

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) Publication number:

0 521 588 A2

(12)

EUROPEAN PATENT APPLICATION(21) Application number: **92202891.5**(51) Int. Cl.⁵: **H01B 3/44**, C08L 27/18,
C08L 29/10(22) Date of filing: **26.04.91**

This application was filed on 22 - 09 - 1992 as a
divisional application to the application
mentioned under INID code 60.

(30) Priority: **27.04.90 GB 9009407**
27.04.90 US 515302(43) Date of publication of application:
07.01.93 Bulletin 93/01(60) Publication number of the earlier application in
accordance with Art.76 EPC:(84) Designated Contracting States:
DE ES FR GB IT SE

(71) Applicant: **W.L. GORE & ASSOCIATES, INC.**
551 Paper Mill Road P.O. Box 9206
Newark, Delaware 19714-9206(US)
Applicant: **W.L. GORE & ASSOCIATES (UK)**
LTD
1 Bell Yard
London WC2A 2JP(GB)

(72) Inventor: **Mortimer, William Patrick**
53 Crocus Court
Conowingo, MD 21918(US)

(74) Representative: **Horne, Martin Grenville et al**
Cruikshank & Fairweather 19 Royal
Exchange Square
Glasgow G1 3AE Scotland(GB)

(54) **Electrical insulating material.**

- (57) An electrical insulating composite material comprises an intimate admixture of
- (a) 5-90 weight percent of a thermoplastic copolymer of tetrafluoroethylene and perfluoro (propyl vinyl ether); and
 - (b) 90-5 weight percent of coagulated dispersion type polytetrafluoroethylene (PTFE), or of porous expanded PTFE.

Tape made from the composite material may be porous expanded tape or non-porous tape. The tape is wrapped around a conductor (C) and sintered at 320-450 ° C. A dual-wrap construction having layers (A, B) of both porous expanded tape and of non-porous tape give particularly good dynamic cut-through and scrape resistance properties.

EP 0 521 588 A2

TECHNICAL FIELD

The present invention relates to an electrical insulating composite material, particularly though not exclusively for insulating wire. The invention also includes a method of forming the insulating material, and insulated conductors.

DESCRIPTION OF PRIOR ART

The use of polytetrafluoroethylene (PTFE) or copolymers formed from tetrafluoroethylene (TFE) and perfluoro (propyl vinyl ether) (PPVE) is well known for the insulation of wire. These polymers have good heat resistance, high resistance to solvent attack and good dielectric properties. These attributes are desirable where high reliability is required, for example in aerospace applications.

Other desirable attributes for such applications include mechanical properties such as resistance to abrasion and resistance to cut-through of insulation by sharp edges. However, the properties of the aforesaid materials are poor in these respects.

Attempts have been made in the past to improve the mechanical properties of TFE base polymers by including additives such as glass spheres, silica flake, etc. However, the improvements achieved with such compositions are generally limited and often at the expense of other desirable features, for example leading to degradation of electrical properties or mechanical properties such as flexibility.

Attempts have also been made in the past to improve the mechanical properties of the fluoropolymers by mixing with other polymers having better mechanical properties, such as polyphenylene sulphide, polyphenylene oxide, etc. However, these other polymers are in general incompatible with fluoropolymers so that there is difficulty in producing intimate blends.

It is an object of the present invention to mitigate these problems.

SUMMARY OF THE INVENTION

The present invention provides an electrical insulating composite material which comprises an intimate admixture of:

- (a) 5-90 weight percent of a thermoplastic copolymer of tetrafluoroethylene and perfluoro (propyl vinyl ether); and
- (b) 90-5 weight percent of polytetrafluoroethylene (PTFE) selected from the class consisting of coagulated dispersion type PTFE and porous expanded PTFE.

The composite material itself may be non-porous or may be expanded to produce porous material.

