

SILANE-CROSSLINKED POLYOLEFIN RESIN COMPOSITION AND  
INSULATED CABLE COVERED WITH THE COMPOSITION  
FIELD OF THE INVENTION

The present invention relates to a silane-  
crosslinked resin composition which comprises a base  
polymer, an organic unsaturated silane, a free radical  
5 generating agent, a silanol condensation catalyst and, if  
necessary, other additional ingredients melt-blended with  
one another and to an insulated cable wherein the electric  
wire has been covered with the composition.

RELATED ART

10 Widely known simple methods for crosslinking  
polyethylene include chemical crosslinking, electron beam  
irradiation crosslinking, and warm water crosslinking  
(which proceeds with an organic silane compound as the  
medium). The warm water crosslinking method, one of the  
15 above-mentioned methods, as compared with chemical  
crosslinking and electron beam irradiation cross-linking,  
has advantages in that the cost of the crosslinking  
apparatus is markedly low and the crosslinking can be  
easily controlled. A representative and widely known  
20 example of the method of warm water crosslinking of  
polyethylene is the so-called silane crosslinking method  
which comprises graft-reacting an organic unsaturated  
silane onto the polyolefin in the presence of a free

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radical generating agent to effect silane grafting and then contacting the silane-grafted polymer with water in the presence of a silanol condensation catalyst to effect crosslinking. This method is disclosed, for example, in  
5 JP-B-48-1711 and JP-A-57-49109.

However, the warm water crosslinking method, which is lower in apparatus cost than the other crosslinking methods, has the disadvantage of requiring much time and cost for crosslinking treatment. When  
10 electric wire is covered with a water-crosslinkable resin composition, the crosslinking reaction proceeds only very slowly at ordinary temperatures and hence the crosslinking needs to be promoted in a warm water of about 80°C or in a high-temperature, high humidity vessel. Even under such  
15 conditions, it takes approximately full one day for the promotion and hence a vast capital expenditure is necessary for the crosslinking treatment facility. Therefore, even if the apparatus cost is very low, the great expenditure necessary for the crosslinking treatment cost results in  
20 the diminishment of the above-mentioned advantage of the method.

Accordingly, various attempts have hitherto been made to shorten the time necessary for crosslinking treatment of electric wire extrusion-covered with a water-  
25 crosslinkable resin. For example, JP-A-57-208006 and JP-A-62-106947 disclose a method of promoting crosslinking by adding a catalyst and/or an auxiliary agent to a modified silane compound. JP-A-60-254520 discloses a method which

comprises, at the time of crosslinking a water-crosslinkable resin-covered wire, improving the contact of the resin with water thereby to shorten the crosslinking time. Further, JP-A-4-331241 discloses a method wherein  
5 the crosslinking treatment of a water-crosslinkable resin-covered wire is conducted in an ultrasonic wave environment to promote the diffusion of water to the inside of the water-crosslinkable resin and thereby to shorten the crosslinking treatment time. All of the above-mentioned  
10 methods, however, merely serve to shorten the time necessary for crosslinking treatment with warm water or steam and cannot eliminate the water crosslinking step itself.

Moreover, the warm water crosslinking of  
15 polyethylene has a disadvantage in that its effect in improving the heat resistance of the resin is lower than in the chemical crosslinking and electron beam irradiation crosslinking. Therefore, cases have been increasing wherein linear, medium to low density polyethylene is used  
20 as the base resin to improve the heat resistance effectively. However, the use of linear, medium to low density polyethylene, which has a higher melting point and a higher melt viscosity than low density polyethylene or the like, as the base resin is apt to cause problems of  
25 generating heat in the extruder to result in premature crosslinking and of forming extrudates of rough surface owing to the friction with the die.

An example wherein linear, medium to low density polyethylene alone is used as the raw material is disclosed in JP-A-7-130238. This method, however, is to give a stable processability and not to eliminate the water crosslinking step.

#### SUMMARY OF THE INVENTION

The object of the present invention is, overcoming the above-mentioned problems, to provide a silane-crosslinked polyolefin resin composition which is excellent particularly in the smoothness of the extrudate surface and in the heat resistance, and further to provide an insulated cable which can be prepared by sheathing an electric wire extrusion-covered with the silane-crosslinked polyolefin resin composition immediately after the covering.

The present inventors have made extensive study to solve the above-mentioned problems and resultantly formed that the object can be attained by using a specific crosslinked polyolefin.

Thus, according to the present invention, there is provided (i) a silane-crosslinked polyolefin resin composition comprising (1) a base polymer, (2) a carrier polymer A incorporated with an organic unsaturated silane represented by the formula  $RR'SiY_2$ , wherein R is a monovalent olefinic unsaturated hydrocarbon group, Y is a hydrolyzable organic group and R' is a monovalent hydrocarbon group other than aliphatic unsaturated



hydrocarbon groups or is the same as Y, and with a free radical generating agent and (3) a carrier polymer (B) incorporated with a silanol condensation catalyst and with an anti-oxidant, wherein the base polymer contains a

5 linear, medium to low density polyethylene with a degree of dispersion (Mw/Mn) of 4 or more, has an average density of  $0.915 \text{ g/cm}^3$  -  $0.935 \text{ g/cm}^3$  and shows a heat deformation percentage (JIS K 6723) after melt-kneading of not more than 40%.

10 In the silane-crosslinked polyolefin resin composition (i), preferably the base polymer comprises a mixture of 45 - 100 parts by weight of a linear, medium to low density polyethylene with a degree of dispersion (Mw/Mn) of 4 or more and 0 - 55 parts by weight of a high  
15 density or low density polyethylene, or the base polymer comprises 75 - 100 parts by weight of a linear, medium to low density polyethylene with a degree of dispersion (Mw/Mn) of 4 or more and 0 - 25 parts by weight of at least one polyolefin selected from the group consisting of ethylene-  
20 ethyl acrylate copolymer (EEA), ethylene-vinyl acetate copolymer (EVA), ethylene-methyl methacrylate copolymer (EMMA), hydrogenated block copolymer obtained by hydrogenating a block copolymer comprising a polymer block consisting mainly of at least one vinylaromatic compound  
25 and a polymer block consisting mainly of at least one conjugated diene compound, and the mixture thereof.

