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(54) Title of the Invention: **High temperature insulated wire or cable**
Abstract Title: **Insulated wire or cable**

(57) A wire or cable comprises a core 10 and a polymeric sheath, wherein the sheath includes:
(i) an inner fire resistant layer 14 of a polymer matrix in which mica particles are dispersed;
(ii) an intermediate layer 16 comprising a wrapped film 15 of a polymer containing aromatic rings and having a melting point of at least 3500C and a glass transition temperature of at least 150 °C; and
(iii) a wrapped or extruded outer layer 18 of a fluoropolymer.

The intermediate layer 16 may be composed of a poly aryl ether ketone PAEK, or a blend or alloy thereof.

Examples of PAEK's that may be used are PEK, PEEKK, PEKEKK, PEKK, PEKKK.

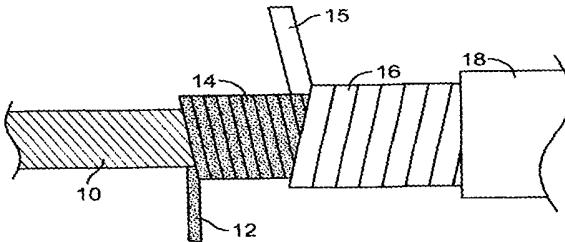


Fig. 1

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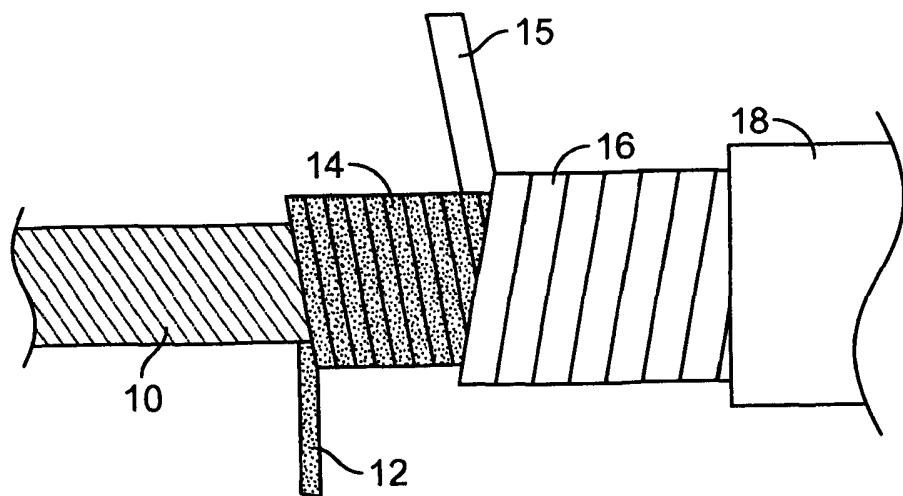


