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54 Refractory coated article.

57 An article of manufacture, for example an electrical conductor, as on the surface of a metal part an adherent, dense refractory keying layer and, on the keying layer a further electrically insulating refractory layer that has been formed by a faster deposition method.

The keying layer is preferably formed by a vacuum deposition processing, e.g. sputtering evaporation, ionplating or chemical vapour deposition, and the further refractory layer is preferably formed by a sol-gel deposition method, plasma ashing method, a solution coating method or a plasma spraying method. The articles are particularly suitable for high temperature wires.

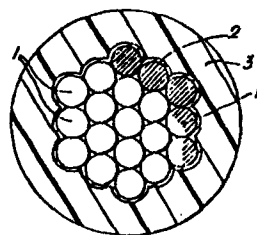


Fig. 1.

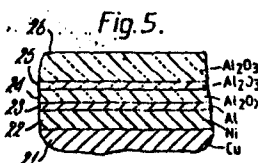


Fig. 5.

Refractory Coated Article

This invention relates to articles that are formed from metal, for example from copper or copper alloys, and especially to such articles that may be subjected to high temperatures.

One area in which the present invention is particularly applicable is that of electrical wires and cables. For example so called "magnet wire" which is used in electromagnet windings in transformers, motors and other equipment, may experience severe temperature excursions under overload conditions in service. Also, in certain fields where cables are used, for example in military, marine or offshore applications, it is desired to use cables that are capable of functioning for a period of time during a fire without failing. Such cables are called circuit integrity cables or signal integrity cables depending on their use. The previously proposed circuit and signal integrity cables have generally used the principle that the individual conductors should be separated from one another by mica tapes or by large volumes of packing materials or silicones or by combinations thereof in order to prevent the formation of short circuits during a fire, with the result that the previously proposed cables are relatively heavy or large or both.

The present invention provides an article of manufacture which has at least a part that is formed from a metal the article having, on a surface of that part, an adherent dense refractory keying layer and, on the keying layer, a further refractory layer that has been formed by a relatively fast deposition method.

By the phrase "relatively fast deposition method" is meant that the rate of deposition of the further refractory layer, measured for example in micrometres of thickness per unit time, is greater than the rate of deposition of the refractory keying layer. The properties of refractory coatings are known to depend significantly on the method by which they are formed or deposited onto a substrate, and in general, the techniques that exhibit the lowest deposition rates will form refractory layers having relatively high density, i.e. not being porous, and having higher adhesion to metallic substrates. Preferably the refractory keying layer has been formed by a vacuum deposition process, e.g. a sputtering, evaporation, ion plating, or chemical vapour deposition, and the further refractory layer preferably has been formed by a sol-gel deposition method, a plasma ashing method, a solution coating method or a plasma spraying method e.g. a flame spraying method, or may be formed by another, faster, vacuum deposition process.

According to the invention it is possible to form articles having a refractory coating which, although being relatively thick and so having good electrical insulation characteristics, also exhibits very good adhesion to the underlying metal even when subjected to mechanical or thermal stresses.

Preferably, the refractory keying layer is substantially contaminant-free, that is to say, it contains only those species that are intended in order for the layer to fulfill its intended function, and contains substantially no species that result from the manufacturing process. An important feature of the refractory keying layer is good control of composition to optimise the high temperature performance of the article. The composition is totally inorganic and therefore does not rely on conversion processes to occur during exposure to normal or emergency high temperature service, as is the case for example in many mica filled or glass filled silicone resin systems. The composition is also improved by removing the use of polymeric binders to support inorganic materials which may be consolidated by firing processes to form the inorganic insulation. Similarly, articles in which the refractory coatings have been formed by electrochemical conversion of metal layers e.g. by anodising an aluminium layer, do not form part of the invention, such layers usually being porous and often being heavily contaminated with ionic residue from the electrolytic solutions e.g. sulphates from sulphuric acid anodisation processes.

Preferably the underlying metal from which the part of the article is formed has a melting point of at least 800°C, more preferably at least 900°C, and especially at least 1000°C. The present invention is particularly applicable to articles in which the metal is copper or an alloy thereof for example wire and cable that need to be capable of functioning at high temperatures for significant lengths of time without failure e.g. circuit and signal integrity cable and

magnet wire, and the invention will be described below with reference to wire and cable.

In the case where the article comprises an electrical wire or cable, so that the underlying copper forms the conductor of the cable, the conductor may be a single, solid conductor or it may be a stranded conductor in which individual strands are laid together to form a bundle which preferably contains 7, 19 or 37 strands. Where the conductor is stranded it is preferred for the bundle to be coated rather than the individual strands, that is to say, the refractory coating extends around the circumference of the bundle but not around the individual strands so that substantially only the outwardly lying surfaces of the outermost layer of strands are coated.

This form of conductor has the advantage that the inter strand electrical contact is retained and the dimensions of the bundle are kept to a minimum (since the thickness of the coating may constitute a significant proportion of the strand dimensions for fine gauge conductors) and also it aids the formation of good electrical connections, e.g. crimp connections, to the conductor because a large proportion of the surface of the strands, and the entire surface of the strands in the central region of the conductor, will be uncoated by the refractory layer.

If a circuit or signal integrity cable is formed according to the invention from a stranded conductor, it has the advantage that it is very flexible as compared with other signal and circuit integrity cables, especially if a stranded conductor is used. The abi-

lity of the wire to be bent around tight bends (small bend radii) without deleterious effect is partly due to the fact that the layer providing the integrity is thinner than with other signal and circuit integrity cables. However, when the conductor is a stranded conductor it may be bent around tight bends without undue stress on the surface of the strands because the strands are displaced from a regular hexagonal packing at the apex of the bend thereby exposing uncoated areas of the strands to the eye. It is highly surprising that even though uncoated strands may be exposed when the wire conductor is bent there is no electrical contact between adjacent stranded conductors. It is believed that in this case the integrity is retained because the profile of a stranded conductor is not cylindrical but rather is in the form of a hexagon that rotates along the length of the conductors, so that adjacent stranded conductors will touch one another only at a few points along their length, which points are always provided by the outwardly oriented part of the surface of the strands in the outer layer of the conductors. It is these points of contact that are always provided with the refractory coating.

The further refractory layer preferably has a thickness of at least 0.5, more preferably at least 1 and especially at least 2 micrometres. The exact thickness desired will depend on a number of factors including the type of layer and the voltage rating of the wire, circuit integrity cables usually requiring a somewhat thicker coating than signal integrity cables and sometimes above 15 micro-metres. The lower limits for the layer thickness are usually determined by the required voltage rating of the wire whilst the upper

limits are usually determined by the time, and therefore the cost, of the coating operation.

The refractory keying layer will usually be thinner than the further refractory layer, and preferably has a thickness of not more than 0.5 micrometres and most preferably not more than 0.3 micrometres, but usually at least 0.1 micrometres.