In the silane-crosslinked polyolefin resin

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composition (i), more preferably the carrier polymer A is selected from the group consisting of ethylene-ethyl acrylate copolymer (EEA), ethylene-methyl methacrylate copolymer (EMMA), hydrogenated block copolymer obtained by  
5 hydrogenating a block copolymer comprising a polymer block consisting mainly of at least one vinylaromatic compound and a polymer block consisting mainly of at least one conjugated diene compound, and the mixtures thereof, the carrier polymer B is selected from the group consisting of  
10 polyethylene, polypropylene and ethylene- $\alpha$ -olefin copolymer, and the total amount of the carrier polymers A and B is 3-15% by weight relative to the whole polymers.

There is also provided an insulated cable wherein the wire has been covered with the above-mentioned silane-  
15 crosslinked polyolefin resin composition which is obtained by covering wire with the resin composition and then covering the covered wire with a sheath material.

According to the present invention, there is further provided (ii) a silane-crosslinked polyolefin resin  
20 composition comprising (1) a base polymer and (2) a carrier polymer C incorporated with an organic unsaturated silane represented by the formula  $RR'SiY_2$ , wherein R is a monovalent olefinic unsaturated hydrocarbon group, Y is a hydrolyzable organic group, and R' is a monovalent  
25 hydrocarbon group other than aliphatic unsaturated hydrocarbon groups or is the same as Y, with a free radical generating agent and with a silanol condensation catalyst, wherein the base polymer contains a linear, medium to low



density polyethylene with a degree of dispersion ( $M_w/M_n$ ) of 4 or more, has an average density of  $0.915 \text{ g/cm}^3 - 0.935 \text{ g/cm}^3$  and shows a heat deformation percentage (JIS K 6723) after melt-kneading of not more than 40%.

- 5                    In the silane-crosslinked polyolefin resin composition (ii), preferably the base polymer comprises a mixture of 45 - 100 parts by weight of a linear, medium to low density polyethylene with a degree of dispersion ( $M_w/M_n$ ) of 4 or more and 0 - 55 parts by weight of high density
- 10 or low density polyethylene, or the base polymer comprises a mixture of 75 - 100 parts by weight of a linear, medium to low density polyethylene with a degree of dispersion ( $M_w/M_n$ ) of 4 or more and 0 - 25 parts by weight of at least one polyolefin selected from the group consisting of
- 15 ethylene ethyl acrylate copolymer (EEA), ethylene-vinyl acetate copolymer (EVA), ethylene-methyl methacrylate copolymer (EMMA), hydrogenated block copolymer obtained by hydrogenating a block copolymer comprising a polymer block consisting mainly of at least one vinylaromatic compound
- 20 and a polymer block consisting mainly of at least one conjugated diene compound, and the mixtures thereof, said mixture having an average density of  $0.915 \text{ g/cm}^3 - 0.935 \text{ g/cm}^3$ , the carrier polymer A is selected from the group consisting of ethylene-ethyl acrylate copolymer (EEA),
- 25 ethylene-methyl methacrylate copolymer (EMMA), hydrogenated block copolymer obtained by hydrogenating a block copolymer comprising a polymer block consisting mainly of at least



one vinylaromatic compound and a polymer block consisting mainly of at least one conjugated diene compound, and the mixtures thereof, and the amount of the carrier polymer C is 4 - 13% by weight relative to the whole polymers.

5           There is also provided an insulated cable obtained by covering wire with the above-mentioned silane-crosslinked polyolefin resin composition and then covering the covered wire with a sheath material.

          According to the present invention, there is  
10   furthermore provided (iii) a silane-crosslinked polyolefin resin composition comprising a base polymer, an organic unsaturated silane represented by the formula  $RR'SiY_2$ , wherein R is a monovalent olefinic unsaturated hydrocarbon group, Y is a hydrolyzable organic group and R' is a  
15   monovalent hydrocarbon group other than aliphatic unsaturated hydrocarbon groups or is the same as Y, a free radical generating agent and a silanol condensation catalyst, wherein the base polymer contains a linear, medium to low density polyethylene with a degree of  
20   dispersion ( $M_w/M_n$ ) of 4 or more, has an average density of  $0.915 \text{ g/cm}^3$  -  $0.935 \text{ g/cm}^3$  and shows a heat deformation percentage (JIS K 6723) after melt-kneading of not more than 40%.

          The silane-crosslinked polyolefin resin  
25   composition (iii) preferably comprises a mixture of 45 - 100 parts by weight of a linear medium to low density polyethylene with a degree of dispersion ( $M_w/M_n$ ) of 4 or more and 0 - 55 parts by weight of high density or low



density polyethylene or comprises a mixture of 75 - 100 parts by weight of a linear, medium to low density polyethylene with a degree of dispersion ( $M_w/M_n$ ) of 4 or more and 0 - 25 parts by weight of at least one polyolefin  
5 selected from the group consisting of ethylene-ethyl acrylate copolymer (EEA), ethylene-vinyl acetate copolymer (EVA), ethylene-methyl methacrylate copolymer (EMMA), hydrogenated block copolymer obtained by hydrogenating a block copolymer comprising a polymer block consisting  
10 mainly of at least one vinyl aromatic compound and a polymer block consisting mainly of at least one conjugated diene compound, and the mixtures thereof.

More preferably, the base polymer comprises a mixture of 5 - 100 parts by weight of granular polymer and  
15 0 - 95 parts by weight of pellet-formed polymer.

There is also provided an insulated cable obtained by covering wire with the above-mentioned silane-crosslinked polyolefin resin composition and then covering the covered wire with a sheath material.

