Title: CONDUCTIVE SURFACING FILMS AND PROCESSES FOR PRODUCING SAME

FIG. 2.

Abstract: The present invention provides processes of forming electrically conductive coatings on composite surfaces, more particularly to airplane composites for lightning protection and static electricity dissipation, and articles produced in the process and objects derived from such processes.
CONDUCTIVE SURFACING FILMS AND PROCESSES FOR PRODUCING SAME

BACKGROUND

TECHNICAL FIELD

[0001] The present invention provides processes of forming electrically conductive coatings on composite surfaces, more particularly to processes of forming electrically conductive surfaces on airplane composite parts for lightning protection and static electricity dissipation, and articles used in the process and objects derived from such processes.

BRIEF DESCRIPTION OF RELATED TECHNOLOGY

[0002] Materials for protection against electromagnetic interference, accumulation of static electricity, and/or lightning strike mitigation are useful in a number of applications, and are commonly used, for example, in airplanes and other aircraft. The ability to effectively manage lightning strikes on composite materials that form structural panels for wings, fuselages, fuel tanks, and other components of an aircraft structure is an important consideration for the safety of an aircraft.

[0003] Carbon fiber reinforced plastic (CFRP) is one type of composite material used for skin, spar and rib installations on aircraft. Such composite materials are highly desirable for use as structural components due to their lower mass, while possessing excellent structural rigidity and high strength. However, composite materials are not highly conductive and cannot dissipate the energy from a lightning strike as efficiently as traditional metal body components used in many conventional aircraft. For example, a CFRP structure is about 2000 times more resistive than most metals, and consequently CFRP is more prone to electrical breakdown when subjected to currents from lightning strikes, especially at interfaces and fasteners.

[0004] A number of approaches to protecting aircraft having non-conductive composite parts from lightning damage are in current practice or have been proposed. Failure to take such precautions can result in catastrophic failures to the composite structure, including puncturing the surfaces or damage to underlying structures or other sensitive equipment, like hydraulic lines and fuel tanks, as well.
[0005] One such solution is to completely cover the outer surface area of each non-conductive panel that is vulnerable to lightning with a conductive metal liner. Alternatively, copper foils or wire grids have been applied to the part lay-up of the composite skin prior to curing. These traditional solutions use metals because of their high conductivity and their ability to dissipate high electrical charges associated with lightening. But such protection comes at a cost of undesirable weight or machinability constraints. In some cases, the metal portions of the surfacing films may be as heavy as, or exceed, the surfacing film itself.

[0006] Moreover, not all parts of aircraft are equally prone to lightning strikes, and so may not require such high levels of protection. For example, leading edges suffer statistically greater lightning “hits” than do trailing portions of the aircraft. Replacing heavier metal panels, foils, or wire grids at statistically less vulnerable positions with physically lighter options may give some relief.

[0007] Dissipation of static is also an important consideration, even during construction. For example, during construction of secondary structures for aerospace applications, such as wing-to-body fairings on an aircraft, a high static charge can build up in service due to airflow over the insulative part because of the glass fiber material used as a support in the fairings. In order to alleviate this static charge build up, carbon filled paint can be sprayed over the secondary structure such that when it is attached to the aircraft, the secondary structure can become grounded and the static charge is dissipated.

[0008] Though this practice is satisfactory to achieve the desired goal, it adds additional material and labor costs, and reduces throughput due to the necessity of applying the carbon filled paint and drying it. Thus, it would be desirable to provide a way in which static charge build up could be eliminated or at least minimized in a more efficient and effective way.

[0009] Accordingly, there is a need for alternative lighter-weight lightning protection or static dissipation systems. Other desirable features and characteristics of the present invention will become apparent from the subsequent detailed description and the appended claims, taken in conjunction with the accompanying drawings and the foregoing technical field and background.
SUMMARY

[0010] The present invention is directed toward methods of forming electrically conductive coatings on conductive surfaces, the materials and intermediates used or developed in such methods, and the articles resulting from the use of such methods and intermediates.

[0011] In certain embodiments, an assembly of the present invention comprises a fabric having first and second opposing surfaces and a curable resin adjacent to the first surface, said resin comprising conductive filler, wherein said first surface of the fabric is characterized by a porosity or interstitial spacing, which allows, on heating, at least a portion of the curable resin to flow into and/or through the fabric and which prevents or inhibits the movement of the conductive filler therein or therethrough.

[0012] In other embodiments, an assembly of the present invention comprises a fabric having first and second opposing surfaces, a membrane, and a curable resin, said resin comprising conductive filler, wherein the membrane is interposed between the first surface of the fabric and the curable resin, said membrane characterized by a porosity that allows, on heating, the passage of at least a portion of the curable resin through the membrane into the fabric, and that inhibits the passage of the conductive filler therethrough.

[0013] In still other embodiments, an assembly of the present invention comprises a membrane and a layer of curable resin adjacent thereto, where the resin comprises conductive filler, and the membrane has a porosity that allows, on heating, the passage of at least a portion of the curable resin into the membrane, and that inhibits the passage of the conductive filler therein or therethrough.

[0014] Other embodiments provide a kit for providing a conductive surface to a substrate, said kit comprising (a) a curable resin; (b) a conductive filler; (c) a fabric having first and second opposing surfaces, the first surface characterized by a porosity which allows, on heating, the flow of the resin into the fabric and which prevents or inhibits the movement of the conductive filler therein; and optionally (d) a membrane, (e) a resin absorbent material, and/or (f) instructions as to the application of the combination of the fabric and curable resin to a substrate to provide a conductive surface on said substrate. In other embodiments, the kit comprises (a) a curable resin (b) a conductive filler; (c) an optional fabric; (d) a membrane characterized by a porosity which allows, on heating, the flow of the resin and which prevents or inhibits the movement of the conductive filler therethrough; and optionally (e) a resin absorbent material,
and/or (f) instructions as to the application of the combination of the fabric and curable resin to a substrate to provide a conductive surface on said substrate.

[0015] The present invention also provides embodiments for a process of providing a conductive surface to a substrate which comprise the steps of: (a) applying a fabric assembly to a substrate surface to form a fabric-substrate assembly, said fabric assembly comprising a fabric having first and second opposing surfaces, whose first surface has adjacent thereto a curable resin comprising a conductive filler, such that the curable resin is interposed between the fabric and the substrate surface; (b) subjecting the fabric-substrate assembly to conditions sufficient to promote the flow of at least a first portion of the curable resin into the fabric, thereby providing a resin-impregnated fabric and concentrating the conductive filler within a second portion of the curable resin, said second portion of curable resin remaining interposed between the resin-impregnated fabric and the substrate surface; and (c) curing the second portion of the resin containing the concentrated conductive filler such that it adheres to the substrate. Other embodiments provide that the fabric assembly further comprises a membrane interposed between the fabric and the curable resin containing the conductive material, wherein the membrane allows, on heating of the assembly, the passage of at least a portion of the curable resin into or through the membrane into the fabric, but which prevents or inhibits the movement of the conductive filler therethrough. Still other embodiments further comprise removing the resin-impregnated fabric, either before or after the curing step.

