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[54] **SHEET-LIKE NONWOVEN WEB AND FLEXIBLE ARTICLE OF POLYESTER AND AROMATIC POLYAMIDE STAPLE FIBERS**

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[52] **U.S. Cl.**..... **161/150,** 57/140 BY, 117/138.8 F, 117/138.8 N, 161/151, 161/152, 161/227, 161/231, 161/170, 161/156, 161/214, 161/165, 174/68.5

[51] **Int. Cl.**..... **D04h 1/04,** B32b 7/04

[58] **Field of Search** ..... 161/150, 170, 151, 169, 161/152, 227, 214, 231, 156, 165; 174/68.5; 57/140 BY; 117/138.8 F, 138.8 N

[56] **References Cited**

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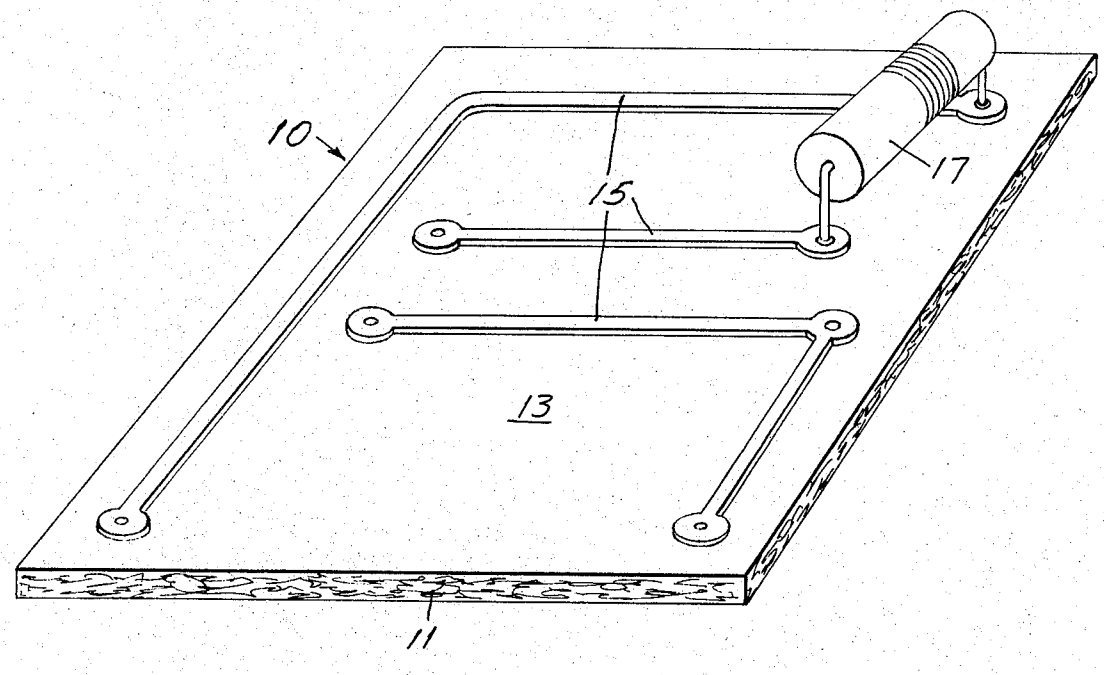
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[57] **ABSTRACT**

The disclosed laminate is suitable for use in the art of printed circuitry and comprises an electrically conductive layer and a nonwoven backing layer. The nonwoven backing has unusual dimensional stability under a wide variety of conditions and preferably comprises a blend of at least 15 wt. % polyester staple and at least 10 wt. % aromatic polyamide staple. This blend is impregnated with a thermosettable resin.

5 Claims, 1 Drawing Figure


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SHEET-LIKE NONWOVEN WEB AND FLEXIBLE ARTICLE OF POLYESTER AND AROMATIC POLYAMIDE STAPLE FIBERS

This application is a division of copending application Ser. No. 152,591, filed June 14, 1971, now abandoned, which is a continuation-in-part of Ser. No. 53,120 filed July 8, 1970, now abandoned.

This invention relates to impregnated, fibrous, paper-like sheets used as flexible printed circuit backings. An aspect of this invention relates to a critical blend of chemically diverse fibers which provide a synergistic dimensional stability effect. A still further aspect of this invention relates to a laminate of metal foil and a nonwoven backing, the backing comprising a critical blend of polyester and aromatic polyamide fibers.

