

DESCRIPTION

Title of Invention

METHOD FOR PREVENTING MUTUAL ADHESION OF PELLETS FOR SOLAR
5 CELL SEALING MATERIALS

Technical Field

The present invention relates to a method for
preventing the mutual adhesion of pellets for solar cell
10 sealing materials, and the like.

Background Art

Methods for preventing the mutual adhesion of
pellets by coating the surfaces of the pellets with
15 inorganic compound powder or a low molecular-weight
polyethylene wax are known (Japanese Unexamined Patent
Application Publication No. 1-288408, Japanese Unexamined
Patent Application Publication No. 2001-342259, and
Japanese Examined Patent Application Publication No. 2-
20 014934).

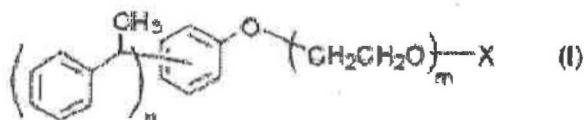
Summary of Invention

The present invention includes the following
inventions.

25 [1] A method for preventing the mutual adhesion of

pellets for solar cell sealing materials, in which a water-based emulsion comprising an ethylene-unsaturated ester copolymer and a surfactant containing no metals is imparted to pellets for solar cell sealing materials.

5 [2] The method according to [1], in which the surfactant containing no metals comprises at least one surfactant selected from the group consisting of a surfactant represented by the formula (I) and a surfactant that has a different structure from the surfactant
10 represented by the formula (I), has at least one group selected from the group consisting of an oxyethylene group and an oxypropylene group, and is a liquid at 10°C to 50°C:



wherein, in the formula (I), X represents a hydrogen atom
15 or $-\text{SO}_3\text{M}$, M represents a hydrogen atom or NH_4 , n represents an integer of 1 to 3, and m represents an integer of 1 to 100.

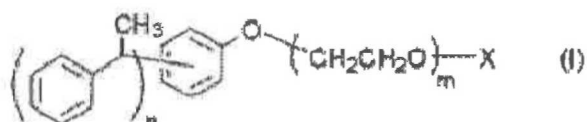
[3] The method according to [3], in which the surfactant containing no metals comprises the surfactant
20 represented by the formula (I).

[4] The method according to [2] or [3], in which the surfactant containing no metals comprises the surfactant represented by the formula (I) and the surfactant that has

a different structure from the surfactant represented by the formula (I), has at least one structure selected from the group consisting of an oxyethylene group and an oxypropylene group, and is a liquid at 10°C to 50°C.

5 [5] A mutual adhesion inhibitor of pellets for solar cell sealing materials, comprising an ethylene-unsaturated ester copolymer and a surfactant containing no metals.

[6] The mutual adhesion inhibitor according to [5], in which the surfactant containing no metals comprises at least one surfactant selected from the group consisting of a surfactant represented by the formula (I) and a surfactant that has a different structure from the surfactant represented by the formula (I), has at least one structure selected from the group consisting of an oxyethylene group and an oxypropylene group, and is liquid at 10°C to 50°C:



wherein, in the formula (I), X represents a hydrogen atom or $-\text{SO}_3\text{M}$, M represents a hydrogen atom or NH_4 , n represents an integer of 1 to 3, and m represents an integer of 1 to 100.

[7] The mutual adhesion inhibitor according to [6], in which the surfactant containing no metals comprises the

surfactant represented by the formula (I).

[8] The mutual adhesion inhibitor according to [6] or [7], in which the surfactant containing no metals comprises the surfactant represented by the formula (I)

5 and the surfactant that has a different structure from the surfactant represented by the formula (I), has at least one structure selected from the group consisting of an oxyethylene group and an oxypropylene group, and is a liquid at 10°C to 50°C.

10 [9] The mutual adhesion inhibitor according to any one of [5] to [8], in which an average particle diameter is not less than 0.01 μm and not more than 30 μm .

[10] A pellet for solar cell sealing materials, in which the mutual adhesion inhibitor according to any one
15 of [5] to [9] has adhered to the surface thereof.

[11] A method for producing a pellet for solar cell sealing materials having a mutual adhesion inhibitor adhered to the surface of the pellet for solar cell sealing materials, in which a water-based emulsion
20 comprising an ethylene-unsaturated ester copolymer and a surfactant containing no metals is imparted to the surface of the pellet for solar cell sealing materials.

[12] A solar cell sealing material obtained by using the pellet for solar cell sealing materials according to
25 [10].

Mode for Carrying Out the Invention

<Water-based emulsion>

A water-based emulsion comprises an ethylene-
5 unsaturated ester copolymer and a surfactant containing no
metals.

<Ethylene-unsaturated ester copolymer>

The water-based emulsion comprises an ethylene-
unsaturated ester copolymer.

10 The content rate of a structural unit derived from
the unsaturated ester of the ethylene-unsaturated ester
copolymer is preferably not less than 10 mass% and not
more than 35 mass%, more preferably not less than 15 mass%
and not more than 30 mass%, and still more preferably not
15 less than 18 mass% and not more than 30 mass% from the
viewpoint of improving workability and transparency. If
the ethylene-unsaturated ester copolymer includes
structural units derived from two or more of the
unsaturated esters, the total of the content rates of all
20 structural units derived from the unsaturated esters
included in the ethylene-unsaturated ester copolymer is
considered as the content rate of the structural unit
derived from the unsaturated ester.

Examples of the unsaturated ester include carboxylic
25 acid vinyl ester, and unsaturated carboxylic acid alkyl

ester. Examples of the carboxylic acid vinyl ester include vinyl acetate, and vinyl propionate. Examples of the unsaturated carboxylic acid alkyl ester include methyl acrylate, ethyl acrylate, butyl acrylate, methyl
5 methacrylate, ethyl methacrylate, and glycidyl methacrylate.

Examples of the ethylene-unsaturated ester copolymer include an ethylene-vinyl acetate copolymer, an ethylene-vinyl propionate copolymer, an ethylene-methyl acrylate
10 copolymer, an ethylene-ethyl acrylate copolymer, an ethylene-butyl acrylate copolymer, an ethylene-methyl methacrylate copolymer, an ethylene-ethyl methacrylate copolymer, an ethylene-glycidyl methacrylate copolymer, and an ethylene-vinyl acetate-methyl methacrylate
15 copolymer.

