate, potassium t-butyrate, sodium t-butyrate and sodium amylate; and phosphine compounds such as triphenylphosphine.

[0027]

The polymerization temperature when a block copolymer is produced is preferably -10 to 150°C, and more preferably 30 to 120°C.

The time required for the polymerization is, though depending on the condition, preferably within 48 hours, and more preferably 0.5 to 10 hours.

The atmosphere of a polymerization system is preferably an inert gas atmosphere such as nitrogen gas.

The polymerization pressure suffices if being in the range enough to maintain the monomer and solvent in a

liquid phase in the above polymerization temperature range, and is not especially limited.

Further it is preferable that a state is made in which impurities, such as water, oxygen and carbon dioxide gas, inactivating a catalyst and a living polymer in the polymerization system are not mingled.

[0028]

<Hydrogenation reaction>

The block copolymer is obtained by the above-mentioned <polymerization reaction>, thereafter a proton donor such as an alcohol or water is added, and thereafter the resultant is subjected to a hydrogenation reaction using a hydrogenation catalyst described later, to thereby obtain the hydrogenated block copolymer.

[0029]

The hydrogenation catalyst is not especially limited, and conventionally known ones of (1) carried heterogeneous hydrogenation catalysts in which carbon, silica, alumina, diatomaceous earth or the like carries a metal such as Ni, Pt, Pd or Ru, (2) so-called Ziegler type hydrogenation catalysts using a transition metal salt such as an organic acid salt or an acetylacetone salt of Ni, Co, Fe or Cr, and a reducing agent such as an organoaluminum, and (3) homogeneous hydrogenation catalysts including so-called organometal complexes of Ti, Ru, Rh, Zr or the like are used.

Specific hydrogenation catalysts usable are, for example, hydrogenation catalysts described in Japanese Patent Publication Nos. 42-8704, 43-6636, 63-4841, 1-37970, 1-53851 and 2-9041. Preferable hydrogenation catalysts include a titanocene compound and/or a mixture thereof with a reductive organometal compound.

The titanocene compounds usable are compounds described in Japanese Patent Laid-Open No. 8-109219, and examples thereof may include compounds having at least one ligand having a (substituted) cyclopentadienyl skeleton such as biscyclopentadienyltitanium dichloride or monopentamethylcyclopentadienyltitanium trichloride, an indenyl skeleton or a fluorenyl skeleton.

Examples of the reductive organometal compound may include organic alkaline metal compounds such as organolithiums, organomagnesium compounds, organoaluminum compounds, organoboron compounds and organozinc compounds.
[0030]

The hydrogenation reaction is carried out preferably in the temperature range of 0 to 200°C, and more preferably 30 to 150°C.

The pressure of hydrogen used in the hydrogenation reaction is made preferably 0.1 to 15 MPa, more preferably 0.2 to 10 MPa, and still more preferably 0.3 to 5 MPa.

The hydrogenation reaction time is preferably 3 min to 10 hours, and more preferably 10 min to 5 hours.

The hydrogenation reaction can use any of a batch process, a continuous process, and a combination thereof.

[0031]

The total hydrogenation ratio after the hydrogenation of unsaturated double bonds based on a conjugated diene compound incorporated in a block copolymer before being hydrogenated can be selected optionally according to the purpose, and is not especially limited. Preferably 70 % or more, more preferably 80 % or more, and still more preferably 95 % or more of unsaturated double bonds based on a conjugated diene compound in a block copolymer may be hydrogenated, and only a part thereof may be hydrogenated.

In the case where only a part thereof is hydrogenated, the hydrogenation ratio is preferably 10 % or more and less than 70 %, more preferably 15 % or more and less than 65 %, and still more preferably 20 % or more and less than 60 %.

The hydrogenation ratio of a hydrogenated block copolymer is measured by a nuclear magnetic resonance instrument (NMR).

[0032]

As described above, the hydrogenated block copolymer constituting the hydrogenated block copolymer crumb according to the present embodiment has a main peak molecular weight of 200,000 to 600,000.

The main peak molecular weight can be controlled by regulating the amount of a polymerization initiator.

[0033]

(Treatment of obtaining a hydrogenated block copolymer crumb)

<Step of obtaining an aqueous slurry>

After the solution of the hydrogenated block copolymer is obtained as described above, as required, the catalyst residual is removed, and then, the solution of the hydrogenated block copolymer is placed in a hot water under stirring; and the solvent is removed by steam stripping, to thereby obtain an aqueous slurry in which a hydrogenated block copolymer crumb is dispersed in water.

The treatment method in the steam stripping is not especially limited, and a conventionally known method can be employed.

In the steam stripping, a crumbing agent may be used; and the crumbing agent to be used is usually an anionic surfactant, a cationic surfactant or a nonionic surfactant.

