

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952

DECLARATION IN SUPPORT OF AN APPLICATION FOR A PATENT

In support of an application made by: RAYCHEM LIMITED

for a patent for an invention entitled: WIRE

I, ROBERT LEONARD HALL

of 2 HILLCREST CLOSE, HILLSIDE AVENUE, SWINDON, WILTSHIRE, SN1 4LS

do solemnly and sincerely declare as follows:

1. I am authorised by the above mentioned applicant for the patent to make this declaration on its behalf.

2. The names and addresses of each actual inventors of the invention is as follows:

SHAUN MICHAEL BARRETT of 39 Corby Avenue, Lakeside, Swindon, Wiltshire, SN3 1PS and MICHAEL JOSEPH LUDDEN of 12 Casson Road, Swindon, Wiltshire, SN3 4QF

and the fact(s) upon which the applicant is entitled to make this application are as follows:

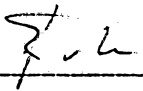
By Assignment of the application from the inventors to the applicant.

3. The basic application(s) as defined by Section 141 of the Act was(were) made as follows:

Country United Kingdom on 10 July 1987
in the name of RAYCHEM LIMITED

4. The basic application(s) referred to in the preceding paragraph of this Declaration was (were) the first application(s) made in a Convention country in respect of the invention the subject of this application.

Declared at SWINDON, WILTSHIRE this 20th day of FEBRUARY 19 88

Signed:  ROBERT LEONARD HALL

Position: AUTHORISED SIGNATORY

GRIFFITH HACK & CO., G.P.O. BOX 4164, SYDNEY N.S.W 2031
AUSTRALIA

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(56) Prior Art Documents
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US 4576694
GB 1064401

(57) Claim

1. An electrical wire which comprises an elongate electrical conductor and an insulating mineral layer electrolytically formed on the conductor from a chemically delaminated weathered mica, the mineral forming the mineral layer having a dominant x-ray reflection at approximately 10 Angstroms characteristic of the mica basal spacing.

PCT

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(54) Title: WIRE (57) Abstract An electrical wire comprises an elongate electrical conductor and an insulating mineral layer electrolytically formed on the conductor from a chemically delaminated weathered mica, the mineral forming the mineral layer having a dominant x-ray reflection at approximately 10 Angstroms characteristics of the mica basal spacing. The chemically delaminated weathered mica layer is able to adhere well to the electrical conductor and exhibits good electrical insulating properties at high temperatures. The wire is capable of functioning for long periods at very high temperatures e.g. during a fire, due to the presence of the weathered mica layer. This document contains the amendments made under Section 49 and is correct for printing.		

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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.

According to the present invention, there is provided an electrical wire which comprises an elongate electrical conductor and an insulating mineral layer

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electrolytically formed on the conductor from a chemically delaminated weathered mica, the mineral forming the mineral layer having a dominant x-ray reflection at approximately 10 Angstroms characteristic of the mica basal spacing.

It is known that several 2:1 layer phyllosilicate minerals form interlayer complexes with a wide range of charged and uncharged species of both organic and inorganic origins e.g. alkylammonium ions, amino acids and amino acid cations. The inclusion of intercalating species between the layers of the macrocrystal usually results in changes to the basal spacing which can be measured by X-ray diffraction techniques. Under certain circumstances an additional swelling can take place whereby further intercalation, by a wide range of polar and non-polar solvents, occurs. In special cases the degree of expansion can be so extensive as to produce 'gel-like' samples. The application of mild mechanical action to these extensively swollen systems can lead to the production of colloidal dispersions of the mineral on a dispersing solvent, this process being known as "chemical delamination".

This effect can be particularly apparent in a range of mica-type complexes containing n-alkylammonium ions, with water as a dispersing solvent. Whether additional interlayer expansion occurs depends on the layer charge density separating successive layers on the mineral and the length of the alkyl chain of the associated intercallants.

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Minerals with a surface charge density in the range of 0.5 to 0.9, saturated with certain short chain n-alkylammonium ions e.g. n-propyl, n-butyl and isoamyl, behave exceptionally well in that they show extensive interlayer swelling in water. Crystals which show this type of behaviour can increase in volume by up to 30 times their original volume and remain coherent and 'gel-like'. This action can be used to produce a colloidal dispersion of thin high aspect ratio platelets. In the case in which the starting mineral is of a homogenous nature the composition of the colloid will be consistent. However, if mixed layer minerals are used then there can be a wide variation of platelet composition and characteristics throughout the colloidal dispersion. Fractionation techniques, including sedimentation, can be used to isolate components of the dispersion which exhibit different chemical and physical characteristics from each other and from the parent mineral. If the colloid is subjected to mild mechanical shearing, delamination will occur in the swollen crystals along the macroscopically swollen cleavage plane where the interlayer forces are minimised. Such a process is described for example in British patent No. 1,593,382 to ICI.