The melt flow rate (MFR) of the ethylene-unsaturated ester copolymer is preferably not less than 4 g/10 minutes and not more than 100 g/10 minutes from the viewpoint of improving workability. The upper limit of MFR is more
20 preferably 40 g/10 minutes or less. The lower limit of MFR is more preferably 5 g/10 minutes or more. MFR is measured using the method specified by JIS K7210-1995 under conditions of a temperature of 190°C and a load of 21.18 N.

25 Examples of the ethylene-vinyl acetate copolymer

include SUMITATE KA-40 (manufactured by Sumitomo Chemical Co., Ltd.), examples of the ethylene-methyl methacrylate copolymer include ACRYFT WH303 and ACRYFT WH302 (both manufactured by Sumitomo Chemical Co., Ltd.), and examples
5 of the ethylene-glycidyl methacrylate copolymer include BONDFAST E and BONDFAST CG5001 (both manufactured by Sumitomo Chemical Co., Ltd.).

The content of the ethylene-unsaturated ester copolymer is, with respect to the total amount of the
10 water-based emulsion, ordinarily 80 mass% or less, preferably 70 mass% or less, and more preferably 60 mass% or less, and is, for example, 10 mass% or more, preferably 15 mass% or more, more preferably 20 mass% or more, and still more preferably 30 mass% or more.

15 The ethylene-unsaturated ester copolymer can be manufactured by carrying out a radical polymerization reaction of an ethylene and an unsaturated ester as monomers using a radical polymerization initiator. Examples of a polymerization tank (polymerization reactor)
20 in which the radical polymerization reaction takes place include a vessel reactor and a tubular reactor.

<Other resins>

The water-based emulsion may also comprise a resin or resins other than the ethylene-unsaturated ester
25 copolymer.

Examples of the other resins include a variety of polymers and copolymers, such as a polyolefin-based resin, an acrylic resin (PMMA), a polyvinyl chloride (PVC), a polyvinylidene chloride, a polystyrene (PS), a polyvinyl acetate (PVAc), a polytetrafluoroethylene (PTFE), an acrylonitrile butadiene styrene resins (ABS resins), and an AS resin as well as modified polymers and modified substances. These may be solely used, or two or more of these may be blended.

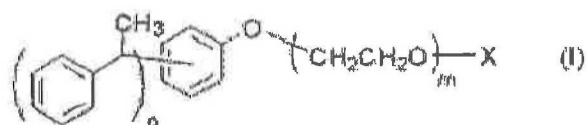
10 <Surfactant>

The surfactant refers to an amphipathic molecule that serves as an emulsifier, and the surfactant containing no metals in the present invention refers to the amphipathic molecule containing no counter metal cations. Surfactants containing no metals may be used individually or in combination. Preferably, the surfactants are used in combination.

Examples of the surfactant containing no metals include a high-molecular surfactant and a low-molecular surfactant, including a cationic surfactant, an anionic surfactant, a nonionic surfactant, and an amphoteric surfactant thereof. The anionic surfactant and the nonionic surfactant are preferred, and the anionic surfactant is more preferred.

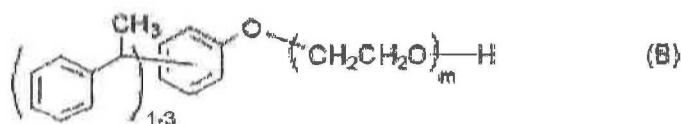
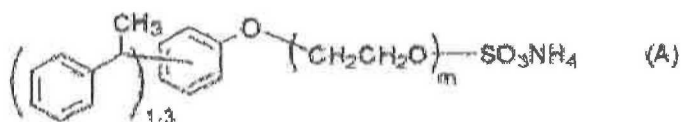
25 The surfactant represented by the formula (I) is

preferable.



(In the formula (I), X represents a hydrogen atom or $-\text{SO}_3\text{M}$, and M represents a hydrogen atom or NH_4 . n represents an integer of 1 to 3. m represents an integer of 1 to 100.)

Examples of the anionic surfactant include a sulfuric acid ester salt of a higher alcohol, a higher alkylsulfonate, a higher carboxylate, an alkylbenzene sulfonate, a polyoxyethylene alkylsulfate salt, a polyoxyethylene alkylphenyl ether sulfate salt, a vinyl sulfosuccinate, and a compound represented by the formula (A). The compound represented by the formula (A) is preferred.



Examples of the high-molecular anionic surfactant include acrylic acid, methacrylic acid, a copolymer of esters thereof, and a maleic anhydride-styrene copolymers.

Examples of the cationic surfactant include alkyl

ammonium salts such as a dodecyl trimethyl ammonium salt and a cetyl trimethyl ammonium salt, alkyl pyridium salts such as a cetyl pyridium salt and a decyl pyridium salt, oxyalkylene trialkylammonium salts, dioxyalkylene
5 dialkylammonium salts, and aryltrialkylammonium salts, diaryldialkylammonium salts.

Examples of the nonionic surfactant include polyoxyethylene alkyl ethers such as a polyoxyethylene propylene ether, compounds having a polyoxyethylene structure such
10 as a polyoxyethylene alkyl phenyl ether, a polyethylene glycol fatty acid ester, an ethylene oxide-propylene oxide block copolymer, a polyoxyethylene fatty acid amide, an ethylene oxide-propylene oxide copolymer, a compound represented by the formula (B), and sorbitan derivatives
15 such as polyoxyethylene sorbitan fatty acid ester.

Examples of the high-molecular nonionic surfactant include a polyethylene glycol-polypropylene glycol copolymer.

Examples of the amphoteric surfactant include a
20 lauryl betaine, and a lauryldimethylamine oxide.

Specific examples of the surfactant containing no metals include the surfactant described in Japanese Unexamined Patent Application Publication No. 58-127752, LATEMUL AD-25 (manufactured by Kao Corporation), LATEMUL
25 E-1000A (manufactured by Kao Corporation), and NOIGEN EA-

177 (manufactured by Dai-ichi Kogyo Seiyaku Co., Ltd.).
Among these, LATEMUL E-1000A (manufactured by Kao Corporation) is preferred.