## 20 DESCRIPTION OF THE PREFERRED EMBODIMENTS

The linear medium to low density polyethylene used for the base polymer of the present invention is a copolymer of ethylene of the main component with an  $\alpha$ -olefin obtained by various methods of polymerization, such  
25 as gas phase polymerization, solution polymerization and suspension polymerization, at low, medium or high pressure using various catalysts, such as Ziegler type catalysts and



chromium-based catalysts. The  $\alpha$ -olefin may be a  $C_3 - C_{12}$  olefin, for example, propylene, butene-1, pentene-1, octene-1, 4-methylpentene-1, 4-methylhexene-1, 4,4-dimethylpentene-1, nonene-1, decene-1, undecene-1 and  
5 dodecene-1.

The polyethylene used for the base polymer of the present invention is high density polyethylene or low density polyethylene.

High density polyethylene is an ethylene polymer  
10 obtained by various methods of polymerization, such as gas phase polymerization, solution polymerization and suspension polymerization, at low, medium or high pressure using various catalysts, such as Ziegler type catalysts and chromium-based catalysts.

15 Low density polyethylene refers to an ethylene polymer prepared by high pressure radical polymerization using the tubular method or the autoclave method.

The base polymer of the present invention preferably comprises a mixture of 45 - 100 parts by weight  
20 of a linear, medium to low density polyethylene with a degree of dispersion ( $M_w/M_n$ ) of 4 or more and 0 - 55 parts by weight of high density or low density polyethylene, the mixture having an average density of  $0.915 \text{ g/cm}^3 - 0.935 \text{ g/cm}^3$ . When the average density is lower than  $0.915 \text{ g/cm}^3$   
25 or when the amount of mixed low density polyethylene exceeds 55 parts by weight, the heat resistance tends to decrease; when the average density is higher than  $0.935 \text{ g/}$

cm<sup>3</sup>, the resin composition tends to be stiff and unsuitable for preparing large-size wire and cables.

The polyolefin used for the base polymer of the present invention may be, for example, ethylene-ethyl  
5 acrylate copolymer (EEA), ethylene-vinyl acetate copolymer (EVA), ethylene-methyl methacrylate copolymer (EMMA) and hydrogenated block copolymers obtained by hydrogenating a block copolymer comprising a polymer block consisting  
10 block consisting mainly of at least one vinylaromatic compound and a polymer block consisting mainly of at least one conjugated diene compound, e.g., hydrogenated styrene-isoprene block copolymer (SEPS) and hydrogenated styrene-butadiene block copolymer (SEBS).

The base polymer of the present invention  
15 preferably comprises a mixture of 75 - 100 parts by weight of a linear, medium to low density polyethylene with a degree of dispersion ( $M_w/M_n$ ) of 4 or more and 0 - 25 parts by weight of the above-mentioned polyolefin, the mixture having an average density of 0.915 g/cm<sup>3</sup> - 0.935 g/cm<sup>3</sup>.  
20 When the average density is lower than 0.915 g/cm<sup>3</sup> or when the amount of mixed polyolefin exceeds 25 parts by weight, the heat resistance tends to decrease; when the average density is higher than 0.935 g/cm<sup>3</sup>, the resin composition tends to be stiff and unsuitable for preparing large-size  
25 wire and cables.

In the production process of silane-crosslinked polyolefin resin composition (iii), the base polymer preferably comprises a mixture of 5 - 100 parts by weight



of granular polymer and 0 - 95 parts by weight of pellet-formed polymer. When the amount of the granular polymer is less than 5 parts by weight, the dispersion of the unsaturated organic silane tends to be poor, leading to  
5 occurrence of local crosslinking reaction and resultant development of fish eyes.

The organic unsaturated silane used in the present invention is grafted to the base resin to serve as the crosslinking point between base resin molecules with  
10 each other. The organic unsaturated silane used in the present invention is a compound represented by the formula  $RR'SiY_2$ , wherein R is a monovalent olefinic unsaturated hydrocarbon group, Y is a hydrolyzable organic group and R' is a monovalent hydrocarbon group other than aliphatic  
15 unsaturated hydrocarbon groups or is the same as Y.

Organic unsaturated silanes preferably used are those wherein R' and Y are the same and represented by the formula  $RSiY_3$ , for example, vinyltrimethoxysilane, vinyltriethoxysilane, vinyltributoxysilane,  
20 allyltrimethoxysilane and allyltriethoxysilane. The amount of the silane to be added is 0.1 - 5% by weight, preferably 0.7 - 3% by weight, relative to the total weight of polymers. When the amount is less than 0.1% by weight a sufficient grafting does not take place; when it exceeds 5%  
25 by weight, a defective extrusion tends to occur and moreover it is economically disadvantageous.

The free radical generating agent used in the present invention acts as an initiator for silane grafting

reaction. The free radical generating agent used may be various organic peroxides and peresters which exert a strong polymerization initiating action, for example, dicumyl peroxide,  $\alpha, \alpha'$ -bis(t-butylperoxydiisopropyl)-  
5 benzene, di-t-butyl peroxide, t-butylcumyl peroxide, dibenzoyl peroxide, 2,5-dimethyl-2,5-bis(t-butylperoxy)hexane, t-butyl peroxy-pivalate and t-butyl peroxy-2-ethylhexanoate. The amount of the free radical generating agent to be added is 0.01 - 0.5% by weight,  
10 preferably 0.05 - 0.2% by weight, relative to the total weight of polymers. When the amount is less than 0.01% by weight, the silane grafting reaction does not proceed sufficiently; when it exceeds 0.5% by weight, the extrusion processability tends to be poor and the extrudate surface  
15 also tends to be poor.