Aromatic polyamides having recurring units of the formula

$$-NR_1-Ar_1CO-$$

or the formula

$$-NR_1Ar_1-NR_1CO-Ar_2-CO-$$

(wherein Ar_1 and Ar_2 are the same or different and are divalent aromatic nuclei which are linked meta or para into the recurring units, and wherein R_1 is hydrogen or lower alkyl) can be made into fibers, films, and "fibrids" and are known for their resistance to the degradative effects of high temperature. See U.S. Pat. No. 3,094,511 (Hill, et al.) issued June 18, 1963; U.S. Pat. No. 3,300,450 (Clay) issued Jan. 24, 1967; and U.S. Pat. No. 3,354,127 (Hill, et al.) issued Nov. 21, 1967; see also U.S. Pat. No. 3,203,933 (Hoffman, et al.) issued Aug. 31, 1965 or U.S. Pat. No. 3,225,011 (Preston, et al.), issued Dec. 21, 1965. The aromatic polyamide art contains suggestions relating to the use of such fibers, films, or "fibrids" in electrical insulation, e.g., in printed circuits, see, for example, the aforementioned Hill, et al. patents. Among the fibrous materials described in the prior art are waterleaf-type sheets of "fibrids" and staple fibers (see the aforementioned Clay patent) which ordinarily are calendered to reduce porosity. See British Pat. No. 1,129,097. Further details regarding fibrid structures can be found in U.S. Pat. No. 2,999,788 (Morgan), issued Sept. 12, 1961 and U.S. Pat. No. 2,988,782 (Parrish, et al.), issued June 20, 1961.

It is known to use porous, nonwoven webs of polyester (e.g. polyethylene terephthalate) staple in making electrical insulation and the like. Such nonwoven webs can be impregnated with the heat-curable resins used as electrical insulating varnishes. See U.S. Pat. No. 3,309,260 (Boese) issued May 14, 1967. Electrical insulation of the type disclosed in the aforementioned Boese patent has excellent properties (e.g. high tear strength), but may lack dimensional stability when exposed to high temperatures, e.g., above 230° F. (110° C.). In the printed circuit art, the paper-like backing for the circuit is subjected to processing temperatures of about 250° F. (about 121° C.) or higher, and generally is submerged or floated on a solder bath which is at temperature of, for example, about 400°–500° F. (205°–260° C.). This complex heat history, coupled with other processing steps such as metal-cladding, etching, etc., warps or distorts a polyester or varnish-impregnated polyester backing to the point where it is highly unsatisfactory or even unusable. Attempts to carefully control the heat history and cladding, etching,

or similar processing steps have not been successful in preserving dimensional stability.

The prior art teachings relating to paper-like sheets made from fibers and fibrids of aromatic polyamide and aromatic polyamide films appear to suggest an answer to the dimensional stability problems encountered in the manufacture of paper-like printed circuits. The use of aromatic polyamide films in the manufacture of printed circuits is not practical for thin, sheetlike backings, because such films lack sufficient tear strength and are characterized by high moisture sensitivity. A calendered paper-like sheet made from fibers and/or fibrids of aromatic polyamide (see the discussion of calendering in British Pat. No. 1,129,097), whether treated or untreated with resinous electrical insulating varnishes, has good tear strength but surprisingly suffers about as much distortion due to printed circuit processing and heat history as the polyester insulation. Uncalendered paper-like sheets made from fibers and fibrids of aromatic polyamide, after coating with a resin, make unacceptable printed circuit backings due to their poor tear strength. Apparently the selection of a suitable dimensionally heat stable fiber is only one factor involved in the fabrication of nonwoven webs suitable for use as printed circuit backings.

It is known in the art of making nonwoven webs to blend various fibers; see, for example, column 8 of U.S. Pat. No. 2,723,935 (Rodman), issued Nov. 15, 1955. This knowledge has been extended to the field of fibrid/staple fiber papers; see the aforementioned Morgan and Parrish, et al., patents. However, the blending of fibers would not appear to be a likely prospect for improving the dimensional stability of a nonwoven web subjected to a complex heat history and a variety of processing steps. The dimensional stability and heat resistance of the aromatic polyamides would be hard to improve upon, particularly as compared to relatively heat-sensitive fibers such as polyethylene terephthalate. In any event, the prior art contains no guidelines as to what sort of fiber blends would be suitable in this particular context of printed circuit technology.

Accordingly, this invention contemplates the fabrication of flexible printed circuit backings which will not be adversely affected by the processing (including steps involving elevated temperatures) involved in manufacturing printed circuits.

This invention further contemplates a printed circuit or a similar type of laminate having a nonwoven, paper-like printed circuit backing comprising a blend of fibers which is resistant to distortion, warping, degradation, and other ill effects caused by the heat history of the printed circuit and/or the various chemical and physical steps involved in cladding with an electrically conductive foil, etching the conductive foil, soldering, etc.

Briefly, this invention involves

blending discontinuous aromatic polyamide fibers, e.g. of the type disclosed in the aforementioned Hill, et al. and Clay patents, with at least 25% by weight (or at least 15% by wt. undrawn) discontinuous polyester fiber, e.g., a mixture of drawn and undrawn staple fibers derived from a polymer of an alkylene glycol and an aromatic dicarboxylic acid;

forming a thin (less than about 20 mils or about 0.5 mm), porous (i.e. having a Gurley value, as determined by ASTM test D 726, method A, of less than about 100 seconds per 100 cc. of air for a 5 mil [0.125 mm] layer

of material), nonwoven web from the blend of discontinuous fibers;

impregnating this thin, porous, nonwoven web with a suitable electrically insulating, heat curable or thermosettable organic polymeric synthetic resin; and

processing the impregnated thin, porous, nonwoven web according to the usual practices of printed circuits technology, e.g., laminating or plating with a conductive film, etching, soldering, etc.

