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(54) METHOD FOR THE PRODUCTION OF CROSS-LINKED THERMOPLASTIC OR ELASTOMERIC MATERIALS

(71) We, KABEL- UND METALL-
WERKE GUTENHOFFNUNGSHUTTE
AKTIENGESELLSCHAFT, a body
corporate organised under the laws of
Germany of 271, Vahrenwalder Strasse,
Hannover, Germany, 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 a method of
producing cross-linked thermoplastic or
elastomeric materials, the materials being
cross-linked in the presence of moisture
following the grafting of a silane compound
on to them, and the method being of
particular value for the sheathing of lengths
of longitudinally extended material, e.g. an
electrical cable or wire, or a tube. The
method comprises the steps of mechanically
kneading a mixture of the requisite
ingredients, grafting, degassing (if
necessary), and shaping. The grafting may
be carried out in the presence of one or
more peroxide compounds and/or grafting
or crosslinking activators.

For the purpose of cross-linking in the
presence of moisture, it has been known for
some time to graft alkoxy-silanes on to a
polyethylene chain. The grafting can be
effected by the use of free-radical initiators,
for example peroxides; however, it can also
be effected by mechanical kneading under
certain conditions, free radicals again being
produced (German Published Specification
("Auslegeschrift") No. 1,794,028). Further,
it is known to use, as an alternative to
polyethylene, a rubbery copolymer of
ethylene and vinyl acetate ("EVA") which
can be cross-linked in the presence of
moisture (German Published Specification
("Offenlegungsschrift") No. 2,350,876).

We are concerned here not only with the
cross-linking of thermoplastic materials in
the presence of moisture, but also with the

cross-linking of elastomeric materials,
particularly those which have a good heat
resistance, even though their application to
electrical cables and wires tends to be
restricted to low-voltage insulation, and to
cable sheathing. As is well known, this is
because their electrical properties do not
approach those of non-polar materials,
e.g. polyethylene and ethylene copolymers.

It is an object of the present invention to
make possible the production of improved
cross-linked thermoplastic or elastomeric
materials, the materials being cross-linked
in the presence of moisture following the
grafting of a silane compound on to them.

According to the present invention we
provide a method of producing cross-linked
thermoplastic or elastomeric materials, the
materials being cross-linked in the presence
of moisture following the grafting of a
silane compound on to them, and the
method comprising the steps of
mechanically kneading a mixture of the
requisite ingredients, grafting, degassing (if
necessary), and shaping, in which method
the mixture employed comprises a polymer
composition made up of: (A) at least 50%
by weight of an olefin polymer or
copolymer; and (B) up to 50% by weight of
a modifier, as herein defined, comprising
one or more elastomers and/or other
polymeric substances. The polymer
composition just specified has the
particular advantage of permitting a
considerable degree of regulation or
control over the properties of the cables or
wires, tubes or other products which are
made therefrom. It is thus possible,
according to the particular field(s) of
application of the products, and by an
appropriate choice of polymer composition
and more particularly of the modifier (as
herein defined) present therein, to regulate
the extrudability of the mixture, if, for any
special reasons, the flow behaviour of the
material is of importance. However, it is

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similarly possible to regulate, in a method according to the invention, the stability, flexibility and electrical properties of the product, to suit the requirements of the

5 In the method of the invention the component "A" employed can for example comprise polyethylene, the component "B" employed comprising an elastomer, e.g. an ethylene-propylene rubber (EPR). In this case, in which the ratio of "A" to "B" may for instance be 5:1, and in which an elevated melt viscosity is obtainable, the mixture is particularly suitable for electrical cables and wires. However, it is also possible, and indeed of particular advantage, to employ as component "A" a copolymer of ethylene with a minor proportion of an acrylate, butene, hexene, propylene and/or vinyl acetate; these latter-mentioned comonomers being used singly or in the form of mixtures of two or more thereof. Again, it is possible to employ a component "A" comprising a butene or propylene polymer or copolymer. In each case, as already specified, the component "A" is employed in a proportion of at least 50% by weight.