In the production process of silane-crosslinked polyolefin resin composition (i), the free radical generating agent and the organic unsaturated silane can be incorporated into the carrier polymer A of the present  
20 invention by swelling the carrier polymer A with a liquid mixture of the organic unsaturated silane and the free radical generating agent dissolved therein. At this time, in order to incorporate the silane to a high concentration, the carrier polymer A needs to be preheated, but the  
25 temperature must be not higher than the crystal melting point so that the polymer may not be molten. The carrier polymer A must be in the form of particles and must be a solid compatible with the base polymer to be crosslinked

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and with the organic unsaturated silane. The term "compatible" herein signifies that the carrier polymer A must not easily react with the silane and must be dispersible or soluble in the base polymer. Suitable carrier polymers A should be non-hygroscopic. That is, carrier polymers A which absorb water relatively slowly are preferred to suppress the possibility of premature hydrolysis and condensation of the organic unsaturated silane to the minimum. In any event, substantially no water should be present in the carrier polymer A. The carrier polymer A is ordinarily used in the form of particles, namely granules or pellets, preferably in the form of pellets.

The carrier polymer A used in the present invention may be, for example, ethylene-ethyl acrylate copolymer (EEA), ethylene-methyl methacrylate copolymer (EMMA), hydrogenated block copolymer obtained by hydrogenating a block copolymer comprising a polymer block consisting mainly of at least one vinylaromatic compound and a polymer block consisting mainly of at least one conjugated diene compound, e.g., hydrogenated styrene-isoprene block copolymer (SEPS) and hydrogenated styrene-butadiene block copolymer (SEBS), and the mixtures thereof.

The silanol condensation catalyst used in the present invention may be, for example, such organometallic compounds as dibutyltin dilaurate, stannous acetate, dibutyltin diacetate, dibutyltin dioctoate, lead naphthenate, zinc caprylate, cobalt naphthanate, tetrabutyl

titanate, lead stearate, zinc stearate, cadmium stearate, barium stearate and calcium stearate. The amount of these compounds to be added is 0.01 - 0.2% by weight, preferably 0.02 - 0.1% by weight, relative to the total weight of  
5 polymers. When the amount is less than 0.01% by weight, the crosslinking reaction does not proceed sufficiently, when it exceeds 0.2% by weight, the crosslinking proceeds locally in the extruder at the time of extrusion to cause deterioration of the extrudate appearance.

10 In the production process of silane-crosslinked polyolefin resin composition (i), the silanol condensation catalyst and the antioxidant can be incorporated into the carrier polymer B of the present invention by kneading and granulating them with the carrier polymer B. The carrier  
15 polymer B should be in the form of particles and should be a solid compatible with the base polymer to be crosslinked. The carrier polymer B in the present invention is ordinarily used in the form of particles, namely granules or pellets, preferably in the form of pellets.

20 The carrier polymer B used in the present invention may be, for example, polyethylene, polypropylene, copolymers of olefin with an  $\alpha$ -olefin, the  $\alpha$ -olefin being a  $C_3 - C_{12}$  olefin, e.g., propylene, butene-1, pentene-1, octene-1, 4-methylpentene-1, 4-methylhexene-1, 4,4-  
25 dimethylpentene-1, nonene-1, decene-1, undecene-1 and dodecene-1, and mixtures of these polymers.

In the production process of silane-crosslinked polyolefin resin composition (ii), the free radical



generating agent, silanol condensation catalyst and organic unsaturated silane can be incorporated into the carrier polymer C of the present invention by swelling the carrier polymer C with a liquid mixture obtained by dissolving the  
5 free radical generating agent and silanol condensation catalyst in the organic unsaturated silane. At this time, in order to incorporate the unsaturated silane to a high concentration, the carrier polymer C needs to be preheated, but the temperature must be not higher than the crystal  
10 melting point so that the polymer may not be molten. The carrier polymer C must be in the form of particles and must be a solid compatible with the base polymer to be crosslinked and with the organic unsaturated silane. The term "compatible" herein signifies that the carrier polymer  
15 C must not easily react with the organic unsaturated silane and must be dispersible or soluble in the base polymer. Suitable carrier polymers C should be non-hygroscopic. That is, the carrier polymers C which absorb water relatively slowly are preferred to suppress the possibility  
20 of premature hydrolysis and condensation of the organic unsaturated silane to the minimum. In any event, substantially no water should be present in the carrier polymer C. The carrier polymer C in the present invention is ordinarily used in the form of particles, namely  
25 granules or pellets, preferably in the form of pellets.

The carrier polymer C used in the present invention may be, for example, ethylene-ethyl acrylate

copolymer (EAA), ethylene-methyl methacrylate copolymer (EMMA), hydrogenated block copolymers obtained by hydrogenating a block copolymer comprising a polymer block consisting mainly of at least one vinylaromatic compound  
5 and a polymer block consisting mainly of at least one conjugated diene compound, e.g., hydrogenated styrene-isoprene block copolymer (SEPS) and hydrogenated styrene-butadiene block copolymer (SEBS), and the mixtures thereof.

In the production process of silane-crosslinked  
10 polyolefin resin composition (i), the carrier polymers are added such that the total amount of the carrier polymers A and B is in the range of 3 - 15% by weight relative to the whole polymers. When the amount is less than 3% by weight, a sufficient grafting does not take place; when it exceeds  
15 15% by weight, a defective extrusion tends to take place and moreover it is economically disadvantageous.

In the production process of silane-crosslinked polyolefin resin composition (ii), the amount of the carrier polymer C to be added is in the range of 4 - 13% by  
20 weight relative to the whole polymers. When the amount is less than 4% by weight, a sufficient grafting does not take place; when it exceeds 13% by weight, a defective extrusion tends to take place and moreover it is economically disadvantageous.

25 In all of the production process of silane-crosslinked polyolefin resin compositions (i), (ii) and (iii), if necessary and desired, other conventionally used additives may be added to the present resin composition,



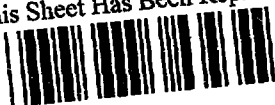
which include, for example, antioxidants, neutralizing agents, ultraviolet absorbers, antistatic agents, pigments, dispersants, thicknesses, corrosion inhibitors, mildewproofing agents, flow regulators and other inorganic  
5 fillers and other synthetic resins.