The above-described surfactants are readily
5 available on the market.

In addition, examples of the preferable surfactant containing no metals include such a surfactant that has at least one structure selected from the group consisting of an oxyethylene group and an oxypropylene group, and is a
10 liquid at 10°C to 50°C. The use of the surfactants is preferred since it is capable of preventing the mutual adhesion of wet pellets by use thereof.

The surfactant may be anionic, cationic, nonionic, or amphoteric, and may have an aromatic group or only have
15 an aliphatic structure. Preferably, the surfactant is nonionic, and only has an aliphatic structure. Among the above-described surfactants, a surfactant having an oxypropylene group is preferred.

Examples of the surfactant include polyoxyethylene
20 alkyl ethers, such as polyoxyethylene propylene ether, polyoxyethylene alkyl phenyl ethers, polyethylene glycol fatty acid esters, ethylene oxide-propylene oxide copolymers, polyoxyethylene fatty acid amides, and polyoxyethylene sorbitan fatty acids. The surfactant is
25 preferably an ethylene oxide-propylene oxide copolymer.

Among the above-described surfactants, a polyethylene oxide-polypropylene oxide block copolymer is more preferred.

The above-described surfactants are readily
5 available on the market. Examples of such commercially available surfactants include PLURONIC L-62, PLURONIC L-64, PLURONIC L-81, and PLURONIC L-92 (manufactured by Adeka Corporation).

The surfactant containing no metals is particularly
10 preferably a combination of a surfactant represented by the formula (I) and a surfactant that has at least one structure selected from the group consisting of an oxyethylene group and an oxypropylene group, and is a liquid at 10°C to 50°C.

15 The content of the surfactant containing no metals is, with respect to 100 parts by mass of the ethylene-unsaturated ester copolymer, normally from 0.1 parts by mass to 50 parts by mass, preferably from 0.1 parts by mass to 20 parts by mass, and more preferably from 0.1
20 parts by mass to 10 parts by mass.

If the water-based emulsion comprises a surfactant that has at least one structure selected from the group consisting of an oxyethylene group and an oxypropylene group, and is a liquid at 10°C to 50°C, and other
25 surfactants containing no metals other than the surfactant,

the content of the surfactant that has at least one structure selected from the group consisting of an oxyethylene group and an oxypropylene group, and is a liquid at 10°C to 50°C, with respect to the total amount of the surfactants containing no metals is normally 0.1 mass% or more, preferably 1 mass% or more, and more preferably 2 mass% or more, and is normally 30% or less, preferably 20% or less, and more preferably 10% or less.

<Basic compound>

10 The water-based emulsion may further comprise a basic compound.

 The basic compound is preferably a compound capable of neutralizing a carboxyl group; and for example ammonia and an organic amine compound are preferable. An organic amine compound having a boiling point of 200°C or lower is particularly preferred when the performance of preventing the mutual adhesion of pellets should be improved by using a water-based emulsion, since the compound can be easily evaporated by ordinary drying.

20 Examples of the organic amine compound include triethylamine, N,N-dimethylethanolamine, aminoethanolamine, N-methyl-N,N-diethanolamine, isopropylamine, iminobispropylamine, ethylamine, diethylamine, 3-ethoxypropylamine, 3-diethylaminopropylamine, sec-
25 butylamine, propylamine, methylaminopropylamine, 3-

methoxypropylamine, monoethanolamine, morpholine, N-methylmorpholine, and N-ethylmorpholine. Among these, N,N-dimethylethanolamine and the like are preferred.

If the water-based emulsion comprises the basic
5 compound, the content thereof is preferably from 1 mass% to 30 mass%, more preferably from 2 mass% to 20 mass%, and still more preferably from 2 mass% to 10 mass% with respect to the ethylene-unsaturated ester copolymer.

<Water>

10 For the water contained in the water-based emulsion, tap water, deionized water, or the like is ordinarily used.

<Solvent>

The water-based emulsion preferably comprises no solvent, but may comprise a solvent. Examples of the
15 solvent include organic solvents such as aromatic hydrocarbons, such as toluene and xylene; aliphatic hydrocarbons, such as hexane; esters, such as ethyl acetate and butyl acetate; ketones such as methyl ethyl ketone and methyl isobutyl ketone; alcohols, such as
20 methanol, ethanol, n-propanol, isopropyl alcohol, and n-butanol; glycol-based solvents, such as ethylene glycol, diethylene glycol, triethylene glycol, and propylene glycol; cellosolve-based solvents, such as methyl cellosolve, cellosolve, butyl cellosolve, dioxane, MTBE
25 (methyl tert-butyl ether), and butyl carbitol; glycol-

based solvents, such as diethylene glycol monomethyl ether, triethylene glycol monomethyl ether, propylene glycol monomethyl ether, and 3-methoxy-3-methyl-1-butanol; glycol ester-based solvents, such as ethylene glycol monomethyl ether acetate, PMA (propylene glycol monomethyl ether acetate), diethylene glycol monobutyl ether acetate, and diethylene glycol monomethyl ether acetate. These may be used individually or in combination.

When the water-based emulsion comprises the solvent, the content thereof is ordinarily from 0.001 parts by mass to 30 parts by mass, preferably from 0.001 parts by mass to 10 parts by mass, and more preferably from 0.001 parts by mass to 5 parts by mass with respect to 100 parts by mass of the ethylene-unsaturated ester copolymer.

<Other components>

The water-based emulsion may contain, as necessary, a stabilizer, such as a phenol-based stabilizer, a phosphate-based stabilizer, an amine-based stabilizer, an amide-based stabilizer, an anti-aging agent, a weathering stabilizer, an anti-settling agent, an antioxidant, a thermal stabilizer, and a light stabilizer; an additive, such as a thixotropic agent, a thickener, a dispersant, an antifoam agent, a viscosity modifier, an antiseptic agent, a weather-resistant agent, a pigment, a pigment dispersant, an antistatic agent, a lubricant, a nucleating agent, a

flame retarder, an oil solution, a dye, and a curing agent (crosslinking agent); a transition metal compound, such as (rutile) titanium oxide and zinc oxide; a pigment, such as carbon black; an inorganic or organic filler, such as a
5 glass fiber, a carbon fiber, a potassium titanate fiber, wollastonite, calcium carbonate, calcium sulfate, talc, a glass flake, barium sulfate, clay, kaolin, fine silica powder, mica, calcium silicate, aluminum hydroxide, magnesium hydroxide, aluminum oxide, magnesium oxide,
10 alumina, and celite; and the like.