The term "weathered mica" is used herein to describe the weathering products of natural mica and includes minerals comprising vermiculite or minerals of a mixed layer type that contain mica layers interspersed with other layers that are formed by weathering. The weathered layers may, in the broadest aspect, comprise any hydratable, layer latticed, expandable silicate structure, e.g. hydrobiotite and

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hydrophlogopite layers, and preferably hydrophlogopite II layers although other layers may instead be present. The hydratable layers may comprise a major part of the original mineral although it is preferred for the major part (by weight) to be formed from unweathered mica layers.

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.

In contrast with weathered mica having a higher degree of cationic replacement, the weathered mica mineral used in accordance with the invention exhibits an x-ray reflection at approximately 10 Angstroms (in fact 10.03 Å) characteristic of mica, and, also in contrast with weathered mica having a higher degree of cationic replacement, does not exhibit any reflection at 14.25 Angstroms characteristic of vermiculite. The mineral will normally also exhibit a reflection at approximately 11.7 Angstroms which is characteristic of the hydrated biotite basal spacing.

Thus, the mineral used in the invention may be regarded as formed from platelets that have a micaeous, or predominantly micaeous interior, and a surface that is formed from a hydrated silicate layer. The platelets preferably have an average thickness of

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not more than 500 Angstroms, more preferably not more than 300 Angstroms, especially not more than 200 Angstroms and most especially not more than 100 Angstroms, but preferably at least 20 Angstroms, more preferably at least 40 Angstroms and especially at least 60 Angstroms.

The wire will normally be provided with an outer protective layer or jacket which will protect the weathered mica layer from mechanical abuse during handling and which is preferably also electrically insulating so that it can provide further electrical insulation during normal operation. The protecting and insulating layer will normally be a polymeric layer which is formed on the coated conductor by an extrusion process although in some cases it may be preferred to apply the insulation by a tape wrapping process for example in the case of polytetrafluoroethylene or certain polyimides. In other cases however, for example in the case of electric motor windings or transformer windings, where very thin, high temperature wire is required, it is possible to dispense with the polymeric insulation altogether.

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 curing step being used if necessary to cure the silicone layer.

The weathered mica dispersion may be formed by a process comprising:

- (a) forming an aqueous dispersion of a weathered mica having a dominant x-ray reflection at approximately 10 Angstroms characteristic of mica;
- (b) contacting the weathered mica with an aqueous solution of intercalating ions washing the dispersion with water in order to swell the weathered mica;
- (c) mechanically shearing the swollen weathered mica; and
- (d) separating components having a thickness greater than 500 Angstroms from the suspension so formed.

In this process the weathered mica ore is usually treated consecutively with an aqueous solution of an alkali metal salt 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 ore then swells up to 3.5 times its original size, usually to about 1.5 to 3 times its original size in

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water, after which 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 in order to separate components of the mineral having different thicknesses. With a mineral having a high degree of weathering, as one moves from the 'fines' to the more coarse fractions composition of the mineral changes significantly, the degree of hydration decreasing through successive layers, the K_2O content increasing and the x-ray diffraction pattern moving closer to that of mica. When partially weathered micas are used, a distinctive increasingly micaceous composition is identified as one moves to the coarse, unprocessable fraction of the mineral. Its x-ray diffraction pattern, TGA trace and elemental composition distinctly identify it as pure mica. In this 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 optionally also the highly hydrated fines. It is therefore possible to generate a dispersion of mica-like platelets as identified by x-ray diffraction utilising the chemical exchangability of weathered interlayers in 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

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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, the greater the proportion of mineral that can be dispersed. The particle size range of the decanted fraction, i.e. the particle dimensions parallel to the silicate layers, typically is between 1 and 250 μm , preferably between 1 and 100 μm .

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 unreproducible 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-

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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.

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

We have found that 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. The use of latex binders is described in our copending International application No. WO 89/00765.