The silane-crosslinked polyolefin resin composition of the present invention is excellent in heat deformation characteristics and can be applied to a variety of uses. Though the heat resistance can be further  
10 improved by subjecting the composition to post-crosslinking treatments, e.g., steam treatment or warm water treatment after extrusion, it is also possible to omit such steps.

Accordingly, the present resin composition is particularly suitably used for producing insulated cables  
15 which require good heat resistance and flexibility. After electric wire has been covered with the present resin composition, the covered wire can be immediately covered with a sheath material without being subjected to a water crosslinking step. For thus purpose, the heat deformation  
20 percentage immediately after extrusion should be not more than 40%. The sheath material used may be, for example, vinyl chloride resin compositions.

The present invention is described in detail below with reference to Examples, which are merely for the  
25 sake of illustration and in no way limit the present invention.

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Preparation of Carrier Polymers A, B and C:

Preparation of carrier polymer A:

First, 100 parts by weight of EEA was charged into a Supermixer, stirred and mixed, and preheated to 5 80°C. Then a liquid mixture obtained by dissolving 2 parts by weight of DCP in 45 parts by weight of VTMO was charged into the Supermixer and was made to impregnate the EEA with stirring in 10 minutes.

Preparation of carrier polymer B

10 One hundred parts by weight of LDPE, 15 parts by weight of DBTDL, 16 parts by weight of an antioxidant and 5 parts by weight of a lubricant were kneaded with a pressure kneader (3ℓ-capacity, mfd. by MORIYAMA SEISAKUSHO) and granulated.

15 Preparation of carrier polymer C:

First, 100 parts by weight of EEA was charged into a Supermixer, stirred and mixed, and preheated to 80°C. Then a liquid mixture obtained by dissolving 2 parts by weight of DCP and 15 parts by weight of DBTDL in 45 20 parts by weight of VTMO was charged into the Supermixer and was made to impregnate the EEA with stirring in 10 minutes.

Examples 1 - 15 and Comparative Examples 1 - 18

In the production process of silane-crosslinked 25 polyolefin resin composition (i) the base polymer, carrier

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polymer A and carrier polymer B were melt-blended in the proportions shown in Tables 1-a and 2-a and extruded into tapes. The heat deformation percentage of the extruded tape immediately after extrusion was evaluated. Further, covered wire extrusion was conducted by using the same composition as in tape extrusion, and the surface smoothness of the extrudate was evaluated. The results of evaluation are shown in Tables 1-b and 2-b.

Examples 6 - 10 and Comparative Examples 9 - 16

10 In the production process of silane-crosslinked polyolefin resin composition (ii), the base polymer and carrier polymer C were melt-blended in the proportions shown in Tables 3-a and 4-a and extruded into tapes. The heat deformation percentage of the extruded tape immediately after extrusion was evaluated. Further, covered wire extrusion was conducted by using the same composition as in tape extrusion, and the surface smoothness of the extrudate was evaluated. The results of evaluation are shown in Tables 3-b and 4-b.

20 Examples 11 - 15 and comparative Examples 17 - 25

In the production process of silane-crosslinked polyolefin resin composition (iii), the base polymer and a mixed solution obtained by dissolving the free radical generating agent and the silanol condensation catalyst in the unsaturated organic silane compound were melt-blended in the proportions shown in Tables 5-a and 6-a and extruded into tapes. At this time, the amount of the mixed solution was regulated by means of a constant delivery pump so as to



give the part by weight shown in the Tables. The extruded tape was used to evaluate the heat deformation percentage. Further, covered wire extrusion was conducted by using the same composition as in tape extrusion and the surface  
5 smoothness of the extrudate was evaluated. The results of evaluation are shown in Tables 5-b and 6-b.

The raw material used were as follows.

- (1) EEA: ethylene-ethyl acrylate copolymer (EA content: 23% by weight, density:  $0.935 \text{ g/cm}^3$ , pellet-formed)
- 10 (2) EVA: ethylene-vinyl acetate copolymer (VA content: 25% by weight, density:  $0.950 \text{ g/cm}^3$ , pellet-formed)
- (3) VTMOs: vinyltrimethoxysilane
- (4) DCP: dicumyl peroxide
- (5) DBTDL: dibutyltin dilaurate
- 15 (6) Antioxidant: phenolic antioxidant/Irganox 1010 (mfd. by Ciba-Geigy Corp.)
- (7) Lubricant: low molecular weight polyethylene/Sanwax 171P (mfd. by Sanyo Kasei K.K.)
- (8) LDPE: low density polyethylene (density:  $0.923 \text{ g/cm}^3$ , pellet-formed)
- 20 (9) L-LDPE (1): linear, medium to low density polyethylene (density:  $0.917 \text{ g/cm}^3$ , degree of dispersion: 7.8, pellet-formed)
- (10) L-LDPE (2): linear, medium to low density  
25 polyethylene (density:  $0.919 \text{ g/cm}^3$ , degree of dispersion: 3.9, pellet-formed)