A surfactant as the crumbing agent is added usually in 0.1 to 3,000 ppm to water in a stripping zone. In addition to the surfactant, a water-soluble salt of a metal such as Li, Na, K, Mg, Ca, Al or Zn may be used as a dispersion aid of the crumb.

[0034]

<Step of recovering a hydrogenated block copolymer crumb>

The aqueous slurry, in which the hydrogenated block copolymer crumb is dispersed in water, obtained by the steam stripping as described above is subjected to dehydration and drying treatments by the following steps, to thereby recover a hydrogenated block copolymer crumb.

The recovery step of the hydrogenated block copolymer crumb carries out <step 1> a dehydration treatment, <step 2> a dehydration treatment and a drying treatment, and <step 3> a drying treatment, which are described later.

In <step 2>, a dehydration treatment and a drying treatment may be carried out using respective independent apparatuses, or may be carried out using a so-called integrated extrusion type drying machine having a structure having a dehydration treatment unit and a drying treatment unit, which are communicated.

[0035]

[Step 1]

The aqueous slurry is subjected to a dehydration treatment to thereby obtain a crumb in which the moisture content is higher than 60 mass % and 80 mass % or lower, and crumb components not passing through a sieve having an aperture of 3.35 mm account for 60 mass % or more of the entire crumb.

The moisture content of the crumb after <step 1> is preferably 62 mass % to 80 mass %, and more preferably 65 mass % to 75 mass %.

After <step 1>, crumb components not passing through a sieve having an aperture of 3.35 mm account for preferably 70 mass % or more, and more preferably 80 mass % or more of the entire crumb.

The dehydration treatment in such <step 1> can be carried out using a rotary screen, a vibration screen or a centrifugal dehydration machine.

The case where the moisture content of an obtained crumb exceeds 60 mass % can suppress the decrease of polymer fluidity in an extruder in <step 2> described later; and the case where the moisture content is made 80 mass % or lower can suppress a thermal load to the polymer crumb in the extruder in <step 2> described later.

Further making crumb components not passing through a sieve having an aperture of 3.35 mm account for 60 mass % or more of the entire crumb allows stably carrying out a dehydration and a drying treatment in <step 2> described later, and thereby allows providing a desired specific surface area and particle diameter distribution of the crumb and achieving excellent compound processability.

[0036]

[Step 2]

The crumb having been subjected to the dehydration treatment and made to have a predetermined moisture content as described above by <step 1> is subjected to a dehydration treatment and a drying treatment in <step 2> to thereby make a crumb having a moisture content of 3 to 30 mass %, which is transferred to <step 3> described later.

The moisture content of the crumb after the <step 2> is preferably 3 to 25 mass %, and more preferably 3.2 to 20 mass %.

The dehydration treatment and the drying treatment may be carried out using respective independent apparatuses, but may be carried out using a so-called integrated extrusion type drying machine having a structure having a dehydration treatment unit and a drying treatment unit, which are communicated.

The extrusion type drying machine is an apparatus to carry out a dehydration treatment and a drying treatment, has a dehydration treatment unit and a drying treatment unit wherein the dehydration treatment unit employs an extruder (extruder type water squeezing machine); and the drying treatment unit employs a kneader type drying machine, a screw expander type drying machine or the like. Particularly an extrusion type drying machine having a constitution having a multi-screw extruder such as a single or a twin screw extruder as the dehydration treatment unit and a screw type drying machine as the

drying treatment unit is preferable from the viewpoint of the dehydration efficiency and the workability.

In order to gently control the dehydration of a crumb, a combination of a single screw extruder and a screw type drying machine is especially preferable.

[0037]

A dehydration apparatus, a drying apparatus, and further an extrusion type drying machine having an integrated dehydration treatment unit and a drying treatment unit, specifically, a screw type extruder, a screw type drying machine, an integrated screw extruder type drying machine and the like, which are for carrying out <Step 2>, may be installed with a vent mechanism and a dehydration slit according to use purposes.

[0038]

Making the moisture content of the crumb to be 3 mass% or higher by <Step 2> allows preventing the crumb from being gelatinized and/or decomposed by the shearing force of an extruder; and making the moisture content to be 30 mass% or lower allows easily controlling the moisture content of a crumb obtained in <Step 3> described later at 1 mass% or lower.

[0039]

It is preferable that the outlet port temperature of an apparatus to carry out the drying treatment in <Step 2>, that is, in the case where the dehydration treatment and the drying treatment are carried out by respective

separate apparatuses, the outlet port temperature of an apparatus to carry out the dehydration treatment is made 120°C or lower, and the outlet port temperature of an apparatus to carry out the drying treatment is made 135 to 175°C.

It is more preferable that the outlet port temperature of the apparatus to carry out the dehydration treatment is made 120°C or lower, and the outlet port temperature of the apparatus to carry out the drying treatment is made 138 to 172°C; and it is still more preferable that the outlet port temperature of the apparatus to carry out the dehydration treatment is made 118°C or lower, and the outlet port temperature of the apparatus to carry out the drying treatment is made 140 to 172°C.