[0016] Yet another embodiment provides a process of providing a conductive surface to a substrate comprising the steps of: (a) applying a curable resin comprising a conductive filler to a substrate; (b) applying a fabric such that the curable resin is interposed between the fabric and the substrate surface to form a fabric-substrate assembly; (c) subjecting the fabric-substrate assembly to conditions sufficient to promote the flow of at least a first portion of the curable resin into the fabric, thereby providing a resin-impregnated fabric and concentrating the conductive filler within a second portion of the curable resin, said second portion of curable resin remaining interposed between the resin-impregnated fabric and the substrate surface; and (d) curing the second portion of the resin containing the concentrated conductive filler such that it adheres to the substrate. Other embodiments further comprise removing the resin-impregnated fabric, either before or after the curing step.
[0017] Another embodiment provides a process of providing a conductive surface to a substrate comprising the steps of: (a) applying a curable resin comprising a conductive filler to a substrate; (b) applying a membrane adjacent to the curable resin to form a substrate-resin-membrane assembly; (c) subjecting the substrate-resin-membrane assembly to conditions sufficient to promote the flow of at least a first portion of the curable resin into the membrane, thereby concentrating the conductive filler within a second portion of the curable resin; and (d) curing the second portion of the resin containing the concentrated conductive filler such that it adheres to the substrate. Other embodiments further comprise removing the resin-impregnated membrane, either before or after the curing step.

[0018] In another embodiment, a process of providing a conductive surface to a substrate comprises the steps of: (a) applying a membrane adjacent to a substrate; (b) applying a curable resin comprising a conductive filler to the membrane to form a substrate-membrane-resin assembly; (c) subjecting the substrate-membrane-resin assembly to conditions sufficient to promote the flow of at least a first portion of the curable resin through the membrane and to the substrate, thereby concentrating the conductive filler within a second portion of the curable resin; and (d) curing the entire assembly such that the resin and membrane both adhere to the substrate.

[0019] Other embodiments of the invention include the various compositions of matter used in or formed by the disclosed methods. For example, other embodiments of the invention include the substrate-fabric compositions formed during the claimed processes and articles having a conductive surface produced by the method of any one of the claimed methods.

BRIEF DESCRIPTION OF THE DRAWINGS

[0020] Figures are provided for illustration only and are not to scale.

[0021] FIG. 1 illustrates an example of the present invention. FIG. 1A illustrates the concept of the substrate / resin layer / fabric assembly. FIG. 1B illustrates the concept of the substrate / filler-enriched resin layer / resin-enriched fabric assembly. FIG. 1C illustrates an embodiment wherein the resin-enriched fabric is removed after curing.

[0022] FIG. 2 illustrates another example of the present invention. FIG. 2A illustrates the concept of the substrate / resin layer (230) containing conductive filler (240) / membrane (220) / fabric assembly (210). FIG. 2B illustrates the concept of the substrate / filler-enriched resin layer / membrane / resin-enriched fabric assembly.
DETAILED DESCRIPTION

[0023] The present invention may be understood more readily by reference to the following detailed description taken in connection with the accompanying Figures and Examples, which form a part of this disclosure. It is to be understood that this invention is not limited to the specific products, methods, conditions or parameters described and/or shown herein, and that the terminology used herein is for the purpose of describing particular embodiments by way of example only and is not intended to be limiting of any claimed invention. Similarly, unless specifically otherwise stated, any description as to a possible mechanism or mode of action or reason for improvement is meant to be illustrative only, and the invention herein is not to be constrained by the correctness or incorrectness of any such suggested mechanism or mode of action or reason for improvement.

[0024] It is to be appreciated that certain features of the invention which are, for clarity, described herein in the context of separate embodiments, may also be provided in combination in a single embodiment. Conversely, various features of the invention that are, for brevity, described in the context of a single embodiment, may also be provided separately or in any subcombination. Finally, while an embodiment may be described as part of a series of steps or part of a more general composition or structure, each said step may also be considered an independent embodiment in itself.

[0025] The present invention provides methods for providing a conductive surface to a substrate, as well as articles and kits used to accomplish such methods, and articles produced by said methods.

[0026] In certain embodiments, an assembly of the present invention comprises a fabric having first and second opposing surfaces and a curable resin adjacent to the first surface, said resin comprising conductive filler, wherein said first surface of the fabric is characterized by a porosity or interstitial spacing, which allows, on heating, at least a portion of the curable resin to flow into and/or through the fabric and which prevents or inhibits the movement of the conductive filler therein or therethrough.

[0027] In other embodiments, assemblies of the present invention are used to provide a conductive surface to a substrate. In certain of these embodiments, the process comprises the steps of: (a) applying a fabric assembly to a substrate surface to form a fabric-substrate
assembly, said fabric assembly comprising a fabric having first and second opposing surfaces, whose first surface has adjacent thereto a curable resin comprising a conductive filler, such that the curable resin is interposed between the fabric and the substrate surface; (b) subjecting the fabric-substrate assembly to conditions sufficient to promote the flow of at least a first portion of the curable resin into the fabric, thereby providing a resin-impregnated fabric and concentrating the conductive filler within a second portion of the curable resin, said second portion of curable resin remaining interposed between the resin-impregnated fabric and the substrate surface; and (c) curing the second portion of the resin containing the concentrated conductive filler such that it adheres to the substrate.

[0028] Other embodiments further comprise removing the resin-impregnated fabric from the substrate, leaving behind a conductive surface on the substrate. This may be done before or after the curing step. If done after, it may be desirable to remove the resin-impregnated fabric at a time removed from the curing process, thereby providing protection of the surface treated substrate from physical, chemical, or photolytic damage during subsequent processing to the substrate (e.g., during assemble of treated pieces into a large article).

[0029] The substrates may be initially non-conductive (e.g., polymer-based) or partially or wholly conductive. If polymer-based, the substrates may comprise uncured, partially cured, or cured thermoset or thermoplastic polymers or resins. The process may be applied to partially or wholly conductive surfaces, for example, in the context of repairing existing, but damaged, conductive surfaces or to increase the total thickness of the conductive layer made by this technology or in conjunction with one or more of the conventional technologies discussed above (e.g., so as to be able to discharge the electrical energy associated with a lightning strike, and/or may be applied).