- (11) L-LDPE (3): linear, medium to low density  
polyethylene (density:  $0.902 \text{ g/cm}^3$ , degree of  
dispersion: 5, pellet-formed)
- (12) L-LDPE (4): linear, medium to low density  
polyethylene (density:  $0.925 \text{ g/cm}^3$ , degree of  
dispersion: 5, pellet-formed)
- (13) L-LDPE (5): linear, medium to low density  
polyethylene (density:  $0.918 \text{ g/cm}^3$ , degree of  
dispersion: 4.5, granular)
- (14) L-LDPE (6) : linear, medium to low density  
polyethylene (density:  $0.920 \text{ g/cm}^3$ , degree of  
dispersion: 3.6, granular)
- (15) HDPE: high density polyethylene (density  $0.950 \text{ g/cm}^3$ ,  
pellet-formed)
- The methods of evaluation are as follows.
- (16) Extruded tape appearance (examination of the presence  
or absence of fish eyes):  
50 mm $\phi$ , single-screw extruder (mfd. by TANABE  
Plastic Machine K.K.) 130-160-180-190-180°C  
L/D: 20, compression ratio: 3.5, tape die:  
width 100 mm, lip clearance: 1 mm,  
screw rotation number: 40 rpm  
tape appearance (fish eye) evaluation:  
evaluated in the order  $\bigcirc > \triangle > \times$ , level  $\bigcirc$   
being judged acceptable
- (17) Heat deformation percentage (%): according to JIS K  
6723

- (18) Extruded covered wire appearance (evaluation of extrudate surface smoothness):

5 50 mm $\phi$  single-screw extruder (mfd. by TANABE  
Plastic Machine K.K.) 130-160-180-190-180°C,  
L/D: 24, compression ratio: 4.0, conductor  
diameter: 0.8 mm $\phi$ , cover thickness 1.00 mm $\phi$ ,  
screw rotation number: 40 rpm,  
covered wire appearance evaluation: evaluated  
in the order  $\bigcirc > \Delta > \times$ , level  $\bigcirc$  being judged  
10 acceptable

- (19) Easiness of winding after wire covering (evaluation of flexibility of cable):

evaluation of covered wire in winding:  
evaluated in the order  $\bigcirc > \Delta > \times$ , level  $\bigcirc$   
15 being judged acceptable

- (20) Overall evaluation:

$\bigcirc$ : all  $\bigcirc$  in (16), (18) and (19), and not  
more than 40% in (17)  
 $\times$ :  $\times$  in any of (16), (18) and (19), or more  
20 than 40% in (17)

Table 1-a

| Ingredient        | Example |    |    |    |    | Comparative Example |    |
|-------------------|---------|----|----|----|----|---------------------|----|
|                   | 1       | 2  | 3  | 4  | 5  | 1                   | 2  |
| L-LDPE (1)        | 50      | 50 | 50 | 80 | 80 |                     | 40 |
| L-LDPE (2)        | 50      |    |    |    |    | 50                  | 60 |
| LDPE              |         | 50 |    |    |    | 50                  |    |
| HDPE              |         |    | 50 |    |    |                     |    |
| EEA               |         |    |    | 20 |    |                     |    |
| EVA               |         |    |    |    | 20 |                     |    |
| Carrier polymer-A | 5       | 5  | 5  | 5  | 5  | 5                   | 5  |
| Carrier polymer-B | 2       | 2  | 2  | 2  | 2  | 2                   | 2  |

Table 1-b

| Result of Evaluation                                  | Example |       |       |       |       | Comparative Example |       |
|-------------------------------------------------------|---------|-------|-------|-------|-------|---------------------|-------|
|                                                       | 1       | 2     | 3     | 4     | 5     | 1                   | 2     |
| Average density of base polymer, (g/cm <sup>3</sup> ) | 0.918   | 0.920 | 0.934 | 0.921 | 0.924 | 0.922               | 0.919 |
| Tape appearance                                       | ○       | ○     | ○     | ○     | ○     | ○                   | ○     |
| Heat deformation percentage, (%)                      | 29      | 20    | 23    | 37    | 33    | 21                  | 24    |
| Extruded wire smoothness                              | ○       | ○     | ○     | ○     | ○     | ×                   | ×     |
| Wire winding evaluation                               | ○       | ○     | ○     | ○     | ○     | ○                   | ○     |
| Overall evaluation                                    | ○       | ○     | ○     | ○     | ○     | ×                   | ×     |

Table 2-a

| Ingredient           | Comparative Example |    |    |    |    |    |
|----------------------|---------------------|----|----|----|----|----|
|                      | 3                   | 4  | 5  | 6  | 7  | 8  |
| L-LDPE(1)            | 40                  | 40 | 70 | 70 |    |    |
| L-LDPE(3)            |                     |    |    |    | 50 |    |
| L-LDPE(4)            |                     |    |    |    |    | 50 |
| LDPE                 | 60                  |    |    |    | 50 |    |
| HDPE                 |                     | 60 |    |    |    | 50 |
| EEA                  |                     |    | 30 |    |    |    |
| EVA                  |                     |    |    | 30 |    |    |
| Carrier<br>polymer-A | 5                   | 5  | 5  | 5  | 5  | 5  |
| Carrier<br>polymer-B | 2                   | 2  | 2  | 2  | 2  | 2  |

Table 2-b

| Result of Evaluation                                  | Comparative Example |       |       |       |       |       |
|-------------------------------------------------------|---------------------|-------|-------|-------|-------|-------|
|                                                       | 3                   | 4     | 5     | 6     | 7     | 8     |
| Average density of base polymer, (g/cm <sup>3</sup> ) | 0.921               | 0.937 | 0.922 | 0.927 | 0.913 | 0.938 |
| Tape appearance                                       | ○                   | ○     | ○     | ○     | ×     | ○     |
| Heat deformation percentage, (%)                      | 42                  | 12    | 60    | 55    | 60    | 19    |
| Extruded wire appearance                              | ×                   | ×     | ×     | ×     | ×     | ×     |
| Wire winding evaluation                               | ○                   | ×     | ○     | ○     | ○     | ×     |
| Overall evaluation                                    | ×                   | ×     | ×     | ×     | ×     | ×     |