The TFE/PPVE copolymer is preferably used in particulate form and preferably has a particle size in the range 1 to 180 microns, especially 20 to 100 microns. The particles may have a wide range of particle sizes and preferably include particles having sizes right across the ranges. However, particles of narrow size range may also be used. The TFE/PPVE copolymer particles preferably have a substantially regular shape, such as oblong or spherical.

The polytetrafluoroethylene component is of the coagulated dispersion type. As is well known, polytetrafluoroethylene (PTFE) can be produced in three quite distinct forms having different properties viz; granular PTFE, coagulated dispersion PTFE, and liquid PTFE dispersions. Coagulated dispersion PTFE is also referred to as fine powder PTFE. In the present invention, the PTFE resin can be used in powder form; or alternatively, the PTFE resin can be coagulated from an aqueous dispersion in the presence of perfluoroalkoxy TFE/PVE copolymer powder or dispersion. The coagulation of PTFE in the presence of a dispersion of the copolymer results in a co-coagulation of PTFE and copolymer. The flocculated mixture may then be decanted and dried.

The electrically insulating material may be used for producing a covering for wire, or other electrically conductive substrate to which bonding is not normally required.

DESCRIPTION OF PREFERRED EMBODIMENTS

One particular aspect of the present invention provides a non-porous electrical insulating material for an electrical conductor comprising an intimate admixture of

5 to 40 weight percent of a thermoplastic copolymer of tetrafluoroethylene and perfluoro (propyl vinyl ether); and

60 to 95 weight percent of coagulated dispersion type polytetrafluoroethylene.

Advantageous, the composite material comprises 5 to 40 wt% of copolymer (and 60 to 95 wt% PTFE);

more particularly 8 to 20 wt% of copolymer (and 80 to 92 wt% of PTFE).

The non-porous material typically has a density of 2.0 to 2.2 g/cc.

There is also provided a method of insulating an electrical conductor comprising;

paste extruding an electrically insulating material formed from an intimate mixture of 5 to 40 weight percent of a particulate thermoplastic copolymer of tetrafluoroethylene and perfluoro (propyl vinyl ether);
and

60 to 95 weight percent of coagulated dispersion type polytetrafluoroethylene;

applying said material to an electrically conductive substrate; and

sintering the material before or after application to the substrate.

The paste extrusion step may be carried out using conventional PTFE extrusion techniques (for example in admixture with a liquid carrier, such as a hydrocarbon). The extruded composition is generally of thin section so as to allow efficient removal of the liquid carrier and formation of a solid material, usually in the form of a sheet, tape or filament. If necessary, the solid material may be mechanically worked, such as by calendering, to modify its shape or thickness prior to application to the substrate.

In the case of wire, usually the solid material in the form of a tape is wrapped around the wire in overlapping turns. The overlapping areas of the material may then be fused together, for example at temperatures of 350 to 450 °C (for 0.5 to 20 minutes). The time will be in correspondence with the temperature employed. Temperatures as low as 320 °C may be used at long sintering times. Lower temperatures tend to minimise degradation of the material. The time and temperature conditions also depend on the construction of the insulated conductor, such as thickness of the insulation and number of cores in the wire.

It has been found that wire electrical insulation made from wrapped and sintered tape produced from the composition has an unexpectedly better cut-through resistance and abrasion resistance than equivalent wire insulation made from fine powder PTFE alone.

A second particular aspect of the invention provides a porous material which is a composite of:

a) 5-90 weight percent of a thermoplastic copolymer of tetrafluoroethylene and perfluoro(propyl vinyl ether), and complementarily, intermingled therewith,

b) 90-5 weight percent of a porous expanded structure of polytetrafluoroethylene.

In one embodiment, the thermoplastic copolymer will constitute about 5-50 weight percent of the composite. In this embodiment, the composite is useful as insulation on wire or cable, especially as electrical insulation.

In another embodiment, the thermoplastic copolymer will constitute about 50-95 weight percent of the composite. In this embodiment, the composite is useful as a reinforced thermoplastic copolymer film.