We have observed that 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, with the result that any wires that have been tested for circuit integrity performance will 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 the binder as the temperature rises and/or to the generation of gaseous conductive species from the binder or any other organic components in the cable, and that this effect rapidly dies away as the carbon so formed is oxidized. However, the detrimental effect on the resistance caused by most of the binders may usually be completely removed by the presence of the thin silicone layer. It is believed that the silicone layer acts as some form of electrical and/or mechanical barrier which prevents the carbonaceous char from the binder forming an electrical short circuit. 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 will normally have completely oxidized away and will no longer have any effect on the wire performance. Thus, according to another aspect, the invention provides a flame resistant electrical wire which comprises a metallic electrical conductor and electrical insulation which comprises an insulating mineral layer that is formed from weathered mica and contains an organic binder, and, located on the mineral layer, a layer of a material that will provide a temporary barrier when the wire is subjected to a fire which will reduce or eliminate the detrimental effect of char formed from the binder on the electrical resistance of the wire insulation.

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 char residue can be measured by the method known as thermogravimetric analysis, or TGA, in which a sample of the latex is heated in nitrogen or other

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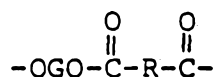
inert atmosphere at a defined rate, e.g. 10°C per minute to a defined temperature and the residual weight, which is composed of char, is recorded. The char residue is simply the quantity of this residual char expressed as a percentage of the initial polymer after having taken into account any non polymeric volatile or non-volatile components. The char residue values quoted above are defined as having been measured at 850°C.

As stated above, an outer protective layer, preferably a polymeric insulating layer, may be provided in order to protect the underlying mineral layer from mechanical abuse and in order to provide the required insulating and dielectric properties during normal use. Examples of polymers that may be used to form the outer layer 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, and styrene/butadiene/styrene, styrene/ ethylene/butadiene/styrene block copolymers and hydrogenated versions of these block 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

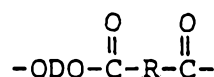
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2,2,4- and 2,4,4-trimethylhexamethylene diamine isomers), polyamides formed from the condensation of one or more bisaminomethylnorbornane isomers with one or more aliphatic, cycloaliphatic or aromatic dicarboxylic acids e.g. terephthalic acid and optionally including one or more amino acid or lactam e.g. ϵ -caprolactam comonomers, polyamides based on units derived from laurilactam, isophthalic acid and bis-(4-amino-3-methylcyclohexyl) methane, polyamides based on the condensation of 2,2-bis-(p-aminocyclohexyl) propane with adipic and azelaic 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-cyclohexanedimethoxy 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, ionomers based on metal salts of methacrylated polyethylene, acrylic elastomers e.g. those based on ethyl acrylate, n-butyl acrylate or alkoxy-substituted ethyl or n-butyl acrylate polymers containing a cure site monomer and optionally ethylene comonomer, and block copolymers having long chain ester units of the general formula:

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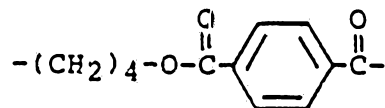


and short-chain ester units of the formula



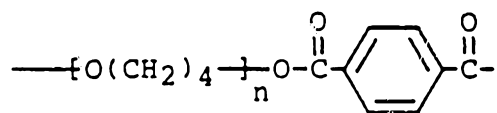
in which G is a divalent radical remaining after the removal of terminal hydroxyl groups from a polyalkylene oxide) glycol, preferably a poly (C₂ to C₄ alkylene oxide) having a molecular weight of about 600 to 6000; R is a divalent radical remaining after removal of carboxyl groups from at least one 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:



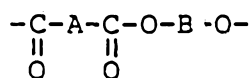
and amorphous, elastomeric polytetramethylene ether terephthalate soft blocks of repeating unit

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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.