In the case of using a so-called two-stage-constitution extrusion type drying machine, in which a dehydration treatment unit and a drying treatment unit are integrated, it is preferable that the temperature of the first-stage outlet port is made 120°C or lower, and the temperature of the second-stage outlet port is made to be 135 to 175°C.

It is more preferable that the temperature of the first-stage outlet port is made 120°C or lower, and the temperature of the second-stage outlet port is made 138 to 172°C; and it is still more preferable that the temperature of the first-stage outlet port is made 118°C

or lower, and the temperature of the second-stage outlet port is made 140 to 172°C.

Setting the temperatures in the above temperature ranges allows stably carrying out the dehydration treatment and the drying treatment, and thereby allows providing a desired specific surface area and particle diameter distribution of the crumb and achieving excellent compound processability.

[0040]

[Step 3]

The crumb obtained in <Step 2> as described above is subjected to a drying treatment using a hot air drying machine to thereby make a crumb having a moisture content of 1 mass% or lower.

The moisture content of the crumb after the <Step 3> is made 1 mass% or lower, preferably 0.95 mass% or lower, and more preferably 0.9 mass% or lower.

Making the moisture content of the dried crumb to be 1 mass% or lower allows preventing appearance faults due to the occurrence of foams, silver streaks and the like in a thermoplastic resin composition obtained after a compounding step.

[0041]

As described above, an aqueous slurry is subjected to a dehydration treatment to thereby obtain a crumb in which the moisture content is higher than 60 mass% and 80 mass% or lower, and crumb components not passing through

a sieve having an aperture of 3.35 mm account for 60 mass% or more of the entire crumb, by <Step 1>; the crumb is subjected to a dehydration treatment and a drying treatment to thereby make the crumb having a moisture content of 3 to 30 mass%, by <Step 2>; and the crumb is subjected to a drying treatment using a hot air drying machine to thereby make the moisture content of the crumb to be regulated at 1 mass% or lower, by <Step 3>.

[0042]

The moisture content and the size of a hydrogenated block copolymer crumb can be determined by methods described in Examples described later.

By specifying the size and the moisture content of a crumb by the above <Step 1> and further specifying the outlet port temperatures of the apparatuses and the moisture contents of the crumbs at the outlet ports by <Step 1> to <Step 3>, the fluidity of the crumb is raised and a reasonably foamed crumb (having a large specific surface area) can be obtained. Further, the pulsating flow in the apparatuses is suppressed and uniform crumbs containing few fine powdery crumbs (passing through a sieve having an aperture of 0.425 mm and being sandy and hard) and few large-particle diameter crumbs (not passing through a sieve having an aperture of 3.35 mm and having nonuniform foams) can be obtained.

The hydrogenated block copolymer crumb according to the present embodiment has a specific surface area of 0.3

to 1.0 m²/g. Components passing through a sieve having an aperture of 3.35 mm and not passing through a sieve having an aperture of 0.425 mm account for 80 mass% or more of the entire crumb.

In order to obtain such a crumb, it is especially effective that the size and the moisture content of a crumb before <Step 2> are regulated and the dehydration and the drying conditions in <Step 2> are optimized.

In detail, if the moisture content of a crumb after <Step 1> is too low, 60% or lower, the dehydration excessively progresses in <Step 2> to thereby reduce the fluidity. By contrast, if the moisture content is too high, higher than 80%, or with respect to the crumb size, crumb components not passing through a sieve having an aperture of 3.35 mm are too few, the stable dehydration and drying treatments cannot be carried out in <step 2>, also resulting in not providing good fluidity.

In <Step 2>, if the moisture content of the crumb is too high, the load in <Step 3> becomes large; and if the moisture content of the crumb is too low, the fluidity of the crumb decreases, foams become nonuniform, and the crumb sizes become nonuniformized. In order to prevent the decrease of the fluidity of the crumb, the nonuniformization of foams and the nonuniformization of the crumb sizes by further excessive drying, the outlet port temperature of the apparatus in the drying treatment in <Step 2> is preferably made 135 to 175°C.

Therefore, as described above, it is effective that the moisture content of the crumb is regulated to be higher than 60 mass% and 80 mass% or lower, and crumb components not passing through a sieve having an aperture of 3.35 mm are made to account for 60 mass% or more of the entire crumb, in <Step 1>, and the moisture content of the crumb is controlled to be 3 to 30 mass%, in <Step 2>.

[0043]

[Polymer composition using the hydrogenated block copolymer crumb]

The hydrogenated block copolymer crumb according to the present embodiment is compounded using a predetermined thermoplastic resin and a softening agent such as a process oil to thereby fabricate a thermoplastic composition to become a material utilizable to various types of applications described later.

