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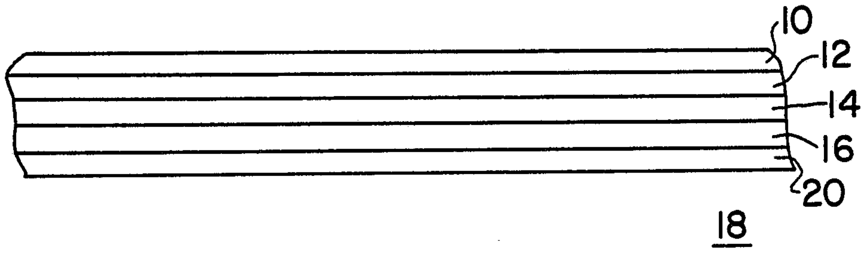

(57) Abstract

A multilayer "leather-like" laminated composite with improved qualities of chemical resistance after abrasion, toughness and flexibility is disclosed. The basic building block is comprised of a fluoropolymer film combined with an impregnated non-woven substrate. A four layer composite is disclosed which is made of a first layer of film (10) principally comprising PTFE laminated to a second layer (12) comprising an impregnated non-woven substrate, a third barrier layer (14) laminated to the non-woven substrate and a fourth layer of woven glass (16) substrate coated with a fluoropolymer is laminated to the barrier layer. In addition, a five layer embodiment adds a layer of fluoropolymer-containing film (20) adhered to the fourth layer of woven glass substrate. The composites are useful in the manufacture of protective articles and garments in which flexible, abrasion and chemical resistance qualities are desired.

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Description

FLEXIBLE MULTILAYER FLUOROPOLYMER LAMINATE

Background of the Invention

This invention relates to flexible fluoropolymer-containing composites. More particularly, the invention relates to "leather-like" multilayer laminated composites which exhibit improved qualities of abrasion resistance, chemical permeation resistance, toughness and flexibility. The invention further relates to protective articles, including garments, made from such improved composites.

Protective articles currently available provide varying degrees of chemical resistance. Garments can be made from non-woven spun-bonded polyethylene (TYVEK) or polyester (SONTARA), and from laminates of TYVEK with polyethylene or SARAN. In addition, materials such as butyl or neoprene elastomers, fluoroelastomers and chlorinated polyethylene can be used in protective articles. For example, U.S. Patents Nos. 4,421,878 and 4,423,183 teach that cured fluoroelastomer films (VITON) may be useful in coating safety apparel. These materials, however, are permeable to or degraded by some classes of chemicals, and are not resistant to the complete spectrum of toxic and hazardous materials encountered in hostile environments. Furthermore, garments made from these materials require flame resistant oversuits where both chemical and fire protection are necessary.

In U.S. Patent No. 4,165,404, a process is taught for producing coated laminates of knit or woven fabrics with a thick fluorinated copolymer sheet using an interlayer of low melt viscosity copolymer. The composites thus formed are not sufficiently flexible for use in garments, and are structured as to be specifically suitable for molding rigid articles.

Fire retardant protective garments have been made using spun lace reinforcements such as Nomex® SL. Such materials exhibit questionable chemical resistance behavior, however, related to the substantial internal porosity of the spun lace. Previous efforts at coating Nomex® spun-lace fabrics to achieve a material which is both chemically and fire resistant have resulted in mechanically deficient products.

It is often desirable for protective articles, including garments, to be able to withstand the deleterious effects of abrasion and flexing while still maintaining superior resistance to chemical permeation. Such protective articles must be able to withstand this mechanical action in order to meet specifications promulgated by the National Fire Protection association (NFPA). Certification to such specifications is intended to provide assurance that the protective articles used by firefighters and other safety personnel are characterized by performance which is satisfactory during extremely severe use conditions.

Prior art protective composites, as described above, exhibit poor abrasion resistance. For example, after surface abrasion with 80 grit sandpaper in accordance with NFPA test standard 1991, CHALLENGE® 5200, a fluoropolymer based composite manufactured in accordance with the teachings of U.S. Patent 4,943,473 and which has excellent chemical permeation resistance, suffers severe surface abrasion which substantially disrupts one of the chemically resistant layers, resulting in breakthrough of aggressive solvents such as carbon disulfide or methylene chloride (at a rate of 0.14ug/cm^2-min) within minutes. As a consequence, in order to protect the chemically resistant material from abrasion and to meet NFPA certification requirements, it is necessary to use costly and cumbersome protective oversuits. These oversuits also cause the process of decontamination of the suit after exposure to chemicals to be much more involved and difficult. It is therefore desired to improve the permeation resistance after abrasion of laminated composites to provide suitable materials for fabrication into protective articles and garments for use in a potentially abrasive environment without the need for additional protective oversuits.

Other prior art products which exhibit poor resistance to chemical permeation after abrasion include (a) suits made from thick, elastomeric materials, such as neoprene or chloroprene, which rely upon the bulk of the elastomer to provide chemical resistance for a satisfactory period of time, and (b) suits made from fluoropolymer films laminated to nonwoven substrates. Prior art products of type (a) are disadvantageous in that they are heavy, retain body heat, are attacked by some chemicals, or are able to absorb some chemicals into the body of the suit. Prior art products of type (b) are disadvantageous in that they are difficult to fabricate and can be very prone to damage through snagging and tearing.

