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(57) Abstract

An electrical wire comprises a metallic electrical conductor, an insulating mineral layer electrolytically formed on the conductor from a chemically delaminated layered silicate, and an overlying layer of polymeric insulation, the layer of polymeric insulation having an inner surface comprising a material that exhibits a carbonaceous char residue of not more than 15 % by weight, preferably, substantially 0 % by weight. Wires having insulation with relatively low carbonaceous char are able to pass circuit integrity tests such as IEC 331 in which the cable is held at 900°C.

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ELECTRICAL WIRE

This invention relates to electrical wire and cables.

In certain fields where wire and cables are used, for example in military or mass transit applications, it is desired to use cables which are capable of functioning for a period of time during a fire without shorting or otherwise failing. These cables have been called circuit integrity cables or signal integrity cables depending on their use. The previously proposed cables have generally used the principle that the individual conductors should be separated from one another by mica tapes, by large volumes of packing materials, by relatively thick layers of silicone insulation or by combinations thereof in order to prevent the formation of short circuits during a fire. There is therefore a need for a cable that will retain its integrity for a period of time when subjected to a fire but which is relatively small and lightweight and which is relatively inexpensive to manufacture.

Our copending patent application entitled "Electrical Wire and Cable" filed on even date herewith (Agent's reference RK325) is concerned with an electri-

cal wire in which certain layered silicates are electrolytically formed on the conductor. However, we have found that the ability of such wires to be used as circuit or signal integrity wires can be affected by whatever polymeric insulation is provided.

According to the present invention, there is provided an electrical wire which comprises a metallic electrical conductor, an insulating mineral layer electrolytically formed on the conductor from a chemically delaminated layered silicate, and an overlying layer of polymeric insulation, the layer of polymeric insulation having an inner surface comprising a material that exhibits a carbonaceous char residue of not more than 15% by weight.

We have observed that when such wires are subjected to a circuit integrity test, for example of the type described in IEC331 in which twisted wires are maintained at a high temperature e.g. about 900°C, and the time taken for the wires to short is determined, the wires will usually either fail within the first minute or two or will survive for a number of hours at the test temperature. It is believed that the reduction in resistance of the wire is due to carbonisation of organic components in the wire as the temperature rises and/or to the generation of gaseous conductive species from the organic components in the wire, and that this effect rapidly dies away as the carbon so formed is oxidized. We have observed that the use of polymers that have very high carbonaceous char residues, e.g. polyether ether ketones and other highly aromatic polymers, cause the wire to fail such circuit

integrity tests within one or two minutes, while aliphatic polymers that exhibit low char residues allow the wire to function for hours during the circuit integrity test.

Preferably the polymer will have a char residue of not more than 10% by weight, more preferably not more than 5%, especially not more than 2% by weight and most especially substantially 0%.

The char residue of the polymer components in the electrical wire according to the invention can be measured by the method known as thermogravimetric analysis, or TGA, in which a sample of the polymer is heated in nitrogen or other inert atmosphere at a defined rate, e.g. 10°C per minute to a defined temperature and the residual weight, which is composed of char, is recorded. The char residue is simply the quantity of this residual char expressed as a percentage of the initial polymer after having taken into account any non polymeric volatile or non-volatile components. The char residue values quoted herein are defined as having been measured at 850°C.

Examples of aliphatic polymers that may be used include olefin homopolymers and copolymers of olefins with other olefins and with other monomers e.g. vinyl esters, alkyl acrylates and alkyl alkacrylates, e.g. low, medium and high density polyethylene, linear low density polyethylene and ethylene alpha-olefin copolymers, ethylene/propylene rubber, ethylene vinyl acetate, ethylene ethyl acrylate and ethylene acrylic acid copolymers. A particularly preferred class of low

charring polymers is the polyamides. Preferred polyamides include the nylons e.g. nylon 46, nylon 6, nylon 7, nylon 66, nylon 610, nylon 611, nylon 612, nylon 11 and nylon 12 and aliphatic/aromatic polyamides, polyamides based on the condensation of terephthalic acid with trimethylhexamethylene diamine (preferably containing a mixture of 2,2,4- and 2,4,4-trimethylhexamethylene diamine isomers), polyamides formed from the condensation of one or more bis-aminomethylnorbornane isomers with one or more aliphatic, cycloaliphatic or aromatic dicarboxylic acids e.g. terephthalic acid and optionally including one or more amino acid or lactam e.g. -caprolactam comonomers, polyamides based on units derived from laurinlactam, isophthalic acid and bis-(4-amino-3-methylcyclohexyl) methane, polyamides based on the condensation of 2,2-bis-(p-aminocyclohexyl) propane with adipic and azeleic acids, and polyamides based on the condensation of trans cyclohexane-1,4-dicarboxylic acid with the trimethylhexamethylene diamine isomers mentioned above. Other aliphatic polymers that may be used include polyesters e.g. polyalkylene terephthalate and especially polytetramethylene terephthalate, and cycloaliphatic diol terephthalic acid copolymers e.g. copolymers of terephthalate and isophthalate units with 1,4-cyclohexanedimethyloxy units, polyethers e.g. polybutylene ether copolymers, and especially polyether esters such as those having polytetramethylene ether and poly(tetramethylene terephthalate) blocks; aliphatic ionomers e.g. those based on metal salts of ethylene (meth)acrylic acid copolymers or sulphonated olefins such as sulphonated EPDM, and the like. Preferred

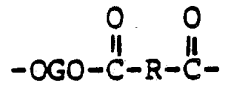
aliphatic polymers include polyethylene, polybutylene terephthalate, and ionomers based on metal salts of methacrylated polyethylene. Blends of any two or more of these polymers or blends with other polymers may be used.