The above-described porosity is essential for ease of impregnation. In order to provide the above-described nonwoven web with the required porosity, it is preferred to avoid blending the fibrids disclosed by Morgan and Parrish, et al., with the discontinuous (i.e. staple) fiber blend, because such fibrids have a tendency to reduce porosity, thereby making impregnation difficult. For optimum porosity (the range of Gurley values defined previously) a staple fiber blend is preferred wherein the fibers are about 0.5 – 10 denier by at least 3 mm. in length. Preferably, the fibers, particularly the fine denier fibers, are monofilaments.

There appears to be no simple or direct theoretical explanation for the improved performance of the nonwoven webs of this invention, and this invention is not, in any event, bound by any theory. It would appear to be contrary to the teachings and experience of the art to strive for greater dimensional stability by diluting heat resistant aromatic polyamide fibers with heat sensitive polyester fibers. The reason for the improved performance of the blend probably involves such factors as compensating for the moisture sensitivity of the aromatic polyamide and/or balancing expansion coefficients of the fibers (and/or the resinous impregnant and/or the conductive film cladding).

For example, it has been found that an impregnated nonwoven web can be made according to this invention such that it has a fairly constant linear thermal expansion coefficient throughout a significantly large temperature range (e.g. room-temperature up to 160° C.). Furthermore, this coefficient can be very close to the linear expansion coefficient for conductive metals such as copper, silver, gold, and aluminum, even though the nonwoven web contains at least 15 wt. % of temperature-sensitive (or heat softenable) fiber.

Reported values for the linear thermal expansion coefficient of various epoxy resins used in impregnating printed circuit backings are generally at least 65×10^{-6} per °C. (All coefficients of linear thermal expansion referred to in this application are expressed as a ratio of inch/inch or cm/cm per degree centigrade.) The reported thermal coefficient values for polyester films are lower than these epoxy resin values and are roughly comparable to some of the higher reported values for commonly used electrical conductors and semiconductors, the thermal coefficients of most of these conductive substances reportedly being in the range of about 5 to about 30×10^{-6} per °C., in rare instances as low as 4 or as high as 33×10^{-6} per °C. The thermal expansion coefficients of most metals, as solids, tend to be independent of temperature, in most cases remaining below 30×10^{-6}/°C. throughout the entire range of temperature relevant to the principles and practice of this invention.

It has now been found that epoxy resin-impregnated nonwoven webs of poly(ethylene terephthalate) fiber can have more than one linear expansion coefficient, depending on the temperature at which the coefficient is determined. For temperatures below 100° C. these values are close to the aforementioned reported values for polyester films, but for the higher temperatures frequently encountered in making laminates of this invention, these values are significantly larger and may be doubled or even tripled, as is shown subsequently in Example 5(C) of this application.

According to reported values, aromatic polyamide fibers and yarns have a linear expansion coefficient value which is in the 5 to 30×10^{-6} per °C. range discussed previously. However, the linear expansion coefficient of paper-like webs made from fibrous poly(m-phenyleneisophthalamide) is, apparently, temperature dependent, though less so than that of the polyester webs discussed previously.

Accordingly, the low and relatively constant values of thermal expansion coefficients for impregnated nonwoven webs used in this invention are not predictable from previously published thermal expansion data on the component parts of the web and appear to be a factor contributing to the surprising dimensional stability effects observed in practicing this invention, e.g., substantial flatness and low shrinkage. In short, thermal expansion data indicate that the combination of the component parts of this invention possesses properties not inherent in these parts individually.

As will be apparent from this description, a high level of dimensional stability is obtained according to this invention by blending a raw nonwoven web from (1) at least 15 weight % discontinuous synthetic fibers which are at least partially heat softenable at temperatures below 200° C., which fibers may have a temperature-dependent linear thermal expansion coefficient, with (2) 10–75% by weight of fibers resistant to temperatures of at least 250° C. which also may have a linear thermal expansion coefficient with some degree of temperature dependency. The raw web thus obtained is then impregnated with a curable resin impregnant which cures to a moisture insensitive, electrically insulative material. This combination of materials can provide a backing with a substantially constant linear expansion coefficient, preferably below 30×10^{-6} per °C., at least throughout a temperature range from normal ambient (20°–25° C.) up to 120° C. and preferably up to 160° C. The impregnated web is clad with an electrically conductive substance (i.e., conductor, or semiconductor), which will ordinarily have a linear thermal expansion coefficient of less than 30×10^{-6} per °C., preferably less than 25×10^{-6} per °C., e.g. nickel, copper, aluminum, and precious metals such as silver and gold. Insofar as the practice of this invention is concerned, these metals have substantially constant, i.e., temperature-independent, thermal expansion coefficients.

For purposes of this application, the term "moisture insensitive" denotes a moisture absorption which is less than the raw fiber blends used in this invention, i.e., less than 6% and preferably less than 5% (by weight) after 3 days at 95% relative humidity.