Fig. 1

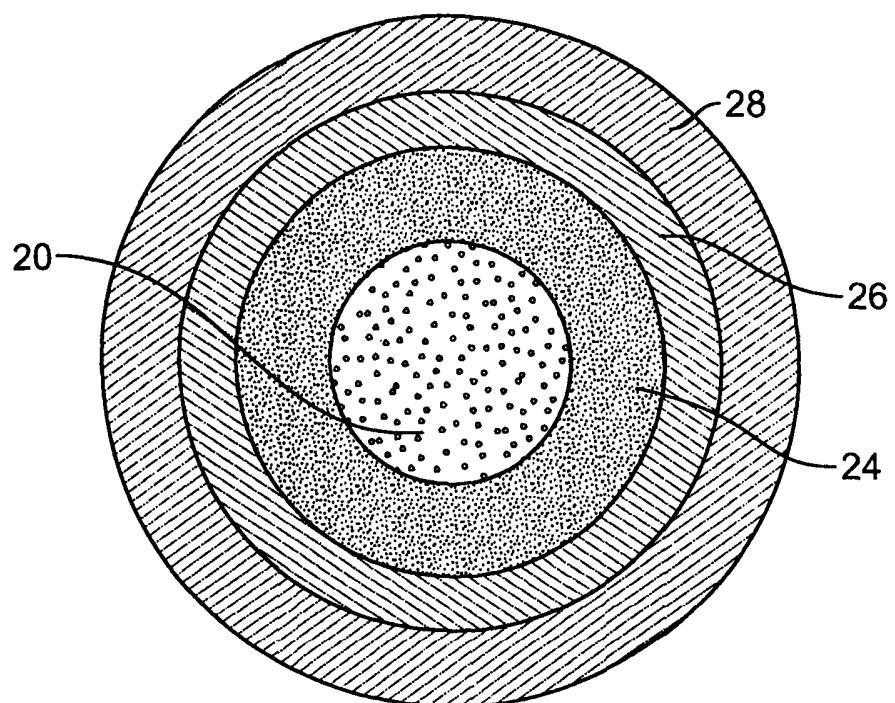


Fig. 2

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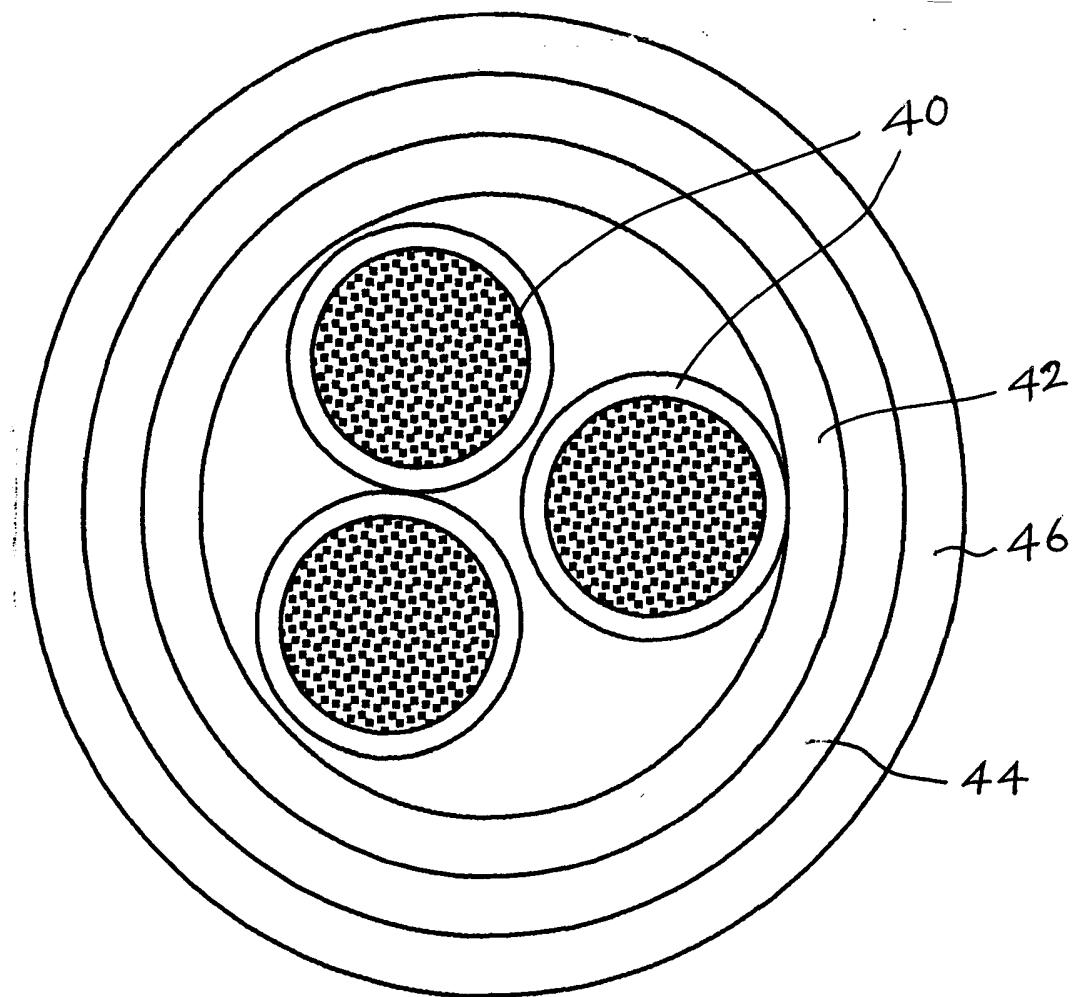