In a compound with a thermoplastic resin such as propylene, and a softening agent such as a process oil, various types of additives can be blended according to the purposes. The kind of the additive is not especially limited as long as being usually used for formulation of thermoplastic resins and rubbery polymers. The additives are, for example, inorganic fillers such as metal hydroxides, silica-based inorganic fillers and metal oxides, organic fillers, antioxidants, ultraviolet absorbents, light stabilizers, lubricants such as stearic

acid, behenic acid, zinc stearate, calcium stearate, magnesium stearate and ethylene bis stearamide, release agents, paraffins, plasticizers, flame retardants, antistatic agents, reinforcing materials such as organic fibers, carbon fibers and metal whiskers, pigments, and colorants.

These additives may be added to a solution of the hydrogenated block copolymer crumb, or may be added in the dehydration step and/or the drying step, or may be added after the drying step.

[0044]

[Applications of the hydrogenated block copolymer crumb]

The hydrogenated block copolymer crumb according to the present embodiment can be utilized as modifying agents of various types of thermoplastic resins, materials for footwear, materials for pressure-sensitive adhesive materials and adhesive materials, asphalt modifying agents, and materials of industrial components such as electric wire cables, automobile components, materials for medical implements, household electric products and their components, electronic devices and their components, household commodities and toys.

Examples

[0045]

Hereinafter, the present invention will be described by way of Examples. The present invention is not limited to the following Examples.

[0046]

Analyses of samples in Examples were carried out by methods shown below.

<(1) Amount of bonded styrene>

A chloroform solution of a measurement sample (a block copolymer fabricated by Production Example 1 described below) was prepared and the amount of bonded styrene (mass %) was measured by detecting an absorption at UV 254 nm by a phenyl group of styrene, by using a spectrophotometer (V-550, made by JASCO Corp.).

[0047]

<(2) Main peak molecular weight>

A tetrahydrofuran solution of a hydrogenated block copolymer was prepared, and a chromatogram of a sample was measured using GPC (HLC-8320, made by Tosoh Corp.) of a polystyrenic gel (Shodex, made by Showa Denko K.K.).

The main peak molecular weight was determined using a calibration curve made using peak molecular weights of commercially available standard polystyrenes.

[0048]

<Vinyl bond content>

A carbon disulfide solution of a measurement sample (a block copolymer fabricated in Production Example 1 described below) was prepared, and an infrared spectrum

was measured in the range of 600 to 1,000 cm^{-1} using an infrared spectrophotometer (Spectrum 100, made by PerkinElmer Japan Co., Ltd.) and the vinyl bond content was determined by the calculation expression of the Hampton method (styrene-butadiene copolymer) from the absorbances in the predetermined wave numbers.

[0049]

<(3) Hydrogenation ratio>

The hydrogenation ratio of a hydrogenated block copolymer was measured using a nuclear magnetic resonance instrument (DPX-400, made by Bruker Corporation).

[0050]

<(4) Moisture content in a crumb>

A hydrogenated block copolymer crumb was heated at 150°C for 8 min by a halogen moisture meter, and the mass loss was determined and the moisture content was calculated by the following expression:

Moisture content (mass %) = a mass loss (amount of moisture in a crumb) between before and after the heating / a mass of a hydrogenated block copolymer crumb before the heating $\times 100$

[0051]

<(5) Specific surface area of a crumb>

An adsorption isotherm by nitrogen of a hydrogenated block copolymer was measured and the specific surface area was determined by the BET multi-point method.

The measurement instrument used was a BELSORP-mini (made by BEL Japan, Inc.) and the measurement was carried out at an adsorption temperature of 77 K.

[0052]

<(6) Crumb size>

A sieve shaker (Octagon Digital, made by Seishin Enterprise Co., Ltd.) was used, and a sieve having an aperture of 3.35 mm was superposed on a sieve having an aperture of 0.425 mm; a crumb was placed on the sieve having an aperture of 3.35 mm, and shaken for 15 min; the amounts of the crumb remaining on the respective sieves and the amounts of the crumb having passed the respective sieves were measured; and the proportion (mass %) of the crumb not having passed through the sieve having an aperture of 3.35 mm, and the proportion (mass %) of the crumb whose size was 0.425 to 3.35 mm were calculated.

[0053]

<(7) Uniformity of oil absorption>

100 g of a paraffin-based process oil (Diana Process Oil PW90, made by Idemitsu Petrochemical Co., Ltd.) colored with an ink dropped therein was placed in 100 g of a hydrogenated block copolymer crumb, and stirred so that the process oil extended in the entire crumb, and thereafter allowed to stand for 10 min.

An image of the entire crumb after the standing-still was binarized, and the areal ratio of a colored portion (a ratio of the crumb having absorbed the oil) was calculated.

[0054]

<(8) Oil holding power>

10 g of a hydrogenated block copolymer crumb was put in a cylindrical vessel having a diameter of about 3 cm; 10 g of a paraffin-based process oil (Diana Process Oil PW90, made by Idemitsu Petrochemical Co., Ltd.) colored with an ink dropped therein was placed on the hydrogenated block copolymer, and allowed to stand for 5 min; and the mass of the crumb not having been colored with the ink was measured.