[0030] As used herein, the term “adjacent” carries the conventional meaning of “near or close, and including, but not necessarily, abutting.” That is, a curable resin that is adjacent to the first surface of the fabric includes those embodiments wherein these two materials physically contact (i.e., abut) one another, and where one or more intermediary layers are interposed between the fabric and the curable resin (for example, a material which dissolves or moves during processing or a membrane, see below).
One of the many features of the present invention is the desirability and ability of
the fabric to attract (e.g., by wicking or capillary action), incorporate, and/or provide passage
through the fabric of a first portion of the curable resin on heating of the resin, while preventing
or inhibiting the movement of the conductive filler into or through said fabric. The resulting
effect is to concentrate the conductive filler within a second portion of curable resin that remains
between the fabric and the substrate.

In certain embodiments, the surface of the fabric which is directed toward the
substrate – i.e., described herein as the first surface – acts as a filtering means, allowing the
movement of the curable resin, while preventing or inhibiting the movement of the conductive
filler, into the fabric. One way in which this may be achieved is for the first surface of the fabric
to have pores or interstitial spacings of a dimension sufficient to allow for the passage of the
curable resin into the fabric, but insufficient to permit or allow for the similar movement of the
conductive filler. Accordingly, the size of the pores or interstitial spacings of the fabric may be
selected or made in relation to the size of the conductive filler, and/or vice versa.

As used herein, the terms “prevent,” “exclude,” or “inhibit” connote an
impediment to movement of the conductive filler into the fabric, and should not be interpreted to
require that all of the filler be prevented, excluded, or otherwise kept from the fabric. Rather, it
is merely sufficient that the movement of the conductive filler be impeded such that, once the
first portion of the curable resin has migrated into the fabric, the concentration of the filler within
the remaining second portion of the curable resin (i.e., remaining after the migration of the first
portion of the curable resin into the fabric) be greater than the first portion of the curable resin,
and/or greater than the concentration of the filler in the original resin. In certain separate
embodiments, these terms reflect that less than about 50 wt%, less than about 25 wt%, less than
about 10 wt%, less than about 5 wt%, or less than about 1 wt% of the original conductive filler
accompanies the first portion of the curable resin into the fabric.

Additional embodiments exist beyond those embodiments wherein the first
surface of the fabric provides the means for allowing entry of the curable resin, while excluding,
preventing, or inhibiting the movement of the conductive filler into the fabric. For example,
other embodiments provide that the fabric contain a membrane, interposed between the fabric
and the curable resin, wherein the membrane serves as an alternate or additional filtering means.
The use of a separate membrane for this purpose provides for greater flexibility in design. For
example, the membrane may be prepared from solid polymer films or tapes by treating with plasma or other conventional perforating treatments, so as to tailor the pore sizes and/or shapes to those not otherwise available from woven or non-woven fabrics. The use of a membrane may also relieve the requirement that the first surface of the fabric provides the necessary filtering function previously described.

[0035] This concept of concentrating the conductive filler material in a layer of curable resin can also be accomplished without the use of a fabric, using the principles described herein. For example, in one embodiment, a process of providing a conductive surface to a substrate comprises the steps of: (a) applying a curable resin comprising a conductive filler to a substrate; (b) applying a membrane adjacent to the curable resin to form a substrate-resin-membrane assembly; (c) subjecting the substrate-resin-membrane assembly to conditions sufficient to promote the flow of at least a first portion of the curable resin into the membrane, thereby concentrating the conductive filler within a second portion of the curable resin; and (d) curing the second portion of the resin containing the concentrated conductive filler such that it adheres to the substrate. Other embodiments further comprise removing the resin-impregnated membrane.

[0036] In another embodiments, a process of providing a conductive surface to a substrate comprises the steps of: (a) applying a membrane adjacent to a substrate; (b) applying a curable resin comprising a conductive filler to the membrane to form a substrate-membrane-resin assembly; (c) subjecting the substrate-membrane-resin assembly to conditions sufficient to promote the flow of at least a first portion of the curable resin through the membrane and to the substrate, thereby concentrating the conductive filler within a second portion of the curable resin; and (d) curing the entire assembly such that the resin and membrane both adhere to the substrate.

[0037] The terms “pores,” “porosity,” or “interstitial spacings” refer to openings in the membrane, fabric, or fabric surface(s) which allow for the movement of the curable resin into and/or through the internal portions of the fabric. These may comprising openings within (e.g., micro-openings) or between (e.g., macro-openings) strands or fibers of the fabric. It should be appreciated that the internal spacing or pore dimensions within the body of the fabric may be different, for example larger, than the pore sizes or interstitial spacings at the first surface of the fabric or the membrane. For example, once the first surface or membrane has discriminated
between the entry of the curable resin to the exclusion of the conductive filler, a larger internal 
pore size or spacing within the body of the fabric may be desirable for the incorporation of larger 
volumes of the curable resin.

[0038] While thus far the ability of the fabric to selectively incorporate a portion of the 
curable resin while inhibiting the incorporation of the conductive filler has been described in 
terms of a size exclusion principle, the invention is not limited to this mechanism, or any other 
particular mechanism or mode of operation, nor to the correctness of any single theory or mode 
of operation. In other embodiments, the surface of the fabric, or the body of the fabric itself, 
may contain features which either complement this size exclusion principle or may provide an 
alternative mechanism. For example, in other embodiments the fabric may optionally comprise 
surfactants or other coatings which either attract and/or enhance the attraction of the curable 
resin into the film or repel and/or enhance the repulsion of the conductive filler or both, for 
example by differences in hydrophobicity / hydrophilicity, lipophobicity / lipophilicity, or 
electrostatic charge. For example, the surface of the fabric may optionally be coated with silica, 
siloxane, aluminum oxide, or metal, or treated with plasma or silane.

[0039] Each individual element of the fabric assemblies described may also be 
considered separate embodiments. That is, individual separate tapes, sheets, or layers of the 
curable resin comprising the conductive filler and/or a fabric may be deemed independent 
embodiments, when used in the processes described herein. These may be provided as 
individual sheets or in continuous rolls. Moreover, processes comprising application of each of 
these individual elements to the substrate before heating and curing the resin may be considered 
separate embodiments. For example, in the processes described herein, the individual articles of 
resin and fabric may be provided separately and may be joined at any time before the heating and 
curing steps, provided the combination of the two materials provides an assembly capable of 
providing the desired effect of providing a conductive surface to the substrate. For example, 
when each of these components is provided separately, a process of providing a conductive 
surface to a substrate may comprise the steps of: (a) applying a curable resin comprising a 
 conductive filler to a substrate; (b) applying a fabric such that the curable resin is interposed 
 between the fabric and the substrate surface to form a fabric-substrate assembly; (c) subjecting 
the fabric-substrate assembly to conditions sufficient to promote the flow of at least a first 
portion of the curable resin into the fabric, thereby providing a resin-impregnated fabric and
concentrating the conductive filler within a second portion of the curable resin, said second portion of curable resin remaining interposed between the resin-impregnated fabric and the substrate surface; and (d) curing the second portion of the resin containing the concentrated conductive filler such that it adheres to the substrate. Additional embodiments may also further comprise removing the resin-impregnated fabric. When used according the methods described herein, the separate tape, sheet, or layer of the curable resin comprising the conductive filler and the fabric may be considered additional embodiments of the invention.

