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[54] **PARTICULATE FILLED COMPOSITE FILM AND METHOD OF MAKING SAME**

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[73] Assignee: **Rogers Corporation**, Rogers, Conn.

[*] Notice: The portion of the term of this patent subsequent to Jun. 18, 2008, has been disclaimed.

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Related U.S. Application Data

[62] Division of Ser. No. 705,624, May 24, 1991, abandoned.

[51] Int. Cl.⁶ **B32B 5/16**

[52] U.S. Cl. **428/323; 428/325; 428/335; 428/901**

[58] Field of Search **428/323, 325, 428/335, 403, 404, 405, 406, 407, 421, 422, 457, 901**

[56] References Cited

U.S. PATENT DOCUMENTS

2,710,266	6/1955	Hochberg	428/268
2,852,811	9/1958	Petricello	264/39
2,923,651	2/1960	Petricello	428/461
2,945,831	7/1960	Evans et al.	260/29.6
2,961,345	11/1960	Petricello	428/212
2,980,965	4/1961	Infantino et al.	18/57
3,054,716	9/1962	Bergstein et al.	264/212
3,054,761	9/1962	Moore et al.	524/491
3,292,725	11/1966	Van Zalingo	264/215
3,518,332	6/1970	Skiarchuk	264/49
3,556,161	8/1970	Roberts	138/141
3,577,508	5/1971	Desaulniers	264/331.15
3,679,614	7/1972	Shah et al.	521/62
3,843,570	10/1974	Murayama	521/62
4,049,589	9/1977	Sakane	521/64
4,112,037	9/1978	Parker et al.	264/126
4,183,991	1/1980	Smiley et al.	428/220
4,196,070	4/1980	Chao et al.	204/226

4,203,848	5/1980	Grandine, II	310/490
4,211,603	7/1980	Reed	428/901 X
4,307,142	12/1981	Blitstein et al.	428/143
4,380,521	4/1983	Moreno et al.	264/49
4,393,119	7/1983	Concamion	428/413
4,409,354	10/1983	Namba et al.	524/431
4,434,116	2/1984	Covitch	264/49
4,500,603	2/1985	Freundlich	428/409
4,555,543	11/1985	Effenberger et al.	428/421
4,610,918	9/1986	Effenberger et al.	428/245
4,692,287	9/1987	Timmons	264/41
4,818,619	4/1989	Stepparola et al.	428/421
4,824,511	4/1989	Hartman et al.	428/209 X
4,847,135	7/1989	Braus et al.	428/138
4,849,284	7/1989	Arthur et al.	428/325
4,883,716	11/1989	Effenberger et al.	428/421
4,888,245	12/1989	Nitzko	428/421

(List continued on next page.)

FOREIGN PATENT DOCUMENTS

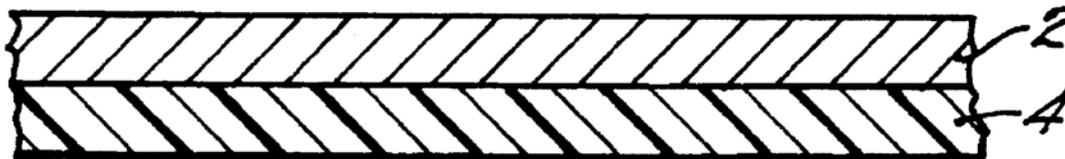
246844	11/1987	European Pat. Off. .
2071112	9/1981	United Kingdom .

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Assistant Examiner—H. Thi Lê
Attorney, Agent, or Firm—Fishman, Dionne & Cantor

[57] ABSTRACT

A particulate filled fluoropolymeric matrix composite article and method of making the same is presented. Preferably, the article comprises an electrical substrate material. The method for making the particulate filled polymeric matrix composite film includes mixing a polymeric matrix material with a dispersion of particulate filler in a carrier liquid to form a casting composition and adjusting the viscosity of the casting composition to retard separation of the particulate filler from the composition. A layer of the viscosity-adjusted casting composition is cast on a substrate and the layer is consolidated to form the particulate filled polymer matrix composite film. Films made by the method include very thin, e.g less than 1.0 mil, fluoropolymeric matrix films highly filled with very small diameter, preferably spherical, particles for use as, e.g. dielectric substrate materials in laminar electrical circuits.

