

PATENT SPECIFICATION

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(54) PROCESS FOR THE PREPARATION OF POLYMER
 COMPOSITIONS WHICH ARE CROSSLINKABLE
 IN THE PRESENCE OF MOISTURE FOLLOWING
 THE GRAFTING ON OF AN ETHYLENICALLY
 UNSATURATED SILANE

(71) We, KABEL- UND METALL-
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 AKTIENGESELLSCHAFT, a body corpor-
 ate organised under the laws of Germany of
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 many, do hereby declare the invention for
 which we pray that a patent may be granted
 to us, and the method by which it is to be
 performed, to be particularly described in
 and by the following statement:—

This invention relates to the preparation
 of compositions comprising a polymer, as
 herein defined, which compositions which are
 crosslinkable in the presence of water follow-
 ing the grafting-on of an ethylenically un-
 saturated silane compound contained there-
 in. The term "polymer" is employed herein
 in a broad sense in that it embraces elasto-
 meric and other polymers, including thermo-
 plastic rubbers (TPR) and other thermo-
 plastic polymers. The present compositions
 may be employed for coating or sheathing
 elongated products, e.g. electrical conductors
 or cables, or pipes. To inhibit premature
 crosslinking due to moisture absorption, and
 to promote extrudate homogeneity and sur-
 face smoothness, the (or at least one) poly-
 mer, as herein defined, is employed in the
 form of a flowable particulate material, e.g.
 powder, grit or granulate. The particles of
 this material are agitated and heated, by
 inter-particle friction and/or by the applica-
 tion of heat from the outside, to a tempera-
 ture below the lower limit of the respective
 crystallite melting range, e.g. to a temperature
 within the range 60—100°C. Before or dur-
 ing this heating, the ethylenically unsaturated
 silane compound and the requisite grafting
 and crosslinking additives, e.g. peroxides or
 activators, are added in liquid form so as to
 penetrate, by diffusion, wholly or partially
 into the individual particles of the said
 material. After the diffusion mixing, the re-
 sulting mixture is cooled, with not more

than that degree of agitation which was em-
 ployed in the heating stage, to a temperature
 at which the volatility of the said silane is
 negligible, and the cooled mixture is charged
 into one or more closed containers until it
 is to undergo grafting.

A process whereby organic polymers,
 following the grafting-on of an alkoxy-silane
 compound, can be cross-linked and hardened
 in the presence of moisture has already been
 described in German Published Specification
 ("Auslegeschrift") No. 1,794,028. In this pro-
 cess the silane may be grafted on to poly-
 ethylene macromolecules, for example. The
 grafting-on of the silane compound can be
 effected in the course of an extrusion operation
 under the influence of a compound which
 affords free radicals, e.g. a peroxide, and at a
 high temperature, e.g. 180°—220°C. In a
 preliminary mixing operation, the silane
 and (e.g.) the peroxide are mixed with the
 polymer concerned, e.g. polyethylene, this
 being in the form of a granulate, and a liquid
 mixture consisting of (e.g.) peroxide and
 silane being drummed with this granulate to
 effect a surface coating of the granules; the
 homogenising of the pre-mix is effected
 subsequently in an extruder, and is followed
 by a granulation of the homogenised material
 thus produced. The granulate, when grafted,
 is blended with (e.g.) a polyethylene com-
 position which contains a crosslinking cata-
 lyst, and the blended material is fed to a final
 shape-imparting extruder, for example for
 coating or sheathing an electrical conductor
 or cable.

In this known process, the surface coating
 technique permits only an inadequately
 homogeneous distribution of the peroxide; it
 is also liable to suffer from a certain degree
 of premature crosslinking, during the cooling
 of the grafted granulate. Accordingly we re-
 gard this known process as by no means
 straightforward. In fact we consider it unsuit-

able, in practice, for applications such as those in the cable industry in which it is necessary to produce continuously insulations for conductors and cables which have to satisfy specific electrical and mechanical requirements. As it comprises so many operations, moreover, including mixing, grafting and granulation, this known process is expensive, in addition to employing moisture-crosslinkable grafted material whose shelf life is limited.