The polymer may include flame-retardants, for example halogenated flame-retardants, but not to such a level that the char residue of the polymer will be increased to above 15% by weight. Normally the polymer will contain not more than 12% by weight halogens, preferably not more than 10% by weight halogens.

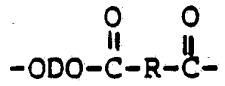
In many cases it may be desirable for the insulation of the wire to include other polymers or polymer compositions in order for example to optimise other properties of the wire, for example its mechanical properties, temperature resistance etc. In such cases it may be appropriate to form the wire insulation as a dual wall insulation having an inner layer or primary insulation and an outer layer or primary jacket. The inner layer should be formed from a polymer or polymer composition having a char residue of not more than 15% by weight, and preferably from one or more of the polymers described above, while the polymer or composition employed for the outer layer may be chosen with other criteria. It may, for example, comprise an aromatic polymer, for example a polyalkylene terephthalate, and especially polytetramethylene terephthalate or it may comprise more highly aromatic polymers having relatively high char residues e.g. greater than 40% and even greater than 50%. This does not mean to say that a high char value is desired for its own sake, but simply

that good mechanical and physical properties of these aromatic polymers including temperature stability and fire retardancy, are usually associated with high char residues. In other cases e.g. in the case of airframe wire where high temperature ratings are necessary, it may be desirable for the outer layer to comprise a halogenated polymer. One class of halogenated polymer that is particularly useful is the fluorinated polymers, preferably those containing at least 10%, more preferably at least 25% fluorine by weight. The fluorinated polymer may be a single fluorine containing polymer or a mixture of polymers one or more of which contains fluorine. The fluorinated polymers are usually homo- or copolymers of one or more fluorinated, often perfluorinated, olefinically unsaturated monomers or copolymers of such a comonomer with a non-fluorinated olefin. The fluorinated polymer preferably has a melting point of at least 150°C, often at least 250°C and often up to 350°C, and a viscosity (before any crosslinking) of less than 10^4 Pa.s at a temperature of not more than 60°C above its melting point. Preferred fluorinated polymers are homo- or copolymers of tetrafluoroethylene, vinylidine fluoride or hexafluoroethylene, and especially ethylene/tetrafluoroethylene copolymers e.g. containing 35 to 60% ethylene, 35 to 60% tetrafluoroethylene by mole and up to 10% by mole of other comonomers, polyvinylidine fluoride, copolymers of vinylidine fluoride with hexafluoropropylene, tetrafluoroethylene and/or hexafluoroisobutylene, polyhexafluoropropylene, and copolymers of hexafluoropropylene and tetrafluoroethylene. Alternatively C_1-C_4 perfluoroalkoxy substituted perfluoroethylene homopolymers and copolymers with the above fluorinated polymers may be used.

Preferred polymers for use in the outer layer as well as the inner layer include polytetramethylene terephthalate, ionomers, e.g. ionomers based on metal salts of methacrylated polyethylene and block copolymers having long chain ester units of the general formula:

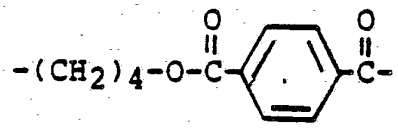


and short-chain ester units of the formula

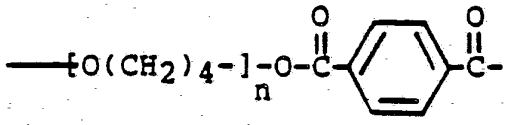


in which G is a divalent radical remaining after the removal of terminal hydroxyl groups from a polyalkylene oxide) glycol, preferably a poly (C_2 to C_4 alkylene oxide) having a molecular weight of about 600 to 6000; R is a divalent radical remaining after removal of carboxyl groups from at least one dicarboxylic acid having a molecular weight of less than about 300; and D is a divalent radical remaining after removal of hydroxyl groups from at least one diol having a molecular weight less than 250.

Preferred copolyesters are the polyether ester polymers derived from terephthalic acid, polytetramethylene ether glycol and 1,4-butane diol. These are random block copolymers having crystalline hard blocks with the repeating unit:

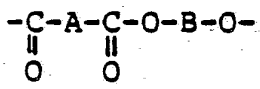


and amorphous, elastomeric polytetramethylene ether terephthalate soft blocks of repeating unit



having a molecular weight of about 600 to 3000, i.e. n = 6 to 40.