40 Claims, 1 Drawing Sheet



U.S. PATENT DOCUMENTS

4,895,756	1/1990	Suzuki	428/317.9	4,990,544	2/1991	Asaumi et al.	428/283 X
4,915,983	4/1990	Lake et al.	430/311 X	5,024,871	6/1991	Arthur et al.	428/209
4,985,296	1/1991	Mortimer, Jr.	428/220	5,061,548	10/1991	Arthur et al.	428/209
				5,077,115	12/1991	Arthur et al.	428/137
				5,198,295	3/1993	Arthur et al.	428/323

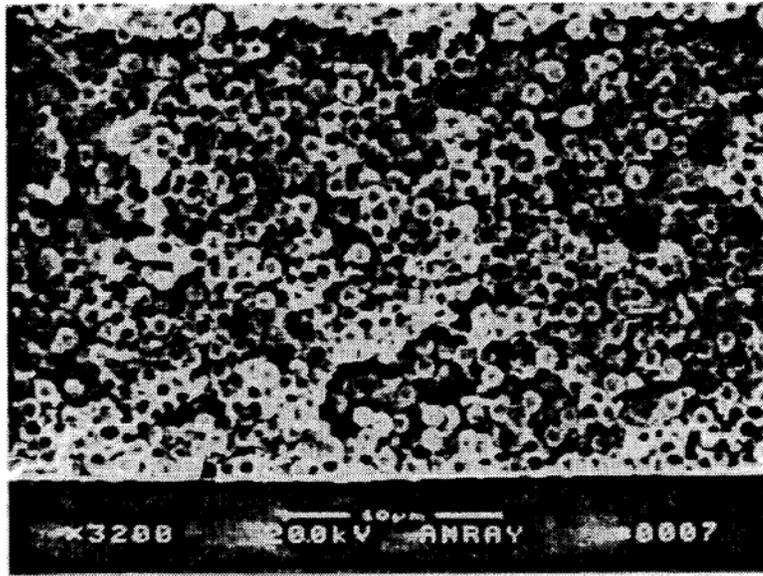


FIG. 1



FIG. 2

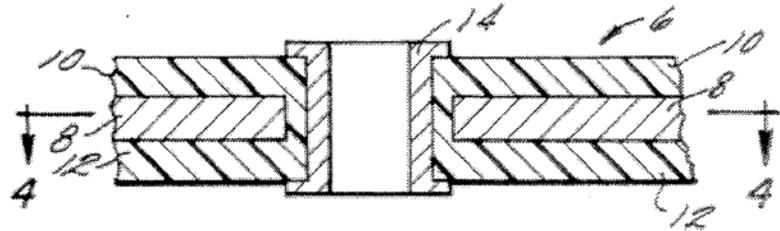


FIG. 3

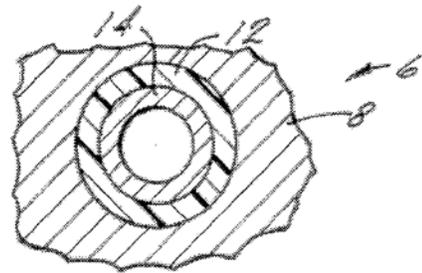


FIG. 4

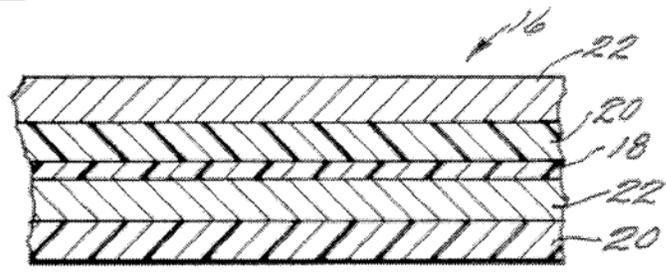


FIG. 5

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PARTICULATE FILLED COMPOSITE FILM AND METHOD OF MAKING SAME

This is a divisional of application Ser. No. 07/705,624 filed on May 24, 1991, now abandoned.