Generally the granulation and storage of grafted material is rather uncertain. Thus, a certain degree of premature crosslinking may easily occur, which renders the processing of the material difficult, or even impracticable. It is to be regarded as a further disadvantage that, after the blending of the grafted material with the crosslinking catalyst, the extrudability of the blended material is considerably impaired if even slight traces of unwanted moisture are present in the material, which possibility can hardly be excluded without increasing costs. In these circumstances, the extruded products are liable to have defects, for instance a rough surface, which, if the products are to be exposed to substantial voltages, may lead to a breakdown.

In view of these difficulties, an alternative procedure has already been proposed, in German Published Specification ("Offenlegungsschrift") No. 2,439,513. In this alternative procedure, which utilises diffusion mixing, the polymer is employed in the form of a flowable particulate material, e.g. a powder, grit or granulate, the particles of this material being agitated and being heated, by inter-particle friction and/or by the application of heat from the outside, to a temperature below the lower limit of the respective crystallite melting range, and the silane compound and the requisite grafting and crosslinking additives being added in liquid form before or during this heating and wholly or partially penetrating, by diffusion, into the individual particles of the said material. This gives a homogeneous distribution of the various substances which are added, and thus the silane, being distributed homogeneously in the above-mentioned material, can duly be grafted on to the polymer molecules subsequently to the diffusion mixing. However this German Specification does not contemplate separation of the addition of antioxidant(s) and peroxide(s) during the procedure in question.

In the above-mentioned diffusion mixing procedure, the fact that the ingredients necessary for crosslinking are already distributed homogeneously in the particulate material before the grafting stage means that in the subsequent processing the extruder need perform no mixing work, or homogenising work, at temperatures below the tempera-

ture at which the grafting catalyst, e.g. a peroxide, first becomes operative. The danger of premature crosslinking is therefore very slight; and the entire length of the extruder is accordingly available for the grafting reaction, this state of affairs permitting a substantially increased output.

However, if the diffusion-mixed material is not fabricated, e.g. extruded, on the spot, but is instead, until it is to undergo grafting, charged into closed containers for storage or transport, it may be found that the shelf life of the diffusion-mixed material is unduly limited. This limitation results from certain side-reactions which may take place even at room temperature, these side-reactions detracting from the effectiveness of the grafting reaction, so that the degree of crosslinking is liable to be reduced.

It is an object of the present invention, therefore, to improve the shelf life of a diffusion-mixed material constituting a precursor of a moisture-crosslinked silane-grafted composition based on a polymer as herein defined.

According to the present invention we provide a process for the preparation of a composition comprising a polymer, as herein defined, which composition is crosslinkable in the presence of moisture following the grafting-on of an ethylenically unsaturated silane compound contained therein, wherein premature crosslinking due to moisture absorption is inhibited, and extrudate homogeneity and surface smoothness are promoted, by employing the (or at least one) polymer, as herein defined, in the form of a flowable particulate material, the particles of this material being agitated and being heated by inter-particle friction and/or by the application of heat from the outside to a temperature below the lower limit of the respective crystallite melting range, e.g. to a temperature within the range 60–100°C, the ethylenically unsaturated silane compound and the requisite grafting and cross-linking additives being added in liquid form before or during this heating and wholly or partially penetrating, by diffusion, into the individual particles of the said material, the resulting mixture being cooled after this diffusion mixing, with not more than that degree of agitation which was employed in the heating stage, to a temperature at which the volatility of the said silane is negligible, and the cooled mixture being charged into one or more closed containers until it is to undergo grafting; in which process one or more antioxidants and one or more peroxides are employed, the antioxidant(s) on the one hand and the peroxide(s) on the other hand being added to the material containing the polymer, as herein defined, independently of and separately from one another, the peroxide(s) being added before or during the heating to the first-mentioned

temperature, and the antioxidant(s) being added during or after the cooling stage.

The invention also includes elongated products, e.g. electrical conductors or cables, or pipes, having a coating or sheath composed of a crosslinked material obtained from a composition prepared by a process as specified in the last preceding paragraph.

The flowable particulate material specified in the last preceding paragraph but one may for instance comprise one or more thermoplastic polymers, e.g. a polyethylene, or one or more thermoplastic rubbers, and may for instance comprise a powder, grit or granulate.