The ratio of a mass (10 g) of the paraffin-based process oil colored with the ink and a mass of the crumb colored with the ink was calculated by the following expression, and an acquired value was taken as an oil holding power:

Oil holding power = a mass (10 g) of the paraffin-based process oil / [an entire mass (10 g) of the crumb - a mass (g) of the crumb not having been colored with the ink]

In this evaluation, a state was made in which out of the crumb stacked in the cylindrical vessel, only the

crumb of the upper part was dyed in the color of the oil, and the crumb of the lower part was not dyed in the color of the oil. If the oil holding power was high, the oil stayed in the crumb of the upper part, meaning that a small amount of the crumb could hold a certain amount of the oil.

[0055]

<(9) Number of unmelted polymers in a compound>

An unmelted polymer refers to a polymer in a state where the crumb is not completely melted and remains as an unmelted polymer in a compound.

24.57 g of a paraffin-based process oil (Diana Process Oil PW90, made by Idemitsu Petrochemical Co., Ltd.) was added to 16.38 g of a hydrogenated block copolymer crumb, and stirred so that the process oil was spread uniformly.

Then, the resultant was allowed to stand at room temperature for 20 min to thereby make the oil to be absorbed.

Thereafter, 9.01 g of a polypropylene (PL500A, made by SunAllomer Ltd.) and 0.04 g of n-octadecyl-3-(3,5-di-t-butyl-4-hydroxyphenyl)-propionate (product name: Irganox 1076) were added thereto, and kneaded at 160°C at 70 rpm for 20 min using a Labo Plastomill (4M150, made by Toyo Seiki Seisaku-sho, Ltd.).

Each at 3 min and 20 min after the initiation of the kneading, 2 g of a compound sample was sampled, and a

sheet having a diameter of about 15 cm and a thickness of about 60 μm was made by compression molding; and the number of fish eyes (unmelted polymers) having a diameter of about 100 μm or larger in the sheet was counted using a magnifying glass ("Meister Loupe LB," made by As One Corp., a magnification: 3.5 times).

Figure 1 shows a cross-sectional photograph of a sheet having a fish eye (unmelted polymer, diameter: A). Actually, the fish eyes were observed as dots on the surface.

The difference in the number of fish eyes (unmelted polymers) between after 3 min (the compound became a uniform state, but unmelted polymers remain) and after 20 min (the unmelted polymers were wholly melted) was taken as the number of unmelted polymers in a compound.

[0056]

(Production Example 1: a method for producing a block copolymer)

An autoclave installed with a stirrer and a jacket and capable of controlling the temperature was used as a reactor; and under a nitrogen gas atmosphere, a cyclohexane solution of 16 parts by mass of styrene from which impurities had been removed, 0.14 parts by mass of tetrahydrofuran, and 0.03 parts by mass of tetramethylenediamine was prepared, and after the temperature of the reactor interior was held at 50°C, 0.06 parts by mass of n-butyllithium as a polymerization

initiator was fed to the reactor to carry out polymerization.

Then, 68 parts by mass of butadiene was fed and polymerization was carried out, and finally, 16 parts by mass of styrene was fed and polymerization was carried out to thereby obtain a block copolymer having an S-B-S structure (S represented a polystyrene block, and B represented a polybutadiene block).

The obtained block copolymer had a styrene content of 32 mass %, a main peak molecular weight of 280,000 and a vinyl bond content of the butadiene moiety of 36 %.

[0057]

(Production Example 2: a method for producing a hydrogenated block copolymer)

100 ppm in terms of Ti of a hydrogenation catalyst (the molecular ratio of bis(η^5 -cyclopentadienyl)titanium dichloride/trimethylaluminum = 1/2) obtained by mixing cyclohexane with a n-hexane solution containing bis(cyclopentadienyl)titanium dichloride and trimethylaluminum, and allowing the mixture to react at room temperature for 3 days, was added to the solution of the block copolymer obtained in the above Production Example 1, and was subjected to a hydrogenation reaction at a hydrogen pressure of 0.7 MPa at a temperature of 95°C for 1 hour. The hydrogenation ratio of the butadiene moiety of the obtained hydrogenated block copolymer was 98 %.

[0058]

[Examples 1 to 4] and [Comparative Examples 1 to 4]

Water as a reaction quenching agent of 5 mol times the amount of n-butyllithium used in the polymerization was added to the solution of the hydrogenated block copolymer obtained in the above Production Examples 1 and 2, and thereafter 0.25 parts by mass of n-octadecyl-3-(3,5-di-t-butyl-4-hydroxyphenyl)-propionate (product name: Irganox 1076) as a stabilizer was added with respect to 100 parts by mass of the hydrogenated block copolymer.