TECHNICAL FIELD

The present invention relates to particulate filled polymer matrix composite materials and methods of manufacturing same and more particularly to thin films of highly filled polymer matrix composite materials.

BACKGROUND OF THE INVENTION

Laminated electrical circuit substrates which include a conductive layer supported on a dielectric fluoropolymer matrix composite layer are known. Driven by the continuing trend toward increasing circuit density, very thin films, e.g. less than about 1.0 mil, of highly filled fluoropolymeric matrix composite substrate materials having a substantially uniform microstructure have become desirable as allowing further reduction in the size of electronic circuits. It is technically and economically difficult to make such materials by known methods.

Fluoropolymer and particulate filled fluoropolymer matrix composite films are made by known papermaking, skiving, casting, melt extrusion and paste extrusion and calendaring processes.

Films produced by paper making processes required fiber reinforcement and are limited to thicknesses greater than about 2 mil.

It is very difficult to produce thin high quality highly filled fluoropolymer matrix films by skiving due to abrasion of the skiving blade by the filler particles and tearing of the film associated with the resistance of the filler particles to the skiving blade.

The filler loading of films made by known casting processes is limited to less than about 15 volume percent.

The high melt viscosity of neat fluoropolymers complicates the production of fluoropolymer films by melt extrusion. Polyvinylidene fluoride (PVF₂) and polychlorotrifluoroethylene (PCTFE) are melt extrudable only within a narrow processing window. Polyvinylfluoride (PVF) film cannot be produced by melt extrusion due to thermal instability. Polytetrafluoroethylene (PTFE) cannot be melt extruded due to its extraordinarily high melt viscosity. Fluorocopolymers are known which provide lower melting temperature and lower melt viscosity at extrusion temperatures, e.g. copolymers of tetrafluoroethylene with hexafluoropropylene (FEP) or with ethylene, copolymers of CTFE with vinylidene fluoride or hexafluoropropylene.

The introduction of fillers further complicates the melt extrusion of fluoropolymers. In the presence of certain fillers, especially at high filler loading level, the melt processability of the melt extrudable fluoropolymers is rapidly degraded due to the increase in melt viscosity associated with the presence of the filler or with filler-catalyzed thermal degradation of the polymer matrix.

A method of making highly filled PTFE composite materials which exhibit excellent physical and electrical properties by paste extrusion and calendaring is set forth in coassigned U.S. Pat. No. 4,849,284 to D. J. Arthur, J. C. Mosko, C. S. Jackson and G. R. Traut, entitled "ELECTRICAL SUBSTRATE MATERIAL", the disclosure of which is

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difficult and economically extremely difficult to produce thin, i.e. less than 2 mils, highly filled, i.e. greater than about 40%, fluoropolymer matrix composite films by the paste extrusion and calendaring process.

What is needed in the art is a method which overcomes the above noted deficiencies of known processing methods.

SUMMARY OF THE INVENTION

A particulate filled fluoropolymer matrix composite article is disclosed. The article includes a fluoropolymer matrix and up to about 95 vol. % filler particles distributed throughout the matrix, wherein said particles have a maximum equivalent spherical diameter of less than about 10 microns.

In an alternative embodiment, a particulate filled fluoropolymer matrix composite article comprises a fluoropolymer matrix and up to about 95 vol. % filler particles distributed throughout the matrix wherein none of the particles have a single linear dimension greater than about 10 microns.

In a preferred embodiment a particulate filled fluoropolymer matrix composite film comprises a nonfibrillated fluoropolymer matrix and greater than about 15 vol. percent filler particles distributed throughout the matrix. The film has a thickness less than about 2 mils and is free of visually evident pin holes or tears.