<Method for producing the water-based emulsion>

The water-based emulsion can be produced by using any known method in the field, such as a post-emulsification method in which a copolymer, after being
15 polymerized, is dispersed in an aqueous medium (for example, a mechanical emulsification method, a forcible emulsification method, a self-emulsification method, a phase-transfer emulsification method, or the like).

Specific examples thereof include (1) a method in
20 which the ethylene-unsaturated ester copolymer and the solvent are injected into a reactor, stirred, and dissolved by heating, and then the surfactant containing no metals, water, and/or the solvent are injected into the reactor, heated, and stirred, while ,before or after this
25 operation, water and/or the solvent, as determined

arbitrarily, are further injected therein and stirred;
(2) a method in which the ethylene-unsaturated ester
copolymer and, as determined arbitrarily, the solvent are
injected into a mixer, stirred, and dissolved by heating,
5 the surfactant containing no metals, water, and/or the
solvent are injected into the mixer, heated, and stirred,
while ,before or after this operation, water and/or the
solvent, as determined arbitrarily, are further injected
therein and stirred.

10 In the above-described production method (1), a
reactor which is to be employed is a container (preferably
a sealed and/or pressure-resistant container) provided
with a heating apparatus capable of heating and a stirrer
capable of applying a shearing force and the like to the
15 contents of the reactor.

An ordinary stirrer can be used for the stirrer.
Examples of the above pressure-resistant container include
a stirrer-equipped pressure-resistant autoclave. The
stirring may be carried out at either normal pressure or
20 reduced pressure, for example. The rotating speed of the
stirrer can be set at approximately from 50 rpm to 1000
rpm, for example. Preferably, the rotating speed is
raised as necessary as the dispersion/stirring of the
water-based emulsion develops.

25 The heating is carried out at a temperature

ordinarily of from 50°C to 200°C, preferably from 60°C to 150°C, and more preferably from 70°C to 100°C.

After the stirring, the solvent is preferably removed by distillation (preferably distillation under
5 reduced pressure or by being pressurized) from the dispersion. For the distillation, a known method in the field can be used. The degree of the reduced pressure or pressurization is approximately from ± 0.001 MPa to 1 MPa, and preferably approximately from ± 0.001 MPa to 0.5 MPa.

10 In the above production method (2), examples of the mixer include a roll mill, a kneader, an extruder, an ink roll, and a Banbury mixer. Particularly, an extruder having one or more screws in a casing or a multi-axis extruder may be used.

15 In the method in which the stirring is conducted with use of the extruder, the melt ethylene-unsaturated ester copolymer and the surfactant containing no metals are mixed together, are continuously supplied to the extruder through a hopper or a supply opening, are melt-
20 kneaded by heating, followed further by water being supplied thereto through at least one supply opening provided in a compression zone, a gauging zone, a deaeration zone, etc. in the extruder, kneading with screws, and then being continuously extruded from a die.

25 If the surfactant containing no metals is used in an

excessive amount, the excess surfactant containing no metals may be separated and removed from the obtained water-based emulsion. The separation or removal of the surfactant containing no metals is done by using a
5 centrifugal separator, a filtration filter having fine pores with an average fine pore diameter smaller than the average particle diameter of a dispersed material contained in the water-based emulsion (preferably a micro filtration membrane having an average pore diameter of
10 from 0.05 μm to 0.5 μm), or an ultrafiltration film, for example.

The obtained water-based emulsion is preferably cooled, which provides a water-based emulsion containing a fine dispersoid. Examples of the cooling method include a
15 method in which the water-based emulsion is left to stand at normal temperature. By use of the method in which the water-based emulsion is left to stand at room temperature, a fine and homogeneous water-based emulsion can be obtained without ethylene-unsaturated ester copolymer and
20 the like agglomerating in the cooling process.

As necessary, the obtained water-based emulsion may be filtered or otherwise, for example, using a filter having differing pore diameters, or the like.

The average particle diameter of the dispersoid
25 contained in the water-based emulsion can be measured in

terms of a volume-based median diameter. The average particle diameter of the dispersoid is ordinarily 30 μm or less, preferably from 0.01 μm to 20 μm , and more preferably from 0.01 μm to 10 μm . The stability on
5 standing is good within the above-described range. The volume-based median diameter refers to a particle diameter at which the value of the integrated particle diameter distribution has reached 50% in terms of volume.

The dispersoid comprises the ethylene-unsaturated
10 ester copolymer and the surfactant containing no metals.

The mutual adhesion inhibitor in the present invention is uniformly present in the dispersoid contained in the water-based emulsion after water being removed therefrom.

15 Since the presence or non-presence of water hardly changes the particle diameter of the dispersoid contained in the water-based emulsion, the average particle diameter of the dispersoid contained in the water-based emulsion and the average particle diameter of the mutual adhesion
20 inhibitor are nearly the same.

<Pellet for solar cell sealing materials>

The pellet for solar cell sealing materials (hereinafter sometimes referred to as the present pellet) is made of an ethylene-unsaturated ester copolymer.

25 The content rate of a structural unit derived from

an unsaturated ester of the above ethylene-unsaturated ester copolymer is preferably not less than 23 mass% and not more than 33 mass%, and more preferably not less than 25 mass% and not more than 32 mass% from the viewpoint of improving workability and transparency. When the ethylene-unsaturated ester copolymer of the present invention includes structural units derived from two or more of the unsaturated esters, the total of the content rates of all structural units derived from the unsaturated esters included in the ethylene-unsaturated ester copolymer is considered as the content rate of the structural unit derived from the unsaturated ester.

Examples of the unsaturated ester are the same as those described above.

Examples of the ethylene-unsaturated ester copolymer in the present pellet are the same as those of the ethylene-unsaturated ester copolymer comprised in the above water-based emulsion.