[0040] As used herein, the term “fabric” refers to a woven or non-woven material, or a combination of such materials. Woven fabrics are preferred. The fabrics may include materials comprising carbon or glass, and/or polyester, polyamide, polyethylene, polypropylene, polyethylenenaphthalate (PEN), polyethylene terephthalate (PET), polybutylene terephthalate (PBT), polyether etherketone (PEEK), polyamide, polyaryletherketone (PAEK), polyethersulfone (PES), polyethylenenimine (PEI), poly (p-phenylene sulfide) (PPS), polyvinyl chloride (PVC), fluorinated or perfluorinated polymer (such as a polytetrafluoroethylene (PTFE or TEFLON), polyvinylidene difluoride (PVDF), a polyvinyl fluoride (PVF or TEDLAR), or a mixture or copolymer thereof. Preferred exemplary fabrics may comprise polyester, polyamide, carbon fibers, glass or other inorganic fibers or KEVLAR. Polyesters, nylons, or mixtures thereof are especially useful.

[0041] Such fabric is typically dimensioned so as to at least define the area to be treated. The fabric size may vary so as to include sheets, layers, or continuous rolls.

[0042] The fabric may comprise single-ply or multi-ply constructions. The invention is well-suited for a variety of surface shapes and contours, including flat or essentially flat panels, curved contours, including convex or concave shapes or surfaces comprising combinations thereof. The fabric assembly, or components thereof, may be applied so as to substantially conform to the contour shape of the substrate, for example by draping over the surface to be treated.

[0043] Where the fabric is woven, the woven fabric comprises tightly woven mono- or multi-filament tows. Tightly woven, high density weaves are preferred so as to provide a smooth finish, compatible with the finish desired for the final product. Accordingly, preferred weaves include a plain weave, a harness satin weave, a crow-foot satin weave, or a twill, with a crow-foot satin weave style being most preferred. The use of polymer membranes as described above
may provide an even smoother final finish than available from even highly calendared, closed weave fabrics.

[0044] The tightness of the weave can be described in terms of warp ends and fill ends per inch, both terms being readily understood by those skilled in the art. Fabrics or films of this invention comprise those which independently contain at least 80 warp ends per inch, or at least 100, 120, 140, or 160 warp ends per inch, and at least 40 fill ends per inch, or at least 60, 80, or 100 fill ends per inch. For example, good results are obtained wherein the fabrics or films contain at least about 80 warp ends per inch and at least about 40 fill ends per inch. Other embodiments include those wherein the fabric is woven with at least 120 warp ends per inch and at least 60 fill ends per inch. Such weaves are commercially available, for example, from Precision Fabrics Group of Greensboro, North Carolina, and those characterized as providing “fine surface impressions” are most preferred. Exemplary compositions include 60004 / 56111 polyester, 51789 / 52006 nylon, and 52008 / 56115 nylon materials. Fiber or yarn thicknesses are such as to provide minimally open weaves, given the warp end / fill end parameters, and consistent with the thickness of the overall fabric.

[0045] The final surface finish of the article can be further improved using fabrics which have been scoured, heat set, and calendared so as to create a smooth tightly woven surface. This calendaring can be done before the application of the curable resin, or as part of the process to apply the resin to the fabric.

[0046] The fabric may also comprise a non-woven, interlocked fabric in which the fibers are derived from staple or continuous filament forms. The fibers may be tow, twisted or untwisted, spun, crimped and the like varieties. The fabrics are interlocked by textile processes such as weaving, knitting, needle punching, latch stitching and adhesive or thermal bonding. It is desirable that the fabric be a lightweight cloth. The fabric should have a weight from about 0.2 oz/yd² to about 2.0 oz/yd².

[0047] These non-woven fabrics are drapable (i.e., conform to the shapes of another surface), opaque and have relatively flat uniform surfaces that do not contribute unwanted patterns to the coated surface of the ultimate prepreg based composite. Cloth fiber types include, for example, polyester, carbon, nylon, and glass, in the form of filament or long staple fibers. The non-woven of choice should be spun-bonded or long staple cross-lapped garneted or carded varieties. The non-woven films are commercially available such as REEMAY (polyethylene
terephthalate fiber) from Reemay, Inc., TYVEC (polypropylene fiber) from Du Pont de Nemours & Co., and CEREX 4007 (nylon fiber) from James River Mills. The carrier cloth may also be made of non-woven staple or continuous carbon or glass fibers. Suitable carbon filament or staple and glass filament or staple carrier cloths are obtainable from International Paper, where an illustrative carbon mat is a non-woven 1" staple fiber carbon cloth of 0.21 oz/yd² weight (ASTM D-1910) bound with polyester resin. Thickness 0.002 inch (ASTM D-1777), Strength (Dry) 1.11 lb/in. M.D., 1.06 lb/in. C.D., Stretch (Dry) 0.67% M.D, 0.79% C.D. (ASTM D-1682).

[0048] Given the non-uniform porosity or interstitial spacings associated with the surfaces of non-woven fabrics, these are more likely to be used or applied in conjunction with a membrane.

[0049] In those embodiments where membranes are employed, the membranes may comprise materials of the same types as described above for the fabric. Membranes need not be woven or non-woven fabrics, but may also comprise solid tapes, films, or other sheet materials, having micro- or nanodimensioned pores. Additionally, in some embodiments, the membranes comprise electrically conductive materials, which may be left on the surface of the substrate after the resin-impregnated fabric is removed, providing additional conductivity to the substrate surface. Especially useful membrane materials include polyether sulfones.

[0050] In order to enhance the penetration of the curable resin into and through the fabric, it may be desirable to locate a resin absorbent material adjacent to the second surface of the fabric. Drawing the curable resin into this resin absorbent material effectively increases the capacity of the fabric to hold the resin, thereby increasing the concentration of the conductive filler at the surface of the substrate. Especially useful resin absorbent materials which may be used for this purpose include plastisols or molecular sieves. Degalan® from Evonik Industry of Darmstadt, Germany is a representative plastisol useful for this purpose.