The term "resistant to temperatures of at least 250° C.," as used in relatin to fibers, means, in its broadest aspect, a fiber which can be exposed to temperatures up to 250° C. (e.g., from floating on a hot solder bath) for 10 seconds or more and exhibit little or no shrinkage due to melting, relief of strains, disorientation of molecular structure, or similar physical or chemical changes. Fibers which satisfy this criterion include the

aromatic polyamides described previously and high-melting and/or degradation-resistant cellulosic fibers, preferably regenerated cellulose fibers such as rayon. Using known spinning techniques, fibers can be made from heat resistant, dimensionally stable polyimides, e.g. polymers formed from aromatic diamines such as 4,4'-diaminodiphenylether and aromatic di-anhydrides such as pyromellitic anhydride. The resulting fibers are resistant to temperatures up to 250° C. and are low in thermal expansion. The heat resistant fibers most preferred for use in this invention, when tested at room temperature after 24 hours exposure to dry air at 260° C., have at least 60% of the pre-exposure breaking strength. These fibers also preferably have a linear expansion coefficient less than about 30×10^{-6} /°C. at temperatures below 120° C.

The raw (i.e. unimpregnated) nonwoven webs used in this invention can be prepared by a series of known steps. First, the desired blend of discontinuous fibers of aromatic polyamide and polyester is made into a nonwoven web, preferably by a conventional air-laying process, e.g., Rando-webbing or garnetting. Second, the fluffy, air-laid nonwoven web is needle-loomed or otherwise processed by increase density and/or provide strength and uniformity. Third, the nonwoven, needle-loomed web is preferably hot pressed and/or calendered to further increase strength by autogenously bonding the web and increasing both density and strength. The length of the staple fibers should be consistent with the objectives of good tear strength and ease of web formation. Rando-webbing, garnetting or equivalent air-laying processes are convenient to use with staple fibers longer than about 0.3 cm and preferably longer than about 1.5 cm. Fibers longer than about 8 or 10 cm are not convenient to use even on a garnett.

Whatever the web-forming technique, it is preferred that the discontinuous aromatic polyamide and polyester fibers of this invention be monofilament staple having filament diameters greater than 5 but less than 35 microns, or roughly 0.5 – 10 denier. The aromatic polyamide staple comprises a polyamide which is preferably of the type disclosed in the aforementioned Hill, et al., and Clay patents, i.e.,

$$+NR_1—Ar_1—NR_1—CO—Ar_2—CO+_n.$$

Among these preferred polymers are those wherein R_1 is hydrogen and Ar is a meta- or para-phenylene radical, e.g. poly(m-phenylene-[diamine]isophthalamide). These preferred polymers substantially maintain their physical properties at temperatures above 300° C. They do not melt, but degrade rapidly above 370° C. The index of polymerization ("n") should be high enough to provide the high molecular weights used in spun filaments. Other aromatic polyamides, e.g. those of the formula $+NR_1—Ar_1—CO+_n$ also are well known in the art for their desirable thermal properties; see the aforementioned Hoffman, et al., and Preston, et al., patents.

The preferred polyester fibers comprise polyesters of the formula

$$+O—A—O—CO—Ar—CO+_n$$

wherein A is a divalent straight chain or cyclic aliphatic radical, Ar is a divalent aromatic radical, e.g. meta- and/or para-phenylene and n is the index of polymerization. These polyesters are prepared in a known manner from difunctional alcohols, e.g. ethylene glycol, propylene glycol, and 1,4-cyclohexanedimethanol, and difunctional carboxylic acids (or esters thereof), e.g., terephthalic acid, isophthalic acid, and mixtures thereof. Fibers and filaments made from these polyesters are readily available, e.g. "Dacron" (a trademark of duPont Co.), which is drawn poly(ethyleneterephthalate). The polyester fiber need not be drawn (i.e., stretched or oriented and crystalline in structure) and can be undrawn (non-oriented and substantially amorphous); in fact, at least some of the polyester staple should be undrawn.

The raw nonwoven webs of this invention can comprise the following fiber blend:

Staple Fiber	Wt. %
Drawn polyester (as described previously)	0 – 60
Undrawn polyester (as described previously)	15 – 60
Aromatic polyamide (as described previously)	10 – 75

An important feature of this fiber blend is that it contains at least 15 wt. % undrawn fibers, which begin to soften at temperatures below 100° C., e.g. 75° C. The balance of the fibers (both the drawn polyester and the aromatic polyamide) do not even begin to soften at such low temperatures. The drawn polyester starts to soften at higher than 200° C., e.g., 250° C., and the aromatic polyamide resists temperatures above 250° C. and even above 300° or 350° C.

The concentration of drawn polyester fiber can and should fall below 10 wt. % (even to zero) as the heat resistant aromatic polyamide fiber concentration approaches 75 wt. %, e.g. 65 wt. % or more. However, as this heat resistant polyamide component approaches the lower limit of 10 wt. %; at least some drawn polyester fiber should then be present to provide more fibers which resist softening in the 150° – 250° C. range. For example, if the concentration of aromatic polyamide fiber is less than 25 wt. %, the drawn polyester fiber concentration should be at least 25 Wt. %. The optimum fiber blend is therefore;

Staple Fiber	Wt. %
Total of drawn + undrawn polyester (for total polyester component, drawn:undrawn ≦ 30/70 at 35 wt. %; drawn;undrawn ≧ 30/70, but < 2:1, at 75 wt. %)	35 – 75
Aromatic polyamide	65 – 25

It should be noted that either excessive aromatic polyamide (more than 75 wt. %) or excessive polyester (drawn + undrawn more than 90%) fiber concentrations will result in a non-woven backing having poor dimensional stability and significant distortion of a metal-clad backing can be expected during printed circuit fabrication procedures.