Fig. 3

HIGH TEMPERATURE INSULATED WIRE OR CABLE

This invention relates to high performance, high temperature and preferably fire resistant wires and cables for use in demanding or extreme conditions such as in drilling or mining, commercial or military aerospace and marine applications and automotive, rail and mass transport. Such cables may be exposed to extremes of temperature as well as to corrosive substances or atmospheres or to fire. High performance wires generally comprise a functional core such as an electrical conductor or optical fibre, and one or more insulating and/or protective coatings. These coatings should be flexible and not too bulky, since wires are required in many cases to be of small diameter.

Various types of polymer are known for use in wire and cable sheaths, such as polytetrafluoroethylene (PTFE) and polyetheretherketone (PEEK). PTFE has the advantage of being very tough as well as chemically inert, with a high softening point, low coefficient of friction and good electrical insulating properties. PEEK has found increasing use in wire and cable sheathing since it has good flame resistance, being self-extinguishing with very low smoke. It also has good elongation, good flexibility in thin sections such as films and good mechanical resistance to dynamic cut-through and scrape abrasion. It can however be susceptible to arc tracking and also to attack by acetone and strong acids. EP-A-572 177 discloses an electrical insulation laminate of porous PTFE and PEEK. The purpose of this is to provide a flexible electrical insulation material for air frame wire insulation which is lightweight with high mechanical strength, thermal resistance and chemical resistance and reduced dielectric constant. There is a demand for wire and cable insulations that are resistant to fire as well as to very high temperatures. One way of imparting such flame resistance is to apply a coating comprising mica particles, typically platelets, dispersed in a polymer matrix. JP-A-2003100149 for example discloses the use of a dispersion of fine mica powder and glass frit in a silicone resin for coating fire resistant cables.

Mica can however add to the cost and accordingly there is a need to

reduce the mica content of cable sheaths. For example, JP-A-2006120456 seeks to avoid the use of mica by combining a glass tape to impart tensile strength and dimensional stability with a silicone tape to impart heat resistance, electrical characteristics and adhesiveness.

JP-A-2000011772 discloses a fire resistant coating made with a cross-linked silicone rubber mixed with aluminium hydroxide and mica powder. There is also a requirement for wires and cables of reduced diameter, which could be achieved by using sheaths of reduced thickness.

GB-A-2460686 discloses a wire having a functional core and a sheath including an inner flameproofing layer comprising mica particles dispensed in a polymer matrix such as silicone, a wrapped film of PEEK and an outer coating of PEEK or another polymer. In this way the required temperature and flame resistance can be obtained with mica confined to one layer of three, with a thickness of preferably not more than 100µm.

There remains however a need for wires and cables which, in addition to high temperature and flame resistance, have improved mechanical properties, especially at high temperatures.

According to the present invention, there is provided a wire or cable comprising a core and a polymeric sheath, wherein the sheath includes:

- a) an inner fire resistant layer of a polymer matrix in which mica particles are dispersed;
- b) an intermediate layer comprising a wrapped film of a polymer containing aromatic rings and having a melting point of at least 350°C and a glass transition temperature of at least 150°C; and
- c) a wrapped or extruded outer layer of a fluoropolymer.

The inner fire-resistant layer (a) comprises mica dispersed in a polymeric matrix such as a polymeric siloxane. This fire-resistant layer may be in the form of a separate layer radially inside the intermediate layer (b). Alternatively it may be combined with a film formed from a tape used to form the intermediate layer.

The fire-resistant layer may have a backing layer, for example a supporting layer of glass fibre or a layer of another polymer such as a polyolefin.