The melt flow rate (MFR) of the ethylene-unsaturated ester copolymer in the present pellet is preferably not less than 4 g/10 minutes and not more than 50 g/10 minutes from the viewpoint of improving workability. The upper limit of MFR is more preferably not more than 40 g/10 minutes. The lower limit of MFR is more preferably not less than 5 g/10 minutes. The MFR is measured using the

method specified by JIS K7210-1995 under conditions of a temperature of 190°C and a load of 21.18 N.

The molecular weight distribution (Mw/Mn) of the ethylene-unsaturated ester copolymer in the present pellet is preferably not less than 2 and not more than 8, and more preferably not less than 2.5 and not more than 4 from the viewpoint of improving workability. The Mw represents the weight-average molecular weight of the above copolymer, and the Mn represents the number-average molecular weight of the above copolymer.

The polyethylene-equivalent weight-average molecular weight of the ethylene-unsaturated ester copolymer in the present pellet is preferably from 40000 to 80000, and more preferably from 50000 to 70000. The polyethylene-equivalent weight-average molecular weight was obtained by determining the polystyrene-equivalent weight-average molecular weight using gel permeation chromatography, and multiplying the polystyrene-equivalent weight-average molecular weight by the ratio of polyethylene to polystyrene in terms of the Q factor (17.7/41.3).

Examples of a method for producing the ethylene-unsaturated ester copolymer in the present pellet are the same as those for the ethylene-unsaturated ester copolymer comprised in the water-based emulsion.

Examples of the shape of the present pellet include

a spherical shape, an oval spherical shape, a cylindrical shape, an oval cylindrical shape, a horn shape, and a rod shape. Regarding the size of the present pellet, the diameter or the length is preferably not less than 3 mm
5 and not more than 5 mm.

<Method for using the water-based emulsion>

By imparting the water-based emulsion to the surface of the present pellet, and removing water therefrom, the present pellet having the mutual adhesion inhibitor
10 adhered to its surface can be obtained. The present pellet to which the mutual adhesion inhibitor has adhered is excellent in mutual adhesion-prevention performance.

Examples of the method for imparting the water-based emulsion to the surface of the present pellet and removing
15 the water therefrom include a method in which the water-based emulsion is sprayed into a hopper or a pneumatic conveying line so as to coat the present pellet with the water-based emulsion, and water is removed therefrom by drying; and a method in which the present pellet and the
20 water-based emulsion are put into a container, stirred, and then dried.

For an industrial scale production, since a certain work such as packing, as part of the packaging step, for example, (including loading into a bag, a drum can, a
25 plastic container, or the like) needs to be done through a

continuous and simplified operation, for example, the mutual adhesion inhibitor is imparted to the present pellet using the following method.

Examples of the method for imparting the water-based emulsion to the surface of the present pellet and removing water therefrom include
5 a method comprising

Step 1a) a step in which the ethylene-unsaturated ester copolymer is extruded from an extruder, and is cut
10 into a pellet shape in water, thereby producing the present pellet,

Step 1b) a step in which while the present pellet is transported to the next step through a pneumatic conveying line, the water-based emulsion is imparted to the surface
15 of the present pellet within the pneumatic conveying line,

Step 1c) a step in which the present pellet having the water-based emulsion imparted to its surface is dried, and the water adhered in Step 1a) is removed therefrom, thereby obtaining the present pellet having the mutual
20 adhesion inhibitor adhered to its surface, and

Step 1d) a step in which the present pellet having the mutual adhesion inhibitor adhered to its surface is packaged,
and

25 a method comprising

Step 2a) a step in which the ethylene-unsaturated ester copolymer is extruded from an extruder, and is cut into a pellet shape in water, thereby producing the present pellet,

5 Step 2b) a step in which the present pellet is transported to a hopper through a pneumatic conveying line,

Step 2c) a step in which the water-based emulsion is imparted to the surface of the present pellet within the hopper,

10 Step 2d) a step in which the present pellet having the water-based emulsion imparted to its surface is dried, and the water adhered in Step 2a) is removed therefrom, thereby obtaining the present pellet having the mutual adhesion inhibitor adhered to its surface, and

15 Step 2e) a step in which the present pellet having the mutual adhesion inhibitor adhered to its surface is packaged.

Step 2d) may be carried out within the hopper of Step 2c).

20 Step b') a step in which the present pellet is drained may be provided between Step 1a) and Step 1b), or between Step 2a) and Step 2b).

The amount of the mutual adhesion inhibitor having adhered to the surface of the present pellet can be
25 obtained by an ultrasonic cleaning in water of the present

pellet having the mutual adhesion inhibitor adhered to its surface, then drying and weighing the mutual adhesion inhibitor which has eluted into water.

Preferably, 0.001 parts by mass to 5 parts by mass of the ethylene-unsaturated ester copolymer comprised in the mutual adhesion inhibitor adhere with respect to 100 parts by mass of the present pellet since it is capable of suppressing the mutual adhesion between the present pellets.

As required, one or more compounds selected from the group consisting of a light-resistant stabilizer, an ultraviolet absorber, an antioxidant, and a lubricant may be kneaded into the pellet, or may adhere to the surface of the present pellet together with the mutual adhesion inhibitor.

Examples of the light-resistant stabilizer include a hindered amine-based compound. Examples of the ultraviolet absorber include a benzophenone-based compound. Examples of the antioxidant include a phenol-based compound, and a phosphorous-based compound. Examples of the lubricant include a fatty acid amide compound, such as oleic amide, erucamide, stearic acid amide, behenamide, ethylene bisoleic acid amide, and ethylene bisstearic acid amide.

<Solar cell sealing material>

A resin product obtained using the present pellet having the mutual adhesion inhibitor of the present invention adhered to its surface shows improved volume intrinsic resistance. Therefore, a sheet or the like produced using the present pellet having the mutual adhesion inhibitor of the present invention adhered to its surface is suitably used as a solar cell sealing material that is used to seal and protect a solar cell element (crystal, poly-crystal, amorphous, and the like).