30 The modifier "B" referred to in the present description and claims is a polymeric or elastomeric component whose properties differ significantly from those of the component "A" employed, and which is derived from a monomer or monomer combination differing qualitatively and/or quantitatively from the monomer or monomer combination from which the component "A" is derived.

40 The nature and proportion of the modifier "B" employed will depend upon the properties required in the product. It may be for example be an elastomer, e.g. an ethylene-propylene rubber (EPR), an ethylene-propylene-diene monomer terpolymer (EPDM), a butyl rubber, or a chlorosulphated polyethylene. However, it may be advantageous in certain cases to employ a modifier "B" comprising a thermoplastic material, for example a polypropylene, a polybutene, a polyisobutylene or a chlorinated polyethylene; the last-mentioned substance is particularly suitable for the production of difficultly inflammable products, on account of its substantial chlorine content.

55 It is possible for the cross-linkable mixture comprising components "A" and "B" to be prepared by mixing component "A" and component "B" and any desired additives (e.g. cross-linking agents, activators and the like) and grafting them in a common grafting step. For this purpose it is possible to form a premixture in a quickly-running mixer, and then to feed the

material thus premixed into an extruder in which grafting takes place. 65

However, it is advantageous in certain cases to directly meter component "A", together with component "B" and any desired additives, to an extruder in which mixing and grafting take place, to degas the grafted material, and, after further homogenisation, to carry out the shaping step in a second extruder. 70

The method of the present invention can be modified in that it may be advantageous (depending upon the desired properties of the cross-linkable grafted material) to mix component "A" with the silane compound and any desired additives, to graft the mixture thus formed, and to blend the modifier, i.e. component "B" (a butyl rubber, for example), with the mixture thus prepared, this modifier being ungrafted. In this way it is possible to ensure that degradation or decomposition of (e.g.) the butyl rubber will not occur. 75 80 85

The method of the present invention can also be modified in that component "A" and component "B" can be brought together after separately grafting these two components by means of similar or dissimilar grafting ingredients (silane and such other grafting ingredients as may be required), and mixing them together after the grafting step. This procedure has the particular advantage that it permits the use of dissimilar grafting ingredients for the two components. 90 95

The following Example illustrates the invention. 100

Example

The following ingredients were mixed together:

	parts	
Polyethylene (1810H)	70—90	105
EPDM (sequence type)	30—10	
Aromatic oil	2—5	
Silane (vinyltrimethoxysilane)	1—5	
Organic peroxide	0.1—0.5	110
Anox HB	0.4	
Naftovin SN/L	0.05	

The resulting mixture was extruded to form a sheath around a length of longitudinally extended material, and was thereupon contacted with water. 115

As a result of the addition of the EPDM, the flexibility of the material is improved, and its heat resistance reaches a satisfactory value very shortly after leaving the extrude die, so that any danger of eccentricity (for example in the sheath of an electrical cable) is reduced. A further advantage is that the corona sensitivity of the polyethylene (component "A") is considerably reduced by the addition of the 120 125

EPDM. The aromatic oil added serves as an extrusion aid or processing aid, and it can also be of value as a voltage stabiliser, thus improving the electrical properties of the product.

WHAT WE CLAIM IS:—

1. Method of producing cross-linked thermoplastic or elastomeric materials, the materials being cross-linked in the presence of moisture following the grafting of a silane compound on to them, and the method comprising the steps of mechanically kneading a mixture of the requisite ingredients, grafting, degassing (if necessary), and shaping, in which method the mixture employed comprises a polymer composition made up of: (A) at least 50% by weight of an olefin polymer or copolymer; and (B) up to 50% by weight of a modifier, as herein defined, comprising one or more elastomers and/or other polymeric substances.
2. Method according to claim 1, in which the component "A" employed comprises polyethylene and the component "B" employed comprises an elastomer.
3. Method according to claim 2, in which the component "B" employed comprises an ethylene-propylene copolymer or an ethylene-propylene-diene monomer terpolymer.
4. Method according to claim 1, in which the component "A" employed comprises a copolymer of ethylene with a minor proportion of an acrylate, butene, hexene, propylene and/or vinyl acetate, these comonomers being used singly or in the form of mixtures of two or more thereof.
5. Method according to claim 1 or 4, in which the component "B" employed comprises a thermoplastic material.