Other preferred aliphatic polymers include those based on polyether and polyamide blocks, especially the so called a "polyether-ester amide block copolymers" of repeating unit:



wherein A represents a polyamide sequence of average molecular weight in the range of from 300 to 15,000, preferably from 800 to 5000; and B represents a linear or branched polyoxyalkylene sequence of average molecular weight in the range of from 200 to 6000, preferably from 400 to 3000.

Preferably the polyamide sequence is formed from alpha,omega-aminocarboxylic acids, lactams or diamine/-dicarboxylic acid combinations having C_4 to C_{14} carbon chains, and the polyoxyalkylene sequence is based on ethylene glycol, propylene glycol and/or tetramethylene

glycol, and the polyoxyalkylene sequence constitutes from 5 to 85%, especially from 10 to 50% of the total block copolymer by weight. These polymers and their preparation are described in UK Patent Specifications Nos. 1,473,972, 1,532,930, 1,555,644, 2,005,283A and 2,011,450A. Blends of these polymers with other polymers and with non-polymeric fillers may be used, for example as described in our co-pending European Specification No. 182629 and our British Application No. 8710927.

The aliphatic polymer preferably has a C:H ratio of not more than 0.9, more preferably not more than 0.75, most preferably not more than 0.65 and especially not more than 0.55.

The electrical wire and its manufacture are the subject of our copending British patent application entitled "Electrical Wire and Cable" filed on even date herewith (Agent's reference RK325), the disclosure of which is incorporated herein by reference.

The layered silicate layer is preferably formed from a weathered mica, by which is meant the weathering products of natural mica and includes minerals comprising vermiculite or minerals of a mixed layer type containing vermiculite layers as a major constituent. It includes any hydratable, layer latticed, expandable silicate structure, and primarily the three layer micas. The layers usually have a thickness of about 10 Angstrom units with the main elemental constituents being magnesium, aluminium, silicon and oxygen. It may be formed by replacement of non-exchangeable

cations, e.g. potassium ions, by exchangeable cations, e.g. sodium or magnesium ions, in mica. Such replacement will normally occur through weathering of mica, but the term includes materials formed by other methods of cation exchange, e.g. by hydrothermal action. The term includes materials such as vermiculites and smectites in which there has been complete replacement of the non-exchangeable cations, and any intermediate materials such as formed by partial replacement of the non-exchangeable cations, provided, as explained below, that it is possible to form a colloidal dispersion from the material. The use of a weathered mica instead of unweathered mica has the advantage that the cohesion of the resulting mineral layer is much larger than that of a deposited mica layer with the result that it is then possible to handle the wire more easily during manufacture and use, and in addition, much higher electrolytic deposition rates can be achieved with lower deposition voltages.

The wire according to the invention may be manufactured in a particularly simple manner by passing an elongate electrical conductor through a dispersion of chemically delaminated weathered mica and applying an electrical potential to the conductor in order to deposit reconstituted weathered mica (hereinafter referred to simply as the "mineral") onto the conductor and drying the conductor and the mineral layer so formed. After the mineral layer has been dried, the silicone layer may be formed on the coated conductor by any appropriate method, e.g. by extrusion or dip-coating and then curing the silicone layer so formed.

The weathered mica dispersion may be formed by treating the weathered mica ore consecutively with an aqueous solution of an alkali metal e.g. a sodium salt, and especially sodium chloride, and an aqueous solution of a further salt, e.g. an organo substituted ammonium salt such as an n-butyl ammonium salt, in order to swell the ore for example as described in British Patent No. 1,065,385, the disclosure of which is incorporated herein by reference. After the ore has been swelled to a number of times its original size in water, it is delaminated for example by means of a mill, a mixer, an ultrasonic agitator or other suitable device to form the majority of the expanded mineral into a colloidal dispersion. The colloidal dispersion so formed can be fractionated by sedimentation into several cuts. With a mineral such as vermiculite or other very highly weathered systems, as one moves from the 'fines' to the more coarse fractions the degree of hydration decreases through successive layers, the K_2O content increases and the x-ray diffraction pattern moves closer to resembling the parent mineral. When partially weathered micas are used a distinctive increasing micaceous component can be easily identified and as one move to the coarse unprocessable fraction of the mineral its x-ray diffraction pattern, TGA trace and elemental composition distinctly identifies it as pure mica. In the latter case it is possible to form a dispersion of predominantly micaceous lamellae by selecting the appropriate fractions of the colloid i.e. by discarding the coarse mica fraction and the highly hydrated vermiculitised fines. It is therefore possible to generate a dispersion of mica-like platelets as identified by XRD, TGA and elemental anaylsis

by utilising the chemical exchangeability of vermiculite interlayers on partially weathered interstratified layered minerals.