In order to optimise the adhesion between the refractory keying layer and the further refractory layer it is preferred for them both to have the same nominal chemical composition, that is to say, they both preferably have the same general chemical formula although, as explained below, the precise stoichiometry of one or both layers may differ from the stoichiometric formula.

In order to improve further the high temperature properties of the article, and especially in the case where the underlying metal is copper or an alloy thereof, it is preferred for the article to include a metallic intermediate layer located between the metal from which the part is formed and the refractory keying layer. The metal is preferably one which forms a good bond between the underlying metal and the refractory keying layer and also, as described in our copending British Application entitled "Temperature Resistant Coated Article" filed on even date herewith (Agent's Ref. RK263) (corresponding to European Application No. 85304871.8), one which acts as a barrier to diffusion of oxygen or copper or both or which acts to reduce stress in the refractory layers imposed by substrate strain resulting from mechanical

or thermal stress. Preferred metallic intermediate layers include those formed from aluminium, titanium, tantalum chrom-ium, manganese, silicon or nickel although other metals may be used. Examples of articles in which they may be used are described in our copending British Patent Application entitled "Electrical Wire & Cable" (Agent's Reference RK264) filed on even date herewith, (corresponding to European Application No. 85304872.6).

In the case of electrical equipment the refractory layers may provide the entire electrical insulation or one or more additional insulating layers may be provided thereon. The additional insulating layer may be inorganic or organic or a combination of inorganic and organic layers may be provided.

In the case of wires according to the invention, the polymeric insulation may be provided in order to provide additional insulation to the conductor during normal service conditions and also to enable the wire to have the desired dielectric properties and other properties e.g. mechanical properties, scuff resistance, colour coding ability etc. However, an important advantage of the present invention is that since a significant proportion of or all the service insulating properties are provided by the refractory coating, the electrical properties of the polymeric insulation are not as critical as with other wire constructions in which the polymeric insulation provides the sole insulation between the conductors. Of the known polymeric materials that are used for electrical insulation, polyethylene probably has the most suitable electrical properties but is highly flammable, and has

poor mechanical properties. Attempts to flame retard polyethylene have either required halogenated flame retardants which, by their nature, liberate corrosive and toxic hydrogen halides when subjected to fire, or have required relatively large quantities of halogen free flame retardants which have a deleterious effect on the electrical properties and often also the mechanical properties of the polymer. Accordingly, an acceptable wire has in the past only been achieved by a compromise between different properties which is often resolved by using a relatively thick-walled polymeric insulation and/or dual wall constructions. Although such forms of polymeric insulation may be used with the wire according to the present invention, the presence of the refractory layer does obviate these problems to a large extent since the polymer used for the insulation may be chosen for its flammability and/or its mechanical properties at the expense of its electrical properties. As examples of polymers that may be used to form the polymeric insulation there may be mentioned polyolefins e.g. ethylene homopolymers and copolymers with alpha olefins, halogenated polymers e.g. tetrafluoroethylene, vinylidene fluoride, hexafluoropropylene and vinyl chloride homo or copolymers polyamides, polyesters, polyimides, polyether ketones e.g. polyarylether ketones, aromatic polyether imides and sulphones, silicones, alkene/vinyl acetate copolymers and the like. The polymers may be used alone or as blends with one another 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, for example a polyvinylidene fluoride layer may be located

on for example a polyethylene layer. The polymers may be uncrosslinked but preferably are 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. anti-oxidants, stabilizers, crosslinking promoters, processing aids and the like. The polymeric insulation may, if desired, contain a filler e.g. hydrated alumina, hydrated titania, dawsonite, silica and the like, and especially a filler that has the same chemical composition, at least under pyrolysis conditions, as the refractory coating, so that the filler in the polymeric insulation will provide additional insulation when the wire or cable is subjected to a fire. A preferred type of polymeric insulation is one that will char, for instance certain aromatic polymers mentioned above, or that will ash e.g. a silicone polymer, when subjected to a fire so that the char or ash, together with the refractory coating, will provide the necessary insulation during a fire. Examples of polymers, compositions, their manufacture and wires using them are described in U.S. Patent Specifications Nos. 3,269,862, 3,580,829, 3,953,400, 3,956,240, 4,155,823, 4,121,001 and 4,320, 224, British Patent Specifications Nos. 1,473,972, 1,603,205, 2,068,347 and 2,035,333, 1,604,405 and in European Patent Specification No. 69,598, the disclosures of which are incorporated herein by reference. In some instances, for example when certain aromatic polymers are used, it may be appropriate to form the insulation on the conductor by a plasma or thermal polymerisation process. Preferably the wire is substantially halogen free.

As stated above, the preferred methods of forming the keying layer include evaporation, plasma assisted chemical vapour deposition and sputtering methods.

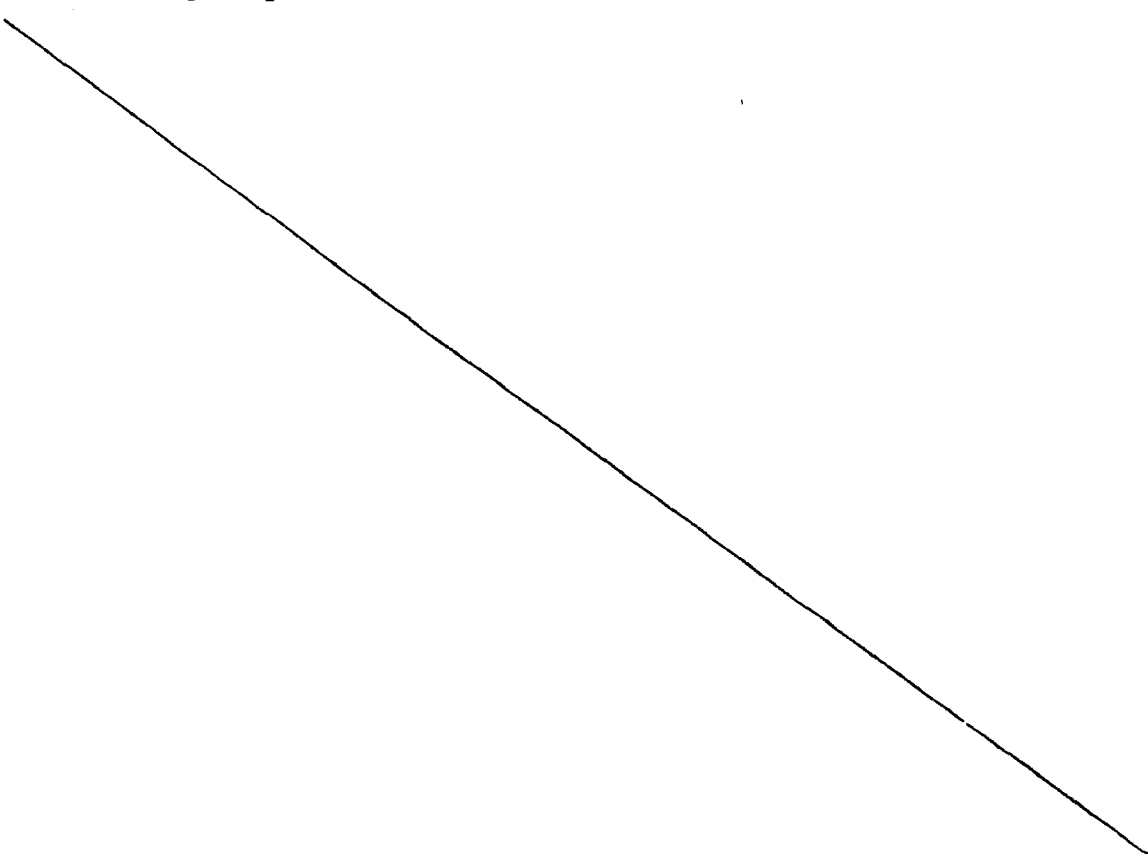
An advantage of using a relatively slow deposition method such as a sputtering method for forming the keying layer is that it allows greater control over the chemical composition and mechanical properties of the keying layer to be exercised. For example, it is often advantageous for the keying layer to be non-stoichiometric since this may increase the adhesion between the keying layer and the underlying layer, and especially if the stoichiometry of the keying layer varies through at least part of its thickness so that stresses that may be induced in the coating, for example due to differential thermal expansion, are not localised to a boundary of the layer and so that different parts of the layer will exhibit different properties. For example, a relatively metal-rich part of the keying layer may exhibit good adhesion to the conductor or intermediate layer while part of the coating having least metal or semi-metal may exhibit the best electrical properties or better adhesion to the further refractory layer.