One method of improving the resistance of a composite to chemical permeation after abrasion is to fabricate the composite with a thick, chemically resistant outer layer. A thick outer layer is less likely to be fully eroded after abrasion. However, the use of a thick outer layer can lead to an increase in the total thickness of the composite and will considerably diminish the flexibility of the composite. Protective articles, including garments made from this thicker and less flexible composite, are then cumbersome and unwieldy in use. Additional problems with such composites include the practical difficulty of fabricating them into articles along with an increased cost of material.

It is therefore an object of the present invention to provide laminated composites whose desired qualities of chemical resistance can withstand the effects of normal abrasion, yet which are tough and flexible such as to be suitable for fabricating protective articles, particularly garments.

This and other objects as described above are achieved by the present invention in a "leather-like" multilayer, multiple substrate material which provides the combination of desirable properties including superior chemical permeation resistance, abrasion resistance, toughness and flexibility.

Summary of the Invention

The composite of the present invention is a flexible fluoroplastic and/or fluoroelastomer containing material comprising wear and abrasion resistant elements with good thermal resistance, chemical stability and recoverable mechanical extensibility; chemically inert elements which serve as a barrier to permeation; and fibrous reinforcements which contribute mechanical strength and dimensional stability to the composite.

The wear and abrasion resistant elements of the invention composite comprise a fluoropolymer impregnated non-woven (including knit) textile which provides a measure of recoverable extensibility with low flexural modulus. This element also exhibits low thermal conductivity which provides heat shielding.

The permeation barrier elements of the present invention are, preferably, fluoropolymer films based on homopolymers of TFE, CTFE, VF_2 and VF or copolymers based upon these monomers or HFP, fluoro-vinyl ethers, ethylene, and propylene. Both thermoplastic and elastomeric polymers as well as alloys of such polymers may be included in such films. Particularly preferred are the multi-layer, fluoropolymer films designated in co-pending U.S. Patent application serial number 497,785 (incorporated herein by reference) which may contain metal, mineral, ceramic or carbonaceous materials within or between individual layers of the multilayer film itself.

Alternative permeation barrier elements can be films based on non-fluoropolymer barrier films. Polymers well known as barrier materials, such as nylon, ethylene/vinyl alcohol resin (EVAL), polyester and polyvinylidene chloride (PVDC) or its copolymers may be used, either as monolayers or as a part of multilayered construction with polyolefins and/or adhesives.

Fibrous reinforcement elements of the invention composites comprise woven or knitted yarns of fiberglass, polyaramid, or other textile elements able to withstand the process temperatures associated with saturation, coating, or lamination, as required, to achieve full consolidation of the invention composite.

Typically, a coated fabric reinforcement may be laminated with one or more barrier elements and one or more wear and abrasion resistant elements. The actual number and location within the composite of each element is dictated by the anticipated environmental conditions of use, required degree of flexibility and thickness, and fabrication methodology envisioned.

For convenience of manufacture, some of the indicated elements may be combined so as to simplify their final incorporation and consolidation into the invention composite. For example, this may be accomplished by lamination.

As a preferred and convenient means of incorporation and final consolidation into a single laminate, the invention composite utilizes PTFE as a thermally activated and pressure sensitive adhesive, as described in co-pending U.S. Patent application ser. no. 305,748 (incorporated herein by reference). However, other laminating methodologies, such as that described in Canadian Patent No. 1,262,676 and in copending U.S. Patent Application serial number 497,785 (incorporated herein by reference) may be used, as well as more conventional adhesive laminating methods. This is limited only by the ability of the adhesives, or the materials of composite construction, to survive the conditions of the consolidation process.

A convenient "building block component" for producing laminates of the present invention is comprised of the fluoropolymer film combined with the impregnated, nonwoven substrate employed as a wear resistant element by lamination. This provides a flexible, extensible, abrasion resistant component whose ease of incorporation into the invention composite is greater than most materials in the prior art. This building block, which combines several critical functions into a single element, has proven useful in the design of many laminates by its combination with a variety of reinforcing elements which define its tensile strength and dimensional stability. It has also proven useful in its own right for its thermal barrier properties.

A particular embodiment of the present invention which implements this "building block" is a four layer laminate construction of a fluoroplastic-containing film, an impregnated non-woven substrate, fluoroplastic film, and woven substrate which displays and exhibits all the aforementioned properties and qualities. Another embodiment of the present invention is a five layer laminate, as disclosed, which is comprised of the four layer laminate and an additional fluoroplastic-containing film next to the woven substrate so as to provide additional chemical permeation resistance as well as comfort to the wearer of a suit.

The first layer is a film of one or more layers in which the principal component is comprised of consolidated polytetrafluoroethylene (PTFE), fluorinated ethylene propylene (FEP), perfluoroalkoxy resin (PFA) or other melt processable fluoropolymer such as polyvinylidene fluoride (PVF), polychlorotrifluoroethylene (PCTFE), ethylenechlorotrifluoroethylene (ECTFE), ethylenetetrafluoroethylene (ETFE), or fluoroelastomer, and containing a layer of unfused polytetrafluoroethylene or fluorinated ethylene propylene or a perfluoroalkoxy ether copolymer with TFE, or other melt processable fluoropolymer on at least one face thereof to promote adhesion upon lamination.