The invention is based on the recognition of the fact that antioxidants and peroxides are liable to deactivate each other, or at least render each other less effective, so as to reduce the efficacy of the silane grafting. To produce a perfect extrudate, however, e.g., a coating or sheath for an electrical conductor or cable or for a pipe, an antioxidant should be present during the grafting reaction, for only in the presence of an antioxidant will undesired reactions, e.g. peroxidic premature crosslinking, be prevented.

In the process of the invention, the one or more antioxidants, preferably in the form of a masterbatch, may for example be added to the respective material during the cooling stage; then, as the diffusion mixing is already substantially concluded, the antioxidant(s), although duly incorporated in the material in question, will not be actually assimilated into the individual particles of this material. The antioxidant(s) can then be directly effective only in the vicinity of the interfaces of the respective material; however, this fact does not prevent good storage of the material. It is advantageous, in this version of the process of the invention, that the cooling stage should comprise cooling to a temperature below 40°C, at which the vapour pressures of the additives or ingredients incorporated in the polymer or elastomer containing material are acceptably low.

In another version of the process of the invention, it has proved particularly advantageous that the antioxidant(s), preferably in masterbatch form, being stored separately from the above-mentioned cooled mixture, are added to the material containing the polymer, as herein defined, after the cooling stage but before its further processing.

With a view to obtaining optimum distribution, it has proved particularly expedient to add the antioxidant(s) in the form of a masterbatch, as already indicated. This masterbatch preferably contains approximately 8% by weight antioxidant. The (or an) antioxidant may for example comprise 2,2,4-trimethylidihydroquinoline or an oligomer thereof. The antioxidant masterbatch may for example be a masterbatch in poly-

ethylene, an ethylene copolymer, or a thermoplastic or other rubber. If desired, the antioxidant masterbatch may be a masterbatch in an already silane-grafted polymer, as herein defined.

In practice, and more particularly when grafting is effected in an extruder which simultaneously serves for imparting a desired final shape, it is advantageous to add the antioxidant masterbatch by means of metered-feed discs immediately before extrusion. Storage periods of ten weeks or more are then permissible without the subsequent crosslinking, or the quality of the extruded product, being jeopardised.

The antioxidant masterbatch may if desired contain one or more colouring additives and/or crosslinking catalysts. This can assist in minimising the moisture sensitivity, during storage, of the material with which the masterbatch is to be compounded. The metered feed-in of the masterbatch can be utilised to obtain significant modifications of the fusion characteristics, viscosity and crosslinking behaviour of the composition obtained when the masterbatch has been added.

It is frequently particularly advantageous in the process of the invention that the preparation of the mixture which is to be charged into the above-mentioned one or more containers should be effected in a mixing apparatus having both heating and cooling capabilities. For this purpose use may be made of high-speed mixers; these are closed mixing devices within which stirring elements can be rotated by electric motors at high speed, e.g. 500 to 3000 r.p.m. If the required temperature in the heating stage is achieved by agitation, entailing collision and friction of the particles of the respective material, the particles may begin to fuse superficially yet the high speed of rotation will prevent agglomeration of the particles; even so, the superficial softening accelerates the diffusion mixing effect. The diffusion of the silane and crosslinking additives takes place slowly at the beginning of the heating stage, but at temperatures of 70 to 90°C a high speed of diffusion can be obtained. Any resultant reduced pressure in the system can be compensated by introducing an inert gas. The diffusion mixing can be monitored by following the current taken by the electric motors which drive the mixing elements. Thus, a considerable increase in this current takes place towards the end of the diffusion mixing as a result of incipient superficial fusion of the particles concerned and the diminishing lubricant action of the liquid additives employed.

Whether or not this mixing technique is adopted, the diffusing-in of the silane and the other additives can be promoted (even at a substantially lower stirring speed) by supplying heat to the mixer, i.e. by providing for

the temperature required for this diffusing-in to be attained by heat transfer from the outside.

The crosslinking additives may be dissolved in the silane, and, either at once or after a preliminary drying at elevated temperature, may be added by means of an automatic metering-in pump. It has also proved advantageous in many cases to flush the mixing apparatus beforehand with an inert gas, whereby air is removed, the mixing apparatus being of a construction permitting it to be gastightly closed.