Preferably the insulating refractory coating is formed from an electrically insulating infusible or refractory metal or semi-metal oxide or nitride and the invention will be described below in many cases with respect to oxides and nitrides although other refractory coatings are included. By the term "infusible" or "refractory" is meant that the coating material in its bulk form should not fuse or decompose when subjected to a temperature of 800°C, for 3 hours. Preferably the

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oxide or nitride should be able to withstand higher temperatures also, for example it should be able to withstand a temperature of 1000°C for at least 20 to 30 minutes. The preferred oxides are those of aluminium, titanium, tantalum and silicon or mixtures thereof with themselves or with other oxides and the preferred nitrides are those of aluminium and silicon. Thus, for example, the use of mixed metal oxides for the refractory coating are also encompassed by the present invention.

If desired, the stoichiometry of the keying layer may vary continuously throughout the thickness of the layer or it may contain one or more layers or strata of relatively uniform stoichiometry. Thus the keying layer may have an outer region of relatively uniform stoichiometry and preferably of a relatively high oxygen or nitrogen content in order to exhibit the optimum electrical properties or adhesion to the further refractory layer. The relative thicknesses of the non-



uniform and uniform layers may vary widely. For example the major part of the keying may have a non-uniform stoichiometry or the major part of the layer's thickness may be of uniform stoichiometry, in which latter case the non-uniform part of the layer could even be considered as an intermediate layer that improves adhesion of the rest of the layer especially at high temperatures. If the underlying metal- or semi-metal-rich part of the keying layer is intended to improve the adhesion of the refractory coating, its particular composition will depend on the composition of any underlying layer, and in some cases it may be desirable for the metal or semi-metal rich part to consist substantially entirely of the metal or semi-metal so that there is a gradual change from the metal or semi-metal to the oxide or nitride. This is particularly preferred if the system includes an underlying layer of the same metal or semi-metal.

The precise stoichiometry of the uniform top layer can be determined experimentally using wavelength dispersive electron microprobe analysis or by using x-ray photoelectron spectroscopy (XPS). The composition of the coating as it changes from metal to refractory throughout its depth can be assessed using Auger electron spectroscopy (AES) in which the film is continuously sputtered away to expose fresh surface for composition analysis.

The variation in stoichiometry is not limited to a variation in the metal or semi-metal/oxygen or nitrogen proportions. In addition or alternatively the relative proportions of two different metals or semi-metals may be varied so that, for example, there is a gradual

change from one metal, which may constitute an intermediate layer, to the oxide or nitride of a different metal.

The outer region of the keying layer preferably has a molar oxygen or nitrogen content that is at least 50%, more preferably at least 65% and especially at least 80% of the oxygen or nitrogen content of that required for the formal stoichiometry of the insulating refractory oxide or nitride. Thus the preferred oxide composition of the outer region may be represented as

MO_x where x is at least 0.75, preferably at least 1 and especially at least 1.25 in the case of aluminium,

at least 1, preferably at least 1.3 and especially at least 1.5 in the case of titanium or silicon, and

at least 1.25, preferably at least 1.6 and especially at least 2 in the case of tantalum.

The most preferred method of forming keying layer in which the composition varies throughout its thickness is a sputtering method.

In the sputtering method, predominantly neutral atomic or molecular species are ejected from a target, which may be formed from the material to be deposited, under the bombardment of inert gas positive ions e.g. argon ions. The high energy species ejected will travel considerable distances to be deposited on the wire

conductor substrate held in a medium vacuum, e.g. 10^{-4} to 10^{-2} mbar. The positive ions required for bombardment may be generated in a glow discharge where the sputtering target serves as the cathode electrode to the glow discharge system. The negative potential (with respect to ground and the glow discharge) is maintained in the case of insulating target materials by the use of radio frequency power applied to the cathode, which maintains the target surface at a negative potential throughout the process. DC power may be applied when the target is an electrically conducting material. The advantage of such techniques is that control over the coating material is greatly enhanced, and the energy of the species ejected is very much higher than with evaporation methods e.g. typically 1 to 10 eV for sputtering as compared with 0.1 to 0.5 eV for evaporation methods. Considerable improvements in interfacial bonding are achieved but the deposition rate in the sputtering process described will be lower than that for electron beam evaporation.

In magnetron sputtering processes the plasma is concentrated immediately in front of the cathode (target) by means of a magnetic field. The effect of the magnetic field on the gas discharge is dramatic. In that area of discharge where permanent magnets, usually installed behind the cathode, create a sufficiently strong magnetic field vertically to the electric field, secondary electrons resulting from the sputter bombardment process will be deflected by means of the Lorentz force into circular or helical paths. Thus the density of electrons immediately in front of the cathode as well as the number of ionised argon atoms bombarding the cathode are substantially in-

creased. There is an increase in plasma density and a considerable increase in deposition rate. Bias sputtering (or sputter ion plating) may be employed as a variation of this technique. In this case the wire conductor is held at a negative potential relative to the chamber and plasma. The bombardment of the wire conductor by Argon ions results in highly cleaned surfaces. Sputtering of the target material onto the wire conductor throughout this process results in a simultaneous deposition/cleaning mechanism. This has the advantage that the interfacial bonding is considerably improved. In sputter ion plating systems both target and the wire conductor are held at a negative potential. In this case the relative potentials are balanced to promote preferential sputtering of the target material. The target voltage will be typically less than 1kV, dependent on system design and target material. The wire substrate, may be immersed in its own localised plasma dependent upon its bias potential, which will be lower than that of the target. The exact voltage/power relationship achieved at either target or substrate is dependant upon many variables and will differ in detail from system to system. Typical power densities on the target are 10-20W/cm². The load to the substrate may be substantially lower, often as little as 5% of the target load.