This hydrogenated block copolymer solution was subjected to a steam stripping at 95°C for 1 hour. The steam stripping was carried out by adding a styrene-maleic anhydride copolymer Na salt (hereinafter, a crumbing agent A) of the amount shown in Table 1 as a crumbing agent.

The concentration of the hydrogenated block copolymer crumb in the obtained aqueous slurry was 5 mass %.

Then, the aqueous slurry containing the hydrogenated block copolymer crumb obtained in the above was transported to a vibrating screen having an aperture of 1 mm, and subjected to a dehydration treatment (<step 1>); and thereafter, the moisture content of the hydrogenated block copolymer crumb having been subjected to <step 1>

was measured by the method of the above (4), and the crumb size was measured by the method of the above (6).

The moisture content (mass %) and the crumb size (a proportion of components not passing through a sieve having an aperture of 3.35 mm) (mass %) of the hydrogenated block copolymer crumb obtained by <step 1> are shown in the following Table 1.

[0059]

For the hydrogenated block copolymer crumb, in Examples 1 to 4 and Comparative Examples 1 to 4, the dehydration treatment and the drying treatment were carried out using respective separate apparatuses.

First, the hydrogenated block copolymer crumb was fed to a single-screw extruder type water squeezing machine, and extruded at a screw rotation frequency of about 80 rpm to carry out a dehydration treatment (the first stage of <step 2>).

The outlet port temperature of the single-screw extruder type water squeezing machine is shown in the following Table 1.

Then, the hydrogenated block copolymer crumb obtained in the above was fed to a single-screw type expander drying machine, and extruded at a screw rotation frequency of about 80 rpm to carry out a drying treatment (the second stage of <step 2>).

The outlet port temperature of the single-screw type expander drying machine and the moisture content of the obtained crumb are shown in the following Table 1.

[0060]

Thereafter, the hydrogenated block copolymer crumb obtained in the above was subjected to a drying treatment with a hot air at about 90°C using a vibrating transport drying machine (<step 3>).

The moisture content, the specific surface area, the crumb size, the oil absorption uniformity, the oil holding power, and the number of unmelted polymers in the compound of the dried crumb finally obtained are shown in the following Table 1.

[0061]

Whereas the crumbs of Examples 1 to 4 gave good oil absorption uniformities, exhibited high oil holding powers, and had the numbers of unmelted polymers in the compound of 10 or less, the crumbs of Comparative Examples 1 to 4 could not give practically good oil absorption uniformities, and exhibited low oil holding powers, and had the numbers of unmelted polymers in the compound of 15 or more.

[0062]

[Table 1]

		Example 1	Example 2	Example 3	Example 4	Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4
Steam stripping condition	Crumbing agent (ppm / hydrogenated block copolymer)	A	A	A	A	A	A	A	A
		450	450	500	450	450	400	300	350
(Step 1) Aqueous slurry dehydration treatment	Moisture content of crumb (mass %)	75	62	80	70	70	80	45	75
	Crumb size Components not passing through a sieve having an aperture of 3.35 mm (mass %)	85	85	90	85	85	80	80	75
(Step 2) Dehydration and drying treatments	[First stage] Single-screw extruder type water squeezing machine								
	Outlet port temperature (°C)	98	105	107	110	135	85	125	110
	[Second stage] Single-screw type expander drying machine								
	Outlet port temperature (°C)	135	140	155	170	185	130	180	185
	Moisture content of outlet port crumb (mass %)	10.5	5.5	4.8	3.2	2.1	35	2.5	3.5
(Step 3) Crumb after hot air drying	Moisture content of crumb (mass %)	0.88	0.52	0.42	0.2	0.15	0.92	0.3	0.21
	Specific surface area (m ² / g)	0.42	0.45	0.55	0.55	0.35	0.15	0.35	0.38
	Crumb size 0.425 to 3.35 mm (mass %)	100	96	82	95	70	100	65	75
	Oil absorption uniformity (%)	75	73	76	72	63	61	59	65
	Oil holding power	3.1	2.9	3.2	3	2.2	2	2.1	2.3
The number of unmelted polymers in compound		9	9	8	8	15	16	18	14

[0063]

[Examples 5 to 8] and [Comparative Examples 5 to 9]

Water as a reaction quenching agent of 5 mol times the amount of n-butyllithium used in the polymerization was added to the solution of the hydrogenated block copolymer obtained in the above Production Examples 1 and 2, and thereafter 0.25 parts by mass of n-octadecyl-3-(3,5-di-t-butyl-4-hydroxyphenyl)-propionate (product name: Irganox 1076) as a stabilizer was added with respect to 100 parts by mass of the hydrogenated block copolymer.

This hydrogenated block copolymer solution was subjected to a steam stripping at 95 °C for 1 hour. The steam stripping was carried out by adding a crumbing agent A of the amount shown in Table 2 as a crumbing agent.

The concentration of the hydrogenated block copolymer crumb in the obtained aqueous slurry was 5 mass %.