The second layer is adhered to the first layer and comprises a nonwoven substrate impregnated with fluoropolymer, fluoroelastomer, silicone, alloy or blend thereof.

The third layer, adhered to the second layer, is a film of one or more layers in which the principal component is consolidated polytetrafluoroethylene, fluorinated ethylene propylene, perfluoroalkoxy resin or other melt processable fluoropolymer such as polyvinylidene fluoride, polychlorotrifluoroethylene, ethylene-chlorotrifluoroethylene, ethylenetetrafluoroethylene or fluoroelastomer and having layers of unfused polytetrafluoroethylene, fluorinated ethylene propylene, perfluoroalkoxy resin and/or other melt processable fluoropolymer on both faces thereof to promote adhesion during lamination.

The fourth layer is adhered to the third layer and comprises a woven glass substrate coated with fluoropolymer, fluoroelastomer, silicone, alloy or blend thereof.

In the five-layer embodiment, a fifth layer is added by adhering a film to the fourth layer; this layer comprises a film of one or more layers in which the principal component is consolidated polytetrafluoroethylene, fluorinated ethylene propylene, perfluoroalkoxy resin or other melt processable fluoropolymer such as polyvinylidene fluoride, polychlorotrifluoroethylene, ethylene-chlorotrifluoroethylene, ethylene-tetrafluoroethylene or fluoroelastomer, and has a layer of unfused polytetrafluoroethylene, fluorinated ethylene propylene, perfluoroalkoxy resin or other melt processable fluoropolymer on at least one face thereof to promote adhesion during lamination.

Another variant uses the "building block" laminate with a fluoropolymer film laminated to the reverse side to provide two-sided protection, flexibility, extensibility, barrier properties and thermal resistance.

Brief Description of the Drawings

FIG. 1 is a cross sectional view of the fluoropolymer film/ impregnated nonwoven substrate "building block" of the present invention;

FIG. 2 is a cross sectional view of a four layer embodiment of a multilayer composite of the present invention; and

FIG. 3 is a cross sectional view of a five layer embodiment of a multilayer composite of the present invention.

Preferred Embodiments and Method of Making the Composites

The composites according to the invention are made by lamination techniques well known in the art, as described in the Examples which follow herein.

Referring generally to Figure 1, a basic building block 2 of the invention is shown. The building block 2 is comprised of a fluoropolymer film 4 combined with an impregnated nonwoven substrate 6.

In Figure 2, a four layer composite 8 is shown in accordance with the present invention. A first layer 10 comprises a film of one or more layers in which the principal component is comprised of consolidated polytetrafluoroethylene (PTFE), fluorinated ethylene propylene (FEP), perfluoroalkoxy resin (PFA) or other melt processable fluoropolymer such as polyvinylidene fluoride (PVF), polychlorotrifluoroethylene (PCTFE), ethylenechlorotrifluoroethylene (ECTFE), ethylenetetrafluoroethylene (ETFE), or fluoroelastomer, and containing a layer of unfused polytetrafluoroethylene or fluorinated ethylene propylene or a perfluoroalkoxy ether copolymer with TFE, or other melt processable fluoropolymer on at least one face thereof to promote adhesion upon lamination.

A second layer 12 is adhered to the first layer 10 and comprises a nonwoven substrate impregnated with fluoropolymer, fluoroelastomer, silicone, alloy or blend thereof.

A third layer 14, adhered to the second layer 12, is a film of one or more layers in which the principal component is consolidated polytetrafluoroethylene, fluorinated ethylene propylene, perfluoroalkoxy resin or other melt processable fluoropolymer such as polyvinylidene fluoride, polychlorotrifluoroethylene, ethylene-chlorotrifluoroethylene, ethylenetetrafluoroethylene or fluoroelastomer and having layers of unfused polytetrafluoroethylene, fluorinated ethylene propylene, perfluoroalkoxy resin and/or other melt processable fluoropolymer on both faces thereof to promote adhesion during lamination.

A fourth layer 16 is adhered to the third layer 14 and comprises a woven glass substrate coated with fluoropolymer, fluoroelastomer, silicone, alloy or blend thereof.

Figure 3 shows a five layer composite 18 of the present invention. The layers 10, 12, 14 and 16 are as in the four layer composite 8. A fifth layer 20 is laminated to the fourth layer 16 and comprises a film of one or more layers in which the principal component is consolidated polytetrafluoroethylene, fluorinated ethylene propylene, perfluoroalkoxy resin or other melt processable fluoropolymer such as polyvinylidene fluoride, polychlorotrifluoroethylene, ethylene-chlorotrifluoroethylene, ethylene-tetrafluoroethylene or fluoroelastomer, and has a layer of unfused polytetrafluoroethylene, fluorinated ethylene propylene, perfluoroalkoxy resin or other melt processable fluoropolymer on at least one face thereof to promote adhesion during lamination.