The preferred technique that is used to apply the oxide or nitride coating is a reactive bias sputtering method in which reactive gas is introduced into the vacuum chamber in addition to argon so that the oxide/nitride of the target material, which in this case is a metal or semi metal rather than the oxide/nitride will be deposited. Experimental results have shown that the

level of reactive gas and its admission rate have a significant effect on deposition rates. The precision control of partial pressure of the reactive gas and the analysis of the sputtering atmosphere in a closed loop control system is considered highly desirable. Apart from the simultaneous deposition/cleaning advantages mentioned above, the ion bombardment of the substrate enhances surface reaction between the reactive gas and depositing species, resulting in more efficient formation of the coating with the required stoichiometry.

Partial pressure of reactive gas is determined experimentally but will normally be between 2 and 25% but sometimes up to 30%, the exact level depending on the required stoichiometry of the coating and deposition rate. Reactive sputtering is also the preferred technique because it facilitates alterations to the stoichiometry of the coating. For example, an intermediate "layer" of the pure metal used for the oxide/nitride coating may be deposited in such a way that there is no defined boundary between the conductor metal, oxide/nitride metal and oxide/nitride layers.

The vacuum chambers and ancillary equipment, including micro-processor gas control units and a variety of targets used in these methods may be purchased commercially. Many variations in design are possible but most employ the use of "box" shaped chambers which can be pumped down to high vacuum for use in any of the vacuum deposition processes mentioned. Systems are normally, but not exclusively, dedicated to one deposition process. One system which may be employed to coat wire uses air to air transfer techniques for passage of the wire conductor through the

deposition chambers and employs one or more ancillary vacuum chambers either side of the main deposition chamber.

These ancillary chambers are held at progressively higher pressures as they extend from deposition chamber to air. This reduces the load on individual vacuum seals. The system described has the advantage of continuous feed of the wire conductor over batch process arrangements. In the vacuum deposition chamber the pressure is held constant at a pressure normally between 10^{-4} and 10^{-2} Torr.

The targets employed are commercially available Planar Magnetron Sputtering sources. Their size may vary widely, and targets in excess of 2 metres in length may be employed. Between two and four such sources may be arranged opposite one another so as to surround the wire conductor passing through the chamber or to sputter from at least two sides. The arrangement may be employed in series to increase wire throughput rates. As described above a negative bias is applied to the magnetron to initiate the sputtering process. The wire may be held at a lower negative bias as described earlier.

Refinements to the system can, if desired, be employed. For example, the use of an intermediate vacuum station between the air (input side) and the deposition chamber may be employed to generate an Argon ion glow discharge which cleans the wire conductor surface by ion bombardment prior to its entry into the vacuum deposition chamber and also heats the wire conductor.

Further intermediate chambers can be employed between the cleaning and deposition chamber to deposit intermediate layers.

Conditions may be controlled to produce any of the conductor coatings described above in which no defined boundaries occur between the layers. For example an intermediate "layer" of the pure metal used for the refractory coating may be deposited in such a way that there is no defined boundary between the conductor metal, the intermediate layer and the oxide or nitride coating. In a similar fashion additional chambers can be employed between the deposition chamber and air (output side) to deposit different metal, metal oxide or metal alloys onto the refractory coating for improved lubrication or wear resistance.

Evaporation and the related processes of activated evaporation and ion plating offer alternative techniques for deposition of either the keying layer or the further refractory layer.

Evaporation of the coating material is achieved by heating the material such that its vapour pressure exceeds 10^{-2} mbar. Evaporation temperatures vary according to coating material, e.g. 1300-3500°C for refractory metal oxides, the chamber pressure being usually 10^{-4} to 10^{-6} mbar. Similar wire transport systems to those described may be used to hold the substrate about 30-40 cm above the source. Several heating methods exist e.g. resistive, inductive, electron beam impingement etc. although the preferred method is an electron beam source where a beam of high energy electrons e.g. 10,000eV impinge onto the coating

material contained in a water-cooled crucible. The use of multi-pot crucibles or twin source guns, enable multiple layers and graded stoichiometry layers to be deposited with the aid of electronic monitoring and control equipment.

Compound coatings can be made either by direct evaporation from that compound e.g. Al_2O_3 or by reactive evaporation, e.g. aluminium evaporated into a partial pressure of oxygen to give aluminium oxide. Variations in the process exist either to promote reactions or adhesion, e.g. Activated reactive evaporation (ARE) can be used to increase the reaction probability between the evaporant and the reactive gas.

In ion-plating, negative bias applied to the substrate in an inert gas promotes simultaneous cleaning/deposition mechanisms for optimising adhesion as described in the sputtering process. Bias levels of -2kV are typically used but these can be reduced to suit wire substrates. Alternatively, high bias can be applied to a plate positioned behind the traverse wire to achieve a similar effect. As operating pressures are higher in the ion plating technique, e.g. 10^{-3} to 10^{-2} mbar, gas scattering results in a more even coating distribution. To protect the filament the electron beam gun in the ion plating technique is differentially pumped to maintain vacuum higher than 10^{-4} mbar.

In the Plasma assisted chemical vapour deposition (PACVD) method the substrate to be coated is immersed in a low pressure (0.1 to 10 Torr) plasma of the appropriate gases/volatile compounds. This pressure is maintained by balancing the total gas flow-rate against

the throughput of the pumping system. The plasma is electrically activated and sustained by coupling the energy from a power generator through a matching network into the gas medium. Thin films have been successfully deposited from direct current and higher frequency plasmas well into the microwave range. At high frequencies the energy may be capacitatively or inductively coupled depending on chamber design and electrode configuration. Typically a 13.56 MHz radio-frequency generator would be used having a rating which would allow a power density of between 0.1 - 10W/cm² in a capacitatively-coupled parallel-plate type reactor. The substrate, which could be set at a temperature of up to 400°C, may be grounded, floating or subjected to a dc voltage bias as required. Typically deposition rates for this technique can be favourably compared with those obtained by sputtering. The deposition of alumina may be achieved by immersing a substrate in a plasma containing a volatile alumina compound (e.g. Tri-methyl aluminium or Aluminium butoxide) and oxygen under appropriate processing conditions.

After the keying layer has been formed, the further refractory insulating coating is applied. As stated above the further refractory insulating coating may be formed on the vacuum deposited refractory coating by any technique which is relatively fast, for example sol-gel, flame sprayed, or evaporated coatings.