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The polymers may be used alone or in blends with one another or with other polymers and may contain fillers e.g. silica and metal oxides e.g. treated and untreated metal oxide flame retardants such as hydrated alumina and titania. The polymers may be used in single wall constructions or in multiple wall constructions e.g. as described in British Patent Application No. 2,128,394A the disclosure of which is incorporated herein by reference. The polymers may be uncrosslinked or may be crosslinked for example by chemical cross-linking agents or by electron or gamma irradiation, in order to improve their mechanical properties and to reduce flowing when heated. They may also contain other materials e.g. antioxidants, stabilizers, cross-linking promoters, processing aids and the like. In some cases the polymer insulation or at least the inner wall of the insulation may be substantially halogen-free. In addition, it has been found that certain halogen-containing polymers may generate electrically conductive species during a fire and so cause the wire to fail prematurely. In those cases the insulation preferably contains not more than 5% by weight halogens, especially not more than 1% by weight halogens and most especially not more than 0.1% by weight halogens. However, in other cases, for example in the case of airframe wire where high temperature ratings are desirable, it may be appropriate for the outer wall or primary jacket of the insulation to include 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 10⁴ Pa.s at a temperature of not more than 60°C above its melting point. Preferred fluorinated polymers are homo- or copolymers of tetrafluoroethylene, vinylidene 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, polyvinylidene fluoride, copolymers of vinylidene fluoride with hexafluoropropylene, tetrafluoroethylene and/or hexafluoroisobutylene, polyhexafluoropropylene, and copolymers of hexafluoropropylene and tetrafluoroethylene. Alternatively C₁-C₄ perfluoroalkoxy substituted perfluoroethylene homopolymers and copolymers with the above fluorinated polymers may be used.

In addition, the polymeric insulation, or the inner layer of any polymeric insulation, preferably has a carbonaceous char residue of not more than 15% by weight as determined by thermogravimetric analysis. Such wires are the subject of our British patent application No. 8716308 from which International Application No. WO 89/00763 claims priority.



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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

Figures 3a to d are x-ray powder diffraction patterns of the different micaceous minerals.

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

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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.

Figures 3(a) to (d) are x-ray powder diffraction patterns of different micaceous minerals with increasing degrees of weathering. Figure 3(a) is the pattern from mica, figure 3(b) from the mineral used according to the invention, figure 3(c) from a mineral having a higher degree of weathering.

By comparison of the figures it can be seen that the pattern formed from mica exhibits a characteristic mica basal spacing peak 31 around 10 Angstroms, and that the mineral used according to the invention (figure 3(b)) also exhibits the 10 Angstrom peak, but also has a peak 32 at about 11.8 Angstroms that is characteristic of the hydrated biotite basal spacing. The mica will have a water content of 0.5% by weight as measured by thermogravimetric analysis at 400°C, and a molar potassium to magnesium ratio (K/Mg) of 0.5. The mineral used according to the invention, (figure 3(b)) has a water content of 2% by weight and a K/Mg ratio of 0.35.

As the degree of weathering increases, so that the K/Mg ratio becomes 0.2 and the water content increases to 8% by weight, the 10 Angstrom mica, and 11.8 hydrated biotite, peaks disappear, and new peaks at about 12.6 Angstrom, 33, and at 14.4 Angstroms, 34, appear, the latter peak corresponding to the vermiculite basal spacing.

Figure 3(d) shows the diffraction pattern of the mineral deposited from the working colloid. By comparing figure 3(d) with figure 3(b), it can be seen that the intensity of the 10 Angstrom reflection 31 is decreased relative to that of the hydrobiotite reflection 32, reflecting the removal of the unprocessed mica during sedimentation of the colloid.

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 having a powder x-ray diffraction pattern as shown in figure 3(b), 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.

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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 sup-

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port 300V phase-to-phase for the entire test at 900°C without failing (i.e. without blowing a 3A fuse).

Examples 2 to 5

Example 1 was repeated with the exception that the following binders were used:

Example 2	polyvinyl acetate
Example 3	acrylic copolymer emulsion
Example 4	polyvinylidene chloride
Example 5	vinylpyridine terminated styrene-butadiene-styrene rubber

The wire was tested as described in Example 1 and in each case the wires were able to support 300V phase-to-phase at 900°C for 3 hours.

Example 6

Example 1 was repeated with the exception that the silicone layer was formed from the following composition an extended polydimethyl siloxane based formulation.

The silicone composition was room-temperature extruded onto the coated conductor to give a 75 to 100 micrometre thick layer and was vulcanised in a tube furnace at 300°C (20.5 second residence time).

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The wire was tested as described in Example 1 and supported 300V phase-to-phase for 3 hours at 900°C.

Example 7

Example 6 was repeated with the exception that the plating voltage of the deposition bath was 15.5V (300mA) which gave a mineral layer thickness of 40 micrometres.

The wire supported 440V phase-to-phase for 3 hours at 900°C.