Table 3-a

| Ingredient        | Example |    |    |    |    | Comparative Example |    |
|-------------------|---------|----|----|----|----|---------------------|----|
|                   | 6       | 7  | 8  | 9  | 10 | 9                   | 10 |
| L-LDPE (1)        | 50      | 50 | 50 | 80 | 80 |                     | 40 |
| L-LDPE (2)        | 50      |    |    |    |    | 50                  | 60 |
| LDPE              |         | 50 |    |    |    | 50                  |    |
| HDPE              |         |    | 50 |    |    |                     |    |
| EEA               |         |    |    | 20 |    |                     |    |
| EVA               |         |    |    |    | 20 |                     |    |
| Carrier polymer-C | 5       | 5  | 5  | 5  | 5  | 5                   | 5  |

Table 3-b

| Result of Evaluation                                  | Example |       |       |       |       | Comparative Example |       |
|-------------------------------------------------------|---------|-------|-------|-------|-------|---------------------|-------|
|                                                       | 6       | 7     | 8     | 9     | 10    | 9                   | 10    |
| Average density of base polymer, (g/cm <sup>3</sup> ) | 0.918   | 0.920 | 0.934 | 0.921 | 0.924 | 0.922               | 0.919 |
| Tape appearance                                       | ○       | ○     | ○     | ○     | ○     | ○                   | ○     |
| Heat deformation percentage, (%)                      | 26      | 19    | 27    | 37    | 32    | 29                  | 14    |
| Extruded wire smoothness                              | ○       | ○     | ○     | ○     | ○     | ×                   | ×     |
| Wire winding evaluation                               | ○       | ○     | ○     | ○     | ○     | ○                   | ○     |
| Overall evaluation                                    | ○       | ○     | ○     | ○     | ○     | ×                   | ×     |

Table 4-a

| Ingredient           | Comparative Example |    |    |    |    |    |
|----------------------|---------------------|----|----|----|----|----|
|                      | 11                  | 12 | 13 | 14 | 15 | 16 |
| L-LDPE (1)           | 40                  | 40 | 70 | 70 |    |    |
| L-LDPE (3)           |                     |    |    |    | 50 |    |
| L-LDPE (4)           |                     |    |    |    |    | 50 |
| LDPE                 | 60                  |    |    |    | 50 |    |
| HDPE                 |                     | 60 |    |    |    | 50 |
| EEA                  |                     |    | 30 |    |    |    |
| EVA                  |                     |    |    | 30 |    |    |
| Carrier<br>polymer-C | 5                   | 5  | 5  | 5  | 5  | 5  |

Table 4-b

| Result of Evaluation                                  | Comparative Example |       |       |       |       |       |
|-------------------------------------------------------|---------------------|-------|-------|-------|-------|-------|
|                                                       | 11                  | 12    | 13    | 14    | 15    | 16    |
| Average density of base polymer, (g/cm <sup>3</sup> ) | 0.921               | 0.937 | 0.922 | 0.927 | 0.913 | 0.938 |
| Tape appearance                                       | ○                   | ○     | ○     | ○     | ×     | ○     |
| Heat deformation percentage, (%)                      | 42                  | 10    | 50    | 50    | 65    | 8     |
| Extruded wire appearance                              | ×                   | ×     | ×     | ×     | ×     | ×     |
| Wire winding evaluation                               | ○                   | ×     | ○     | ○     | ○     | ×     |
| Overall evaluation                                    | ×                   | ×     | ×     | ×     | ×     | ×     |

Table 5-a

[illegible]

Table 5-b

| Result of Evaluation                                  | Example |       |       |       |       | Comparative Example |       |
|-------------------------------------------------------|---------|-------|-------|-------|-------|---------------------|-------|
|                                                       | 11      | 12    | 13    | 14    | 15    | 17                  | 18    |
| Average density of base polymer, (g/cm <sup>3</sup> ) | 0.918   | 0.920 | 0.934 | 0.921 | 0.924 | 0.923               | 0.920 |
| Tape appearance                                       | ○       | ○     | ○     | ○     | ○     | ○                   | ○     |
| Heat deformation percentage, (%)                      | 27      | 19    | 26    | 33    | 31    | 22                  | 27    |
| Extruded wire appearance                              | ○       | ○     | ○     | ○     | ○     | ×                   | ×     |
| Wire winding evaluation                               | ○       | ○     | ○     | ○     | ○     | ○                   | ○     |
| Overall evaluation                                    | ○       | ○     | ○     | ○     | ○     | ×                   | ×     |

Table 6-a

[illegible]

Table 6-b

| Result of Evaluation                                  | Comparative Example |       |       |       |       |       |       |
|-------------------------------------------------------|---------------------|-------|-------|-------|-------|-------|-------|
|                                                       | 19                  | 20    | 21    | 22    | 23    | 24    | 25    |
| Average density of base polymer, (g/cm <sup>3</sup> ) | 0.921               | 0.937 | 0.922 | 0.927 | 0.910 | 0.937 | 0.917 |
| Tape appearance                                       | ○                   | ○     | ○     | ○     | ×     | ○     | ×     |
| Heat deformation percentage, (%)                      | 44                  | 16    | 57    | 59    | 55    | 17    | 42    |
| Extruded wire appearance                              | ×                   | ×     | ×     | ×     | ×     | ×     | ×     |
| Wire winding evaluation                               | ○                   | ×     | ○     | ○     | ○     | ×     | ○     |
| Overall evaluation                                    | ×                   | ×     | ×     | ×     | ×     | ×     | ×     |

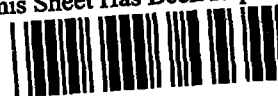
As is apparent from Tables 1-b to 6-b, the resin compositions of Examples 1 - 15 are excellent in extrusion processability and extrudate surface smoothness (extruded wire appearance) and show a very high heat resistance.

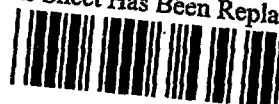
5 That is, the heat deformation percentage is not more than 40% immediately after extrusion and hence the crosslinking treatment step can be eliminated. Furthermore, it can be seen that these resin compositions give good processability and heat resistance for any of the crosslinking methods  
10 used. On the contrary, the resin compositions of Comparative Examples are all unsatisfactory in surface smoothness and are ill balanced between the extrusion processability and the heat resistance.