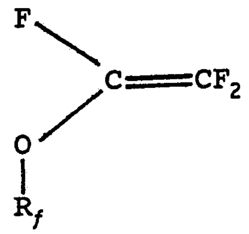
The term "fluoroplastic" as used herein shall encompass both hydrogen-containing fluoroplastics and hydrogen-free perfluoroplastics, unless otherwise indicated. Fluoroplastic means polymers of general paraffinic structure which have some or all of the hydrogen replaced by fluorine, including <u>inter alia</u> polytetrafluoroethylene (PTFE), fluorinated ethylene propylene (FEP) copolymer, perfluoroalkoxy (PFA) resin, homopolymers of polychlorotrifluoroethylene (PCTFE) and its copolymers with TFE or VF_2, ethylenechlorotrifluoroethlyene (ECTFE) copolymer and its modifications, ethylenetetrafluoroethylene (ETFE) copolymer and its modifications, polyvinylidene fluoride (PVDF), and polyvinylfluoride (PFV).

Similarly, the term "fluoroelastomer" as used herein shall encompass both hydrogen-containing fluoroelastomers as well as hydrogen-free perfluoroelastomers, unless otherwise indicated. Fluoroelastomer means any polymer with elastomeric behavior or a high degree of compliance, and containing one or more fluorinated monomers having ethylenic unsaturation, such as vinylidene fluoride, and one or more comonomers containing ethylenic unsaturation. The fluorinated monomer may be a perfluorinated mono-olefin, for example hexafluoropropylene, tetrafluoroethylene, and perfluoroalkyl vinyl ethers, e.g. perfluoro (methyl vinyl ether) or (propyl vinyl ether). The fluorinated monomer may be a partially fluorinated mono-olefin which may contain other substitutes, e.g. chlorine or hydrogen, the mono-olefin is preferably a straight or branched chain compound having a terminal ethylenic double bond. The elastomer preferably consists of units derived from fluorine-containing monomers. Such other monomers include, for example, olefins having a terminal ethylenic double bond, especially ethylene and propylene. The elastomer will normally consist of carbon, hydrogen, oxygen and fluorine atoms.

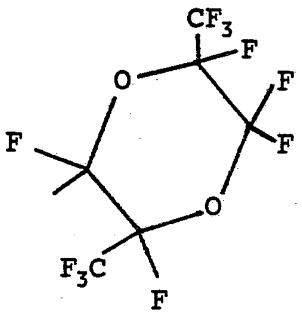
Any fluoropolymer component may contain a functional group such as carboxyl, and sulfonic acid and salts thereof, halogen as well as a reactive hydrogen on an alkyl side chain.

Preferred elastomers are copolymers of vinylidene fluoride and at least one other fluorinated monomer, especially one or more of hexafluoropropylene, pentafluoropropylene, tetrafluoroethylene and chlorotrifluoroethylene. Available fluoroelastomers include copolymers of vinylidene fluoride and hexafluoropropylene, and terpolymers of vinylidene fluoride, hexafluoropropylene and tetrafluoroethylene, sold by DuPont as VITON and by 3M as FLUOREL and by Daiken as DAIEL. Additionally, elastomeric copolymers of vinylidene fluoride and chlorotrifluoroethylene are available from 3M as Kel-F. The use of AFLAS, which is a copolymer of TFE and propylene, as manufactured by Asahi, is also contemplated.

Preferred perfluoroelastomers include elastomeric copolymers of tetrafluoroethylene with perfluoro alkyl comonomers, such as hexafluoropropylene or perfluoro (alkyl vinyl ether) comonomers represented by F



in which R_f is a perfluoroalkyl or perfluoro (cyclo-oxa alkyl) moiety. Particularly preferred are the perfluorovinyl ethers in which R_f is selected from the groups $—CF_3$, $—CF_3F_7$,



, or $-\left[CF_2\underset{\displaystyle CF_3}{CF}O\right]_N CF_2CF_2SO_2X$

where n=1-4 and X=H, Na, K or F. Particularly contemplated is KALREZ is a copolymer including TFE and perfluoromethylvinyl ether (PMVE). If desired, and is well known in the art, fillers or additives such as pigments, plasticizers, stabilizers, softeners, extenders, and the like, can be present in the matrix composition. For example, there can be present substances such as graphite, carbon black, titanium dioxide, alumina, alumina trihydrate, glass fibers, beads or microballoons, carbon fibers, magnesia, silica, asbestos, wollastonite, mica, and the like.

Substrates used according to the invention may be any suitable flexible material capable of withstanding the conditions used to form the laminate. Examples of suitable substrates include, <u>inter alia</u>, glass, fiberglass, ceramics, graphite (carbon), PBI (polybenzimidazole), PTFE, polyaramids, such as Kevlar® and Nomex®, metal such as copper or steel wire, polyolefins such as Tyvek, polyesters such as Reemay, polyamides, polyimides, thermoplastics such as KYNAR and TEFZEL, polyphenylene sulfide, polyether oxides, polyether sulfones, polyether ketones, novoloid phenolic fibers such as KYNOL, cotton, asbestos, and other natural as well as synthetic textiles. The substrate may comprise a yarn, filament, monofilament, or other fibrous material either as such is assembled as a textile, or any woven, non-woven such as spun-laced, spun-bonded, or stitch bonded, or knitted material. The substrate may alternatively comprise a film or paper. No treatment of the fabric is required, although coated fabrics may be employed if desired.

The following examples are submitted to illustrate but are not intended to limit the present invention as described herein.