Example 8

Example 1 was repeated with the exception that the silicone used was a dip-coated solventless silicone (sylgard 184) applied to a thickness of 70 micrometres. The wire supported 300V phase-to-phase for 3 hours at 900°C.

Example 9

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

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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 10

Example 9 was repeated with the exception that the PBT/Surlyn layer contained no flame retardant (decabromodiphenyl ether/Sb₂O₃) 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 tereph- thalate block copolymer	30
ethylene bis-tetrabromo- phthalimide	10
antimony trioxide	4
magnesium hydroxide	20

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

Example 11

Example 7 was repeated with the exception that the low density polyethylene insulation was replaced by the additional layer of Example 10. The wire supported 440V phase-to-phase for 3 hours at 900°C.

Example 12

Example 6 was repeated with the exception that the low density polyethylene insulation was replaced with a 100 micrometre thick layer of un-flame retarded high density polyethylene. The wire supported 300V phase-to-phase for 3 hours at 900°C.

CLAIMS:

1. An electrical wire which comprises an elongate electrical conductor and an insulating mineral layer electrolytically formed on the conductor from a chemically delaminated weathered mica, the mineral forming the mineral layer having a dominant x-ray reflection at approximately 10 Angstroms characteristic of the mica basal spacing.
2. A wire as claimed in claim 1, wherein the mineral layer has a water content in the range of from 0.7% to 6% by weight.
3. A wire as claimed in claim 2, wherein the mineral layer has a water content in the range of from 1 to 4% by weight.
4. A wire as claimed in any one of claims 1 to 3, wherein the mineral layer has a molar potassium to magnesium ratio in the range of from 0.25 to 0.45.
5. A wire as claimed in claim 4, wherein the molar potassium to magnesium ratio is in the range of 0.3 to 0.4.
6. A wire as claimed in any one of claims 1 to 5, wherein the mineral layer exhibits an x-ray reflection at approximately 11.7 Angstroms characteristic of the hydrated biotite basal spacing.
7. A wire as claimed in any one of claims 1 to 6, wherein the mineral has a surface charge density in the range of from 0.5 to 0.9.

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8. A wire as claimed in any one of claims 1 to 7, which includes a silicone polymer layer on top of the mineral layer.