A porous fluoropolymer film comprising a nonfibrillated fluoropolymer matrix having a void volume of greater than about 15 vol. % and a thickness of less than about 2 mils is disclosed.

A method for making a particulate filled polymer matrix composite film is disclosed. The method comprises mixing the polymer with a dispersion of the particulate filler in a carrier liquid to provide a casting composition, wherein the casting composition includes relative amounts of polymer and filler effective to provide a film having greater than 15 volume percent filler casting a layer of the casting composition onto a substrate and consolidating the cast layer to form the particulate filled polymer matrix composite film.

A casting composition is also disclosed. The casting composition includes a mixture of liquid carrier, a polymeric matrix material, and particles of a filler material.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 shows a photomicrograph of a cross sectional view of a particulate filled polymer matrix composite film of the present invention.

FIG. 2 shows a laminar circuit substrate made by the process of the present invention.

FIG. 3 shows a cross sectional view of a conductive through-hole communicating between layers of a portion of a laminated electrical circuit.

FIG. 4 shows a cross sectional view taken along lines 4—4 of FIG. 3.

FIG. 5 shows a cross sectional view of a portion of a laminar electrical circuit.

DETAILED DESCRIPTION OF THE INVENTION

Suitable fluoropolymer matrix materials include fluorinated homopolymers, e.g. polytetrafluoroethylene (PTFE) and polychlorotrifluoroethylene (PCTFE) and fluorinated

monomer selected from the group consisting of hexafluoropropylene and perfluoroalkylvinylethers, copolymers of tetrafluoroethylene with a monomer selected from the group consisting of vinylidene fluoride, vinyl fluoride and ethylene, and copolymers of chlorotrifluoroethylene with a monomer selected from the group of hexafluoropropylene, perfluoroalkylvinylethers, vinylidene fluoride, vinyl fluoride and ethylene. Blends of the above listed fluoropolymers and terpolymers formed from the above listed monomers are also suitable as the fluoropolymer matrix material of the present invention.

Alternatively, polymer matrix material of the present invention may comprise a thermoplastic or thermosetting polymer other than a fluoropolymer. Suitable alternative polymeric matrix materials include, e.g. polyolefins, polyimides, epoxy resins and cyanate esters. Specific examples of suitable polymer matrix materials include polyethylene, polymethylpentene, and polybutadiene.

The particulate filler material of the present invention may include any organic or inorganic particulate material. The terms "particulate" and "particles" as used herein are intended to include fibers. Suitable inorganic filler materials include, e.g. glass particles, ceramic particles, metallic particles, carbon particles and mineral particles. Specific examples of suitable particles include glass beads, glass microspheres, glass fibers, silica particles, carbon black, titanium dioxide particles and barium titanate particles. Silica particles, particularly amorphous fused silica particles and silica particles made by a sol gel process, and glass particles, are preferred filler particles for applications, e.g. dielectric layers of laminar electrical circuits, requiring a low dielectric constant.

Specific examples of suitable polymeric particulate fillers include polymethylmethacrylate particles, polystyrene particles and polyimide particles. Suitable polymeric particles, e.g. LARC-TP1 (Rogers, Corp.), P-84 (Lenzing).

The shape of the filler particles, the size of the filler particles and the size distribution of the filler particles are important parameters with regard to characterizing the particle filled composite article of the present invention.

In a preferred embodiment of the present invention all particles of the particulate filler exhibit an equivalent spherical diameter of less than about 10 microns (μm). As used herein the "equivalent spherical diameter" of a filler particle is the diameter of a sphere which occupies the same volume as that occupied by the filler particle.

In an alternative preferred embodiment of the present invention, each of the filler particles exhibit no single linear dimension greater than about 10 μm .