In a typical process, the dispersion is permitted to stand for between 1 and 60 minutes, preferably 5 to 20 minutes, and the top fraction decanted to supply the working colloid. In many instances where partially weathered mica is employed, it will not be possible for all the mineral to be brought into suspension since the weathering process does not occur uniformly throughout the mineral, and the greater the degree of weathering or cationic replacement, the greater the proportion of mineral that can be dispersed. The particle size range of the decanted fraction typically is between 1 and 250 um, preferably between 1 and 100 um. Preferably the suspension has a concentration of at least 0.5 and especially at least 1% by weight although lower concentrations may be used provided that the concentration is not so low that flocculation occurs. The maximum concentration is preferably 8% and especially 4% by weight, beyond which the relatively high viscosity of the suspension may lead to unreproduceable coatings. The conditions that are employed to form the suspension will depend among other things on the particular type of mineral that is employed.

In order to coat the conductor, it is passed continuously through a bath containing the mineral suspension while being electrically connected as an anode with respect to a cathode that is immersed in the suspension, so that the weathered mica platelets are reconstituted electrolytically on the conductor in the

form of a gelatinous coating. The fact that the coating is gelatinous and therefore electrically conductive means that it is not self-limiting in terms of the coating thickness and therefore enables relatively thick coatings to be formed. The plating voltage will depend on a number of factors including the residence time of the conductor in the bath, the desired coating thickness, the electrode geometry, the bath concentration and the presence or otherwise of other species, especially ionic species, in the bath. The plating voltage will normally be at least 5V, more preferably at least 10V and especially at least 20V since lower voltages usually require very long residence times in the bath in order to achieve an acceptable coating thickness. The voltage employed is usually not more than 200V and especially not more than 100V since higher voltages may lead to the production of irregular coatings and poor circulation of the coating layer, to oxidation of the anode or electrolysis of the bath water and hence a poorly adhered coating. Such plating voltages will usually correspond to a current density of 0.1 to 6 mA mm^{-2}.

After the coated wire has left the bath, and preferably before being contacted by any rollers or other parts of the equipment, the coating is dried in order to remove residual water from the gel. This may be achieved by hauling the coated wire through a hot-air column or a column heated by infrared sources or hot filaments. Additional columns may be used if desired. The wire may then be hauled off for final use or to be provided with an outer protective insulation. The orientation of the platelets in a direction parallel to

the underlying conductor means that relatively rapid drying methods can be used to collapse the gel to leave an integral, self-supporting inorganic layer.

The silicone polymers used for forming the silicone polymer layer are preferably elastomeric and adapted for coating conductors by extrusion or dip-coating. It is preferred to use elastomers rather than solvent based resins because the resin will impregnate the mineral layer at least to some extent which will normally require a long drying period during manufacture of the wire. In addition it has been found that the use of a silicone elastomer layer will improve the fire performance of the wire as described below.

Suitable forms of silicone polymer from which silicone elastomers may be derived include polymers of which at least some of the repeating units are derived from unsubstituted or substituted alkyl siloxanes, for example, dimethyl siloxane, methyl ethyl siloxane, methyl vinyl siloxane, 3,3,3-trifluoropropyl methyl siloxane, polydimethyl siloxane, dimethyl siloxane/-methyl vinyl siloxane co-polymers, fluoro silicones, e.g. those derived from 3,3,3-trifluoropropyl siloxane. The silicone polymer may be, for example, a homopolymer or a copolymer of one or more of the above siloxanes, and is advantageously polydimethyl siloxane or a copolymer of dimethyl siloxane with up to 5% by weight of methyl vinyl siloxane. Silicone modified EPDM, such as Royaltherm (available from Uniroyal) and room temperature vulcanising silicones are also suitable materials.

The silicone elastomer may, if desired, contain fillers, for example reinforcing fillers, flame retardants, extending fillers, pigments, and mixtures thereof. For example, suitable fillers include diatomaceous earth and iron oxide. It will be appreciated that such fillers may be used in addition to a reinforcing filler such as silica that is added to silicone polymer to form the silicone elastomer.

Other materials such as antioxidants, U V stabilisers, thermal stabilisers, extending silicone oils, plasticisers and cross-linking agents, may be included.

Improvements in the mechanical performance of the wire may be achieved if a binder is incorporated in the mineral coating which can improve processability of the mineral-clad conductor.

The material chosen for the binder should be inert, i.e. it should not corrode the conductor metal or react with the mineral coating and preferably it improves the bonding of the mineral layer to the conductor metal. It should also be electrophoretically mobile and non-flocculating. The binder may be dispersible in the medium that is used to form the mineral suspension (water), for example it may comprise a water-dispersed latex, e.g. a styrene/butadiene/carboxylic acid latex, a vinyl pyridine/styrene/butadiene latex, a polyvinyl acetate emulsion, an acrylic copolymer emulsion or an aqueous silicone emulsion. It is preferred to use binders in the form of emulsions because they may be dried quickly with only a few seconds residence time in the drying tower, whereas

with aqueous solutions much longer drying times are necessary, and, if drying is forced, bubbles may be formed in the mineral layer that will cause imperfections in the resulting dried layer. In addition at least some binders that are hydrophobic have the advantage that they can prevent or reduce the uptake of moisture by the mineral layer after it has been dried. This is particularly useful where the weathered mica has a relatively high degree of cationic replacement, i.e. where it contains a relatively high degree of vermiculite, so that undesired exfoliation of the mineral layer when subjected to a fire can be eliminated. The binder is preferably non-curable since curable binders do not significantly improve the performance of the wire and will normally reduce the speed at which the wire can be manufactured.