The moisture sensitivity and flexibility of the raw webs is also a significant factor in this invention. The water absorption of a raw web containing less than 75 wt. % aromatic polyamide fiber (determined on a bone-dry specimen conditioned for 3 days at 95% relative humidity) is less than about 6% and can easily be brought below 5% by increasing the polyester fiber component. The moisture absorption can be further reduced by selecting a moisture-insensitive thermosettable resin, e.g., the resins described in U.S. Pat. No.

3,027,279 (Kurka, et al.), issued Mar. 27, 1962. However, problems caused by the moisture sensitivity of webs containing more than 75% aromatic polyamide fibers are not eliminated by resin coating or impregnating. When such high-polyamide, resin-coated or -impregnated webs are metal-clad and subjected to the conditions of soldering, serious blistering of the metal cladding occurs. This blistering is substantially eliminated by the fiber blends of this invention, particularly with the lower aromatic fiber concentrations. It is not necessary to resort to minimum aromatic polyamide fiber content to eliminate solder blistering, however. For example, no visible blistering occurs with a web containing 50% poly(m-phenylene isophthalamide) and 50% poly(ethyleneterephthalate) staple fiber and impregnated with the Kurka, et al., polymer, even though this impregnated web has a moisture absorption of about 2% (3% for the raw web).

The raw (unimpregnated) web must be porous to permit impregnation. The Gurley value (ASTM test D 726, method A) for the raw webs preferably is less than 100 seconds per 100 cc of air when determined on a single 0.125 mm layer of nonwoven material. The raw web is preferably not so open or so loosely laid as to have no Gurley value whatever, however. If 10 thicknesses of nonwoven material of this invention are super-imposed, and 300 cc instead of 100 cc of air are forced through the resulting 1.25 mm thickness of material, a Gurley value of at least 0.5 second and generally at least 1 or 2 seconds will be observed. In industrial practice, the raw web has a thickness of less than about 0.5 mm and preferably less than about 0.4 mm. The weight of a 2880 or 3000 square foot ream of the raw web can range from about 45 to about 75 pounds, i.e. about 75 – 135 g/m^2, preferably 50–65 lbs. per 2,880 ft.^{2} ream (23–30 kg per 260 m^2). Greater thicknesses could result in an undue loss of flexibility after metal-cladding of the backing. It is essential for rapid, efficient, and continuous printed circuit manufacture that the metal-clad backing (the metal-clad, impregnated web) be flexible enough to be passed around rolls and the like. A backing web or film that was stiffer than 10 mil (.25 mm) biaxially oriented poly(ethyleneterephthalate) film (e.g. 10 mil "Mylar" film, trademark of E. I. duPont and Company) would be insufficiently flexible for continuous industrial printed circuit manufacture; in fact, the flexibility of 5 mil (.13 mm) "Mylar" (which measures 700 mg on the "Gurley Stiffness Tester" available from W. and L. E. Gurley Co. of Troy, N.Y.) is considered about standard for flexible backings now used in industry. The printed circuit backings of this invention are at least as flexible as 10 mil (0.25 mm) Mylar film and can be more or less flexible than 5 mil (.13 mm) Mylar, depending on the flexibility of the resin impregnant, etc. In some printed circuit applications, the backing can be as flexible as desired; in others, a minimum stiffness, e.g. a Gurley Stiffness value of more than 100 mg. is required. A typical circuit backing of this invention has a Gurley Stiffness value of about 500 mg.

The class of thermosettable resins used to impregnate the raw webs of this invention are any of those prior art resins which can be cured, without undue shrinkage, to form coatings or layers with good electrical insulative properties, low moisture sensitivity, and good thermal and mechanical properties, including good flexibility. Prior to cure, the resin composition should be fluid enough to impregnate a porous web. Resins which cure by a condensation mechanism that liberates water (e.g. urea-aldehyde, melaminealdehyde, and phenol-aldehyde resins) are less preferred, since moisture absorbed in the web can cause blistering during a soldering operation. Thermosettable polyurethanes and silicones can be used, as can thermosettable (unsaturated) polyesters, acrylic resins, and the like. A problem with curable polyesters is that shrinkage can occur during curing and must be taken into account. Curable epoxy systems, e.g., conventional polyhydric phenol-polyglycidyl ether compositions, are suitable insulating impregnants. A particularly suitable insulative epoxy composition comprises a blend of (1) a branched-chain, acid-terminated polyester of dicarboxylic acid, dihydroxy alcohol and a polyfunctional compound selected from the class consisting of polyhydric alcohols having at least three non-tertiary hydroxyl groups and polybasic acids having at least three carboxyl groups, not more than one-half of the total of said acids and alcohols containing aromatic rings, which polyester contains an average of 2.1 to 3.0 carboxyl groups per molecule, has an acid number of 15-125, a hydroxyl number of less than 10, and is free from ethylenic unsaturation in its skeletal chain, and (2) an epoxy compound containing on the average at least 1.3 groups readily reactive with the carboxyl group, at least one of which groups is the oxirane group, said groups being separated by a chain of at least two carbon atoms, the chain being free from ethylenic unsaturation. See U.S. Pat. No. 3,027,279 (Kurka, et al.), issued Mar. 27, 1962. For example, an epoxy-polyester composition of this type can comprise a blend of (1) a polyester derived from adipic acid, isophthalic acid, propylene glycol, and trimethylol propane, and (2) a liquid epoxy resin such as the polyglycidyl ether of bisphenol A or resorcinol, the condensation product of 1,1,2,2-tetrakis (4-hydroxylphenyl)ethane and epichlorohydrin, limonene dioxide, cyclopentadiene dioxide, vinyl cyclohexene dioxide and/or 3,4-epoxy-6-methylcyclohexylmethyl-3,4-epoxy-6-methylcyclohexane carboxylate.