This aspect of the invention also provides a process for preparing the composites which comprises mixing the thermoplastic copolymer with a dispersion of the coagulated fine powder polytetrafluoroethylene resin or with a dispersion of the fine powder and coagulating the solids to obtain a resin blend, preparing pellets of the resin blend, forming a tape of the pellets and stretching the tape until a desired degree of porosity is attained in the resulting composite.

In a preferred embodiment a flocculated mixture of the TFE/PPVE copolymer and PTFE, in particulate form, is lubricated for paste extrusion with an ordinary lubricant known for use in paste extrusion, and is pelletized. The pellets are preferably aged at 40-60 °C and are then paste extruded into a desired shape, usually a film. The extruded shape is then stretched, preferably in a series of at least two stretch steps while heating at between 35-360 °C until a desired degree of porosity is attained. The porosity occurs through the formation of a network of interconnected nodes and fibrils in the structure of the stretched PTFE film, as more fully described in U.S. Patent 3,953,566. The density of the porous material will usually be less than 2.0 g/cc.

At the stretch temperatures employed, the TFE/PPVE copolymer melts and, depending on the amount present, may become entrapped in the pores or nodes formed, may coat the nodes or fibrils, or may be present on the outer surface of the membrane formed. Most likely a combination of each embodiment occurs, depending on whether the copolymer and the PTFE remain as distinct moieties.

The porous composite is useful as an insulation covering for wire and cable, particularly in electrical applications. In tape form, the composite can simply be wrapped around the wire or cable in overlapping turns. It is believed that the presence of the TFE/PPVE copolymer aids in adhering the layers of tape wrap to one another. The porous composite can be sintered either before or after wrapping if desired to improve cohesiveness and strength of the tape per se. Once the porous composite is prepared, it can be compressed, if desired, to increase the density of the composite. Such compression does not significantly affect the increased matrix strength that is associated with expanded porous PTFE. Compression improves properties such as dielectric strength and cut-through resistance.

It has been found that wire and cable insulation made from the non-porous or porous composites of this invention have unexpectedly better cut-through resistance, strength and abrasion resistance than insulation made from the TFE/PPVE copolymer alone or from non-expanded PTFE.

A third particular aspect of the present invention provides an insulated electrical conductor, which comprises a wire having wrapped around it two adjacent layers of the composite material, one layer being formed of non-porous composite material and the second layer being formed of porous composite material.

Generally, the layers are applied in the form of tapes wrapped (preferably counter-wrapped) around the wire in overlapping turns. The layers may also be applied longitudinally with a longitudinal overlapping seam. Preferably, sintering takes place after the two tapes have been applied; so that the layers become fused into an integral structure. Sintering may be brought about under the conditions previously described.

It has been found that generally speaking the non-porous non-expanded material has good electrical (particularly dielectric) properties; whilst the porous expanded material (whether compressed after expansion or not) has good mechanical properties (particularly cut-through resistance). Surprisingly these properties are retained in the two-layer insulated electrical conductor notwithstanding sintering, so that an insulating layer having both good mechanical and electrical properties is obtained.

Either the porous or the non-porous layer may be adjacent the wire. Placing the non-porous layer adjacent the wire facilitates stripping of the wire when a connection is to be made. Placing the non-porous layer uppermost allows better overprinting (e.g. for colour coding).

If required more than two layers of material may be used, for example non-porous/porous/non-porous which provides good stripping and printing characteristics.

Also, one or more porous or non-porous layers of the material of the present invention may be wrapped together with one or more layers of conventional expanded or non-expanded PTFE tape prior to sintering. In particular, the combination of layers of non-porous composite material with conventional expanded PTFE; and the combination of layers porous composite material with non-expanded PTFE may be used.

EXAMPLES

Embodiments of the present invention will now be described by way of example only. Figure 1 shows a wire construction.