EXAMPLE 1

A commercially available spunlaced non-woven Nomex® (SL™ obtained from DuPont) was impregnated with an aqueous formulation of PTFE (Teflon™ 30. DuPont) and colloidal graphite (Aquadag™ E, Achseon Colloids) containing 7% graphite by weight based on total solids. The specific gravity of the PTFE/graphite formulation was 1.10. The impregnation equipment used was the two-stage vertical oven designed to dry, bake and fuse the impregnated solids in the substrate as described in copending U.S. Patent Application Ser. No. 305,748.

The non-woven Nomex® SL is characterized as follows:

Type:	E-88
Style:	307
Weight:	0.7 oz/yd^2
Thickness:	4.5 mile
Width:	20 inches

The Nomex® SL was initially heat set at 680°F before the impregnation. Impregnation of the substrate was accomplished by a single application of the PTFE/graphite formulation. The degree of substrate saturation in this process was controlled by the web speed and solids content of the formulation. The oven temperatures used to evaporate the water and bake out the surfactants from the saturated web and leave the PTFE solids in an unfused state were as follows:

Dry Zone:	250°F
Bake Zone:	570°F
Speed:	5 fpm

The product obtained from this operation is a non-woven Nomex® substrate impregnated with unfused PTFE/graphite micro-particulate solids. This product may then be used for further processing into a leathery product by lamination with a fluoropolymer film to at least one face of the impregnated Nomex® SL. The average weight of this impregnated intermediate is approximately 2.80 oz/yd^2 at a thickness of about 7.5 mils. The conditions described above resulted in a finished web width of 16.5 inches.

In a separate operation, PTFE film was prepared by a multi-layer dispersion casting process such that the last PTFE layer cast remained unfused while the first four PTFE layer were fused. The first two fused layers consisted of PTFE derived from Teflon 30, obtained from E. I. DuPont, having a combined thickness of 0.3 mils. The third and fourth layers consisted of PTFE derived from a formulation of Teflon 30 containing 4.5% by weight based on total solids of carbon black (Velveteen Black, obtained from Kohnstamm) having a combined thickness of 0.3 mils. The fifth layer consisted of PTFE (derived from Teflon 30) having a thickness of 0.4 mils. Consequently, this multi-layer film consisted of a fused region having a thickness of 0.6 mils, and an unfused region at one of its surfaces having 0.4 mil thickness.

The PTFE impregnated Nomex® described above was then combined with the aforementioned film using a laminator which had one compressible fiber role rotating between two heated steel rolls with a face width of 50 inches. The film was adhered to each face of the impregnated substrate by placing the unfused PTFE face of each of the two film specimens and the impregnated Nomex® in direct contact under the following conditions:

Hydraulic Pressure:	1650 psig (6" diameter hydraulic cylinders)
Web Speed:	3.0 fpm
Fiber Roll Temp:	180°F
Bottom Steel Roll Temp:	350°F

While modest, the adhesion or tack so developed between the films and the substrate was sufficient to enable subsequent consolidation by thermal activation of the laminate at ambient pressure (free sintering). This consolidation was accomplished in an oven which was in-line with the hot rolls described above and under the following conditions:

Zone 1:	250°F
Zone 2:	670°F
Zone 3:	ambient
Web Speed:	3.0 fpm

Following this high temperature activation and consolidation of the unfused PTFE in the composite, the films were tenaciously bonded to the substrate yielding a leathery like material with unusual physical properties. Physical characterization was as follows:

Property	Units	Value
Weight	oz/y^2	6.45
Thickness	.001"	6.0
PTFE Content	%	82.82
Density (calc)	-	1.437 (void content ≈ 30% calc)
Breaking Strength		
Machine	lb/in	28.0 (does not yield)
Transverse	lb/in	9.4 (yields at 7.4 lb/in; i.e., 78% ult-strength
Ult-Elongation	%	
Machine Direction		21 (does not yield)
Transverse		75 (yields at ≈ 15%; i.e., 71% of ult. elongation)

Recoverable Tensile Deformation (Transverse)

<u>At Room Temperature</u>	%	54 at 8.0 lb/in stress (i.e., 85% ultimate strength)
		64+ at 7.0 lb/in stress (i.e., 74% ultimate strength)
		68 at 6.0 lb/in stress (i.e., 64% ultimate strength)
		96 at 5.0 lb/in stress (i.e., 53% ultimate strength)

The polymeric composition of this material confers upon it good thermal and chemical stability, while its mechanical behavior is characterized by substantially recoverable deformation when extended in tension. This "leathery" behavior allows it to be used as such where its conformability and deformability lends itself to subsequent thermal molding in a manner not possible with coated, woven textiles. Additionally, it exhibits good thermal resistivity by virtue of its composition and void content.

<u>EXAMPLE 2</u>

A laminate intended to exhibit improved chemical barrier properties after abrasion with 80 grit sandpaper was made, based upon PTFE impregnated commercially available spunlaced Nomex® SL extruded FEP film from DuPont, cast multilayered fluoropolymer films, and PTFE coated, woven fiberglass fabric. The mating faces of the impregnated or coated elements of the laminates as well as each film element were comprised of Teflon FEP resin, even though the bulk of each element, other than the extruded film, was Teflon PTFE. This was done to explore FEP as the main adhesive element in the overall laminate.