Like the presence of an organic polymeric insulation, the presence of a polymeric binder has a detrimental effect on the electrical resistance of the mineral layer, usually during the first one or two minutes that the wire is subjected to a fire, after which the effect becomes insignificant. However, the silicone layer appears to act as some form of electrical and/or mechanical barrier which prevents the char from the binder and/or from the polymeric insulation forming an electrical short circuit in a number of cases. Thus, for the first minute or so of the test, the electrical performance of the wire is usually dominated by that of the silicone layer. By the time the silicone layer has ashed, the char from the binder and polymeric insulation will normally have completely oxidized away and will no longer have any effect on the wire performance.

The binder is preferably used in quantities in the range of from 5 to 30%, and especially from 10 to 25% by weight based on the weight of the weathered mica. The use of smaller quantities may not sufficiently improve the processability of the conductor and/or may not improve the adhesion of the mineral layer to the metal conductor adequately while the use of larger quantities of binder may lead to the generation of too much char for the silicone layer to mask. Also, it is preferable not to use binders such as neoprene that generate large quantities of char. Preferably the binder has a carbonaceous char residue of not more than 15%, more preferably not more than 10% and especially not more than 5%.

The polymeric insulation of the wire is preferably cross-linked. In general, however, the aromatic polymers will exhibit a lower degree of crosslinking than the alphatic polymers, and in many cases the aliphatic polymers may be highly crosslinked while the aromatic polymers remain substantially uncrosslinked.

The polymeric composition may be cross-linked, for example, by exposure to high energy radiation. Radiation cross-linking may be effected by expos-ure to high energy irradiation such as an electron beam or gamma-rays. Radiation dosages in the range 20 to 800 kGy, preferably 20 to 500 kGy, e.g. 20 to 200 kGy and particularly 40 to 120 kGy are in general appropriate depending on the characteristics of the polymer in question. For the purposes of promoting cross-linking during irradiation, preferably from 0.2 to 15 weight per cent of a prorad such as a poly-functional vinyl or

allyl compound, for example, triallyl cyanurate, triallyl isocyanurate (TAIC), methylene bis acrylamide, metaphenylene diamine bis maleimide or other cross-linking agents, for example as described in U.S. patents Nos. 4,121,001 and 4,176,027, are incorporated into the composition prior to irradiation.

The polymers used for the various layers may include additional additives, for example reinforcing or non-reinforcing fillers, stabilisers such as ultra-violet stabilisers, antioxidants, acid acceptors and anti-hydrolysis stabilisers, pigments, processing aids such as plasticizers, halogenated or non-halogenated flame retardants, fungicides and the like.

The wire according to the invention may be formed using most commonly available electrical conductor materials such as unplated copper and copper that has been plated with tin, silver or chromium. In addition, if desired the conductor may be coated with an electrically conductive refractory layer, for example as described in European Patent Application No. 190,888, the disclosure of which is incorporated herein by reference.

One embodiment of a wire in accordance with the present invention and a method of manufacturing it will now be described by way of example with reference to the accompanying drawing, in which:

Figure 1 is an isometric view of part of a wire in accordance with the invention with the thicknesses of the layers of insulation exaggerated for the sake of clarity; and

Figure 2 is a schematic view of apparatus for forming the wire of figure 1; and

Figure 3 is an isometric view of part of another wire in accordance with the invention.

Referring to the accompanying drawings, an electrical wire 1 comprises a 22 AWG seven strand copper conductor 2 which has been coated with a 50 micrometre thick layer 3 of a partially weathered mica, a 50 micrometre thick silicone polymer layer 3' and followed by a 0.15mm thick extruded layer of polymeric insulation 4 based on a blend of polytetramethylene terephthalate and a polytetramethylene ether terephthalate/polytetramethylene terephthalate block copolymer.

The wire may be formed by means of the apparatus shown schematically in figure 2. In this apparatus the conductor 2 is fed into a bath 5 that contains a colloidal suspension of the weathered mica and binder, the suspension being fed from a supply bath 5', and agitated in order to maintain uniform mixing of the dispersion. The conductor passes down into the bath, around a roller 6 and then vertically upwards as it leaves the bath. A hollow tube 7 is positioned around the part of the conductor that leaves the bath and a hollow electrode 8 is located inside the hollow tube 7 so that the weathered mica is deposited on the rising part of the conductor. This prevents the mineral coating so formed being damaged as the conductor is passed around roller 6.

After the coated conductor leaves the bath it passes through a drying tower 8 about 1.5 metres in length that is heated by a counter current of warm air so that the top of the drying tower is at a temperature of about 200°C while the bottom is at about 160°C. After the mineral coating has dried the coated conductor is passed through a coating pot 10 that contains a silicone polymer. After a layer of silicone polymer is applied to the wire, it is passed through a further warm air drying tower 11 arranged to have a temperature of about 130°C at the top and 90°C at the bottom.