An additional outer layer (c) of a fluoropolymer is provided for additional strength, flexibility and/or flame resistance. This outer layer may for example comprise polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF), ethylenetetrafluoroethylene, (ETFE), polyfluoroalkoxy (PFA) or copolymers or blends or alloys of any of these. This outer layer may be fixed or may be sintered, preferably at a temperature of 350° to 420°C.

The wrapped film forming the intermediate layer (b) may for example comprise a polyaryl ether ketone (PAEK) or a blend or alloy thereof. These comprise chains of aromatic rings with some linked by oxygen atoms and others by carbonyl groups. Those suitable for the purposes of the invention have higher melting points and glass transition temperatures than PEEK.

Examples of PAEK's having the required melting point T_m and glass transition temperature (T_g) are set out in Table 1 below, in which the polymers are identified by their abbreviated names where E stands to ether and K for ketone and Φ indicates a benzene ring, so that for example PEKK is polyetherketoneketone. The preferred polymers are those in which the ratio of ketone linkages to ether linkages is 1:1 or greater, these compounds having the higher T_g and T_m .

Table 1

Polymer	Structure	T _g (°C)	T _m (°C)
PEK	$-(\text{O}-\text{C}_6\text{H}_4-\text{O})_n$	163	361
PEEKK	$-(\text{O}-\text{C}_6\text{H}_4-\text{O}-\text{C}_6\text{H}_4-\text{O}-\text{C}_6\text{H}_4-\text{O})_n$	154	358
PEKEKK	$-(\text{O}-\text{C}_6\text{H}_4-\text{O}-\text{C}_6\text{H}_4-\text{O}-\text{C}_6\text{H}_4-\text{O}-\text{C}_6\text{H}_4-\text{O})_n$	173	371
PEKK	$-(\text{O}-\text{C}_6\text{H}_4-\text{O}-\text{C}_6\text{H}_4-\text{O})_n$	165	391
PEKKK	$-(\text{O}-\text{C}_6\text{H}_4-\text{O}-\text{C}_6\text{H}_4-\text{O}-\text{C}_6\text{H}_4-\text{O})_n$	175	439

The intermediate layer may have a thickness of 10 to 100 μm , more preferably 25 to 75 μm . In some embodiments, each of the three layers (a) to (c) has the thickness of 25 to 75 μm . The layer may comprise a blend or alloy containing at least 50%, and more preferably 65%, of PAEK.

Polymers that may be blended or alloyed with the PAEK include those made up of heterocyclic units containing a six-membered ring fused to a five-

membered ring, for example polyimide, polybenzimidazole, polybenzoxazole and polybenzothiazole and copolymers thereof.

The intermediate layer (b) could comprise two layers of said aromatic or heterocyclic polymer with a layer of mica between them.

The coatings described above can be applied to numerous different types of core, notably conductive wires or cables, for example copper, which may be nickel or tin coating or silver-plated, aluminium, typically copper-clad aluminium, silver or steel. For other purposes, non-metallic cores such as carbon fibre or polymeric or ceramic cores may be used. The cable may be single core or multi-core or may comprise a twisted pair of wires, a multi-strand core or a braid. Any of these cores may be coated with copper, nickel, tin or silver.

Preferred embodiments of the invention will now be described with reference to the accompanying drawings wherein:

FIG.1 shows how an insulated wire according to the present invention can be made by wrapping a PAEK and other polymeric tapes;

FIG.2 is a cross-section through a multi-coated wire in accordance with a first embodiment of the invention; and

FIG.3 is a cross-section through a coated wire in accordance with a second embodiment of the invention.

Referring first to Fig.1, a multi-stranded conductor 10, which may for example be of copper, uncoated or coated with nickel, silver or tin, aluminium, which may be copper clad, steel or a non-metallic cable such as carbon fibre, polymer fibre or ceramic fibre has a three-layer sheath applied to it by winding and extrusion. A first tape 12, for example of silicone with mica platelets distributed in it, is wound on spirally to form a first wound coating 14. Then a second tape 15, for example of a polyaryletherketone, is wound on spirally to form a second coating 16. Finally an outer layer of another polymer is applied, for example by extrusion or tape wrapping. The inner and intermediate layers 14, 16 could be formed from a single combined wrapped tape. Similarly, all three layers could be wrapped as a composite film.