For extremely thin films and in applications where a substantially uniform microstructure is an important characteristic of the film, it is preferred that all particles of the particulate filler exhibit an equivalent spherical diameter of less than about 5 μm . Alternatively, it is preferred that all particles of the particulate filler exhibit no single linear dimension greater than about 5 μm .

In a preferred embodiment of the present invention each of the filler particles is substantially spherical. The use of spherical filler particles provides improved processability by minimizing the filler surface area for a given particle size and filler loading. Furthermore, spherical particles provide isotropic properties to the film since the spherical particles do not become oriented during processing.

In a preferred embodiment of the present invention, the filler particles of the film are of a uniform size. The use of a monodisperse filler, i.e. wherein all the filler particles are

of substantially the same size, provides a more homogeneous film having substantially uniform properties throughout.

In a particularly preferred embodiment of the present invention, the filler particles comprise spherical silica particles of a substantially uniform size, i.e. all particles within plus or minus 10% of a nominal particle diameter. A pure silica powder known as GELSIL® produced by Geltech, Inc. and specified as :1 micron sphere size ($\pm 10\%$); density of 2.2 grams/cm³; free of hard agglomerations, has been found to be particularly suitable for use in the practice of the present invention.

The particulate filler material may be treated with a surface treatment to improve the moisture resistance and improve the mechanical properties of the composite film of the present invention.

The hydrophobic coating of the present invention may comprise any coating material that is thermally stable, exhibits a low surface energy, and improves the moisture resistance of the composite of the present invention. Suitable coating materials, include conventional silane coatings, titanate coatings and zirconate coatings. Preferred silane coatings include: phenyltrimethoxysilane, phenyltriethoxysilane, 3,3,3-trifluoropropyltrimethoxysilane, (tridecafluoro-1,1,2,2-tetrahydrodecyl)-1-triethoxysilane and mixtures thereof. Further examples of suitable fluorinated silane compounds are set forth in coassigned U.S. application Ser. No. 279,474, filed Dec. 2, 1988 and entitled "FLUOROPOLYMER COMPOSITE" by D. J. Arthur and G. S. Swei, the disclosure of which is incorporated herein by reference. Suitable titanate coatings include: neopentyl(diallyl)oxytrineodecanoyl titanate, neopentyl(diallyl)oxytri(dioctyl)phosphate titanate. Suitable zirconate coatings include: neopentyl(diallyl)oxytri(dioctyl)pyrophosphate zirconate and neopentyl(diallyl)oxytri(N-ethylenediamino)cetyl zirconate. Further examples of suitable titanate and zirconate coatings are set forth in coassigned U.S. application Ser. No. 483,501, filed Feb. 21, 1990, now U.S. Pat. No. 5,024,871, and entitled "CERAMIC FLUOROPOLYMER", by D. J. Arthur and G. S. Swei, the disclosure of which is incorporated herein by reference.

The hydrophobic coating is used in an amount effective to render the surfaces of the filler particles hydrophobic and compatible with the matrix material. The amount of coating relative to the amount of inorganic particles coated will vary with the surface area coated and density of the inorganic particles. Preferably, the coated inorganic particles of the present invention include from about 0.5 parts by weight (pbw) hydrophobic coating: 100 pbw inorganic particles to about 25 pbw hydrophobic coating: 100 pbw inorganic particles.

The polymer matrix material of the present invention is mixed with a first carrier liquid. The mixture may comprise a dispersion of polymeric particles in the first carrier liquid, a dispersion, i.e. an emulsion, of liquid droplets of the polymer or of a monomeric or oligomeric precursor of the polymer in the first carrier liquid or a solution of the polymer in the first carrier liquid.

The choice of the first carrier liquid is based on the particular polymeric matrix material and the form in which the polymeric matrix material is to be introduced to the casting composition of the present invention. If it is desired to introduce the polymeric material as a solution, a solvent for the particular polymeric matrix material is chosen as the carrier liquid, e.g. N-methyl pyrrolidone (NMP) would be a suitable carrier liquid for a solution of a polyimide. If it is

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