[0051] The curable resin is preferably chemically compatible with the substrate composition, and may be the same or different than the composition of the substrate. While both thermoset and thermoplastic resins (or combinations thereof) can be used, thermoset resins are preferred. The thermosetting resin matrix from which the conductive composite surfacing film is prepared may be selected from a host of materials, though most commonly the matrix may be an epoxy based one. For instance, one or more of diglycidyl ethers of bisphenol A (2,2-bis(4-
hydroxyphenyl)propane), sym-tris(4-hydroxyphenyl)propane, tris(4-hydroxyphenyl)methane, bisphenol F (2,2-bis(4-hydroxyphenyl)methane), tetrabromobisphenol A, their polyepoxide condensation products, cycloaliphatic epoxides, epoxy-modified novolacs (phenol-formaldehyde resins), 3,4-epoxy cyclohexyl methyl-3,4-epoxy cyclohexane carboxylate, vinyl cyclohexene dioxide, 2-(3,4-epoxy cyclohexyl-5,5-spiro-3,4-epoxy) cyclohexane-meta-dioxane, bis(3,4-epoxy cyclohexyl) adipate and the epoxides derived from the reaction of epichlorohydrin with aniline, o-, m- or p-aminophenol, and methylene dianiline, may be used individually or in combination as the thermosetting resin matrix.

[0052] The epoxy resin chosen may be a fluid or viscous liquid at room temperature (or at moderately elevated temperatures) but when heated to temperatures below its cure temperature, must become sufficiently fluid as to be able to migrate through the membrane and/or into the fabric.

[0053] The chosen thermoset resin should preferably cure at 350°F (177°C) and 250°F (121°C), as the aerospace industry demands. Nevertheless, within the scope of this invention, thermoset resins (e.g., epoxies) may be chosen as a matrix, where the cure temperature differs from these two cure temperature points, if that is what the intended purpose desires.

[0054] Desirably, when epoxy resins are used as the thermosetting matrix, hardeners may be used to cure the epoxy resin under thermal conditions. The preferred hardeners are amine compounds, ranging from dicyandiamide, to ureas, to aliphatic and aromatic amines. Illustrative of suitable aliphatic amines include alkylenecamines such as monoethanolamine, ethylenediamine, N-(2-aminoethyl)ethanolamine, diethylenetriamine, piperazine, N-(2-aminoethyl)piperazine, triethylenetetramine, tetraethylenepentamine, pentaethylenetetramine, diaminoethypiperazine, piperazinoethylethylenediamine, 4-aminoethyltriethylenetetramine, tetraethylenepentamine, aminoethylpiperazinoethylethylenediamine, and piperazinoethylidiethylenetriamine.

[0055] Illustrations of suitable aromatic amines are aniline, o-, m- or p-aminophenol, and alkylated versions thereof.

[0056] Other desirable hardeners are the reaction products of dialkylamines, such as dimethylamine, diethylamine, methylethylamine, di-n-propylamine, and the like, with a variety of mono and diisocyanates to form mono and diureas.
Preferred urea hardeners in this regard are those that are the reaction products of dimethylamine with mixtures of 80% 2,4-tolyene diisocyanate and 20% 2,6-tolyene diisocyanate, polymeric isocyanate, p-chlorophenylisocyanate, 3,4-dichlorophenylisocyanate or phenylisocyanate.

Accelerators may also be used and include imidazoles and substituted ureas, examples of which include 2-ethyl-4-methylimidazole and p-chlorophenyl-1,1-dimethyl urea.

The amount of the hardener employed is usually stoichiometrically equivalent on the basis of one amine group per epoxy group in the resin matrix.

Beyond epoxy resins, other common matrix resins may be chosen too, such as bismaleimide (BMI), phenolic, polyester, PMR-15 polyimide, acetylene terminated resins and benzoazines, which are each suitable for use in the practice of the invention, whether alone or in combination.

The benzoazine for instance may be embraced by the following structure:

\[
\begin{array}{c}
\text{R}_1 \\
\text{N} \\
\text{O} \\
\text{X} \\
\text{R}_4 \\
\end{array}
\]

where o is 1-4, X is selected from a direct bond (when o is 2), alkyl (when o is 1), alkyne (when o is 2-4), carbonyl (when o is 2), thiol (when o is 1), thioether (when o is 2), sulfoxide (when o is 2), or sulfone (when o is 2), R₁ is selected from hydrogen, alkyl or aryl, and R₄ is selected from hydrogen, halogen or alkyl.
More specifically, the benzoxazine may be embraced by the following structure:

\[\text{II}\]

where \(X\) is selected from of a direct bond, \(\text{CH}_2\), \(\text{C}(\text{CH}_3)_2\), \(\text{C}=\text{O}\), \(\text{S}=\text{O}\) or \(\text{O}=\text{S}=\text{O}\), and \(R_1\) and \(R_2\) are the same or different and are selected from hydrogen, alkyl, such as methyl, ethyl, propyl and butyl, or aryl.

Representative benzoxazines include:
where $R_1$ and $R_2$ are as defined above.

[0064] Alternatively, the benzoxazine may be embraced by the following structure:

where $p$ is 2, $Y$ is selected from biphenyl (when $p$ is 2), diphenyl methane (when $p$ is 2), diphenyl isopropane (when $p$ is 2), diphenyl sulfide (when $p$ is 2), diphenyl sulf oxide (when $p$ is 2), diphenyl sulfone (when $p$ is 2), or diphenyl ketone (when $p$ is 2), and $R_4$ is selected from hydrogen, halogen or alkyl.
Though not embraced by structures I, II or III additional benzoxazines are within the following structures:
where \( R_1 \) are \( R_2 \) are as defined above, and \( R_3 \) is defined as \( R_1 \) or \( R_2 \).

[0066] Examples of these benzoxazines therefore include:
The benzoxazine may include the combination of multifunctional benzoxazines and monofunctional benzoxazines. Examples of monofunctional benzoxazines may be embraced by the following structure:

![Chemical Structure](image)

where R is alkyl, such as methyl, ethyl, propyls or butyls, or aryl, and R₄ is selected from hydrogen, halogen and alkyl.

The thermosetting resin should be present in an amount in the range of about 10 to about 99 percent by weight, such as about 25 to about 75 percent by weight, desirably about 35 to about 65 percent by weight, based on the total weight of the curable resin composition, including the conductive or other filler(s).

The typical thermosetting resin is an A-stage resin. In some cases, however, it may be desirable to use a B-stage resin but in that case, ordinarily it would be in combination with an A-stage resin.

Curing may be accomplished by any conventional method, including thermally or photolytically.

One of the many unique performance features of the present invention is provided by the distribution, packing and orientation of the conductive filler in the resin matrix, and by the ability of the fabric (and/or membrane) to aid in concentrating these conductive fillers at the surface of the substrate before and after curing of the resin.