When the silicone layer has been applied and dried the wire may then be spooled to await the provision of an insulating top-coat or a top-coat may be provided in-line for example by means of an extruder 12.

The feed rate of the conductor 2 to the coating apparatus will depend on the thickness of the intended coating, the electrophoresis potential and the concentration of the weathered mica in the bath. Feed rates in the range of from 2 to 20, and especially 5 to 10 metres per minute are preferred although increases in the feed rate should be possible, for example by increasing the dimensions of the bath in order to maintain the same residence time with higher conductor speeds.

Figure 3 shows another form of wire in accordance with the invention which is the same as that shown in figure 1 but which includes a dual wall insulation comprising a 100 μm thick primary insulation 4' formed from a blend of polytetramethylene terephthalate and

Surlyn, and a 100 μm thick primary jacket formed from a blend of polytetramethylene terephthalate and a polytetramethylene terephthalate/polytetramethylene ether terephthalate block copolymer.

The following Examples illustrate the invention.

In all the Examples the working colloid that was used for coating the conductor was formed as follows: 800 gramms of a weathered mica as used in our co-pending British patent application entitled "Wire" filed on even date herewith (Agent's ref: RK342) was washed with boiling water for about 30 minutes and the resulting liquid was decanted to remove the clay fraction. The mineral was then refluxed for 4 to 24 hours in saturated sodium chloride solution to replace the exchangeable cations with sodium ions. This was then washed with distilled or deionised water to remove excess sodium chloride until no further chloride ions could be observed by testing with silver nitrate. The material was then refluxed for 4 to 24 hours with molar n-butyl ammonium chloride solution followed by further washing with distilled or deionised water until no chloride ions could be detected with silver chloride.

The swollen material was then worked in a Greaves mixer for 30 minutes to shear the mineral and was allowed to stand for 20 minutes to sediment the unprocessed mineral. The top fraction was used as the working colloid.

Example 1

A colloid having 4% by weight weathered mica and 15% by weight carboxylated styrene-butadiene-styrene rubber based on the weight of the weathered mica, was used as the plating bath. A 20 AWG wire was passed through a 40 cm long bath of the colloid at a speed of 5 metres $minute^{-1}$ while the weathered mica was electrophoretically deposited on the conductor at a 4.2V plating voltage and a 165 mA current. The coated wire was then passed through a drying tower as shown in the drawing to form a mineral layer of 30 micrometre dry thickness. The wire was then passed through a bath of a two part silicone (KE1204 ex Shinetsu) and cured again as shown in the drawing to form a 50 micrometre thick silicone layer. Thereafter a 100 micrometre thick single wall insulation formed from low density polyethylene containing 8% by weight decabromodiphenyl ether and 4% antimony trioxide flame retardant was extruded onto the wire.

The wire was tested for circuit integrity by twisting three wires together and connecting each wire to one phase of a three phase power supply, and then heating the wire to 900°C for a test period of three hours in accordance IEC 331. The wire was able to support 300V phase-to-phase for the entire test at 900°C without failing (i.e. without blowing a 3A fuse).

Example 2

Example 1 was repeated with the exception that the low density polyethylene insulation was replaced with a 100 micrometre thick layer comprising:

	parts by weight
polybutylene terephthalate (PBT)	80
Surlyn ionomer	20
decabromodiphenyl ether	8
antimony trioxide	4
Irganox 1010	2
triallyl isocyanurate cross-linking promotor	5

The wire supported 300V phase-to-phase for 3 hours at 900°C.

Example 3

Example 2 was repeated with the exception that the PBT/Surlyn layer contained no flame retardant (decabromodiphenyl ether/Sb_2O_3) and that an additional polymeric layer of thickness 100 micrometres was provided on top of the PBT/Surlyn layer. The additional layer had the composition:

	parts by weight
polybutylene terephthalate (PBT)	70
polybutylene terephthalate-polybutylene ether terephthalate block copolymer	30
ethylene bis-tetrabromophthalimide	10
antimony trioxide	4
magnesium hydroxide	20

The wire supported 300V phase-to-phase for 3 hours at 900°C.

CLAIMS:

1. An electrical wire which comprises a metallic electrical conductor, an insulating mineral layer electrolytically formed on the conductor from a chemically delaminated layered silicate, and an overlying layer of polymeric insulation, the layer of polymeric insulation having an inner surface comprising a material that exhibits a carbonaceous char residue of not more than 15% by weight.

2. A wire as claimed in claim 1, wherein the said material exhibits a char residue of not more than 5% by weight.

3. A wire as claimed in claim 2, wherein the said material exhibits a char residue of substantially 0% by weight.

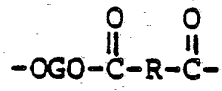
4. A wire as claimed in any one of claims 1 to 3, wherein the said material has an overall molar carbon to hydrogen ratio of not more than 1.15.

5. A wire as claimed in claim 4, wherein the said material has an overall molar carbon-to-hydrogen ratio of not more than 1.0.

