

PATENT SPECIFICATION

(11)

1 486 953

1 486 953

- (21) Application No. 18463/75 (22) Filed 2 May 1975
 (31) Convention Application No. 2.422.914 (32) Filed 11 May 1974 in
 (33) Federal Republic of Germany (DT)
 (44) Complete Specification published 28 Sept. 1977
 (51) INT. CL.² H01B 9/02-13/00
 (52) Index at acceptance
 H1A 2E3D2 3M 5
 (72) Inventors FRITZ GLANDER
 HERMANN UWE VOIGT



(54) ELECTRIC CABLES AND A METHOD OF PRODUCING THEM

(71) We, KABEL- UND METALLWERKE GUTHOFFNUNGSHUTTE AKTIENGESELLSCHAFT, a body corporate organised under the laws of Germany of 271, Vahrenwalder

5 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:—

10 The present invention relates to an electric cable, particularly a high or very high voltage cable, which under an insulation formed from a thermoplastic or elastomeric material has a conductor smoothing formed from a cross-linkable material.

15 A method of cross-linking organic polymerisates by grafting with alkoxy-silane compounds and curing in the presence of moisture is known from German Auslegeschrift No. 1,794,028. In this method a polymer, e.g. polyethylene, is compounded with an alkoxy-silane compound of the formula $R-SiY_3$ under conditions under 20 which free radicals are formed; R is a vinyl group or α -methacryloxypropyl group, and Y is an alkoxy group. During or after this compounding a silanol condensation catalyst may be added. The addition of organic peroxides supplying free radicals is also possible. The material may be processed using, for example, extruders in which homogenising and grafting may be effected.

25 Since compositions thus produced cross-link in the presence of moisture, their granulation and storage raise considerable problems. Thus, premature cross-linking may readily occur, making processing difficult or even impossible. Other difficulties 30 arise when a composition has to be made conductive, by adding carbon black. Since the carbon blacks used hitherto have been hygroscopic, containing moisture removable only with difficulty and incompletely, even 35 by drying processes, the conductive com-

position has not been very suitable for applications involving moisture cross-linking (through siloxane bridges) in the cable industry.

Electric cables and lines, particularly 50 those for high or very high voltages, may have, around the electric conductor, a conductor smoothing intended to avoid increases in electric field strength due to roughness of the surface of the conductor. 55 This conductor smoothing is of particular value if it is cross-linkable; thus its cross-linking, and possibly that of the surrounding insulation also, may be effected after extrusion on to the conductor by passage 60 through a heat-treatment zone, e.g. a continuous vulcanisation ("CV") installation (cf. E. Tunncliffe, "Continuous Vulcanisation of Cables", Trans. I.R.I., 29 (1953), 2). This entails undesirable expense, however, 65 particularly if the insulation is not cross-linkable in the "CV" installation.

It is an object of the present invention, therefore, to provide an electric cable, particularly a high or very high voltage cable, 70 which can be produced with simple means but still meets the relevant electrical requirements.

According to the present invention, we provide an electric cable having a conductor 75 smoothing comprising a cross-linked material and an electrically conductive constituent under an insulation formed from a thermoplastic or elastomeric material, wherein the insulation comprises 80 a grafted polymer cross-linked by the action of moisture, and the cross linked material of the conductor smoothing is cross-linked without externally applied heat, as herein defined. By "externally 85 applied heat" we mean herein heat from outside the cable rather than heat from outside the conductor smoothing. The cable, because of the nature of its insulation, can be produced by simple means, but although 90

no externally applied heat, as herein defined, is relied upon it is still suitable for higher voltages, even for example from 1 kV upwards, because it has a conductor smoothing as just specified.

Preferably the conductor smoothing comprises a thermoplastic or elastomeric material cross-linked by the action of moisture.

In the preferred case just mentioned, the cable may, in accordance with the present invention, be produced by a method wherein the electrically conductive constituent of the conductor smoothing is added to its cross-linkable constituent only during the operation in which the conductor smoothing is applied around the respective conductor.

The invention also includes a method of producing a cable as specified in the last preceding paragraph but two, in which the conductor smoothing is cross-linked by heat, wherein this heat is derived from the heat generated in the insulation when it cross-links by the action of moisture.

The invention further includes a method of producing a cable as specified in the last preceding paragraph but three, in which the conductor smoothing is cross-linked by heat, wherein this heat is provided by the application of UHF radiation.

To prevent moisture absorbed by the conductor smoothing from causing premature cross-linking in the above-mentioned preferred case wherein the conductor smoothing comprises a thermoplastic or elastomeric material cross-linked by the action of moisture, the addition of the electrically conductive constituent, for example carbon black, to the cross-linkable constituent of the conductor smoothing is preferably delayed until a time immediately before, or even (as indicated earlier) during, the operation in which the conductor smoothing is applied around the respective conductor. The carbon black, if used, may for example be added in the form of a carbon black masterbatch (vide infra). The risk of premature cross-linking due to a high moisture content of (e.g.) carbon black in the conductor smoothing is thus substantially reduced. Extrudability is not seriously affected even if (e.g.) 40 parts of carbon black per 100 of polymer (not an unusual proportion) are used to achieve the necessary electrical conductivity.