The inner and intermediate layers are preferably wound spirally around the core with an overlap of 40 to 70%, preferably 48 to 58%

Fig.2 shows a cross-section through a cable to which a three-layer sheath has been applied, for example as described in relation to Fig.1. The innermost layer 24, immediately surrounding the cable 20, is a mica-containing sheath to impart flame resistance. This may for example be a mica-containing silicone tape which may be backed with a glass fibre and/or with a polyethylene layer. This layer may be applied in single or multiple layers of the same or different thicknesses.

The second layer 26 comprises polyaryletherketone wound tape having a thickness of 10 to 100 μ m. The PAEK may be used alone or blended or alloyed with other polymers that preferably contain at least 50%, and more preferably at least 65%, of PAEK.

The outer layer 28 can be either extruded or wrapped. It provides an encapsulation layer to form an additional layer of protection to the cable. Any of the polymers, polymer blends or alloys listed above for this layer can be used. PTFE for example could sintered to provide exceptional chemical resistance as required by the aerospace market.

The synergistic combination of mica-containing polymer and PAEK in this embodiment can provide a high temperature, fire resistant wire with potentially low weight and low overall diameter. The mica can provide insulation and fire resistance up 1000°C, and in combination with the PAEK provides improved mechanical properties including dynamic cut-through resistance, even at high temperatures, non burning characteristics and very low smoke emission. The manufacturing process, which could include high temperature sintering, must support semi-crystallinity in the structural PAEK layer

The two layers 24 and 26 may be applied as a preformed single composite wrapped layer formed from a single or double mica layer on a film or tape of the aromatic polymer having the required high T_m and T_g values. The mica component may for example comprise a mica/silicone tape, with or without a polyethylene layer. For the outer fluoropolymer layer 28, the range of contents

may be the same as in the embodiment described above. Again, the outer layer may be sintered.

As illustrated in Fig. 3, a wrapped PAEK film 44, or a wrapped film of a blend or alloy of PAEK with one or more other polymers such as a heterocyclic polymer, can be used as a structural layer for a wide variety of wire or cable constructions. This could include a conductor with another polymeric insulation, a complete cable construction with or without a braid, such as a twisted pair or a quad of twisted pairs such as Cat 7 cable. In the embodiment illustrated in Fig. 3, the PAEK intermediate layer is formed around a three-core cable 40 with a flameproofing or fire-resistant insulation layer 42 of mica particles in a matrix of silica or the like. An outer protective layer 46 can have a composition selected from the same ranges as the protective layers 18 and 28 of the embodiments described above.

CLAIMS:

1. A wire or cable comprising a core and polymeric sheath, wherein the sheath includes:
 - (a) an inner fire resistant layer of a polymer matrix in which mica particles are dispersed;
 - (b) an intermediate layer comprising a wrapped film of a polymer containing aromatic rings and having a melting point of at least 350°C and a glass transition temperature of at least 150°C; and
 - (c) a wrapped or extruded outer layer of a fluoropolymer.
2. A wire or cable according to claim 1 wherein the wrapped intermediate film (b) has a thickness of 10 to 100µm.
3. A wire or cable according to claim 2 wherein the wrapped intermediate film has a thickness of 25 to 75µm.
4. A wire or cable according to claim 3 wherein each of the three layers (a), (b) and (c) around the core has a thickness of 25 to 75µm.
5. A wire or cable according to a preceding claim wherein the intermediate layer (b) comprises a polyaryl ether ketone (PAEK) or a blend or alloy thereof.
6. A wire or cable according to claim 5 wherein the PAEK has a ratio of ketone to ether groups linking the aromatic rings of at least 1:1.
7. A wire or cable according to claim 5 wherein the wrapped PAEK film comprises a blend or alloy containing at least 50% by weight of PAEK.
8. A wire or cable according to claim 6 wherein the wrapped PAEK film comprises a blend or alloy containing at least 65% by weight of PAEK.

9. A wire or cable according to any one of claims 5 to 8 wherein the PAEK of the intermediate layer is blended or alloyed with a polymer of heterocyclic units containing a six-membered ring fused with a five-membered ring.