Example 1 (non-porous tape)

181g (9wt %) of the TFE/PPVE copolymer powder of wide particle size distribution which had been screened to a particle size in the range 1-150 microns was added to 1.81kg (91wt %) of Hostaflon (Registered Trade Mark) 2023 PTFE resin powder and tumbled in a Pascall tumble mixer at 40 revs/min for 60 minutes.

620 ml of Shellsol (Registered Trade Mark) TD liquid hydrocarbon was then added to this powder mixture and tumbled for a further 30 minutes to form a paste. The paste was then left overnight before being compressed at 200 psi into a 4 inch diameter pellet. The pellet was left for 24 hours at a temperature of 35 to 39 °C before extrusion on a standard PTFE ram extruder at room temperature.

The extrudate of thickness 0.035 inch (890 microns) was then calendered down to 0.004 inch (101 microns) in three stages, using rollers heated to approximately 50 °C. The 0.004" tape was slit and wrapped on to 22 AWG (American Wire Gauge) 19 strand silver plated electrical wire conductor, to an insulation wall thickness of 0.008" (200 microns) and sintered in air at 400 °C for 0.5 minute.

A similar wire sample was made using only the PTFE resin for comparison.

Both wire samples were tested for dynamic cut-through resistance and scrape abrasion resistance according to the test method given in BS G 230 (British Standard, Group 230). The results are given in Table 1 and demonstrate the improvement in the mechanical performance of the PTFE wire insulation when blended with TFE/PPVE copolymer over and above that of the base PTFE resin.

Table 1

SAMPLE	DYNAMIC CUT THROUGH in Newtons (N) (Room Temperature)	SCRAPE ABRASION (4 Newtons Load) (Room Temperature)
A	63	2,000 cycles
B (comparison)	28	200 cycles
Sample A: 22 AWG, 19 strand, silver plated copper conductor with 0.008" wall of PTFE and TFE/PPVE blended insulation material. (according to Example 1). Sample B: 22 AWG, 19 strand, silver plated copper conductor with 0.008" wall of PTFE insulation.		

Example 2 (non-porous tape)

1.2Kg of TFE/PPVE copolymer powder of particle size was dispersed in 3.75Kg of Shellsol (Trademark) TD liquid hydrocarbon.

This was achieved by grinding the suspension in a colloid mill down to approximately 0.002" (50 microns + 12 microns). The resultant slurry was added to 13.61Kg of Hostafon (Trade mark) 2023 PTFE resin and tumbled for 7 minutes.

The powder/lubricant mixture was then compressed into a 4 inch pellet. Tape of thickness 0.003" (75 microns) was made from the resultant pellet by a similar method to that described in Example 1.

Example 3 (expanded tape)

302g. (16.7 wt.%) of a tetrafluoroethylene/perfluoro(propyl vinyl ether) copolymer powder (PFA powder) was added to 1.5 liters of methanol and diluted with 20.1 liters of deionized water to form a dispersion. This was mixed for 30 seconds in a baffled 5 gallon container.

Next, 6500g. of aqueous dispersion containing 1600g. (12.8 wt.%) of dispersion-produced poly-tetrafluoroethylene was mixed with the PFA powder dispersion. Then, 6.4g. polyethylene imine was added to coagulate the solids from the mixture. After about 20 seconds of stirring, the phases separated. The clear liquid was decanted and the remaining solids dried at 160 °C for 24 hours.

The solids, in particulate form, were lubricated with mineral spirits (19% by weight) and pelletized under vacuum. The pellets were aged at 49 °C for about 24 hours, and were then extruded into tape. The tape was calendared to a thickness of 16.5 mil. and then dried to remove lubricant.

The dried tape was stretched in three steps. In the first stretch step, the tape was expanded longitudinally 93% (1.93 to 1) at 270 °C at an output rate of 105 feet per minute. In the second step, the tape was expanded longitudinally at a rate of 20:1 at 290 °C at an output rate of 3.8 feet per minute. In the third step, the tape was expanded longitudinally at a ratio of 2:1 at 325 °C at an output of 75 feet per minute.