As used herein, “conductive filler” generally refers to those materials which, provide for the conduction of electricity or the dissipation of electrical charge when placed in physical or electrical with one another (but see also below).

The conductive filler may be selected from a variety of different materials provided the materials have the capacity to conduct electricity. Among the many materials suitable for use as the conductive filler herein are various metals, graphite and carbon. In certain embodiments, the conductive filler comprises a metal, such as aluminum, copper, nickel, palladium, platinum, silver, tin, tungsten, or mixtures thereof in the form of flake, powder, wire, nanowire, or fibril. In other embodiments, the conductive filler comprises a glass, silica, or other mineral filler coated with such a metal. In still other embodiments, the conductive filler
comprises carbon in the form of fiber, graphite, graphene, and/or nanotubes. Nanotubes may be single-, double-, or multiwalled, and/or filled or doped with additionally conductive materials. Indeed, carbon black is a desirable conductive filler. Various commercial sources of carbon black exist. For instance, Cabot, Colombian Chemicals, Continental Carbon, Degussa Engineered Carbon, and Sid Richardson are but a few. These manufacturers offer carbon black in a variety of different particle size distributions, surface areas, and aspect ratios, for instance.

[0074] The conductive filler may be initially distributed homogeneously or heterogeneously through the curable resin. When the distribution of the filler is heterogeneous through the thickness of a curable resin layer, it may be preferred that the concentration of the conductive filler in the curable resin layer be higher nearer the surface destined to be applied to the substrate than that nearer or destined to be nearer the fabric (and/or membrane). Such a thickness gradient might be achieved, for example, by applying the conductive filler(s) to one surface of a preformed film, tape, or sheet of curable resin, and then providing conditions that allow the conductive filler(s) to migrate into and become incorporated within the resin without allowing the conductive filler(s) to homogeneously distribute throughout the resin composition. The resulting curable resin layer would have a higher concentration of conductive filler nearer one first surface than nearer the other surface. If a curable resin layer was already adhered to a fabric (or membrane) through one surface, application of the filler to the opposing curable resin surface and subsequent incorporation could provide the desired result. In another method, the final curable resin (i.e., that to be applied to the substrate) could comprise a laminate of two or more sub-layers of resin, each sub-layer comprising a different concentration of conductive filler(s), and arranged to form the desired gradient of conductive filler(s) concentration.

[0075] While the specific focus of the present invention is directed toward electrical conductivity, the skilled artisan should appreciate that the inventive concept (of providing a concentrated filler profile adhered to the substrate) is not limited to electrically conductive fillers. Accordingly, the invention also provides for embodiments where the so-called “conductive filler” comprises semiconductive materials, inorganic ceramics (e.g., thermally conductive carbides, nitrides, oxides, or mixtures thereof), piezoelectrics (e.g., ferrites, niobates, titanates, tungstates, zirconates, or mixtures thereof), when used individually, in mixtures, or mixtures with genuinely electrically conductive materials.
The curable resin may also include fillers, other than the conductive ones, which are either inorganic or organic, examples of which include zinc oxides; siliceous fillers encompassing the silicates such as wollastonite, micas, silicas such as fumed silica, quartz, fused silica, precipitated silicas, xerogels, aerogels ceramics such as hollow (or gas filled) silica / alumina (glass) microspheres and polymeric ones. Particle sizes from about 1 to about 120 microns are useful.

When desired, a thickening agent can also be employed with the curable resin matrix. Such materials are well known in the art, and include for instance oxides and hydroxides of the metals of Group I, II and III of the Periodic Table. Illustrative examples of thickening agents include magnesium oxide, calcium oxide, calcium hydroxide, zinc oxide, barium oxide, magnesium hydroxide and the like, including mixtures of the same. When used, thickening agents are normally employed in proportions of from about 0.1 to about 6 weight percent, based upon weight of the thermosetting resin matrix.

Additional flow reductions are provided by thixotroping agents such as fumed silica. Illustrative of thixotropic agents are high surface area fumed silicas and organosilyl blocked fumed silicas, and the like.

These inventive conductive curable resin compositions can be made by conventional mixing of the components in standard mixing equipment ordinarily used to mix viscous compositions. For example, they may be mixed in a Ross Double Planetary Mixer, provided with vacuum construction and jacketing to control temperature and de-aerate the mixture. Mixing is typically effected by blending components, and vacuum pumping to remove entrained air. The temperature chosen at which to blend is variable depending on the viscosity of the formulation to effect dispersion and then combination thereof with the filler component(s). Such procedures are well within the knowledge base of those persons of ordinary skill in the art.

To this point, the various embodiments have been described in terms of the methods of providing conductive surfaces and the individual components useful in the application of those methods. It should also be appreciated that the articles and various intermediate articles resulting from the process are also considered embodiments of the present invention. In particular, the invention contemplates use of these conductive surfaces for the protection against lightening strikes, especially wherein the conductive surface is sufficiently conductive to be able to dissipate the electrical energy of a lightning strike. Exemplary articles
which include the conductive surfaces described herein include an airplane or jet, a wind turbine blade, or a ship mast.

[0081] Other embodiments of the present invention also include those kits, packages or containers containing the necessary components to enable the processes described, said kits, packages or containers optionally providing written instructions as to how to process these materials. For example, a kit may comprise (a) a curable resin (b) a conductive filler; (c) a fabric having first and second opposing surfaces, the first surface characterized by a porosity or interstitial spacing which allows, on heating, the flow of the resin into the fabric and which prevents or inhibits the movement of the conductive filler therein; and optionally (d) a membrane, (e) a resin absorbent material, and/or (f) instructions as to the application of the combination of the fabric and curable resin to a substrate to provide a conductive surface on said substrate. A kit may also comprise (a) a curable resin (b) a conductive filler; (c) a membrane characterized by a porosity which allows, on heating, the flow of the resin and which prevents or inhibits the movement of the conductive filler therethrough; and optionally (d) a fabric; (e) a resin absorbent material, and/or (f) instructions as to the application of the combination of the fabric and curable resin to a substrate to provide a conductive surface on said substrate.

[0082] In such kits, the curable resin may be in the form of a liquid, either containing the conductive filler or with the conductive filler separately provided to be mixed with the curable resin, prior to being applied to the fabric. In other embodiments, the curable resin may be in the form of a film, tape, or sheet, with the conductive resin dispersed homogeneously or heterogeneously within or on one surface of the film, tape, or sheet. Similarly, the kit may contain a separate membrane, to be applied to either a film, tape, or sheet of a curable resin or to the fabric, or the membrane may be pre-attached to either a film, tape, or sheet of a curable resin or to the fabric. These kits may be directed for original application or for repair of existing equipment.
Examples

[0083] The following example(s) is intended to be illustrative only, and not limiting to the scope of the invention.