The weight ratio of web to impregnant in the backings of this invention ranges from 1:1 to 1:4 and is preferably about 2:3.

The resulting impregnated backings of this invention can be provided with a conductive layer on one or both surfaces in a conventional manner, e.g., with suitable adhesives or by an electroless plating process which provides enough of a metal deposit to permit electroplating. Suitable conductive layers include foils of copper, aluminum, nickel, silver, gold, or suitable transition metals. The thickness of the metal foil is commonly on the order of about 0.02 – 0.05 mm. The resulting impregnated, nonwoven web/metal foil laminate is, as has been pointed out, particularly useful for forming a printed circuit, though it can itself serve as a capacitor or as a structural material, e.g., a protective or heat reflective lining. After metal cladding, a conductor pattern can be provided on the nonwoven backing by selectively etching off portions of the metal foil in a conventional manner. The etched laminates can then be floated upon or immersed in a solder bath for several seconds in the conventional manner, the temperature of the solder bath being at least 230° C. and even as high as 340° C. This solder bath treatment is conventionally used to solder on previously attached electrical or electronic circuit connections and/or com-

ponents such as resistors, transistors, semiconductor diodes, capacitors, etc. The resulting printed circuit is illustrated in the Drawing. This circuit **10** comprises a nonwoven fibrous web **11.** One surface **13** of this web supports electric circuit portions **15,** and a circuit component **17** is electrically connected between two of the circuit portions.

For both single-clad (foil/web) and double-clad (foil/web/foil) laminates, it is highly desirable that the nonwoven backing be at least semi-transparent to facilitate inspection by the manufacturer for proper adherence of cladding and/or register of top and bottom cladding. It is a feature of this invention that the nonwoven webs are inherently transparent or semitransparent.

As the skilled technician will readily appreciate, printed circuit manufacturing technology places severe demands upon the dimensional stability of the backing and the adherence of the metal cladding thereto. For purposes of this description, the following measurement has been devised to compare the distortion of various backings of this invention and the prior art:

1. an impregnated, double-clad laminate is prepared in a standardized manner, the cladding being 1.4 mils (.035 mm) of copper;

2. the laminate of step (1) is cut to a 3 inch × 3 inch (7.62 cm × 7.62 cm) test sample size;

3. one side of the laminate is protected with masking tape and all of the copper cladding is etched (with ammonium persulfate etchant solution) from the other side to maximize distortion. The etched laminate is dried for 30 minutes at room temperature. The first measurement of distortion is them made;

4. the laminate of step (3) is heated to 250° F. (121° C.) for 30 minutes to simulate typical printed circuit processing steps. The second measurement of distortion is then made;

5. the laminate of step (4) is immersed for 10 seconds in a tin-lead solder bath maintained at 450° F. (232° C.). A third measurement of distortion is made after this step.

The distortion measurements are made by placing the etched and/or heated 3 inch × 3 inch (7.62 cm × 7.62 cm) sample which would be more or less warped or curved, on a flat surface so that the concave curved surface of the sample will form an arch over the flat surface. The distance from the flat surface to the top of the arch is the "distortion." A distortion of less than about 0.125 inch (about 3.2 mm) is considered very good.

Solder blistering is tested for by conditioning the laminate of step (3) with controlled humidity conditions and subjecting the preconditioned laminate to step (5). Any blistering which occurs is caused by escaping moisture which blows or puffs up or otherwise delaminates the copper.

In addition to the lack of solder blistering and distortion, another desirable feature of the metal-clad laminates of this invention is their low shrinkage. This low shrinkage is further evidence of good dimensional stability. Still another desirable property of the backings of this invention is good tear strength.

The invention is illustrated by the following nonlimiting Examples.