The resulting porous tape was then subjected to heat at 330 °C for about 6 seconds.

It was then compressed to almost full density. The bulk density was 2.0 gm/cc.

Example 4 (expanded tape)

The procedure of Example 3 was followed, except that in the first stretch step the stretch was at 1.9 to 1 instead of 1.93 to 1, and in the second stretch step the temperature was 300 °C, and, in the third stretch step, the temperature was 360 °C.

The tape was not compressed. The resulting density was 0.7 gm/cc.

Example 5 (mechanical properties)

Expanded tapes produced by the method given in Example 3 that had been compressed to almost full density to a thickness of 0.0007" (18 microns) were slit and wrapped onto 20 AWG, 19 strand silver plated electrical wire conductor, to an insulation wall finished thickness of 0.003" (75 microns) post-sinter.

The insulated wire was then heat treated in air at 350 °C for 15 minutes, to fuse the insulation material.

The resultant wire was tested for dynamic cut-through resistance according to the test method given in BS G 230.

BS G 230 (British Standard Group 230) is a test specification for general requirements for aircraft electrical cables. Test results are given in Table 2.

Table 2

Sample	Dynamic Cut-Through in Newtons (N) at Room Temperature
20 AWG, 19 strand, silver plated copper conductor, with 0.003" wall of fused insulation tape.	91
	92
	65
	89
	Average = 84

Example 6 (mechanical properties)

The expanded tape made by the method given in Example 3 was slit and a 0.15mm thick layer (0.1mm post-sinter) was wrapped (layer A) on to 20 AWG (American Wire Gauge) 19 strand nickel plated copper conductor (C).

Tape made by the method given in Example 2 was slit and then a 0.20mm thick layer (0.15mm post-sinter) was counter-wrapped (layer B) on the above insulated wire (See Figure 1). Counter-wrapping means that the tapes were wound as spirals of opposite hand.

The resultant composite wire was then sintered in air at 400 °C for 1.5 minutes. The insulation had a final post-sinter thickness of 0.25mm. Similar insulated wires were made with only the tape manufactured as in Example 3 or Example 4.

For the purposes of comparison, separate samples of conductor were insulated with standard PTFE or with TFE/PPVE jackets (Samples 1 and 2 respectively).

The overall diameter of all samples was maintained at 1.5mm, resulting in similar wall thicknesses to allow the samples to be compared with one another.

The mechanical properties, with respect to scrape abrasion and cut through resistance of the insulated wire samples, were measured according to the test method given in BS G 230. The results are given in Table 3 and show the overall improvement in the mechanical properties of the composite insulation materials when compared with the individual homogeneous insulation materials.

Table 3

	DYNAMIC CUT THROUGH		SCRAPE ABRASION	
	in Newtons (N)		8 Newtons	4 Newtons
			Load	Load
<u>Sample</u>	<u>Room Temperature</u>		<u>(Room Temperature)</u>	
1 (comparison)	35	12	310	
2 (comparison)	45	46	610	
3	56	54	1,900	
4	115	66	260	
5	81	120	10,000	
<u>Sample 1</u>	20AWG, 19 strand, nickel plated copper conductor with 0.25mm wall of PTFE insulation.			
<u>Sample 2</u>	20AWG, 19 strand, nickel plated copper conductor with 0.25mm wall of TFE/PPVE insulation.			
<u>Sample 3</u>	20AWG, 19 strand, nickel plated copper conductor with 0.25mm wall of PTFE and TFE/PPVE blended insulation material (according to Example 2).			
<u>Sample 4</u>	20AWG, 19 strand, nickel plated copper conductor with 0.25mm wall of (expanded and			

densified) PTFE and TFE/PPVE blended insulation material
(according to Example 3).