The cross-linkable grafted polymer for the insulation is preferably prepared (see our U.K. Patent Application No. 7611/75) Serial No. 1486952 by adding to the desired polymeric material in the form of free-flowing granules which are kept in movement and under the crystalline melting range (preferably at temperatures from 60 to 100°C) one or more cross-linking agents

which partly or wholly penetrate, by diffusion, into the surfaces of the granules, and thus contribute to homogeneous distribution in the still free-flowing material. A grafted polymer produced by this method, in comparison with the material previously mentioned, shows a considerable improvement in quality, and improved processability.

The danger of premature cross-linking of the conductor smoothing due to ingredients containing moisture, e.g. carbon black, can be further reduced by adding the latter in masterbatch form, i.e. in the form of a previously prepared blend with a small portion of the respective polymer (i.e. a portion so small that any premature cross-linking in it could be tolerated). The masterbatch can advantageously be metered directly into the feed hopper of an extruder whereby the conductor smoothing is applied around the respective conductor.

It is also advantageous to use grades of carbon black (e.g. those sold under the trade name Ketjenblack EC) which need only be added in relatively small amounts (e.g. 10 to 15%) to impart adequate electrical conductivity to a polymeric material. (The words "Ketjenblack EC" are a registered Trade Mark). Thus, the resistivity of a mixture containing only 10 parts (per 100 of polymer) of Ketjenblack EC, for example, is below 100Ω cm. Since the amount of moisture introduced by 10 parts of carbon black is substantially smaller than with the proportion of 30 parts customarily used, the degree of premature cross-linking due to moisture in the case of this grade of carbon black is lower, and therefore the extrudability of the conductor smoothing material is better.

Another possible way of keeping premature cross-linking due to absorbed moisture at a low level is to use a carbon black having a mean particle size of from 70 to 100 mμ, preferably 95 mμ, and a mean surface area of 15 to 30 m²/g, preferably from 20 to 25 m²/g, measured by the BET method, i.e. the method of Brunauer, Emmet & Teller, described in J. Amer. Chem. Soc., 60 (1938), page 309 (cf. B.S. 4359, part I, 1969). The relatively coarse grain of this carbon black keeps the absorption of moisture to a minimum, and conductivity can be adequate for the purpose of radiation protection for electric cables, for example, and also welding with other materials (these being thermoplastic materials) can be straightforward.

The influence of moisture on the initiation of cross-linking and the danger of premature cross-linking can be further reduced by the addition of one or more substances which are capable of binding water more strongly (even at elevated temperatures) than (e.g.)

porated. These substances include, for any carbon black which is to be incorporated, grades of calcium oxide such as those sold under the trade name "Rheno-sorb". The substances just mentioned may be added either in plain form or in coated form, or again in the form of a masterbatch. In this case the amount of these water-binding substances should preferably be such that their water-binding power has no, or a minimal, adverse effect upon the desired cross-linking by the action of moisture whereby the insulation or semi-conductive layer is formed.

Another possible technique for producing cables having a cross-linked conductor smoothing, and a polyethylene insulation which is moisture-cross-linked, comprises the microwave heating of a conductor smoothing containing one or more peroxides. This can be effected by passing the core through an UHF radiation unit after the insulation has been applied. The strong microwave absorptivity of a carbon-black-containing conductor smoothing causes intense heating, so that the thermal decomposition of the peroxide(s) and consequently cross-linking can be effected without the use of a "CV" installation. The polyethylene insulation can thereafter be cross-linked by normal moisture addition, independently of the UHF irradiation.

Another advantageous feature of the invention is that direct use can be made of the heat content of (e.g.) an extruded polyethylene insulation to cross-link a peroxide-containing conductor smoothing, instead of UHF heating. In this case also the use of a steam "CV" installation can be dispensed with, and the insulation can be cross-linked by simple addition of water. This technique is particularly valuable when the extrusion temperature is high, i.e. above 200°C. A temperature of this order is generally liable to be required when grafting and extrusion are effected in one step.

The invention will be explained more fully with reference to the accompanying drawing, the single Figure of which is a diagrammatic cross-section of a core of a polyethylene high-tension cable in accordance with the present invention.

In the drawing, a conductor 1 comprising a multiplicity of stranded individual wires is surrounded by a conductor smoothing 2 formed from a cross-linkable polymeric material and carbon black, surrounded by

an insulation 3 comprising an organic polymer modified by the grafting on to it of alkoxy-silane moieties, cross-linked in the presence of moisture. The insulation 3 is applied by means of an extruder, and the heat produced by the extrusion and grafting is sufficient to effect the cross-linking of the conductor smoothing 2 without external heat. Thus the advantages of using materials cross-linked in the presence of moisture are extended to cables for which they were hitherto unsuitable because of the high moisture absorption of the carbon black present in the conductor smoothing provided in these cables.