9. A wire as claimed in any one of claims 1 to 8, which includes an organic polymeric insulating layer.

10. A wire as claimed in any one of claims 1 to 9, wherein the mineral layer includes an organic binder.

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Fig.1

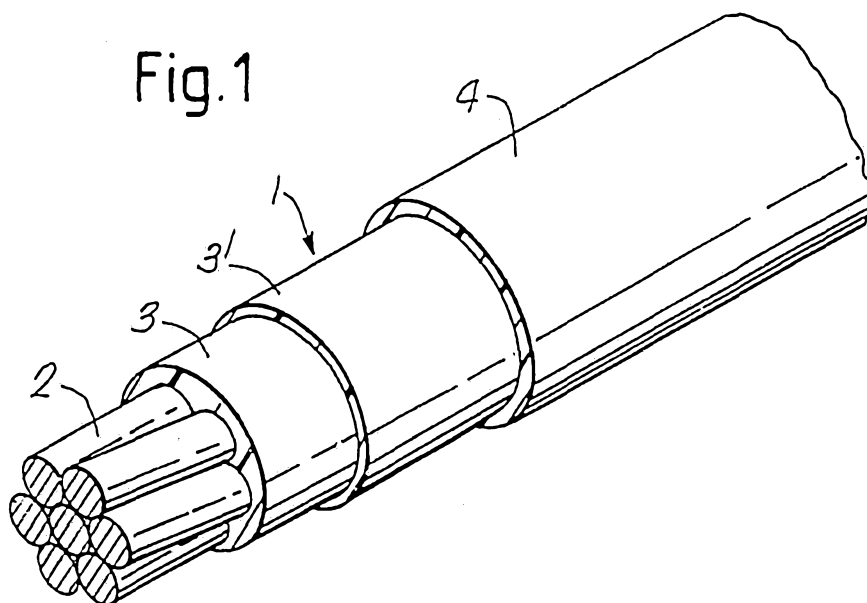
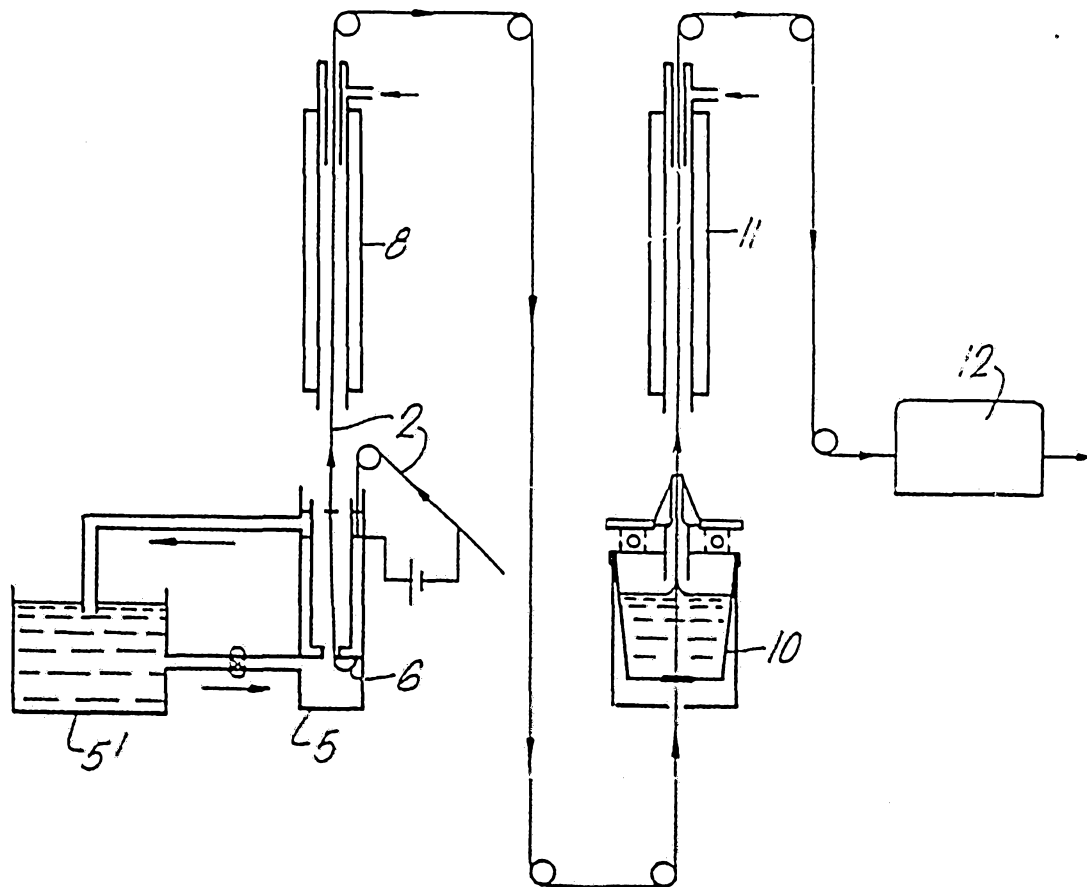


Fig.2.



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Fig. 3a.