Examples of the method for producing a sheet-shaped solar cell sealing material include a method in which the present pellet having the ethylene-unsaturated ester copolymer imparted to its surface is processed using a T-die extruder, a calendar molder, or the like. In a step of processing into a sheet may be added a light-resistant stabilizer, an ultraviolet absorber, an antioxidant, a lubricant, a crosslinking agent, a crosslinking aid, an anti-fog additive, a plasticizer, a surfactant, a colorant, an antistatic agent, a flame retarder, a crystal nucleating agent, and the like.

Examples

The present invention will be described in more detail by showing examples as below. The "parts" and "%" appearing in the examples are based on mass unless

otherwise specifically stated.

The measurement, evaluation, etc. of physical properties were carried out using the following methods.

<Concentration of non-volatile component (unit:%)>

5 The concentration of a non-volatile component in the water-based emulsion was measured using a method equivalent to JIS K-6828-1.

<Average particle diameter (unit: μm)>

10 The average particle diameter of the dispersoid comprised in the water-based emulsion was measured in terms of a volume-based median diameter obtained at a particle refraction index of 1.50, using a laser diffraction-type particle size distribution measurement apparatus LA-950V2 (manufactured by Horiba Ltd.).

15 <Content rate of structural unit derived from vinyl acetate (unit: mass%)>

20 The content rate of the structural unit derived from vinyl acetate of the ethylene-unsaturated ester copolymer is a value obtained when the total of the content rate of the structural unit derived from ethylene and the content rate of the structural unit derived from vinyl acetate are set at 100 mass%, and it was measured according to JIS K7192.

<Melt flow rate (MFR, unit: g/10 minutes)>

25 The melt flow rate of the copolymer was measured

using the method specified by JIS K7210-1995 under conditions of a temperature of 190°C and a load of 21.18 N.

<Example 1>

<Production example 1 of water-based emulsion>

5 Into a 1 L separable flask reactor having a stirrer, a thermometer, and a reflux cooling tube, 200 parts of toluene and 100 parts of an ethylene-unsaturated ester copolymer (A-1) [ethylene-methyl methacrylate copolymer, ACRYFT WH303 manufactured by Sumitomo Chemical Co., Ltd.]
10 were put and were stirred at 95°C. Next, 33.3 parts of LATEMUL E-1000A (30% aqueous solution, manufactured by Kao Corporation) were added dropwise, as a surfactant, to the reactor over ten minutes. After stirring for five minutes, 16.7 parts of a 28% ammonia aqueous solution were injected,
15 followed by further stirring for another five minutes. Next, the stirring was continued while 300 parts of ion-exchange water were added dropwise to the reactor over 30 minutes, thereby obtaining a milk white dispersion liquid.

 The obtained dispersion liquid was injected into a 2
20 L eggplant flask, was distilled under reduced pressure using an evaporator, and was filtered using a 200-mesh nylon net, thereby obtaining a water-based emulsion (E-1) comprising the ethylene-unsaturated ester copolymer (A-1) and the surfactant. The (volume-based) average particle
25 diameter of a dispersoid comprised in the obtained water-

based emulsion (E-1) was 1.35 μm , and the concentration of the non-volatile component was 43%.

<Production example 1 of a pellet for solar cell sealing materials>

5 An ethylene-vinyl acetate copolymer was synthesized in an autoclave-type reactor using t-butyl peroxy 2-ethylhexanate as a initiator under conditions of a reaction temperature of from 188°C to 195°C, a reaction pressure of from 180 MPa to 185 MPa, and a feed gas
10 composition (ethylene: 63 wt% to 68 wt% and vinyl acetate: 37 wt% to 32 wt%) to produce a pellet for solar cell sealing materials (P1) made of the ethylene-vinyl acetate copolymer (vinyl acetate content of 32 mass%, MFR of 37, pellet mass of 32 g).

15 <Production example 1 of a pellet for solar cell sealing materials (Q1) having a mutual adhesion inhibitor adhered to its surface>

 Into a polyethylene container were put 100 parts of the pellet for solar cell sealing materials (P1) and 0.698
20 parts (0.3 parts in terms of solid content) of the water-based emulsion (E-1) (non-volatile component concentration of 43%), which were then stirred for five minutes, and were further dried for two hours while dry nitrogen was blown in, thereby obtaining a pellet for solar cell
25 sealing materials (Q1) having a mutual adhesion inhibitor

adhered to its surface.

<Production example 2 of a pellet for solar cell sealing materials (Q2) having a mutual adhesion inhibitor adhered to its surface>

5 A pellet for solar cell sealing materials (Q2) having a wet mutual adhesion inhibitor adhered to its surface was obtained in the same manner as <the production example 1 of Q1> except that the drying was not conducted.

<Mutual adhesion test>

10 Into a 60 mm x 85 mm zipper-equipped plastic bag, 32 g of the pellet (Q1) was put, and the zipper was closed. Next, a load of 100 g/cm² was applied to the bag at 40°C, and the bag was held to stand for 24 hours, and then at 5°C for another 24 hours. After that, the load was removed,
15 and the bag was held to stand at 23°C for 24 hours. Subsequently, the bag was torn, and the pellet (Q1) was taken out, observed, and evaluated with samples O and X.

O: No mutual adhesion of the pellets.

Δ: 5 to 50 particles of the pellet mutually adhered.

20 X: 51 or more particles of the pellet mutually adhered.

<Flowability test>

 Into a plastic funnel with its bottom sealed with a parafilm was put 100 g of the pellet (Q2), which then was
25 left to stand at 40°C for 24 hours.

Thereafter, the temperature was brought to room temperature. Then, the sealed parafilm was removed, and the duration of time (flowing time) consumed for all the pellets to drop out of the funnel was measured for
5 evaluation with symbols O and X.

O: All pellets dropped in less than 30 seconds.

Δ: All pellets dropped in 30 seconds to less than 3 minutes.

X: None of the pellets dropped even after 3 minutes
10 lapsed.