According to the present invention, a silane-  
15 crosslinked polyolefin resin composition excellent in extrudate surface smoothness and heat resistance can be provided. When the resin composition is used for covering electric wire the water-crosslinking step can be omitted and a sheath can be immediately applied onto the covered  
20 wire to form a cable. Resultantly, the productivity of the cable can be greatly improved and moreover the production cost can be markedly reduced. Thus, the present invention greatly contributes to the production of insulated cables.

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WHAT IS CLAIMED IS:

1. A silane-crosslinked polyolefin resin composition comprising (1) a base polymer, (2) a carrier polymer A incorporated with an organic unsaturated silane represented by the formula  $RR'SiY_2$ , wherein R is a monovalent olefinic unsaturated hydrocarbon group, Y is a hydrolyzable organic group and R' is a monovalent hydrocarbon group other than aliphatic unsaturated hydrocarbon groups or is the same as Y, and with a free radical generating agent and (3) a carrier polymer B incorporated with a silanol condensation catalyst and with an antioxidant, wherein the base polymer contains a linear, medium to low density polyethylene with a degree of dispersion ( $M_w/M_n$ ) of 4 or more, has an average density of  $0.915 \text{ g/cm}^3 - 0.935 \text{ g/cm}^3$  and shows a heat deformation percentage, determined according to JIS K 6723, after melt-kneading of not more than 40%.

2. A silane-crosslinked polyolefin resin composition comprising a base polymer and a carrier polymer C incorporated with an organic unsaturated silane represented by the formula  $RR'SiY_2$ , wherein R is a monovalent olefinic unsaturated hydrocarbon group, Y is a hydrolyzable organic group and R' is a monovalent hydrocarbon group other than aliphatic unsaturated hydrocarbon groups or is the same as Y, with a free radical generating agent and with a silanol condensation catalyst, wherein the base polymer contains a linear, medium to low density polyethylene with a degree of dispersion ( $M_w/M_n$ ) of 4 or more, has an average density of  $0.915 \text{ g/cm}^3 - 0.935 \text{ g/cm}^3$  and shows a heat deformation





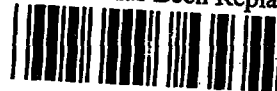
percentage, determined according to JIS K 6723, after heat-kneading of not more than 40%.

3. A silane-crosslinked polyolefin resin composition comprising a base polymer, an organic unsaturated silane represented by the formula  $RR'SiY_2$ , wherein R is a monovalent olefinic unsaturated hydrocarbon group, Y is a hydrolyzable organic group and R' is a monovalent hydrocarbon group other than aliphatic unsaturated hydrocarbon groups or is the same as Y, a free radical generating agent and a silanol condensation catalyst melt-blended with one another, wherein the base polymer contains a linear, medium to low density polyethylene with a degree of dispersion (Mw/Mn) of 4 or more, has an average density of  $0.915 \text{ g/cm}^3 - 0.935 \text{ g/cm}^3$  and shows a heat deformation percentage, determined according to JIS K 6723, after melt-kneading of not more than 40%.

4. The silane-crosslinked polyolefin resin composition according to any of the claims 1 - 3 wherein the base polymer comprises a mixture of 45 - 100 parts by weight of a linear, medium to low density polyethylene with a degree of dispersion (Mw/Mn) of 4 or more and 0 - 55 parts by weight of a high density or low density polyethylene.

5. The silane-crosslinked polyolefin resin composition according to any of the claims 1 - 3 wherein the base polymer comprises a mixture of 75 - 100 parts by weight of a linear medium to low density polyethylene with a degree of dispersion (Mw/Mn) of 4 or more and 0 - 25





parts by weight of at least one polyolefin selected from the group consisting of ethylene-ethyl acrylate copolymer (EEA), ethylene-vinyl acetate copolymer (EVA), ethylene-methyl methacrylate copolymer (EMMA), hydrogenated block copolymer obtained by hydrogenating a block copolymer comprising a polymer block consisting mainly of at least one vinylaromatic compound and a polymer block consisting mainly of at least one conjugated diene compound, and the mixtures thereof.

6. The silane-crosslinked polyolefin resin composition according to claim 3 wherein the base polymer comprises a mixture of 5 - 100 parts by weight of granular polymer and 5 - 100 parts by weight of pellet-formed polymer.

7. The silane-crosslinked polyolefin resin composition according to claim 1 wherein the carrier polymer A is selected from the group consisting of polyethylene, polypropylene and copolymers of ethylene with at least one  $\alpha$ -olefin.

8. The silane-crosslinked polyolefin resin composition according to claim 1 wherein the carrier polymer B is selected from the group consisting of ethylene-ethyl acrylate copolymer (EEA), ethylene-methyl methacrylate copolymer (EMMA), hydrogenated block copolymer obtained by hydrogenating a block copolymer comprising a polymer block consisting mainly of at least one vinylaromatic compound and a polymer block consisting



mainly of at least one conjugated diene compound, and the mixture thereof.

9. The silane-crosslinked polyolefin resin composition according to claim 1 wherein the total amount of the carrier polymers A and B is 3 - 15% by weight relative to the whole polymers.

10. The silane-crosslinked polyolefin resin composition according to claim 2 wherein the carrier polymer C is selected from the group consisting of polyethylene, polypropylene and copolymers of ethylene with at least one  $\alpha$ -olefin.

11. The silane-crosslinked polyolefin resin composition according to claim 2 wherein the amount of the carrier polymer C is 4 - 13% by weight relative to the whole polymers.

12. An insulated cable wherein the electric wire has been covered with the silane-crosslinked polyolefin resin composition according to any of the claims 1 - 11.

13. An insulated cable which is obtained by covering electric wire with the silane-crosslinked polyolefin resin composition according to any of the claims 1 - 11 and then covering the covered wire with a sheath material.



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