10. A wire or cable according to claim 8 wherein said heterocyclic units comprise units of polyimide, polybenzimidazole, polybenzoxazole and/or polybenzothiazole.

11. A wire or cable according to any preceding claim wherein the wrapped intermediate film (b) comprises two layers of said aromatic or heterocyclic polymer with a layer of mica between them.

12. A wire or cable according to any preceding claim wherein the matrix of the fire resistant inner layer (a) comprises a silicon rubber or a polymeric siloxane.

13. A wire or cable according to any preceding claim wherein the fire resistant inner layer is formed from a wrapped tape.

14. A wire or cable according to claim 13 wherein the wrapped tape of a fire resistant material forming the inner layer has a supporting or backing layer.

15. A wire or cable according to claim 14 wherein the wrapped layer of fire resistant material is a glass fibre-backed tape.

16. A wire or cable according to any one of claims 13 to 15 wherein said inner layer and said intermediate layer are formed from a single combined wrapped tape.

17. A wire or cable according to any preceding claim wherein said outer layer (c) is formed of a fluoropolymer selected from polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF), ethylenetetrafluoroethylene (ETFE), polyfluoroalkoxy (PFA) or blends or alloys of any of these.

18. A wire or cable according to any preceding claim wherein the outer protective polymer layer is sintered or fused.

19. A wire or cable according to any preceding claim wherein the intermediate layer is at least partly sintered or fused.

20. A wire or cable according to any preceding claim wherein the core is a polymeric, carbon fibre or ceramic core.

21 A wire or cable according to any one of claims 1 to 19 wherein the core is a conductive metallic core.

22. A wire or cable according to claim 20 wherein the core is of copper, aluminium, silver or steel.

23. A wire or cable according to any preceding claim wherein each of said layers (a) to (c) is an individually wrapped layer.

24. A wire or cable according to any one of claims 1 to 21 wherein two or three of said insulating layers are applied in the form of a laminated composite film.

25. A wire or cable according to claim 23 or claim 24 wherein said insulating layers and/or laminated composite film are spirally bound onto the core with an overlap of 40 to 70%.

26. A wire or cable according to claim 26 wherein said overlap is 48 to 58%.

27. A wire or cable according to any one of claims 1 to 22 wherein the outer protective layer is formed by extrusion.

28. A method of making an insulated wire or cable which comprises the steps of spirally winding onto an elongate core an inner layer or a polymeric matrix in which mica particles are dispersed, an intermediate layer comprising a wrapped film of a polymer containing aromatic or heterocyclic rings and having a melting point of at least 350°C and a glass transition temperature of 150°C, applying an outer layer of a fluoropolymer by wrapping or extrusion and sintering at least said outer layer.

29. A method according to claim 26 wherein said sintering takes place at a temperature in the range from 350 to 420°C.

30. A composite insulating tape or tape construction comprising a first fire resistant layer of a polymer matrix in which mica particles are dispersed, an intermediate second layer of a polymer containing aromatic and/or heterocyclic rings and having a melting point of at least 350°C and a glass transition temperature of at least 150°C and a third layer of PTFE.

Application No: GB1008268.3

Examiner: Peter Easterfield

Claims searched: 1 to 30

Date of search: 13 July 2010

Patents Act 1977: Search Report under Section 17

Documents considered to be relevant:

Category	Relevant to claims	Identity of document and passage or figure of particular relevance
Y	at least claim 1	WO 89/00757 A1 (RAYCHEM)
Y	at least claim 1	WO 89/00764 A1 (RAYCHEM)
Y	at least claim 1	WO 89/00762 A1 (RAYCHEM)

Categories:

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.

Field of Search:

 Search of GB, EP, WO & US patent documents classified in the following areas of the UKC^X:

Worldwide search of patent documents classified in the following areas of the IPC

H01B

The following online and other databases have been used in the preparation of this search report

WPI, EPODOC, TXTE

International Classification:

Subclass	Subgroup	Valid From
H01B	0003/42	01/01/2006