<Preparation of sheet>

One hundred (100) parts by mass of the pellet (Q1),
0.4 parts of t-butyl peroxy 2-ethylhexyl carbonate
(PERBUTYL E, manufactured by NOF Corporation, one-hour
15 half-life temperature of 121°C: organic peroxide as
crosslinking agent),

0.9 parts of triarylisocyanurate (TAIC, manufactured
by Tokyo Chemical Industry Co., Ltd.: crosslinking aid),

0.12 parts of γ-methacryloxypropyl trimethoxysilane
20 (Silquiest A-174, manufactured by Momentive Performance
Materials inc.: silane coupling agent),

0.3 parts of 2-hydroxy-4-n-octoxybenzophenone
(Sumisorb 130, manufactured by Sumika Chemtex Co., Ltd.,
average particle diameter of 178 μm), and

25 0.08 parts of bis(2,2,6,6-tetramethyl-4-

pyperidyl)sebacate (Tinuvin770 DF, manufactured by BASF Ltd.)

were kneaded for five minutes using a labo plasto mill, then, were kept pressed for five minutes at a pressure of 2 MPa using a 150°C hot presser, and were cooled for five minutes using a 30°C cooling presser, thereby producing a sheet (S1) having a thickness of approximately 500 μm .

<Volume intrinsic resistance ($\Omega\cdot\text{cm}$)>

The sheet (S1) was installed in a large-diameter electrode for a flat specimen (manufactured by DKK-Toa Corporation, SME-8310), was subjected to a voltage of 500 V, and the resistance value after the lapse of one minute was measured using a digital insulation meter (manufactured by DKK-Toa Corporation, DSM-8103), thereby calculating the volume intrinsic resistance value on the basis of the resistance value.

<Light transmittance (%)>

The light transmission spectrum of the sheet (S1) in the thickness direction was measured using a spectrophotometer (manufactured by Shimadzu Corporation, UV-3150), and the average value of light transmittance in a wavelength range of 400 nm to 1200 nm was obtained.

<Example 2>

A water-based emulsion (E-2) was produced in the same manner as Example 1 except that the ethylene-

unsaturated ester copolymer (A-1) was changed to an ethylene-unsaturated ester copolymer (A-2) [ethylene-methyl methacrylate copolymer, ACRYFT WH302, manufactured by Sumitomo Chemical Co., Ltd.], and it was then evaluated.

5 <Example 3>

A water-based emulsion (E-3) was produced in the same manner as Example 1 except that the ethylene-unsaturated ester copolymer (A-1) was changed to an ethylene-unsaturated ester copolymer (A-3) [ethylene-vinyl acetate copolymer, MFR of 9, vinyl acetate concentration of 18 wt%, manufactured by Sumitomo Chemical Co., Ltd.], and it was then evaluated.

 <Example 3-1>

To the water-based emulsion (E-3), 4 parts of PLURONIC L-64 (manufactured by Adeka Corporation) were added and well stirred, thereby producing a water-based emulsion (E-3-1), which was then evaluated.

 <Example 3-2>

To the water-based emulsion (E-3), 6 parts of PLURONIC L-64 (manufactured by Adeka Corporation) were added and well stirred, thereby producing a water-based emulsion (E-3-2), which was then evaluated.

 <Example 4>

A water-based emulsion (E-4) was produced in the same manner as Example 1 except that the ethylene-

unsaturated ester copolymer (A-1) was changed to an ethylene-unsaturated ester copolymer (A-4) [ethylene-methyl methacrylate copolymer, ACRYFT CM5021, manufactured by Sumitomo Chemical Co., Ltd.], and it was then evaluated.

5 <Production example 1 of high-molecular weight anionic surfactant aqueous solution>

 Into a four-neck flask equipped with a stirrer was put a reflux cooling tube, a thermometer, and a dropping funnel, 30.0 parts of acrylic acid, 60 parts of ethyl
10 acrylate, 10.0 parts of lauryl methacrylate, and 150 parts of isopropyl alcohol. After nitrogen gas replacement, polymerization was performed at 80°C for three hours using 0.6 parts of 2,2'-azoisobutyronitrile as an initiator. Following neutralization with 37.9 parts of a 28% ammonia
15 aqueous solution, while distilling the isopropyl alcohol, water was added for replacement, thereby ultimately obtaining an aqueous solution (X-1) of a neutralized substance comprising a viscous acrylic polymer having 30% of a non-volatile component.

20 <Example 5>

 The ethylene-unsaturated ester copolymer (A-1) is continuously supplied at a rate of 100 parts/hour through a hopper of a same-direction rotary-engaging twin-screw extruder (manufactured by Ikegai Tekko Co., Ltd., product
25 name of PCM45, three shallow screw groove-type, L/D of 30).

While continuously supplying a substance obtained by adding 113.2 parts of water to 26.8 parts (8 parts of a non-volatile component) of the aqueous solution (X-1), under pressure by a gear pump at a rate of 140 parts/hour from a supply opening provided in a vent section in the same extruder, extrusion is continuously performed at a heating temperature of 130°C, thereby obtaining a milk white water-based emulsion (E-5). If an evaluation is conducted in the same manner as in Example 1, the same results as those in Example 1 are obtained.

<Example 6>

An aqueous solution (X-2) of a neutralized substance comprising a viscous acrylic polymer containing 30% of a non-volatile component is obtained in the same manner as in the <the production example 1 of high-molecular weight anionic surfactant aqueous solution> except that 21.6 parts of acrylic acid, 30 parts of ethyl acrylate, 56.8 parts of butyl methacrylate, and 18.2 parts of a 28% ammonia aqueous solution are used; and furthermore, a water-based emulsion (E-6) is obtained using the same method as in <Example 5>. If an evaluation is conducted in the same manner as in Example 1, the same results as those in Example 1 are obtained.

<Comparative Example 1>

An evaluation was carried out in the same manner as

in Example 1 except that instead of the water-based emulsion (E-1), 0.30 parts by mass of silica (SYLYSIA 430, manufactured by Fuji Silysia Chemical Ltd., average particle diameter of 2.9 μm) was used unground.

5 <Comparative Example 2>

An evaluation was carried out in the same manner as in Example 1 except that instead of the water-based emulsion (E-1), 0.10 parts by mass of calcium stearate (manufactured by Kyodo Chemical Co., Ltd., average
10 particle diameter of 9.3 μm) was used unground.

<Reference Example>

An evaluation was carried out in the same manner as in Example 1 except that the water-based emulsion was not used.