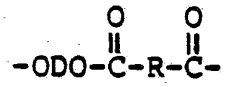
6. A wire as claimed in any one of claims 1 to 5, wherein the said material comprises an olefin homo- or copolymer, a polyamide, a polyester or an ionomer.

7. A wire as claimed in claim 6, wherein the said material comprises polyethylene, a crystalline

polyamide, a polyamide derived from terephthalic acid and one or more trimethylhexamethylene diamine isomers, an ionomer based on a metal salt of methacrylated polyethylene, polybutylene terephthalate or a block copolymer having long-chain ester units of the general formula:



and short-chain ester units of the formula



in which G is a divalent radical remaining after the removal of terminal hydroxyl groups from a polyalkylene oxide) glycol, preferably a poly (C_2 to C_4 alkylene oxide) having a molecular weight of about 600 to 6000; R is a divalent radical remaining after removal of carboxyl groups from at least one dicarboxylic acid having a molecular weight of less than about 300; and D is a divalent radical remaining after removal of hydroxyl groups from at least one diol having a molecular weight less than 250.

8. A wire as claimed in any one of claims 1 to 7, which includes a halogen-containing flame retardant.

9. A wire as claimed in claim 8, wherein the said material includes up to 10% by weight halogen.

10. A wire as claimed in any one of claims 1 to 9, wherein the polymeric insulation includes an aromatic polymer.

11. A wire as claimed in any one of claims 1 to 10, wherein the polymeric insulation comprises an inner layer and an outer layer, the inner layer having a char residue of not more than 15% by weight.

12. A wire as claimed in any one of claims 1 to 11, wherein the outer layer includes an aromatic polymer.

13. A wire as claimed in claim 11 or claim 12, wherein the outer layer exhibits a char residue of at least 20% by weight.

14. A wire as claimed in claim 13, wherein the outer layer exhibits a char residue of at least 50% by weight.

* * * * * *

Fig.1

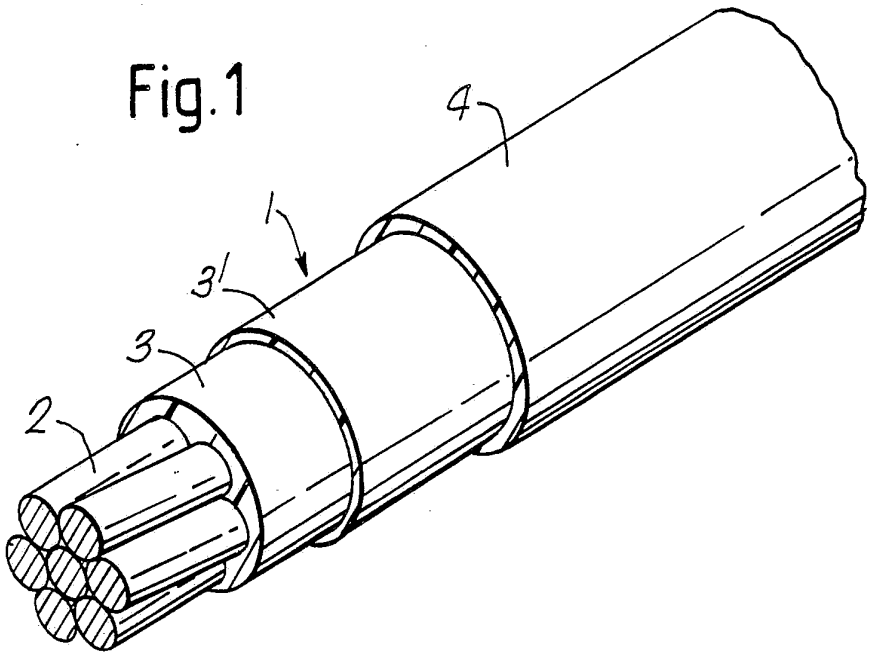


Fig.2.