The sol-gel process involves the hydrolysis and polycondensation of a metal alkoxide, for example, silicon tetraethoxide, titanium butoxide or aluminium butoxide to produce an inorganic oxide gel which is converted to an inorganic oxide glass by a low temper-

ature heat treatment. The metal alkoxides can be used as precursors to inorganic glass preparation via the sol-gel route. The alumina gel can be prepared by adding an alkoxide of aluminium, such as aluminium secondary butoxide, to water which is heated to a temperature above 80°C and stirred at high speed. Approximately two litres of water per mole of alkoxide are suitable quantities. The solution is maintained at 90°C and approximately 0.5 - 1 hour after the addition of the alkoxide a quantity of acid, for example 0.07 moles of hydrochloric acid per mole of alkoxide, is added to peptise the sol particles. The sol is maintained at the boiling temperature to evaporate excess butanol and reflux conditions are established and maintained until peptisation is complete. The sols can be reduced in volume by removal of water until a viscosity suitable for wire coating is reached.

Wires are provided with the alumina gel for subsequent conversion to an inorganic insulation by a dip or extrusion process. In this process the wire is drawn through the gel prepared to a suitable viscosity, as described above, such that a controlled thickness of gel adheres to the wire. The thickness is best controlled by wiping excess gel from the wire using sizing dies. The gel coated wire then undergoes suitable drying and firing stages to convert the coating into an inorganic oxide glass. The precise conditions with respect to temperature and residence time in the various stages of conversion are dependent upon the gel composition prepared and its tolerance to relatively rapid changes in its environment. Porosity and integrity of the coating can be significantly affected by these stages. A suitable conversion process would

include drawing the wire through drying ovens in which the temperature is controlled at approximately 80°C and subsequently through progressive heat treatment stages which expose the wire for a few minutes to temperatures of 300°C to 500°C. The required exposure times are dependent upon the initial thickness of the gel coating, but the general guidelines above are used with the recommendation that the drying process is carried out as slowly as practical. It may be desirable to build thickness in a multipass process in which several thin layers are deposited sequentially.

Flame (or plasma) spraying involves injecting a powder of the refractory compound into a high temperature, high velocity gas stream. This process occurs within a specially designed gun or torch, and the refractory compound is ejected as a molten or semi-molten spray. This spray condenses to form a dense refractory film when it strikes a substrate. The high temperature gas stream can be produced either by controlled burning of a combustible mixture of gases (e.g. acetylene and oxygen), or by striking a low voltage high current arc in an inert gas (e.g. argon) between metal electrodes.

Flame spraying torches are available commercially, and comprise a powder dispenser, gas flow controls, and a shaped nozzle. Several powder dispensing methods are used, including gravity and Archimedean screw. The gas temperature may reach several thousand °C. Plasma spraying is very similar to flame spraying, but the heat source is supplied by an electric arc. In addition to gas control, a special dc power supply is needed that can deliver up to 1000A at 100V. The

cathode is often made of thoriated tungsten, and the anode is usually water-cooled copper. A plasma jet is blown out of the torch nozzle, and refractory powder is injected into this jet. The temperature of the plasma jet may be more than 10000°C, and the gas velocity is up to 1000m/sec.

Several variations on the above methods exist including, for example, detonation gun coating and low pressure spraying. In a detonation gun, pulses of powder are melted and accelerated by the controlled explosion of acetylene-oxygen within a water-cooled cylindrical chamber. This gives high gas velocities (several thousand m/sec), leading to improved coating adhesion. Low pressure plasma spraying is similar to conventional plasma spraying, except the plasma jet (with molten powder) escapes into a rough vacuum, giving a denser, less contaminated coating.

After the keying layer and further refractory layer have been deposited on the wire conductor it may be desirable to coat the oxide layer with a thin coating of a polymeric resin or lacquer in order to provide mechanical protection and a barrier against water or electrolytes during service. Further polymeric insulation may then be extruded onto the coated conductor by methods well known in the art.

In order to form a circuit or signal integrity cable the appropriate wires according to the invention may simply be laid together and be enclosed in a jacket. If desired the wires may be provided with a screen or electromagnetic interference shield before the cable jacket is applied. Thus a cable may be

formed in a continuous process by means well known in the art by braiding the wire bundle and extruding a cable jacket thereon. Any of the materials described above for the wire polymeric insulation may be used although halogen-free compositions e.g. compositions as described in the U.K. Patent Specifications Nos. 1,603,205 and 2,068,347A mentioned above are preferred. It is of course possible to employ additional means for providing integrity of the cable such as mica tape wraps, but these are not necessary nor are they desirable in view of the increased size and weight of the cable.

The present invention is also suitable for forming flat cables which, as will be appreciated, are not susceptible to being wrapped with mica tape. Thus it is possible by means of the present invention to form flat cables that are capable of functioning as circuit and signal integrity cables.

Several embodiments of the invention and a method of production thereof will now be described by way of example with reference to the accompanying drawings in which:

Figure 1 is a cross-section through one form of wire according to the present invention;

Figure 2 is a cross-section through a signal integrity cable employing the wires of figure 1;

Figure 3 is a cross-section through part of a flat conductor flat cable;

Figure 4 is a schematic view of part of the sputtering apparatus showing its wire handling mechanism; and

Figure 5 is a schematic section through part of the thickness of article in accordance with the invention.

Referring to figure 1 of the drawings a 26 AWG stranded copper conductor formed from 19 copper strands 1 is coated with a 0.5 micrometre thick keying layer of aluminium oxide by the sputter ion plating method described above and a further refractory aluminium oxide layer 6 micrometres thick by the sol-gel method described above, both layers being indicated by reference numeral 2. Before deposition of the aluminium oxide, the outer surface of the stranded conductor was provided with a 3 micrometre thick layer of aluminium (not shown). A coating 3 based on a polyetherimide sold under the trade name "ULTEM" is then extruded on the oxide coated conductor to form a polymeric "insulating" layer of mean wall thickness 0.2 mm.

Figure 2 shows a signal integrity cable formed by laying together seven wires shown in figure 1, forming an electromagnetic interference screen 4 about the bundle by braiding and then extruding thereon a jacket 5 based on a halogen-free composition as described in British Patent Specification No. 2,068,347 Example 1A.

The cable so formed is particularly lightweight and has a relatively small overall diameter in relation to the volume of the copper conductor.

Figure 3 shows a flat conductor flat cable comprising an array of flat copper conductors 1 with a 100 mil (2.54 mm) spacing. Each copper conductor 1 is provided with a 3 micrometre thick aluminium intermediate layer (not shown), an 0.5 micrometre thick alumina keying layer thereon and a 6 micrometre thick further alumina layer thereon as described above, both alumina layers shown by reference numeral 2, and the coated conductors are embedded in a single polymeric insulating layer 3 formed for example from the polyether imide sold under the trade name "ULTEM" or from a polyether ether ketone or polyether ketone.