Sample 5 20AWG, 19 strand, nickel plated copper
conductor with 0.25mm wall of composite
insulation consisting of 0.1mm of PTFE and
TFE/PPVE blended material (according to
Example 3) and 0.15mm PTFE and TFE/PPVE
blended material (according to Example 2)
fused together.

Example 7 (electrical performance)

When Samples 4 and 5, manufactured by the method given in Example 5 are subject to the High Voltage Immersion Test given in BS G 230, Test Method 16a, the following test results are obtained:

Sample 4	3.5 KV
Sample 5	5 KV

From these test results it is apparent that Sample 5, containing the dual counter-wrapped tapes manufactured by the methods given in Examples 2 and 3, has improved electrical properties with respect to voltage withstand characteristics over and above that of Sample 4.

Thus, for overall mechanical and electrical performance the dual, counter-wrapped construction is the preferred construction.

Example 8 (expanded/non-porous dual wrap)

Expanded tape made by the method given in Example 3 was slit and a 50 microns thick (post-sinter thickness) layer (A) was wrapped onto 20AWG (American Wire Gauge) 19 strand nickel plated copper conductor (C)..

Tape made by the method given in Example 2 was slit and a 150 microns thick (post-sinter thickness) layer (B) was then counter-wrapped on the above insulated wire.

The resultant composite wire was then fused by heat treatment in air at 350 °C for 20 minutes.

Figures of 113 - 151 cycles to failure (8 Newton load), and 110 - 130 Newtons were obtained when tested respectively, at room temperature, for scrape abrasion and dynamic cut-through resistance, according to Test Methods 30 and 26 given in BS G 230.

Example 9 (non-porous/expanded dual wrap)

Tape made by the method given in Example 2 was slit and a 150 microns thick (post-sinter thickness) layer (A) was wrapped onto 20AWG (American Wire Gauge) 19 strand nickel plated copper conductor (C).

Expanded tape made by the method given in Example 3 was slit and a 50 microns thick (post-sinter thickness) layer (B) was counter-wrapped on the above insulated wire.

The resultant composite wire was then fused by heat-treatment in air for 1.5 minutes at 400 °C followed by 20 minutes at 350 °C.

When tested to Test Methods 16a, 26 and 30 in BS G 230, the results in Table 4 were obtained.

Table 4

Test	Test Method	Result
High Voltage	BS G 230	5 KV
Immersion Test	Test 16a	
Dynamic Cut-Through	BS G 230	139 N
Scrape Abrasion	Test 26 (Room Temperature)	
	BS G 230	95 Cycles
	Test 30 (8N Load, Room Temperature)	

Claims

1. A composite sheet material of a porous membrane of expanded polytetrafluoroethylene (PTFE) and a thermoplastic copolymer of tetrafluoroethylene and perfluoro(propylvinylether) wherein at least a portion of the thermoplastic copolymer is entrapped within the pores of the porous polytetrafluoroethylene.
2. A material according to claim 1 which comprises 5 to 95 wt.% of copolymer.
3. A material according to claim 1 which comprises 50 to 95 wt.% of copolymer.
4. A material according to any preceding claim which has a density less than 2.0 g/cc.
5. A material according to any preceding claim in which the porous structure has been compressed to increase its density.
6. An insulated electrical conductor which comprises a wire (C) having an electrically insulating layer (A) formed of a film or tape of a material according to claim 1 around the wire.
7. A conductor according to claim 6 which has been sintered.
8. A process for preparing a composite material which comprises mixing 5-90 wt.% of a thermoplastic copolymer of tetrafluoroethylene and perfluoro(propylvinylether) with a dispersion of coagulated polytetrafluoroethylene resin comprising 90-5 wt.% of polytetrafluoroethylene, coagulating the solids to form a resin blend, preparing pellets from the resin blend, forming a tape from the pellets, and stretching the tape until a desired degree of porosity is attained in the resulting porous composite.
9. A process according to claim 8 which further comprises compressing the porous composite material.

FIGURE 1