The spunlaced non-woven Nomex® SL was characterized as follows:

Type:	E-88 (from E.I. DuPont)
Style:	307
Weight:	0.7 oz/yd^2
Thickness:	4.5 mils
Width:	41 inches

Impregnation of the Nomex® SL was accomplished on the two-stage vertical oven designed to dry, bake and fuse the impregnated solids in the substrate as in Example 1. The initial impregnation was achieved by an application of an aqueous formulation of PTFE (Teflon® 30, DuPont) with 7% by weight based on total solids of colloidal graphite (Aquadag™, Acheson Colloids). The specific gravity of the formulation was 1.5 g/cc. The degree of substrate saturation in this process was controlled by the web speed and solids content of the formulation. The oven temperatures were set to achieve an unfused layer of solids in the substrate. The conditions were as follows:

Zone	Temperature °F	Speed, fpm
1	200	
2	190	4.5
3	200	
4	380	
5	505	
6	450	
7	ambient	

A further impregnation of this PTFE Nomex® was achieved by an application of FEP dispersion (Teflon TE-9503, DuPont) at a specific gravity of 1.15, to serve as an adhesive layer in a subsequent lamination process. The oven conditions were as follows:

Zone	Temperature	Speed, fpm
1	180	
2	200	6.7
3	205	
4	370	
5	500	
6	410	
7	ambient	

The resulting substrate was somewhat less flexible than the PTFE/graphite impregnated substrate of Example 1. The actual build achieved by each application are as follows:

Application	Weight oz/yd^2	Thickness, mils
PTFE/Graphite	2.50	7.5
FEP	4.40	9.5

Two of the three films used in this laminated composite were made using a multi-layer dispersion casting process. Each of these films contain four internal layers of pigmented PTFE sandwiched between a PFA copolymer on one face and an FEP copolymer on the other face. These copolymers layers serve both as a melt adhesive and as permeation barrier layers. All six layers were thermally consolidated by melting and quenching in the process of their manufacture. The overall thickness of the films was 1.9 mils, 0.1 mil of which was comprised of a PFA layer and 0.3 mil of which was an FEP layer. The remaining 1.5 mils consist of pigmented PTFE, on film was pigmented blue, the other white. The third film used in this laminate product was a commercially available extruded FEP film from DuPont at a thickness of 1.0 mil.

The other textile-based element used in this multilayered composite was a PTFE coated, style 116 fiberglass fabric based on PTFE derived from Teflon 30 with a surface comprised of FEP derived from TE-9503 and having a total weight of 9.5 oz/yd^2. The FEP topcoat weight was 0.9 oz/yd^2.

A laminated composite was made using these films and impregnated or coated textiles according to techniques, previously described in the embodiment of this patent and Canadian Patent No. 1262676. The equipment used for lamination was a continuous belt laminator. The construction of the composite from these elements was as follows:

Layer 1	-	1.9 mil cast, blue pigmented PTFE film with an FEP adhesive layer
Layer 2	-	impregnated Nomex® SL with PTFE/graphite and FEP adhesive layer
Layer 3	-	1.0 mil extruded FEP film,
Layer 4	-	PTFE coated style 116 fabric with an FEP adhesive layer,
Layer 5	-	2.9 mil coat, white pigmented PTFE film with an FEP adhesive layer.

The conditions used to effect lamination by the continuous belt laminator were as follows:

Platens	Temperatures, °F	Speed, fpm
1	375	2.0
2	465	
3	520	
4	555	

The resulting laminated composite had the following physical properties:

Test	Mean Value	Method
Weight (oz/yd_2)	22.0	ASTM D751
Thickness (mils)	19.3	ASTM D751
Breaking Strength (pli) (warp)	288.8	ASTM D751
Breaking Strength (pli) (fill)	238.3	
Flexford Strength (pli) (warp)	258.0	Birdair Method LP78
Flexford Strength (pli) (fill)	210.2	
Breaking Strength Retention (warp	89%	N/A
Breaking Strength Retention (fill)	88%	N/A
Trapezoidal Strength (%) (warp)	8.3	ASTM D4851
Trapezoidal Strength (%) (fill)	7.4	

Peel Adhesion (lbs)	6.2	LAM 5200 LP-62
Stiffness (mgcm)	83,687	ASTM D1388-84
Burst Strength (psi)	532	ASTM D751 Method A

The permeability of this five element, multilayered composite was tested following its subjection to abrasion by 80 grit sandpaper, according to the procedures of NFPA 1991 for vapor protective suits. Carbon disulfide and methylene chloride were used as chemical challenge agents in these tests. No detectable breakthrough (permeation at a rate >0.14) to either agent was observed for sixty minutes at which point the test was terminated.

EXAMPLE 3

A laminated composite was made which was intended to have improved flexibility and chemical barrier properties after abrasion according to the procedures of NFPA 1991 for vapor protective suits (Sections 5.2, 5.5 and 5.5). The materials used in connection of this laminate were commercially available spunlaced Nomex® SL, extruded FEP film from DuPont, dispersion cast multilayered fluoropolymer films, and style 116 woven fiberglass coated with PTFE dispersion.