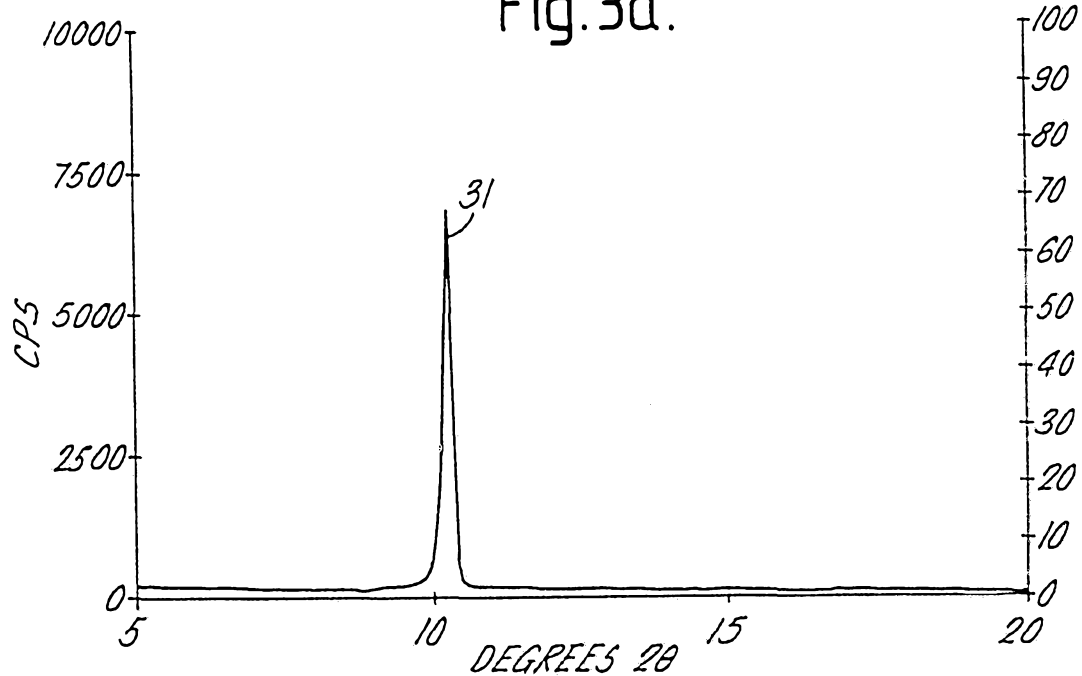
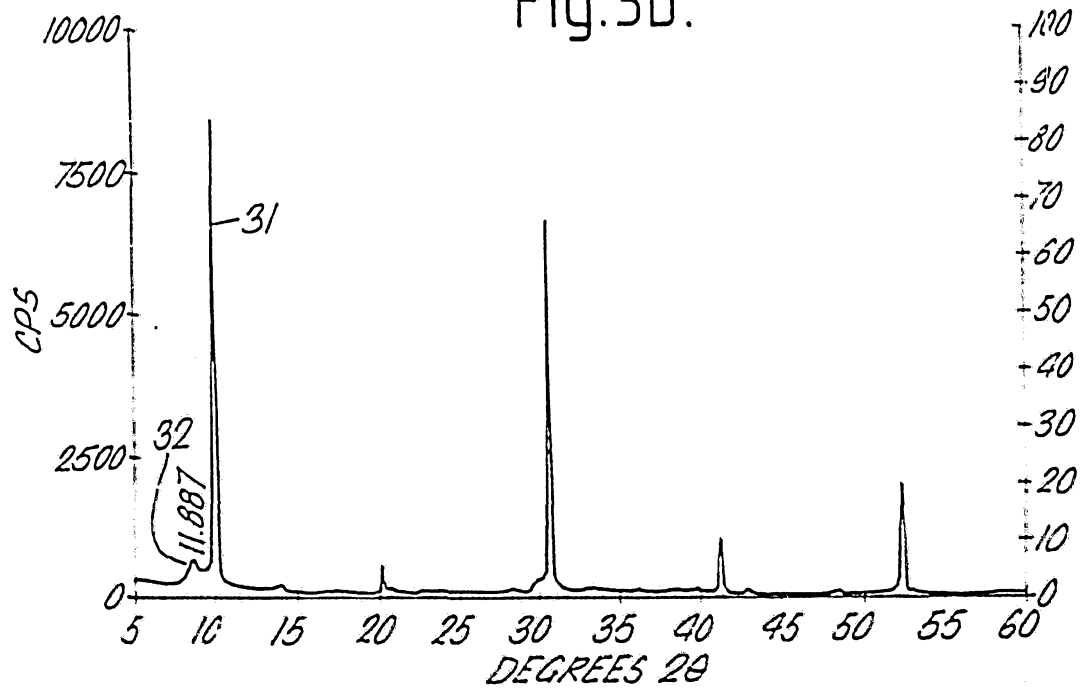


Fig. 3b.



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Fig. 3c.