After mixing, the mixed material, which may be at (e.g.) 90–100°, can be transferred to a cooling mixer; cooling can then be effected at a lower mixing speed than that of the heating stage, and, after a sufficiently low temperature has been attained, charging into metal drums, for example, can be carried out. As indicated earlier herein, the antioxidants can be added in the course of the cooling stage, or antioxidant addition may be deferred, the antioxidant(s) being stored preferably in the form of an antioxidant masterbatch separately from the other mixed material, to be added immediately before extrusion. If use is made of e.g. an antioxidant masterbatch containing approximately 8% by weight antioxidant, this will provide approximately 0.4% by weight antioxidant in the product when the proportion of masterbatch is 5% by weight of the polymer, as herein defined.

EXAMPLE

One example of a formulation which may be employed in preparing a moisture-crosslinkable composition in accordance with the present invention is the following:

	parts by weight
polyethylene (MT8)	100
2,2,4 - trimethyldihydroquinoline	0.5
tert.-butylperoxyisobutylate	0.12
1,3 - bis - (tert. - butylperoxy-isopropyl) - benzene	0.04
triethyl cyanurate	0.06
vinyltrimethoxysilane	2.6
diethyl tin dilaurate	0.05

WHAT WE CLAIM IS:—

1. Process for the preparation of a composition comprising a polymer, as herein defined, which composition is crosslinkable in the presence of moisture following the grafting-on of an ethylenically unsaturated silane compound contained therein, wherein premature crosslinking due to moisture absorption is inhibited, and extrudate homogeneity and surface smoothness are promoted, by employing the (or at least one) polymer, as herein defined, in the form of a flowable particulate material, the particles of this

material being agitated and being heated by inter-particle friction and/or by the application of heat from the outside to a temperature below the lower limit of the respective crystallite melting range the ethylenically unsaturated silane compound and the requisite grafting and crosslinking additives being added in liquid form before or during this heating and wholly or partially penetrating, by diffusion, into the individual particles of the said material, the resulting mixture being cooled after this diffusion mixing, with not more than that degree of agitation which was employed in the heating stage, to a temperature at which the volatility of the said silane is negligible, and the cooled mixture being charged into one or more closed containers until it is to undergo grafting; in which process one or more antioxidants and one or more peroxides are employed, the antioxidant(s) on the one hand and the peroxide(s) on the other hand being added to the material containing the polymer, as herein defined, independently of and separately from one another, the peroxide(s) being added before or during the heating to the first-mentioned temperature, and the antioxidant(s) being added during or after the cooling stage.

2. Process according to claim 1, in which the first-mentioned temperature is within the range 60 to 100°C.

3. Process according to claim 1 or 2, in which the flowable particulate material comprises at least one thermoplastic polymer.

4. Process according to claim 3, in which the flowable particulate material comprises a polyethylene.

5. Process according to claim 1 or 2, in which the flowable particulate material comprises at least one thermoplastic rubber.

6. Process according to claim 1, 2, 3, 4 or 5, in which the flowable particulate material comprises a powder, grit or granulate.

7. Process according to any preceding claim, in which the one or more antioxidants are added to the material containing the polymer, as herein defined, during the cooling stage.

8. Process according to claim 7 in which the cooling stage comprises cooling to a temperature below 40°C.

9. Process according to any of claims 1 to 6, in which the one or more antioxidants are added to the material containing the polymer, as herein defined, after the cooling stage but before its further processing.

10. Process according to any preceding claim, in which the one or more antioxidants are added in the form of an antioxidant masterbatch in polyethylene, an ethylene copolymer, or a thermoplastic or other rubber.

11. Process according to claim 10, in which the antioxidant masterbatch contains approximately 8% by weight antioxidant.

12. Process according to claim 10 or 11,

the temperature required for this diffusing-in to be attained by heat transfer from the outside.

5 The crosslinking additives may be dissolved in the silane, and, either at once or after a preliminary drying at elevated temperature, may be added by means of an automatic metering-in pump. It has also proved advantageous in many cases to flush the mixing apparatus beforehand with an inert gas, whereby air is removed, the mixing apparatus being of a construction permitting it to be gastightly closed.