6. Method according to any of the preceding claims, in which the components "A" and "B" are mixed and are grafted in a common grafting step.

7. Method according to any of claims 1 to 5, modified in that the component "A" is grafted after addition of the requisite additives, and thereafter the modifier "B" is blended, in ungrafted form, with it.

8. Method according to any of claims 1 to 5, modified in that component "A" and component "B" are separately grafted by means of similar or dissimilar grafting ingredients, and are mixed together after the grafting step.

9. Method according to any of the preceding claims, in which grafting is carried out in the presence of one or more peroxide compounds and/or grafting or cross-linking activators.

10. Method according to any of the preceding claims, in which the shaping step comprises applying the material to be shaped, so as to form a sheath, around a length of longitudinally extended material.

11. Method according to claim 10, in which the sheath is formed around an electrical cable or wire, or around a tube.

12. Method according to claim 10, employing a mixture whose composition is substantially as set forth in the foregoing Example.

13. A product comprising a cross-linked thermoplastic or elastomeric material, produced by a method according to any of the preceding claims.

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EPDM. The aromatic oil added serves as an extrusion aid or processing aid, and it can also be of value as a voltage stabiliser, thus improving the electrical properties of the product.

WHAT WE CLAIM IS:—

1. Method of producing cross-linked thermoplastic or elastomeric materials, the materials being cross-linked in the presence of moisture following the grafting of a silane compound on to them, and the method comprising the steps of mechanically kneading a mixture of the requisite ingredients, grafting, degassing (if necessary), and shaping, in which method the mixture employed comprises a polymer composition made up of: (A) at least 50% by weight of an olefin polymer or copolymer; and (B) up to 50% by weight of a modifier, as herein defined, comprising one or more elastomers and/or other polymeric substances.

2. Method according to claim 1, in which the component "A" employed comprises polyethylene and the component "B" employed comprises an elastomer.

3. Method according to claim 2, in which the component "B" employed comprises an ethylene-propylene copolymer or an ethylene-propylene-diene monomer terpolymer.

4. Method according to claim 1, in which the component "A" employed comprises a copolymer of ethylene with a minor proportion of an acrylate, butene, hexene, propylene and/or vinyl acetate, these comonomers being used singly or in the form of mixtures of two or more thereof.

5. Method according to claim 1 or 4, in which the component "B" employed comprises a thermoplastic material.

6. Method according to any of the preceding claims, in which the components "A" and "B" are mixed and are grafted in a common grafting step.

7. Method according to any of claims 1 to 5, modified in that the component "A" is grafted after addition of the requisite additives, and thereafter the modifier "B" is blended, in ungrafted form, with it.

8. Method according to any of claims 1 to 5, modified in that component "A" and component "B" are separately grafted by means of similar or dissimilar grafting ingredients, and are mixed together after the grafting step.

9. Method according to any of the preceding claims, in which grafting is carried out in the presence of one or more peroxide compounds and/or grafting or cross-linking activators.

10. Method according to any of the preceding claims, in which the shaping step comprises applying the material to be shaped, so as to form a sheath, around a length of longitudinally extended material.

11. Method according to claim 10, in which the sheath is formed around an electrical cable or wire, or around a tube.

12. Method according to claim 10, employing a mixture whose composition is substantially as set forth in the foregoing Example.

13. A product comprising a cross-linked thermoplastic or elastomeric material, produced by a method according to any of the preceding claims.

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