WHAT WE CLAIM IS:

1. An electric cable having a conductor smoothing comprising a cross-linked material and an electrically conductive constituent under an insulation formed from a thermoplastic or elastomeric material, wherein the insulation comprises a grafted polymer cross-linked by the action of moisture, and the cross-linked material of the conductor smoothing is cross-linked without externally applied heat, as herein defined.

2. A cable according to claim 1, wherein the cross linked material of the conductor smoothing comprises a thermoplastic or elastomeric material cross-linked by the action of moisture.

3. A method of producing a cable according to claim 2, wherein the electrically conductive constituent of the conductor smoothing is added to its cross-linkable constituent only during the operation in which the conductor smoothing is applied around the respective conductor.

4. A method of producing a cable according to claim 1 in which the conductor smoothing is cross-linked by heat, wherein this heat is derived from the heat generated in the insulation when it cross-links by the action of moisture.

5. A method of producing a cable according to claim 1 in which the conductor smoothing is cross-linked by heat, wherein this heat is provided by the application of UHF radiation.

6. A cable produced by a method according to claim 3, 4 or 5.

For the Applicant,
CARPMAELS & RANSFORD,
Chartered Patent Agents,
43 Bloomsbury Square,
London. WC1A 2RA



porated. These substances include, for any carbon black which is to be incorporated, grades of calcium oxide such as those sold under the trade name "Rheno-sorb". The substances just mentioned may be added either in plain form or in coated form, or again in the form of a masterbatch. In this case the amount of these water-binding substances should preferably be such that their water-binding power has no, or a minimal, adverse effect upon the desired cross-linking by the action of moisture whereby the insulation or semi-conductive layer is formed.

Another possible technique for producing cables having a cross-linked conductor smoothing, and a polyethylene insulation which is moisture-cross-linked, comprises the microwave heating of a conductor smoothing containing one or more peroxides. This can be effected by passing the core through an UHF radiation unit after the insulation has been applied. The strong microwave absorptivity of a carbon-black-containing conductor smoothing causes intense heating, so that the thermal decomposition of the peroxide(s) and consequently cross-linking can be effected without the use of a "CV" installation. The polyethylene insulation can thereafter be cross-linked by normal moisture addition, independently of the UHF irradiation.

Another advantageous feature of the invention is that direct use can be made of the heat content of (e.g.) an extruded polyethylene insulation to cross-link a peroxide-containing conductor smoothing, instead of UHF heating. In this case also the use of a steam "CV" installation can be dispensed with, and the insulation can be cross-linked by simple addition of water. This technique is particularly valuable when the extrusion temperature is high, i.e. above 200°C. A temperature of this order is generally liable to be required when grafting and extrusion are effected in one step.

The invention will be explained more fully with reference to the accompanying drawing, the single Figure of which is a diagrammatic cross-section of a core of a polyethylene high-tension cable in accordance with the present invention.

In the drawing, a conductor 1 comprising a multiplicity of stranded individual wires is surrounded by a conductor smoothing 2 formed from a cross-linkable polymeric material and carbon black, surrounded by

an insulation 3 comprising an organic polymer modified by the grafting on to it of alkoxy-silane moieties, cross-linked in the presence of moisture. The insulation 3 is applied by means of an extruder, and the heat produced by the extrusion and grafting is sufficient to effect the cross-linking of the conductor smoothing 2 without external heat. Thus the advantages of using materials cross-linked in the presence of moisture are extended to cables for which they were hitherto unsuitable because of the high moisture absorption of the carbon black present in the conductor smoothing provided in these cables.

WHAT WE CLAIM IS:

1. An electric cable having a conductor smoothing comprising a cross-linked material and an electrically conductive constituent under an insulation formed from a thermoplastic or elastomeric material, wherein the insulation comprises a grafted polymer cross-linked by the action of moisture, and the cross-linked material of the conductor smoothing is cross-linked without externally applied heat, as herein defined.

2. A cable according to claim 1, wherein the cross linked material of the conductor smoothing comprises a thermoplastic or elastomeric material cross-linked by the action of moisture.

3. A method of producing a cable according to claim 2, wherein the electrically conductive constituent of the conductor smoothing is added to its cross-linkable constituent only during the operation in which the conductor smoothing is applied around the respective conductor.

4. A method of producing a cable according to claim 1 in which the conductor smoothing is cross-linked by heat, wherein this heat is derived from the heat generated in the insulation when it cross-links by the action of moisture.

5. A method of producing a cable according to claim 1 in which the conductor smoothing is cross-linked by heat, wherein this heat is provided by the application of UHF radiation.

6. A cable produced by a method according to claim 3, 4 or 5.

For the Applicant,
CARPMAELS & RANSFORD,
Chartered Patent Agents,
43 Bloomsbury Square,
London. WC1A 2RA