Apparatus for use in a batch process for providing the keying layer on a wire conductor substrate is illustrated in Fig. 4. The apparatus comprises a vacuum chamber into which a complete wire transport mechanism which includes wire pay-off reel 2 and take-up reel 3, wire support rolls 10 and tensioning rolls 11 is loaded. The mechanism engages motor drives which control the passage of wire 4 so that the wire traverses a vertically mounted target 5 a number of times. Deposition occurs by the processes previously described. As before, variations in set-up are possible. An additional target (not shown) may be employed on the other side of the wire to increase coating rates and additional targets, e.g. target 6 can be employed to deposit intermediate layers before and/or after deposition of the primary oxide/ nitride coating. Suitable design of the gas inlet system to suit the specific geometries employed can facilitate deposition of layers which have no defined boundaries as described previously. Batch length will depend on chamber dimensions and transport system design.

In the operation of such a batch process wire 4 is transferred from one reel 2 to the other 3 within the chamber. The route taken by the wire may cause it to pass before the smaller ancillary target 6 to deposit an intermediate layer of any desired material. Power to this target, combined with wire speed and the number of passes in front of the target will control the thickness of the intermediate layer deposit. The wire 4 may then pass in front of the larger primary target 5 to deposit the main coating. Again thickness will be dictated by a combination of power, wire speed and a number of passes. The ratio of thicknesses between the intermediate and the primary coating is controlled in the same way. Multi-layers can be built up by reversing the mechanism as desired such that the wire 4 passes back past the targets 5,6 in reverse order. Thickness and composition may be altered in the reverse pass as required, e.g. the process employed at the smaller magnetron may be reactive on the reverse pass to deposit a compound of the metal on the intermediate layer, e.g. Ti and TiN_x . Deposition of layers with no defined boundary between the metal intermediate layers (or substrates) and the oxide/ nitride coatings may be achieved by setting up gradients of reactive gas in front of the primary target, such that wire at the top edge of the target 5 is subjected to deposition in an Argon rich atmosphere which gradually increases in reactive gas content as the wire progresses down the face of the target. A gradient can be achieved by a baffle system (not shown) which progressively leaks oxygen introduced at the bottom end of the target towards the upper end.

A simpler technique for producing the layer with no defined boundary involves use of a multipass process

in which wire 4 is passed back and forth through the system, and with each pass the level of reactive gas is increased to a final level required to obtain the correct stoichiometry. Thus the stoichiometry of the intermediate layer increases in a series of small incremental steps from metal to required stoichiometry. Composite targets may also be used to produce intermediate layers with stoichiometry gradients. In the case of discrete articles, the articles may instead be held in front of the target by means of a rotating sample holder.

Figure 5 is a schematic section through parts of an article according to the invention showing a typical arrangement of layers that may be formed on the copper substrate, the thickness of the layers being exaggerated for the sake of clarity.

A copper substrate 21 is provided with a thick (e.g. 1 to 3 micrometres) layer 22 of nickel followed by a layer 23 of aluminium metal, a layer 24 of non-stoichiometric aluminium oxide Al_2O_x and a layer 25 of stoichiometric aluminium oxide Al_2O_3 , the layers 23, 24 and 25 having been formed e.g. by a sputtering method. An additional, relatively thick layer 26 of aluminium oxide (e.g. of about 5 to 15 micrometres thickness) has been deposited on the layer 25 by a sol-gel method.

Although the layers are clearly demarcated in the drawing by means of lines, it will be appreciated that such boundaries may, and preferably will, not be formed in practise, especially between the copper/aluminium, aluminium/ Al_2O_x and $\text{Al}_2\text{O}_x/\text{Al}_2\text{O}_3$ layers. Indeed, the aluminium, Al_2O_x and stoichiometric alumina layers may

all be formed in the same sputtering process in which case the stoichiometry of the layers will depend on the oxygen gradient used.

The following Examples illustrate the invention:

Examples 1 and 2

Copper conductors were provided with 3.3 micrometres thick aluminium intermediate layer by use of the sputtering apparatus shown schematically in figure 4 of the drawings. The sputtering conditions were as follows: the wire 4 was precleaned by vapour degreasing in 1,1,1-trichloroethane prior to deposition. The cleaning was achieved by passing the wire through a vapour degreasing bath such that a residence time of 3 minutes was achieved. The wire 4 was then loaded into the vacuum chamber. The chamber was then evacuated to a pressure of 1×10^{-6} mbar prior to starting the process. At this stage argon was admitted to attain a pressure of 1.5×10^{-2} mbar whereupon a high frequency (80 kHz) bias potential was applied to the wire handling system which was isolated from ground. A bias potential of -850V was achieved, and the wire was transferred from reel 3 to reel 4 such that a residence time of 10 minutes was achieved. On completion of the cleaning cycle the pressure was reduced to 8.10^{-3} mbar and the deposition process started.

3 kW of DC power was applied to the aluminium target 5. The wire passed from reel 2 to reel 3 being coated as it passed the target 5. Residence time in this region was controlled by wire speed and adjusted to give the required thickness. The roller mechanism

alternated the wire face exposed to the target as it progressed down the target length.

The wire sample of copper conductor coated with aluminium as described above was subsequently coated with aluminium oxide in a similar process. For this second coating, an aluminium oxide target powered with an RF power supply was used. The wire residence time and target power were adjusted to give a constant thickness of aluminium oxide, of about 0.2 micrometres. During deposition of both aluminium and aluminium oxide the copper conductors were held at an appropriate bias potential relative to the chamber to promote adhesion.

Wire samples of copper conductor, in some cases coated with a 3.3 micrometre thickness of aluminium, and in some cases coated with an additional 0.2 micrometre thickness of aluminium oxide as described above, were subsequently coated with a gel-derived aluminium oxide by the sol-gel process described above.

The samples were then tested to determine the adhesion of the top coat as follows. A fixed length of wire was subjected to a tensile stress whilst the strain was continuously recorded. During testing the wire sample was viewed through an optical microscope. When the coating was seen to significantly spall the strain was recorded. The strain value recorded at this point gave a measure of the adhesion of the coating. The composition of the samples and the results obtained are shown in Table No. 1.

Table 1

Example	1(Comparison)	2
Substrate	22 awg Stranded Copper	22 awg Stranded Cu
Metallic Aluminium layer (micrometres)	0	3.3
Vacuum deposited Aluminium Oxide Layer (micrometres)	0	0.2
Sol gel deposited Aluminium Oxide layer (micrometres)	12	12
Adhesion (arbitrary units)	0*	600

* The adhesion of the coating to bare copper was very poor, rendering the samples unable to be tested due to immediate spalling.

The results show a clear improvement in adhesion of the gel derived alumina coating with the vacuum deposited aluminium oxide layer.