Then, the aqueous slurry containing the hydrogenated block copolymer crumb obtained in the above was transported to a vibrating screen having an aperture of 1 mm, and subjected to a dehydration treatment (<step 1>); and thereafter, the moisture content was measured by the method of the above (4), and the crumb size was measured by the method of the above (6). The moisture content (mass %) and the crumb size (a proportion of components

not passing through a sieve having an aperture of 3.35 mm) (mass %) of the hydrogenated block copolymer crumb obtained by <step 1> are shown in the following Table 2.

The hydrogenated block copolymer crumb was fed to a two-stage single-screw extruder in which a dehydration treatment unit (first stage) and a drying treatment unit (second stage) were integrated, and extruded at a screw rotation frequency of about 80 rpm to carry out a dehydration treatment and a drying treatment (the first stage and the second stage of <step 2>).

The two-stage single-screw extruder used had a slit in the dehydration treatment unit of the first stage, but was operated with the slit totally closed in order to hold the moisture in the crumb until the drying treatment unit of the second stage.

The respective outlet port temperatures (a first stage outlet port temperature and a second stage outlet port temperature) of the dehydration treatment unit and the drying treatment unit, and the moisture content of the crumb obtained from the outlet port of the drying treatment unit are shown in the following Table 2.

[0064]

Thereafter, the hydrogenated block copolymer crumb obtained in the above was subjected to a drying treatment with a hot air at about 90 °C using a vibrating transport drying machine to thereby obtain a dried crumb (<step 3>).

The moisture content, the specific surface area, the crumb size, the oil absorption uniformity, the oil holding power, and the number of unmelted polymers in the compound of the hydrogenated block copolymer crumb finally obtained are shown in the following Table 2.

[0065]

Whereas the crumbs of Examples 5 to 8 gave good oil absorption uniformities, exhibited high oil holding powers, and had the numbers of unmelted polymers in the compound of 10 or less, the crumbs of Comparative Examples 5 to 8 could not give practically good oil absorption uniformities, and exhibited low oil holding powers, and had the numbers of unmelted polymers in the compound of 15 or more.

The crumb of Comparative Example 9 had too much an amount of moisture, and could not be placed in the drying machine, making it impossible to carry out the dehydration treatment and the drying treatment.

[0066]

[Comparative Example 10]

<Step 1> and <step 2> were carried out under the same conditions as in Comparative Example 8, and thereafter, <step 3> was not carried out, to thereby obtain a hydrogenated block copolymer crumb.

The moisture content, the specific surface area, the crumb size, the oil absorption uniformity, the oil holding power, and the number of unmelted polymers in the

compound of the obtained crumb are shown in the following Table 2.

Comparative Example 10 could not give a practically good oil absorption uniformity, and exhibited a low oil holding power, and had the number of unmelted polymers in the compound of 15 or more.

[0067]

[Comparative Example 11]

Water as a reaction quenching agent of 5 mol times the amount of n-butyllithium used in the polymerization was added to the solution of the hydrogenated block copolymer obtained in the above Production Examples 1 and 2, and thereafter 0.25 parts by mass of n-octadecyl-3-(3,5-di-t-butyl-4-hydroxyphenyl)-propionate (product name: Irganox 1076) as a stabilizer was added with respect to 100 parts by mass of the hydrogenated block copolymer.

This hydrogenated block copolymer solution was subjected to a steam stripping at 95 °C for 1 hour. The steam stripping was carried out by adding 800 ppm of a polyoxyethylene alkyl ether phosphoric acid (hereinafter, crumbing agent B) as a crumbing agent to the hydrogenated block copolymer.

The concentration of the hydrogenated block copolymer crumb in the obtained aqueous slurry was 5 mass%.

Then, the aqueous slurry containing the hydrogenated block copolymer crumb obtained in the above was transported to a vibrating screen having an aperture of 1 mm, and subjected to a dehydration treatment (<step 1>); and thereafter, the moisture content was measured by the method of the above (4), and the crumb size was measured by the method of the above (6). The moisture content (mass %) and the crumb size (a proportion of components not passing through a sieve having an aperture of 3.35 mm) (mass %) of the crumb obtained by <step 1> are shown in the following Table 2.

The crumb was not subjected to the above-mentioned <step 2>, and was subjected to a drying treatment with a hot air at about 90°C using a vibrating transport drying machine to thereby obtain a dried crumb (<step 3>).

The moisture content, the specific surface area, the crumb size, the oil absorption uniformity, the oil holding power, and the number of unmelted polymers in the compound of the hydrogenated block copolymer crumb finally obtained are shown in the following Table 2.

[0068]

The crumb of Comparative Example 11 could not give a practically good oil absorption uniformity, and exhibited a low oil holding power, and had the number of unmelted polymers in the compound of 15 or more.