[0084] In one set of experiments, a curable resin containing metallic silver was formulated using the ingredients provided in the attached Table.

<table>
<thead>
<tr>
<th>Trade Name</th>
<th>Supplier</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>EPICLON 830 Resin</td>
<td>Daicel (USA), Inc., Fort Lee, NJ</td>
<td>Diglycidy ether, bisphenol F</td>
</tr>
<tr>
<td>HELOXY Modifier 71</td>
<td>Momentive, Columbus, OH</td>
<td>Fatty acids, C18-unsatd., dimers, polymers with epichlorohydrin</td>
</tr>
<tr>
<td>EPON 1001F</td>
<td>Momentive, Columbus, OH</td>
<td>Phenol. 4.4’-(1-methylethyldiene)bis-polymer with 2.2’-[(1-methylethyldiene)bis-(4.1-phenyleneoxymethylene)]bis(oxirane).</td>
</tr>
<tr>
<td>AMICURE 1400</td>
<td>Air Products and Chemicals, Inc., Allentown, PA</td>
<td>Cyanoguanidine</td>
</tr>
<tr>
<td>OMNICURE* U-405</td>
<td>CVC Thermoset Specialties, Moorestown, NJ</td>
<td>Methylene diphenyl bis(dimethyl urea)</td>
</tr>
<tr>
<td>Silver Flake AA-40719</td>
<td>Metalor Technologies USA Corporation, North Attleboro, MA</td>
<td>Silver Flake</td>
</tr>
<tr>
<td>ECCOSPERHERS glass microspheres SID 160Z</td>
<td>Trelleborg Offshore Boston, Inc., Mansfield, MA</td>
<td>Glass microspheres</td>
</tr>
</tbody>
</table>

[0085] The formulated resin was formed into a film of having a thickness of about 5 mils thick. A 3 inch x 3 inch section of film was applied to a piece of FR-4 laminate of the same size. A second 3 inch x 3 inch section of film was applied to a second piece of FR-4 laminate, this second sample piece of FR-4 laminate, onto which a 3 inch x 3 inch piece of Supor 1200, a polyethersulfone membrane (from Pall Corporation) with 1.2 micron pore size, had been applied (i.e., the Supor 1200 was interposed between the FR-4 and the resin).

[0086] The samples were cured using a 90 min ramp from ambient to 350°F, 120 minute hold, 90 min cool down to ambient temperature, at 85 psig.

- 25 -
[0087] The resistivity of the surface was measured using 4-point probes, 1 inch apart, on multiple locations throughout the panel. The first sample, made without the membrane, exhibited an average resistivity of about 15 milliohm. The second sample, made with the membrane, exhibited an average resistivity of about 8 milliohm; i.e., about half of the sample made without the membrane.

[0088] As those skilled in the art will appreciate, numerous modifications and variations of the present invention are possible in light of these teachings, and all such are contemplated hereby. For example, in addition to the embodiments described herein, the present invention contemplates and claims those inventions resulting from the combination of features of the invention cited herein and those of the cited prior art references which complement the features of the present invention. Similarly, it will be appreciated that any described material, feature, or article may be used in combination with any other material, feature, or article.

[0089] The disclosures of each patent, patent application, and publication cited or described in this document are hereby incorporated herein by reference, in their entirety.
What is Claimed:

1. An assembly comprising a fabric having first and second opposing surfaces and a curable resin adjacent to the first surface, said resin comprising conductive filler, wherein said first surface of the fabric is characterized by a porosity which allows, on heating, at least a portion of the curable resin to flow into the fabric and which inhibits the movement of the conductive filler therein.

2. An assembly comprising a fabric having first and second opposing surfaces, a membrane, and a curable resin, said resin comprising conductive filler, wherein the membrane is interposed between the first surface of the fabric and the curable resin, said membrane characterized by a porosity that allows, on heating, the passage of at least a portion of the curable resin through the membrane into the fabric, and that inhibits the passage of the conductive filler therethrough.

3. The fabric assembly of claims 1 or 2 wherein the fabric comprises carbon or glass.

4. The fabric assembly of any one of claims 1-3 wherein the fabric is woven.

5. The fabric assembly of any one of claims 1-4 wherein the fabric further comprises a surfactant.

6. The fabric assembly of any one of claims 1-5 further comprising a resin absorbent material adjacent to the second surface of the fabric.

7. The fabric assembly of claim 6 wherein the resin absorbent material comprises a plastisol or molecular sieve.

8. The fabric assembly of any one of claims 1-7 wherein the curable resin comprises thermoset resin.

9. The fabric assembly of claim 8 wherein the curable resin comprises epoxy, phenolic, or benzoxazine.

10. The fabric assembly of any one of claims 1-9 wherein the conductive filler comprises (a) metal in the form of a flake, powder, wire, nanowire, or fibril, (b) metal coated glass, silica, or other mineral filler, and/or (c) carbon in the form of fiber, graphite, graphene, and/or nanotubes.

11. The fabric assembly of claim 10 wherein the metal comprises aluminum, copper, nickel, palladium, platinum, silver, tin, tungsten, or mixtures thereof.

12. A kit for providing a conductive surface to a substrate, said kit comprising (a) a curable resin; (b) a conductive filler; (c) a fabric having first and second opposing surfaces, the first
surface characterized by a porosity which allows, on heating, the flow of the resin into the fabric and which prevents or inhibits the movement of the conductive filler therein; and optionally (d) a membrane, (e) a resin absorbent material, and/or (f) instructions as to the application of the combination of the fabric and curable resin to a substrate to provide a conductive surface on said substrate.

13. A kit for providing a conductive surface to a substrate, said kit comprising (a) curable resin (b) a conductive filler; (c) a fabric; (d) a membrane characterized by a porosity which allows, on heating, the flow of the resin and which prevents or inhibits the movement of the conductive filler therethrough; and optionally (e) a resin absorbent material, and/or (f) instructions as to the application of the combination of the fabric and curable resin to a substrate to provide a conductive surface on said substrate.

14. The kit of claim 12 or 13, wherein the curable resin comprising conductive filler is in the form of a film, sheet, or tape.

15. The kit of any one of claims 12-14 further comprising a resin absorbent material.

16. A process of providing a conductive surface to a substrate comprising the steps of:

(a) applying a fabric assembly to a substrate surface to form a fabric-substrate assembly, said fabric assembly comprising a fabric having first and second opposing surfaces, whose first surface has adjacent thereto a curable resin comprising a conductive filler, such that the curable resin is interposed between the fabric and the substrate surface;

(b) subjecting the fabric-substrate assembly to conditions sufficient to promote the flow of at least a first portion of the curable resin into the fabric, thereby providing a resin-impregnated fabric and concentrating the conductive filler within a second portion of the curable resin, said second portion of curable resin remaining interposed between the resin-impregnated fabric and the substrate surface; and

(c) curing the second portion of the resin containing the concentrated conductive filler such that it adheres to the substrate.