Examples 3 and 4

The electrical performance of wires prepared as those in example 2, were tested by twisting pairs of identical wires (2 twists per 2.5 cms length) to form a

twisted pair cable, connecting one end of the wires to a 30V peak to peak 1MHz square wave generator, and observing the wave form across a 200 ohm load connected between the wires by means of an oscilloscope. The twisted pair cables were subjected to heating in a propane gas burner having a flat flame 8cm wide. The temperature of the flame just below the twisted pairs was maintained at the required temperature and the time to failure recorded.

In example 3 the sample was found to survive for 70 seconds in a flame at 900°C. In example 4 the wires had still not failed after a flame exposure time of 72 minutes at 650°C. The substrate material onto which the sol-gel derived aluminium oxide was deposited for examples 3 and 4 had a dense 0.2 micrometres coating of vacuum deposited aluminium oxide on its surface. Although this layer is insulating, it was incapable alone of supporting 30V at room temperature.

Examples 5 to 7

22 AWG 19 strand copper wire conductors were provided with sputtered aluminium and aluminium oxide layers using the method detailed in examples 1 and 2. The wires were then transferred to another vacuum chamber equipped with a 25Kw electron beam gun. This chamber was pumped down to a base pressure of 5.10^{-5} mbar, and a further refractory insulating layer of aluminium oxide deposited by electron beam evaporation. The electron beam power was about 6kW (25Kv, 240mA), and the refractory was evaporated directly from highly sintered alumina pieces, contained in a water-cooled copper crucible. The deposition rate of alumi-

nium oxide by evaporation was about 3um/min, much faster than the refractory keying layer deposition rate, which was about 0.01um/min.

Samples manufactured as described above were adhesion tested using the tensile method described in examples 1 and 2. The results are given in Table 2, from which it is clear that a thin refractory keying layer deposited by a relatively slow method improved the adhesion of a further refractory layer deposited by a faster method.

Table 2

Example	Al intermediate layer thickness (um)	Al ₂ O ₃ keying layer thickness (um)	Al ₂ O ₃ further layer thickness (um)	Adhesion (arbitrary units)
5	0	0	7	500
6	0	0.5	7	1200
7	7	0.5	7	2150

The wire of Example 7 was tested for electrical performance as described in Example 3 (900°C) and no failure was recorded after 4 hours, whereas the wire of Example 5 could not be tested due to immediate spalling on immersion in the flame.

CLAIMS:

1. An article of manufacture which has at least a part that is formed from a metal the article having, on a surface of that part, an adherent dense refractory keying layer and, on the keying layer, a further electrically insulating refractory layer that has been formed by a relatively fast deposition method.
2. An article as claimed in claim 1, wherein the further refractory layer has a thickness that is greater than that of the refractory keying layer.
3. An article as claimed in claim 1 or claim 2, wherein the further refractory layer has a thickness greater than 1 micrometre preferably greater than 2 micrometres.
4. An article as claimed in any one of claims 1 to 3, wherein the refractory keying layer and the further refractory layer have the same nominal chemical composition.
5. An article as claimed in any one of claims 1 to 4, wherein the refractory keying layer and/or the further refractory layer comprises a metal oxide preferably an oxide of aluminium, silicon, titanium or tantalum.
6. An article as claimed in any one of claims 1 to 5, wherein the refractory keying layer has been formed by a vacuum deposition process.

7. An article as claimed in claim 6, wherein the refractory keying layer has been formed by a sputter ion plating method, a chemical vapour deposition method or an evaporation method.

8. An article as claimed in any one of claims 1 to 7, wherein the further refractory layer has been formed by a flame spraying method, a sol-gel method, a plasma ashing method or a solution coating method.

9. An article as claimed in any one of claims 1 to 7, wherein the further refractory layer has been formed by an evaporation process.

10. An article as claimed in any one of claims 1 to 9, wherein the metal from which the part of the article is formed comprises copper or an alloy thereof.

11. An article as claimed in any one of claims 1 to 10, which includes a metallic intermediate layer located between the metal from which the part is formed and the refractory keying layer the metallic layer preferably having a thickness of at least 1 micrometre.

12. An article as claimed in claim 11, wherein the intermediate layer has been formed by a vacuum deposition technique, preferably a sputter ion plating method, or by a metal rolling electroplating method or a melt coating method.

13. An article as claimed in claim 11 or claim 12, wherein the intermediate layer is formed from aluminium, silicon, titanium, tantalum, nickel, manganese, chromium or an alloy thereof.

14. An article as claimed in any one of claims 11 to 13, wherein the refractory keying layer comprises an inorganic metal compound and the intermediate layer comprises the same metal as that present in the refractory keying layer.

15. An article as claimed in any one of claims 11 to 14, wherein the intermediate layer is formed from a metal that forms an intermetallic compound with copper when heated.

16. An article as claimed in any one of claims 1 to 15, wherein the refractory keying layer has a stoichiometry that varies throughout at least part of its thickness such that the proportion of metal or semi-metal in the layer decreases towards the outer surface of the layer.