EXAMPLE 1

A. Formation of Raw Nonwoven Web

The following fiber mixture was weighed, then opened and blended together on a fiber blender:

	Parts by Weight
poly(m-phenyleneisophthalamide) Staple (under the trademark "Nomex" aromatic polyamide), 2 denier × 1.5 inches (3.81 cm)	50
undrawn poly(ethyleneterephthalate), 3 denier × 1.5 inches (3.81 cm), available as "Celanese type 450" (trademark)	50

The well blended mixture was then formed into a web on a Rando Webber machine at a speed of about 5 feet per minute (1.52 m/sec.). After the web was formed, it was then passed through a needle loom machine where the light fluffy web was needled for greater strength and uniformity. After this, and in the same operation, the web passed through steel nip rolls which were heated to 375° F. (190° C.). This densified the web, and at this point the web thickness was about 12 mils (0.31 mm). The web was then densified more by running through oil heated calender rolls at 475° F. (246° C.) and 5,000 pounds (2275 kg) nip pressure, two passes. After this operation, the web caliper was 8 mils (.20 mm) and the web weight was 3.0 ounce/sq. yard = 60 pounds per ream (102 g/m²). The web was porous, dense and tough.

B. Formation of Circuit Backing from Raw Web

The raw web produced in Part A of this Example was dip coated with the epoxy-polyester resin of Example 2 of U.S. Pat. No. 3,027,279; i.e., the reaction product of adipic acid/isophthalic acid/propylene glycol trimethylolpropane polyester, an epichlorohydrin-bisphenol A epoxy resin, and tris (2,4,6-dimethylaminomethyl) phenol. This resin coating was cured for 30 minutes at 400° F. (205° C.). The resulting impregnated web had a caliper of 10 mils (.25 mm), good tear strength, and an 80:20 ratio (by weight) of resin-to-fiber (i.e., resin:raw web).

C. Copper Cladding Procedure

An adhesive coat (same resin composition used in Example 1-B) of about 1 mil (0.025 mm) dry thickness (both sides) was applied over the first cured coat. This was dried and B-staged for 20 minutes at 300° F. (149° C.). One ounce per square foot (0.03 g/cm²) Treatment A copper (Circuit Foil Corporation) was then laminated to both sides by passing through the nip of pressure rolls heated to 280° F. (138° C.). One roll was steel; the other was rubber. After laminating, the adhesive was cured 15 minutes at 400° F. (205° C.). The resulting flat, double-clad laminate was flexible and had an overall thickness of 14.8 mils (.392 mm). The copper was found to be securely bonded to the backing.

D. Coefficient of Thermal Expansion

A second copper-clad sample was made according to Parts A through C of this Example. The copper cladding was completely etched off to provide a nonwoven, impregnated web, the overall caliper of the dielectric being 12 mils (0.30 mm). The linear thermal expansion coefficient was measured throughout the temperature range of 30° – 160° C. and found to be 17×10^{-6} per °C. A one ounce per square foot (0.03 g/cm²) Treatment A copper foil (Circuit Foil Corp.), 1.4 mils (0.035 mm) in thickness, was found to have a linear expansion coefficient of 18×10^{-6} per ° C. in this temperature range, a value which agrees well with the literature value of 17×10^{-6}/°C.

EXAMPLES 2–4

The method of Example 1(A) was used to make webs of varying fiber content, with the following exceptions: a garnett machine was used to both blend the fibers and prepare the light, fluffy webs. The densification procedure was with a platen press instead of nip rolls and was as follows:

Examples	Platen Press Conditions
2 and 3	325° F. (163° C.), 500 psi (35 kg/cm²), 15 min.
4	450° F. (232° C.), 500 psi (35 kg/cm²), 15 min.

The fiber blends were:

Example	Staple Fiber	Wt. %
2	"Nomex" (see Example 1(A))	10
	Undrawn polyester (see Example 1(A))	40
	Drawn poly(ethyleneterephthalate) 3 denier × 1.5 in. (3.81 cm.) ("Celanese Type 410")	50
3	"Nomex" (see Example 1(A))	25
	Undrawn polyester (see Example 1(A))	50
	Drawn polyester (see Example 2)	25
4	"Nomex" (see Example 1(A))	75
	Undrawn polyester (see Example 1(A))	25

The resulting raw webs of Examples 2, 3 and 4 measured 4.5, 5.8, and 6 mils (0.114, 0.147, and 0.152 mm) in thickness, respectively.

Example 1, Parts B and C, were followed in making printed circuit backings, except that a platen press was used in the copper cladding procedure, the conditions being 400° F. (205° C.) and 125 psi (8.75 kg/cm²) for 30 minutes. The thickness and resin/raw web ratio of the impregnated webs were measured, as follows:

Example	Thickness, mils	Resin: Raw Web Ratio (by wt.)
2	6.8 (.173 mm)	54:46
3	7.6 (.193 mm)	57:43
4	8.9 (.226 mm)	70:30

EXAMPLE 5

A. Distortion Tests

The distortion test outlined in the portion of the specification preceding these Examples was followed by 3 in. × 3 in. (7.62 × 7.62 cm) samples cut from the laminates of Examples 1–4. To provide a standard of performance for the insulative materials of this invention, the procedure of Example 1 was followed to provide double-clad laminates from the following backings:

Backing (I): An all-polyester web, i.e.

50/50 drawn/undrawn poly(ethylene-terephthalate), as "Kendall M-1482";

thickness, raw web	5 mils (.127 mm)
thickness, impregnated web	7.5 mils (.191 mm)
resin: raw web ratio (by wt.) of impregnated web	57:43

Backing (II): An all "Nomex" (see Example 1(A)) web, i.e.