17. The process of claim 16 further comprising removing the resin-impregnated fabric.

18. The process of claim 16 or 17 wherein the fabric assembly further comprises a membrane interposed between the fabric and the curable resin containing the conductive material, wherein the membrane allows, on heating of the assembly, the passage of at least a portion of the curable
resin through the membrane into the fabric, but which prevents or inhibits the movement of the conductive filler therethrough.

19. The process of claim 15 wherein the substrate is electrically non-conductive.

20. The process of claim 15 wherein the substrate comprises a thermoset or thermoplastic polymer or polymer resin.

21. A process of providing a conductive surface to a substrate comprising the steps of:
   (a) applying a curable resin comprising a conductive filler to a substrate;
   (b) applying a fabric such that the curable resin is interposed between the fabric and the substrate surface to form a fabric-substrate assembly;
   (c) subjecting the fabric-substrate assembly to conditions sufficient to promote the flow of at least a first portion of the curable resin into the fabric, thereby providing a resin-impregnated fabric and concentrating the conductive filler within a second portion of the curable resin, said second portion of curable resin remaining interposed between the resin-impregnated fabric and the substrate surface; and
   (d) curing the second portion of the resin containing the concentrated conductive filler such that it adheres to the substrate.

22. The process of claim 21 further comprising removing the resin-impregnated fabric.

23. A curable resin comprising a conductive filler for use in the process of claim 21 or 22.

24. The curable resin of claim 23 in the form of a film, sheet, or tape.

25. An article having a conductive surface produced by the method of any one of claims 16-24.

26. The article of claim 25 wherein the conductive surface is sufficiently conductive to be able to dissipate the electrical energy of a lightning strike.
A. CLASSIFICATION OF SUBJECT MATTER

H01B 1/20(2006.01)i, H01B 5/14(2006.01)i, B32B 37/00(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

H01B 1/20; B05D 5/12; B32B 27/38; B32B 37/00; B32B 15/04; B32B 37/06; B64D 45/02; B32B 5/16; G01R 31/02; D03D 9/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

cKOMPASS\(^{(K}PO internal) & Keywords: airplane, lightning, conductive, filler, resin, polymer, epoxy, benzoxazine, cure, heat, flow, melt, thaw, impreg, porosity

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>US 2011-0014356 A1 (PORNES, TIMOTHY D. et al.) 20 January 2011 See the abstract, claim 1, and paragraphs [0039], [0055], [0060].</td>
<td>1-3, 12, 14, 16-18, 21-24</td>
</tr>
<tr>
<td>A</td>
<td>US 2009-0075088 A1 (VAIDYANATHAN K. RANUJ et al.) 19 March 2009 See the abstract, claims 1-10, paragraph [0004], and figures 1, 5, 9.</td>
<td>1-3, 12, 14, 16-18, 21-24</td>
</tr>
<tr>
<td>A</td>
<td>US 2010-0209680 A1 (SANG JUN JIE JEFFREY et al.) 19 August 2010 See claims 1-2, 31, and paragraph [0008].</td>
<td>1-3, 12, 14, 16-18, 21-24</td>
</tr>
</tbody>
</table>

Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents:
  "A" document defining the general state of the art which is not considered to be of particular relevance
  "E" earlier application or patent but published on or after the international filing date
  "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of citation or other special reason (as specified)
  "O" document referring to an oral disclosure, use, exhibition or other means
  "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search
17 SEPTEMBER 2012 (17.09.2012)

Date of mailing of the international search report
19 SEPTEMBER 2012 (19.09.2012)

Name and mailing address of the ISA/KR
Korean Intellectual Property Office
189 Cheongsa-ro, Seo-gu, Daejeon Metropolitan City, 302-701, Republic of Korea
Facsimile No. 82-42-472-7140

Authorized officer
HWANG, Yun Koo
Telephone No. 82-42-481-5715

Form PCT/ISA/210 (second sheet) (July 2009)
**INTERNATIONAL SEARCH REPORT**

**Box No. II  Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)**

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. □ Claims Nos.:
   
   because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.: 7, 9, 11, 19-20, and 26
   
   because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
   
   Claims 7, 9, 11, 19-20, and 26 refer to multiple dependent claims that refer to other multiple dependent claims. Therefore, the meaning of the technical feature to which they refer is vague and unclear, and these claims do not meet the requirement of PCT Article 6.

3. ☒ Claims Nos.: 4-6,8,10, 15, and 25
   
   because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

**Box No. III  Observations where unity of invention is lacking (Continuation of item 3 of first sheet)**

This International Searching Authority found multiple inventions in this international application, as follows:

1. □ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. □ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. □ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. □ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

**Remark on Protest**

☐ The additional search fees were accompanied by the applicant’s protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant’s protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.
<table>
<thead>
<tr>
<th>Patent document cited in search report</th>
<th>Publication date</th>
<th>Patent family member(s)</th>
<th>Publication date</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>KR 10-2012-0046164 A</td>
<td>09.05.2012</td>
</tr>
<tr>
<td>US 2009-0075088 A1</td>
<td>19.03.2009</td>
<td>None</td>
<td></td>
</tr>
<tr>
<td>US 2011-0049292 A1</td>
<td>03.03.2011</td>
<td>CN 102001448 A A2</td>
<td>06.04.2011</td>
</tr>
<tr>
<td></td>
<td></td>
<td>EP 2289803 A2</td>
<td>02.03.2011</td>
</tr>
<tr>
<td></td>
<td></td>
<td>EP 1996465 A2</td>
<td>03.12.2008</td>
</tr>
<tr>
<td></td>
<td></td>
<td>WO 2008-048705 A3</td>
<td>29.01.2009</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CA 2752503 A1</td>
<td>19.08.2010</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CN 102317383 A A2</td>
<td>11.01.2012</td>
</tr>
<tr>
<td></td>
<td></td>
<td>JP 2012-518056 A</td>
<td>09.08.2012</td>
</tr>
<tr>
<td></td>
<td></td>
<td>TW 201035994 A A2</td>
<td>01.10.2010</td>
</tr>
<tr>
<td></td>
<td></td>
<td>US 8178608 B2</td>
<td>15.05.2012</td>
</tr>
<tr>
<td></td>
<td></td>
<td>WO 2010-093598 A2</td>
<td>19.08.2010</td>
</tr>
</tbody>
</table>