15 [Table 1]

	Content rate of structural unit derived from unsaturated ester (%)	MFR
A-1	18	7
A-2	15	7
A-3	20	9
A-4	28	450

[Table 2]

	Example 1	Example 2	Example 3	Example 3-1	Example 3-2	Example 4
Water-based emulsion (parts)	E-1 (0.3)	E-2 (0.3)	E-3 (0.3)	E-3-1 (0.3)	E-3-2 (0.3)	E-4 (0.3)
Silica (parts)	-	-	-	-	-	-
Calcium stearate (parts)	-	-	-	-	-	-
Non-volatile component concentration (%)	43	41	42	43	44	49

Average particle diameter (μm)	1.4	1.1	1.7	1.7	1.7	2.2
Mutual adhesion test result	O	O	O	O	O	Δ
Flowability test result	X	X	X	Δ	O	X
Volume intrinsic resistance ($\Omega\cdot\text{cm}$)	2.2E+14	1.8E+14	3.8E+14	3.2E+14	2.8E+14	2.3E+14
Light transmittance (%)	92.3	92.3	92.3	92.3	92.3	92.5

[Table 2]

	Comparative Example 1	Comparative Example 2	Reference Example
Water-based emulsion (parts)	-	-	-
Silica (parts)	0.3	-	-
Calcium stearate (parts)	-	0.3	-
Non-volatile component concentration (%)	100	100	-
Average particle diameter (μm)	2.9	9.3	-
Mutual adhesion test result	O	O	X
Volume intrinsic resistance ($\Omega\cdot\text{cm}$)	2.2E+14	7.4E+13	2.3E+14
Light transmittance (%)	92.0	91.7	92.3

In Examples 1 to 4, the mutual adhesion was prevented, and the volume intrinsic resistances and the light transmittances were the same as those in the Reference Example. On the other hand, in Comparative Example 1, the light transmittance decreased compared with the Reference Example, while in Comparative Example 2, the volume intrinsic resistance decreased compared with the Reference Example.

10

Industrial Applicability

The method of the present invention is useful as a method for preventing the mutual adhesion of pellets for solar cell sealing materials.

Claims

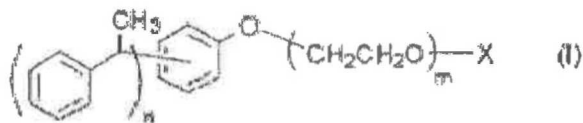
[Claim 1]

A method for preventing the mutual adhesion of
5 pellets for solar cell sealing materials,
wherein a water-based emulsion comprising an
ethylene-unsaturated ester copolymer and a surfactant
containing no metals is imparted to pellets for solar cell
sealing materials.

10

[Claim 2]

The method according to Claim 1,
wherein the surfactant containing no metals
comprises at least one surfactant selected from the group
15 consisting of
a surfactant represented by the formula (I) and
a surfactant that has a different structure from the
surfactant represented by the formula (I), has at least
one group selected from the group consisting of an
20 oxyethylene group and an oxypropylene group, and is a
liquid at 10°C to 50°C:



wherein, in the formula (I), X represents a hydrogen atom

or $-SO_3M$, M represents a hydrogen atom or NH_4 , n represents an integer of 1 to 3, and m represents an integer of 1 to 100.

5 [Claim 3]

The method according to Claim 2,
wherein the surfactant containing no metals
comprises the surfactant represented by the formula (I).

10 [Claim 4]

The method according to Claim 2 or 3,
wherein the surfactant containing no metals
comprises

the surfactant represented by the formula (I) and
15 the surfactant that has a different structure from
the surfactant represented by the formula (I), has at
least one structure selected from the group consisting of
an oxyethylene group and an oxypropylene group, and is a
liquid at 10°C to 50°C.

20

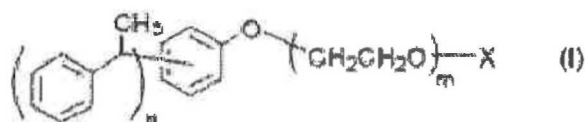
[Claim 5]

A mutual adhesion inhibitor of pellets for solar
cell sealing materials, comprising
an ethylene-unsaturated ester copolymer and
25 a surfactant containing no metals.

[Claim 6]

The mutual adhesion inhibitor according to Claim 5,
wherein the surfactant containing no metals
5 comprises at least one surfactant selected from the group
consisting of

a surfactant represented by the formula (I) and
a surfactant that has a different structure from the
surfactant represented by the formula (I), has at least
one structure selected from the group consisting of an
oxyethylene group and an oxypropylene group, and is a
liquid at 10°C to 50°C:



wherein, in the formula (I), X represents a hydrogen atom
15 or $-\text{SO}_3\text{M}$, M represents a hydrogen atom or NH_4 , n represents
an integer of 1 to 3, and m represents an integer of 1 to
100.

[Claim 7]

20 The mutual adhesion inhibitor according to Claim 6,
 wherein the surfactant containing no metals
 comprises the surfactant represented by the formula (I).

[Claim 8]

The mutual adhesion inhibitor according to Claim 6
or 7,

wherein the surfactant containing no metals
5 comprises

the surfactant represented by the formula (I) and
the surfactant that has a different structure from
the surfactant represented by the formula (I), has at
least one structure selected from the group consisting of
10 an oxyethylene group and an oxypropylene group, and is a
liquid at 10°C to 50°C.

[Claim 9]

The mutual adhesion inhibitor according to any one
15 of Claims 5 to 8,

wherein an average particle diameter is not less
than 0.01 μm and not more than 30 μm .

[Claim 10]

20 A pellet for solar cell sealing materials,
wherein the mutual adhesion inhibitor according to
any one of Claims 5 to 9 has adhered to its surface.

[Claim 11]

25 A method for producing a pellet for solar cell

sealing materials having a mutual adhesion inhibitor
adhered to the surface of the pellet for solar cell
sealing materials,

wherein a water-based emulsion comprising an
5 ethylene-unsaturated ester copolymer and a surfactant
containing no metals is imparted to the surface of the
pellet for solar cell sealing materials.

[Claim 12]

10 A solar cell sealing material obtained by using the
pellet for solar cell sealing materials according to Claim
10.