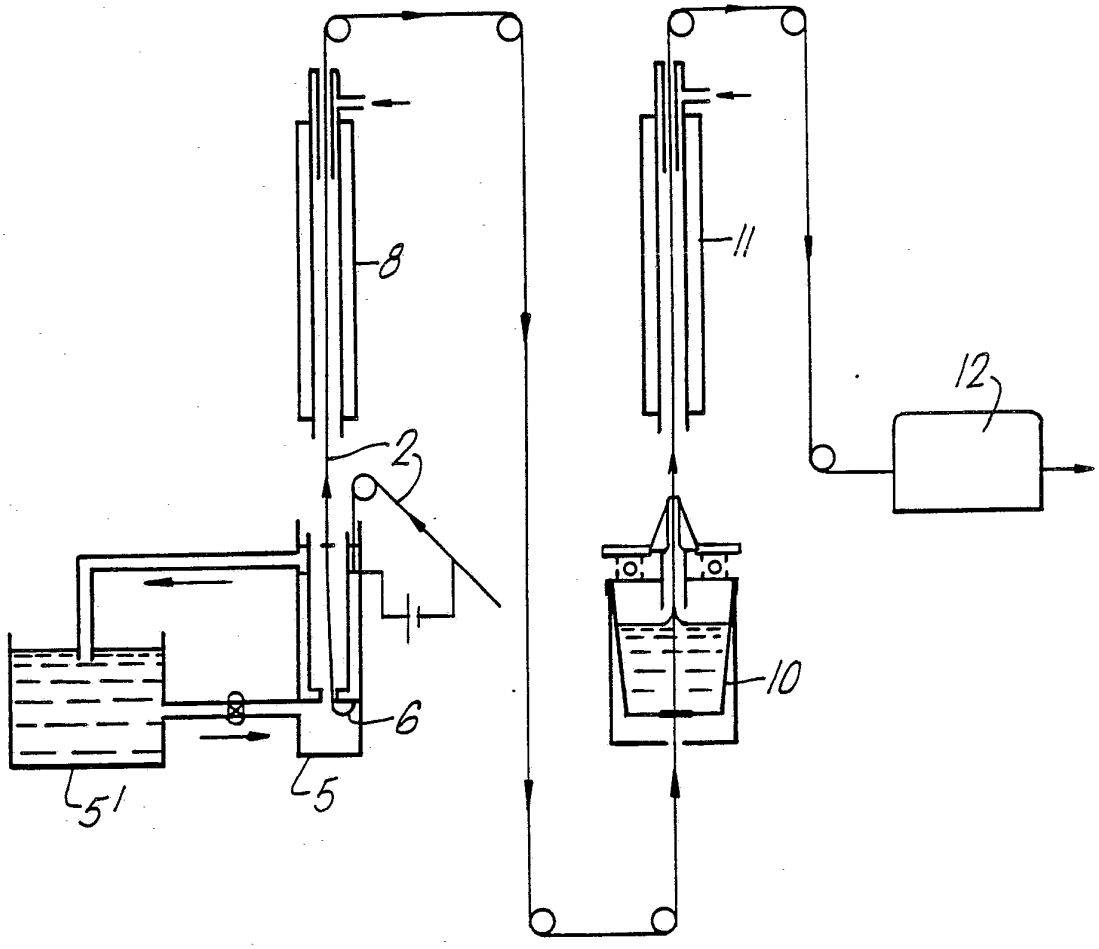
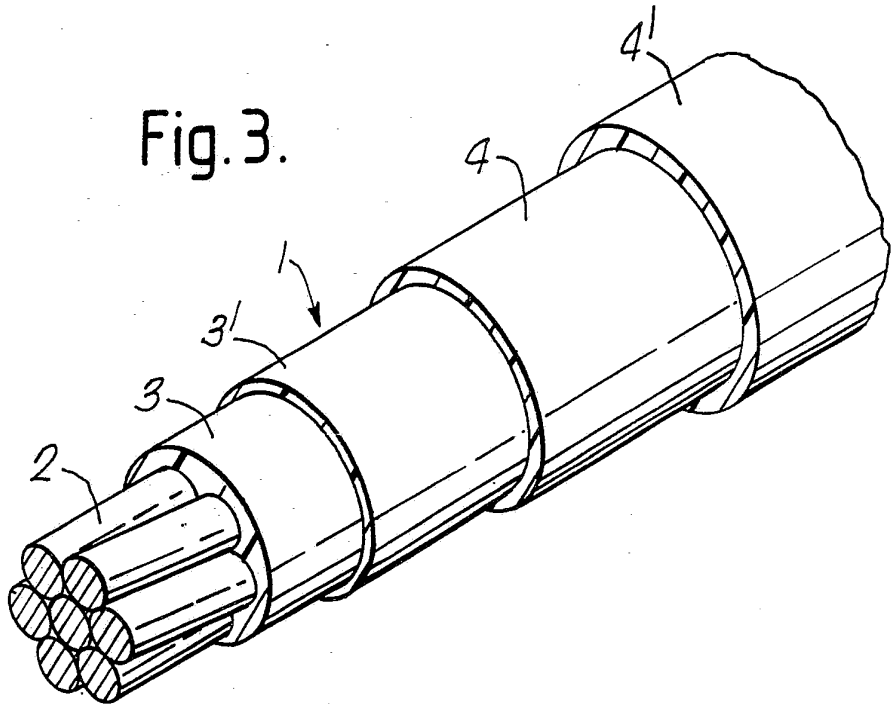


Fig. 3.



INTERNATIONAL SEARCH REPORT

International Application No PCT/GB 88/00549

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [5]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC[4]: H 01 B 7/34; H 01 B 3/04

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
IPC[4]	H 01 B

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category [10]	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
A	GB, A, 2184512 (HEW-KABEL HEINZ) 24 June 1987 see the whole document --	1
A	US, A, 4576694 (E. JIDAI) 18 March 1986 see the whole document --	1
A	GB, A, 1064401 (SIEMENS) 5 April 1967 see the whole document	1

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* Special categories of cited documents: [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
13th September 1988	24. 10. 88
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	P.C.G. VAN DER PUTTEN

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO. GB 8800549 SA 23151

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on 07/10/88
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

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		FR-A- 2591715	19-06-87
		DE-A- 3544810	19-06-87
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		DE-A- 1496986	01-10-70
		CH-A- 443835	
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