[0069]

[Table 2]

		Example 5	Example 6	Example 7	Example 8	Comparative Example 5	Comparative Example 6	Comparative Example 7	Comparative Example 8	Comparative Example 9	Comparative Example 10	Comparative Example 11
Steam stripping condition	Crumbing agent (ppm / hydrogenated block copolymer)	A	A	A	A	A	A	A	A	A	A	B
		500	500	450	450	450	400	400	400	600	400	300
(Step 1) Aqueous slurry dehydration treatment	Moisture content of crumb (mass %)	75	62	80	70	70	80	45	13	90	13	75
	Crumb size Components not passing through a sieve having an aperture of 3.35 mm (mass %)	90	90	85	85	85	80	80	80	60	80	20
(Step 2) Dehydration and drying treatments	Two-stage single-screw type extruder											-
	First-stage outlet port temperature (°C)	98	105	110	118	135	85	125	130	drying was impossible	130	-
	Second-stage outlet port temperature (°C)	143	158	170	172	182	142	180	180		180	-
	Moisture content of second-stage outlet port crumb (mass %)	10	4.8	5.9	3.3	1.8	35	2	0.8		0.8	-
(Step 3) Crumb after hot air drying, in Examples 5 to 8, Comparative Examples 5 to 8 and Comparative Example 11	Moisture content of crumb (mass %)	0.25	0.18	0.45	0.19	0.15	0.85	0.35	0.18		-	0.75
	Specific surface area (m ² / g)	0.6	0.55	0.62	0.45	0.5	0.25	0.4	0.12		0.11	0.2
	Crumb size 0.425 to 3.35 mm (mass %)	96	85	82	95	75	100	78	80		82	80
	Oil absorption uniformity (%)	75	72	75	72	58	64	62	57		53	55
	Oil holding power	3.2	3.1	3.5	3	2.4	2.2	2	2		1.9	1.9
The number of unmelted polymers in compound		7	10	8	8	18	16	15	18		18	17

[0070]

In Table 2, Comparative Example 10 was an example in which after <step 1> and <step 2> were carried out under the same conditions as in Comparative Example 8, <step 3> was not carried out; and properties of the crumb after <step 2> were shown.

In Table 2, for Comparative Example 11, properties of the crumb after <step 1> was carried out, <step 2> was not carried out, and <step 3> was carried out were shown.

[0071]

The present application is based on Japanese Patent Application No. 2010-242313, filed on Oct. 28, 2010 to the Japan Patent Office, the subject of which is incorporated herein by reference.

Industrial Applicability

[0072]

The hydrogenated block copolymer crumb according to the present invention has the industrial applicability as a material for materials for medical implements, household electric products and their components, electronic devices and their components, various types of industrial components such as electric wire cables, automobile components, and toys.

Claims

[Claim 1]

A hydrogenated block copolymer crumb comprising a hydrogenated substance of a block copolymer of a vinyl aromatic hydrocarbon and a conjugated diene,

wherein the crumb satisfies the following (1) to (4):

- (1) a main peak molecular weight is 200,000 to 600,000;
- (2) a moisture content is 1 mass % or lower;
- (3) a specific surface area is 0.3 to 1.0 m²/g; and
- (4) components passing through a sieve having an aperture of 3.35 mm, and not passing through a sieve having an aperture of 0.425 mm account for 80 mass % or more of the entire crumb.

[Claim 2]

A method for producing the hydrogenated block copolymer crumb according to claim 1, comprising the following <step 1> to <step 3>:

<step 1>: a step of subjecting an aqueous slurry containing a hydrogenated block copolymer crumb to a dehydration treatment to thereby obtain a crumb wherein the crumb has a moisture content of higher than 60 mass % and 80 mass % or lower, and crumb components not passing through a sieve having an aperture of 3.35 mm account for 60 mass % or more of the entire crumb;

<step 2>: a step of subjecting the crumb obtained in the <Step 1> to a dehydration treatment and a drying treatment to thereby obtain a crumb having a moisture content of 3 to 30 mass %; and

<step 3>: a step of subjecting the crumb obtained in the <Step 2> to a drying treatment to thereby obtain a crumb having a moisture content of 1 mass% or lower.

[Claim 3]

The method for producing the hydrogenated block copolymer crumb according to claim 2, wherein an apparatus outlet port temperature in the drying treatment in the <Step 2> is made 135 to 175°C (inclusive).

[Claim 4]

The method for producing the hydrogenated block copolymer crumb according to claim 2 or 3, comprising:

using an extrusion type drying machine having a dehydration treatment unit and a drying treatment unit wherein the dehydration treatment unit and the drying treatment unit are communicated, in the <Step 2>;

carrying out the dehydration treatment by the dehydration treatment unit; and

carrying out the drying treatment by the drying treatment unit.

[Claim 5]

The method for producing the hydrogenated block copolymer crumb according to claim 4, wherein an outlet port temperature of the dehydration treatment unit is

120°C or lower, and an outlet port temperature of the drying treatment unit is 135 to 175°C.