Porous nonwoven web comprising 100% "Nomex" fiber bonded with 10 wt. % thermosetting acrylic binder, as "Kendall ST-477.1";

thickness, raw web	3 mils (.076 mm)
thickness, impregnated web	7 mils (.178 mm)
resin: raw web ratio of impregnated web	78:22

The double-clad laminates obtained from Webs (I) and (II) had 1.4 mil (.035 mm) copper foils laminated to each side.

The results of the distortion tests are given in the following table:

TABLE I

DISTORTION OF DOUBLE-CLAD BACKINGS

Laminate	Wt. % "Nomex" in fiber blend	Distortion, flat surface to top of arch, inches (mm) After Etch	250°F. (121°C.) 30 min.	450° F. (232° C.) solder
Double-clad Backing (I)*	0	0.63 (16)	0.88 (22)	1.00 (25.4)
Ex. 2*	10	0.44 (11)	0.82 (21)	0.69 (18)
Ex. 3*	25	0.13 (3.3)	0.13 (3.3)	0.13 (3.3)
Ex. 1*	50	0.09 (2.3)	Flat (0.0)	0.03 (0.8)
Ex. 4**	75	0.33 (8.4)	0.32 (8.1)	0.19 (4.8)
Double-clad Backing (II)**	100	0.38 (9.7)	0.32 (8.1)	0.75 (19)

* Distortion characterized by bowing toward the backing.
** Distortion characterized by bowing toward the unetched copper cladding.

B. Solder Blistering Tests

The soldering blistering test (450° F. [232° C.] solder), also outlined previously, was carried out for an identical set of samples. The samples were etched and dried as described previously and conditioned for 24 hours at 50% relative humidity. Solder blistering was not detectible with 0 – 50 wt. % Nomex fiber content. Some slight solder blistering can occur at 75 wt. % Nomex fiber content. The 100% Nomex sample (Backing (II))) was quite obviously blistered.

The 3 day/95% R.H. moisture absorption of the resin impregnant of Example 5(B) is only about 1%, and this is typical of resinous electrically insulating coating and impregnating compositions.

C. Coefficients of Thermal Expansion

The linear expansion coefficient of Backing (I) was obtained by etching off all the cladding and determining the coefficient in both the machine direction and cross direction of the web at 30° –100° C. and 100° –160° C. The results were as follows:

TABLE II

THERMAL EXPANSION OF ALL-POLYESTER WEB

	Linear Expansion Coefficient, in./in. or cm/cm per °C.	
Temperature Range	Machine Direction*	Cross Direction*
30 – 100° C.	30×10^{-6}	46×10^{-6}
100 – 160° C.	66×10^{-6}	100×10^{-6}

* The terms "machine direction" and "cross direction" refer to the manner of laying of fibers into a web structure, and are determined by the type and operation of the web-making machine.

The reported linear expansion coefficient for Nomex (see Example 1) fiber of yarn is 20×10^{-6} per °C. However, a commercially available 5 mil (0.127 mm) Nomex fibrid paper had, in the machine direction, a linear expansion coefficient of 11×10^{-6}/°C. at 70° –120° C. and 35×10^{-6}/°C. at 120° –155° C. Thus, the expansion coefficient data of webs made according to this invention (see Example 1(D)) further reflects significant advantages in dimensional stability over all-polyester webs (see Table II) and commercially available poly(m-phenyleneisophthalamide) papers.

What is claimed is:

1. A sheet-like nonwoven web impregnated with an electrically insulative, moisture-insensitive thermoset resin, said sheet-like nonwoven web being formed from a fiber blend comprising between 15 and 60 weight % undrawn polyester staple fibers at least partially heat softenable at temperatures below 200° C. 0 up to 60 weight percent drawn polyester staple fiber, and, in intimate admixture with said undrawn polyester staple fibers, at least 10 but no more than about 75 weight % discontinuous aromatic polyamide staple fibers.

2. A sheet-like nonwoven web according to claim **1** wherein said fiber blend contains 25–65 weight percent of said aromatic polyamide staple fibers.

3. A sheet-like nonwoven web according to claim **1** wherein said web is formed from a fiber blend comprising drawn and undrawn polyester staple fiber and heat resistant aromatic polyamide staple fiber, the amount of said drawn polyester staple fiber being no more than twice the amount of said undrawn polyester staple fiber.

4. A flexible, sheet-like article, said article being less than 20 mils in thickness and being at least as flexible as a 10-mil thick biaxially oriented poly (ethylene terephthalate) film said article comprising a sheet-like nonwoven web impregnated with an electrically insulative, moisture-insensitive thermoset resin, said sheet-like nonwoven web, prior to impregnation, having a Gurley value, ASTM Test D 726, Method A, of less than 100 seconds per 100 cc of air per 5 mils of thickness, said sheet-like nonwoven web comprising:

0 – 60 weight per cent drawn polyester staple fiber;

15 – 60 weight per cent undrawn polyester staple fiber, and

10 – 75 weight per cent aromatic polyamide staple fiber,

said sheet-like nonwoven web being autogenously bonded.

5. An article according to claim **4** wherein the amount of said drawn polyester staple fiber is no greater than twice the amount of said undrawn polyester staple fiber.

* * * * *