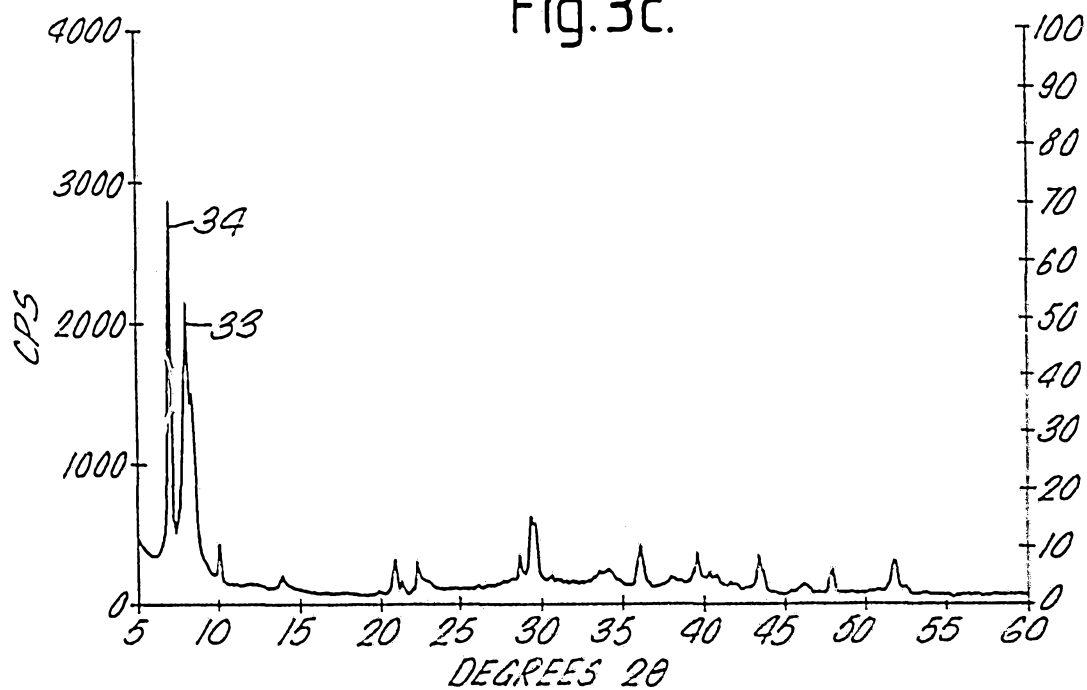
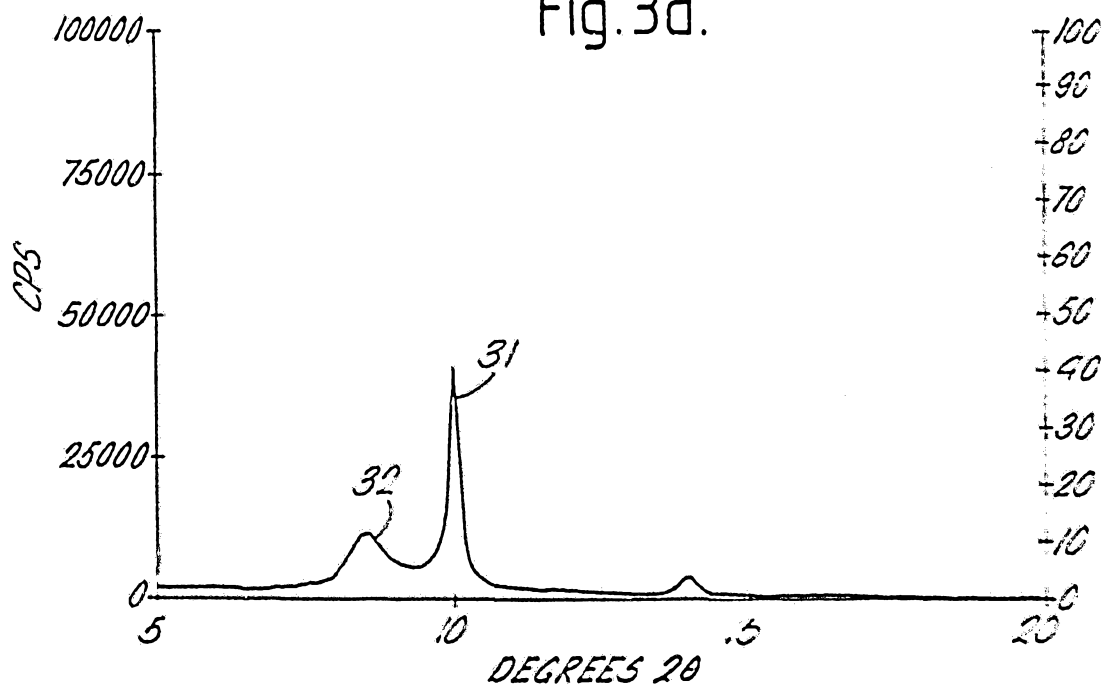
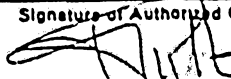


Fig. 3d.



INTERNATIONAL SEARCH REPORT

International Application No PCT/GB 88/00550

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁴		
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
• 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. "A" 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 8800550

SA 23152

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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		DE-A- 3544810	19-06-87
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