17. An article as claimed in any one of claims 1 to 16, which is in the form of an electrical wire.

18. An article as claimed in claim 17, which is provided with an additional outer polymeric insulation.

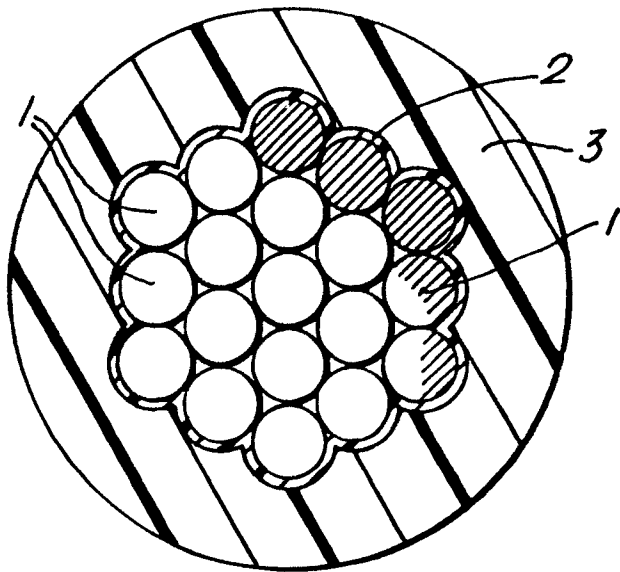
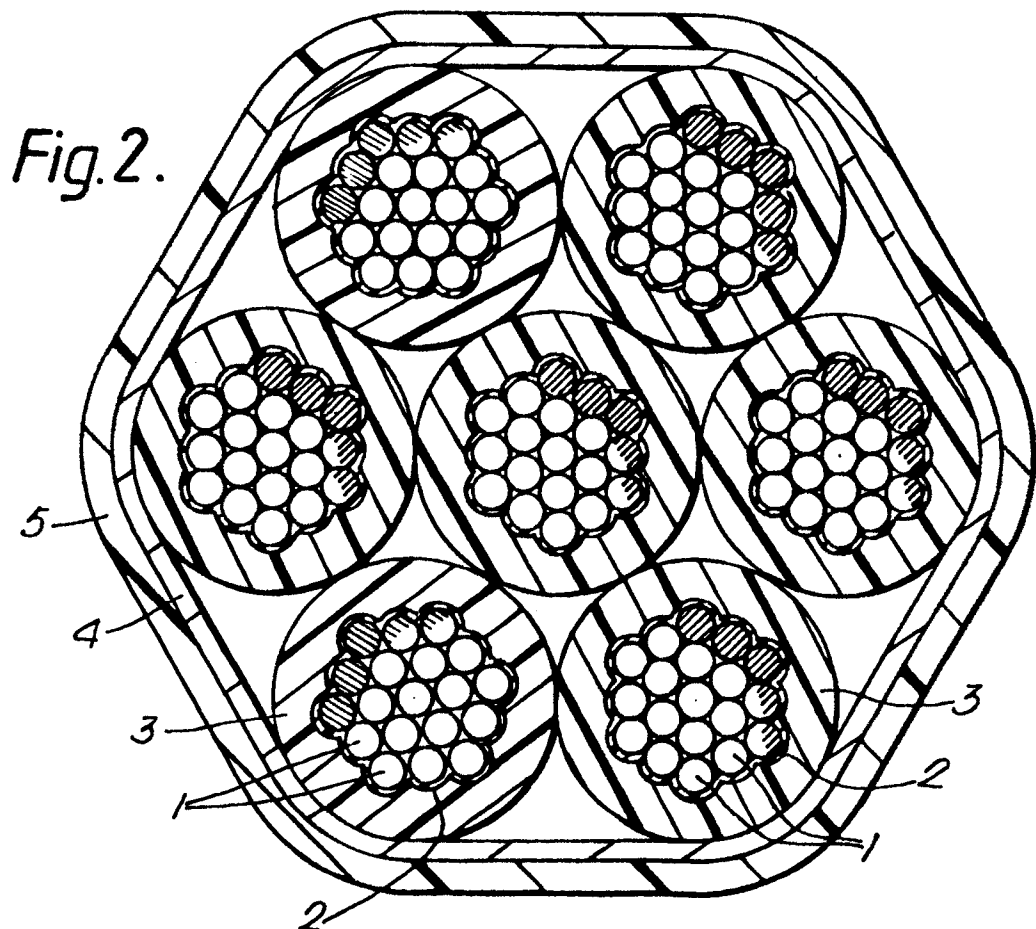
*Fig. 1.**Fig. 2.*

Fig. 3.

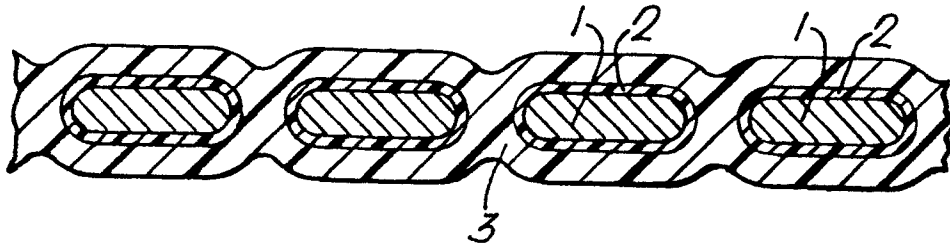


Fig. 4.

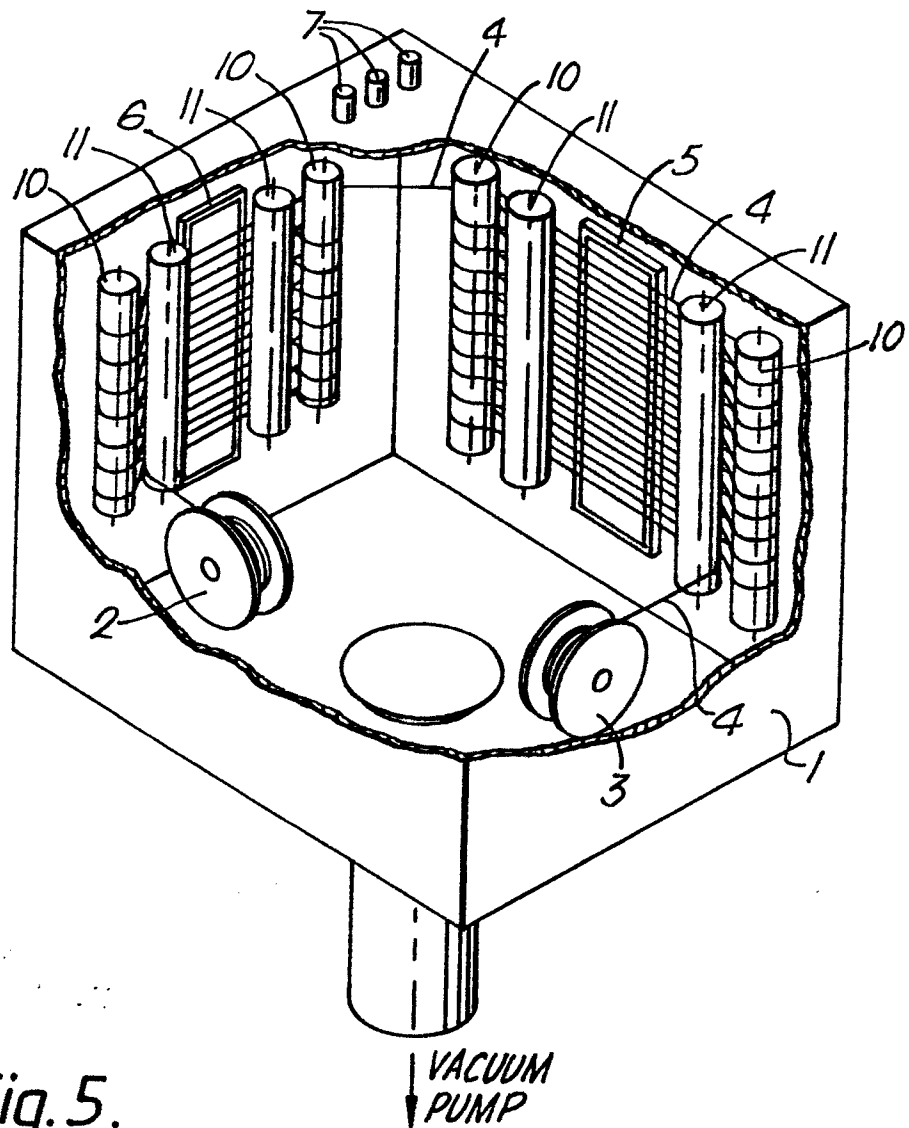


Fig. 5.