10 After mixing, the mixed material, which may be at (e.g.) 90—100°, can be transferred to a cooling mixer; cooling can then be effected at a lower mixing speed than that of the heating stage, and, after a sufficiently low temperature has been attained, charging into metal drums, for example, can be carried out. As indicated earlier herein, the antioxidants can be added in the course of the cooling stage, or antioxidant addition may be deferred, the antioxidant(s) being stored preferably in the form of an antioxidant masterbatch separately from the other mixed material, to be added immediately before extrusion. If use is made of e.g. an antioxidant masterbatch containing approximately 8% by weight antioxidant, this will provide approximately 0.4% by weight antioxidant in the product when the proportion of masterbatch is 5% by weight of the polymer, as herein defined.

35 EXAMPLE

One example of a formulation which may be employed in preparing a moisture-crosslinkable composition in accordance with the present invention is the following:

	parts by weight
polyethylene (MT8)	100
2,2,4 - trimethyldihydroquinoline	0.5
tert.-butylperoxyisononate	0.12
45 1,3 - bis - (tert. - butylperoxyisopropyl) - benzene	0.04
triethyl cyanurate	0.06
vinyltrimethoxysilane	2.6
dibutyl tin dilaurate	0.05

50 WHAT WE CLAIM IS:—

1. Process for the preparation of a composition comprising a polymer, as herein defined, which composition is crosslinkable in the presence of moisture following the grafting-on of an ethylenically unsaturated silane compound contained therein, wherein premature crosslinking due to moisture absorption is inhibited, and extrudate homogeneity and surface smoothness are promoted, by employing the (or at least one) polymer, as herein defined, in the form of a flowable particulate material, the particles of this

material being agitated and being heated by inter-particle friction and/or by the application of heat from the outside to a temperature below the lower limit of the respective crystallite melting range the ethylenically unsaturated silane compound and the requisite grafting and crosslinking additives being added in liquid form before or during this heating and wholly or partially penetrating, by diffusion, into the individual particles of the said material, the resulting mixture being cooled after this diffusion mixing, with not more than that degree of agitation which was employed in the heating stage, to a temperature at which the volatility of the said silane is negligible, and the cooled mixture being charged into one or more closed containers until it is to undergo grafting; in which process one or more antioxidants and one or more peroxides are employed, the antioxidant(s) on the one hand and the peroxide(s) on the other hand being added to the material containing the polymer, as herein defined, independently of and separately from one another, the peroxide(s) being added before or during the heating to the first-mentioned temperature, and the antioxidant(s) being added during or after the cooling stage.

2. Process according to claim 1, in which the first-mentioned temperature is within the range 60 to 100°C.

3. Process according to claim 1 or 2, in which the flowable particulate material comprises at least one thermoplastic polymer.

4. Process according to claim 3, in which the flowable particulate material comprises a polyethylene.

5. Process according to claim 1 or 2, in which the flowable particulate material comprises at least one thermoplastic rubber.

6. Process according to claim 1, 2, 3, 4 or 5, in which the flowable particulate material comprises a powder, grit or granulate.

7. Process according to any preceding claim, in which the one or more antioxidants are added to the material containing the polymer, as herein defined, during the cooling stage.

8. Process according to claim 7 in which the cooling stage comprises cooling to a temperature below 40°C.

9. Process according to any of claims 1 to 6, in which the one or more antioxidants are added to the material containing the polymer, as herein defined, after the cooling stage but before its further processing.

10. Process according to any preceding claim, in which the one or more antioxidants are added in the form of an antioxidant masterbatch in polyethylene, an ethylene copolymer, or a thermoplastic or other rubber.

11. Process according to claim 10, in which the antioxidant masterbatch contains approximately 8% by weight antioxidant.

12. Process according to claim 10 or 11,



* C L M S *

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- in which the antioxidant masterbatch contains one or more colouring additives and/or cross-linking catalysts.
- 5 13. Process according to claim 10, 11 or 12, in which the antioxidant masterbatch is a masterbatch in an already silane-grafted polymer, as herein defined.
- 10 14. Process according to any preceding claim, in which the preparation of the mixture which is charged into the one or more containers is effected in a mixing apparatus having both heating and cooling capabilities.
- 15 15. Process according to claim 1, employing starting materials substantially as specified in the foregoing Example.
16. A polymer or elastomer composition prepared by a process according to any preceding claim.
17. An elongated product having a coating or sheath composed of a crosslinked material obtained from a composition according to claim 16.
18. An electrical conductor or cable having a coating or sheath as specified in claim 17.
19. A pipe having a coating or sheath as specified in claim 17.
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