The spunlaced non-woven Nomex® SL is characterized as follows:

Type:	E-88
Style:	307
Weight:	0.7 oz/yd^2
Thickness:	4.5 mils
Width:	41 inches

The equipment used to impregnate the Nomex® SL was two-stage vertical oven designed to dry, bake, and fuse the impregnated solids in the substrate. The impregnation of the substrate was accomplished by a simple application of an aqueous formulation of FEP (TE-9503, DuPont) containing 6.5% by weight based on total polymer of a silicone oil emulsion (ET-4327, Dow Corning). The degree of substrate saturation was controlled by the web speed and the solids content on the formulation. The specific gravity of the formulation was 1.15 g/cc. The oven temperature were set to dry and bake the water and surfactants from the saturated web and fuse the solids in the substrate. The conditions employed were as follows:

Zone	Temperature °F	Speed, fpm
1	300	
2	300	7.8
3	300	
4	350	
5	500	
6	450	
7	ambient	

The product obtained from this operation was a lightweight, flexible non-woven Nomex® substrate with an FEP impregnated surface. This perfluoropolymer impregnated Nomex® constitutes the abrasion resistant element of the laminated composite. The average weight of this impregnated intermediate is approximately 2.60 oz/yd^2 and its thickness is 8.5 mils.

In a separate operation, PTFE films were prepared by a multilayer dispersion casting process. Their outer surfaces were comprised of TFE copolymers enabling them to be used as melt adhesive layers in lamination and fabrication. The overall thickness of the films was 1.3 mils. The first layer of these films was 0.1 mil PFA (Teflon-335J, DuPont), the second layer was 0.3 mil PTFE (Teflon 30, DuPont). The third and fourth layers were 0.3 mil PTFE with 8% TiO_1 by weight, based on total solids (B5710, Kohnstamm). The fifth layer was a 0.3 mil FEP (TE-9503, DuPont). All five layers were thermally consolidated.

Another film element used to construct this laminated composite was a commercially available 1.0 mil extruded FEP film from E. I. DuPont. The second textile element employed in the construction of this multilayered laminated composite was an impregnated style 116 fiberglass fabric with a total weight of 9.5 oz/yd^2 including an FEP topcoat weighing 0.9 oz/yd^2.

The multilayered laminated composite was prepared using well known techniques, previously described in the embodiment of this patent and Canadian Patent No. 1262676 by means of a continuous, belt laminator. The construction of the composite is as follows:

- 1.3 mil dispersion cast white PTFE film with FEP adhesive layer,
- impregnated Nomex® SL with FEP/silicone adhesive layer,
- 1.0 mil extruded FEP film,
- impregnated style 116 fiberglass fabric with FEP adhesive layer,
- 1.3 mil dispersion cast white PTFE film with FEP adhesive layer.

The conditions for the continuous belt laminator were as follows:

Platens	Temperature °F	Speed, fpm
1	375	2.0
2	480	
3	520	
4	555	

The resulting laminated composite had the following properties:

Test	Mean Value	Method
Weight (oz/yd^2)	18.2	ASTM D751
Thickness (mils)	14.2	ASTM D751
Breaking Strength (pli) (warp)	249	ASTM D751

Breaking Strength (pli) (fill)	213	
Flexford Strength (pli) (warp)	197	Birdair Method LP78
Flexfold Strength (pli) (fill)	176	
Breaking Strength Retention (warp)	79%	N/A
Breaking Strength Retention (fill)	83%	N/A
Trapezoidal Strength (%) (warp)	11.7	ASTM D4851
Trapezoidal Strength (%) (fill)	10.6	
Peel Adhesion (lbs)	5.8	LAM 5200 LP-62
Stiffness (mgcm)	25.8	ASTM D1388-84
Burst Strength (psi)	593	ASTM D751 Method A

The finished composite was tested and found to be certifiable to the 1991 NFPA standards (Sections 5.2, 5.4 and 5.5) for vapor-protective suits for hazardous chemical emergencies, i.e., after abrasion it was found that none of the NFPA 1991 battery of chemicals permeated the material at a rate greater than 0.14 ug/cm_2-min during a one hour test. This multilayer composite design allows for a unique combination of flexibility, chemical protection and abrasion resistance in a protective garment, not obtainable up to now in suits based on a single component.

EXAMPLE 4

A laminate. intended to exhibit improved thermal stability, heat resistance, and chemical protection, was made based upon PTFE impregnated commercially available spunlaced Nomex®/Kevlar® (SL obtained from DuPont), and cast multilayered fluoropolymer film. The mating face of the impregnated elements of the laminate as well as the film element was comprised of uncured Teflon PTFE.

The non-woven Nomex®/Kevlar® SL is characterized as follows:

Type: E-89
Style: 727
Weight: 2.7 oz/yd^2
Thickness: 14.0 mils
Width: 21.5 inches

The Nomex®/Kevlar® SL was initially heat set at 680°F and 5 fpm on a vertical oven designed to dry, bake and fuse impregnated solids into a substrate. The width of the Nomex®/Kevlar® was reduced to 19.25 inches after heat setting. Impregnation was accomplished by a single application of a highly viscosified PTFE (TE-3313, DuPont) formulation, to one face of the substrate only. The high viscosity of the PTFE formulation was used to control the degree of saturation of solids into the porous substrate. The viscosity of the PTFE formulation was modified using an acrylic acid (Acrysol A5E-60, Rohm and Haas), at 0.8% by weight based on total solids, and the measured viscosity was 35,000 cps using a Brookfield RVT spindel #6 at 5 RPM and 78°F. The total weight of the impregnated substrate was 10.9 oz/yd^2. The oven temperatures used to evaporate the water and bake out the surfactants and leave the PTFE solids in an unfused state were as follows:

Dry Zone: 250°F
Cure Zone: 580°F
Web Speed: 5.0 fpm

In a separate operation, PTFE film was prepared by a multilayer dispersion casting process such that the last PTFE layer cast remained unfused while the first four PTFE layers were fused. The first and fourth layers consisted of PTFE derived from Teflon 30, obtained from E.I. DuPont, having a combined thickness of 0.65 mils.

the second and third layers consisted of PTFE derived from a formulation of Teflon 30 containing 5.0% by weight based on total solids of carbon black (Velveteen Black, obtained from Kohnstamm) having a combined thickness of 0.65 mils. The fifth layer consisted of PTFE (derived from Teflon 30) having a thickness of 0.4 mils. Consequently, this multilayer film consisted of a fused region having a thickness of 1.3 mils, and an unfused region at one of its surfaces having a 0.4 mil thickness.

The PTFE impregnated Nomex®/Kevlar® described above was then combined with the aforementioned film using a laminator which had one compressible fiber roll rotating between two heated steel rolls with a face width of 50 inches. The film was adhered to each face of the impregnated substrate by placing the unfused PTFE face of each of the two film specimens and the impregnated Nomex® in direct contact under the following conditions:

Hydraulic Pressure:	1500 psig (6" diameter hydraulic cylinders)
Web Speed:	5.0 fpm
Top Steel Roll Temp:	180°F
Fiber Roll Temp:	180°F
Bottom Steel Roll Temp:	350°F

While modest, the adhesion or tack so developed between the films and the substrate was sufficient to enable subsequent consolidation by thermal activation of the laminate at ambient pressure (free sintering). This consolidation was accomplished in ana oven which was in-line with the hot rolls described above and under the following conditions:

Zone 1:	250°F
Zone 2:	680°F
Zone 3:	Ambient
Web Speed:	5.0 fpm

Following this high temperature activation of the unfused PTFE in the composite, the films were tenaciously bonded to the substrate yielding a leathery like material with unusual physical properties.

Property	Units	Value
Weight	oz/yd^2	13.20
Thickness	.001"	16.5

The foregoing examples and description of the preferred embodiments of the invention has been presented for the purposes of illustration and description. It is not intended to be exhaustive or to limit the invention to the precise forms disclosed. Many modifications and variations are possible in light of the above teaching. It is intended that the scope of the invention be limited not by this detailed description, but rather by the claims appended hereto.

CLAIMS

We claim:

1. A non-woven textile impregnated principally with fluoropolymer.

2. The impregnated non-woven textile of claim 1 in which the textile is aramid.

3. The impregnated non-woven textile of claim 1 in which the textile forms a substrate onto which a film comprising principally PTFE is laminated.

4. The laminated textile of claim 3 in which the PTFE film is bonded to the impregnated non-woven textile substrate with a melt processable adhesive.

5. The laminated textile of claim 3 in which the PTFE film is bonded to the impregnated non-woven textile substrate with a process which uses PTFE as a thermally activated pressure sensitive adhesive.

6. The laminated textile of claim 3 in which the PTFE film comprises as minor components FEP, PFA, ECTFE, CTFE, ETFE, PVF, and/or fluoroelastomer.

7. The laminated textile of claim 3 in which the impregnated non-woven textile substrate is glass.

8. The laminated textile of claim 3 in which the non-woven textile substrate is impregnated principally with PTFE.

9. The laminated textile of claim 3 in which the non-woven textile substrate is impregnated with fluoropolymer, fluoroelastomer, silicone, alloy or blend thereof.

10. The laminated textile of claim 3 in which the film comprises one or more layers of which the principal component is consolidated polytetrafluoroethylene, fluorinated ethylene propylene, perfluoroalkoxy resin or other melt processable fluoropolymer such as polyvinylfluoride, polychlorotrifluoroethylene, ethylene-chlorotrifluoroethylene, ethylene-tetrafluoroethylene or fluoroelastomer, and having a layer of partially fused tetrafluoroethylene, fluorinated ethylene-propylene, perfluoroalkoxy resin or other melt processable fluoropolymer on at least one side thereof to achieve adhesion.

11. The laminated textile of claim 3 in which the film layer contains pigments or other colorants in order to achieve decorative effects in the finished laminate.

12. The laminated textile of claim 3 in which the film layer contains hard polymers, glass or other hard materials to provide improved abrasion and wear resistance.

13. The laminated textile of claim 3 in which the film layer contains an outside surface of melt bondable fluoropolymer to facilitate seaming and fabrication into various articles.

14. The laminated textile of claim 3 further comprising a coated or uncoated woven substrate laminated to the film.

15. The laminated textile of claim 14 in which the coated or uncoated woven substrate is further laminated to a second film.

16. A laminate comprising:

(a) a non-woven textile layer impregnated principally with fluoropolymer;

(b) a barrier layer; and

(c) a woven textile layer to provide dimensional stability.

17. A four layer laminate comprising:

(a) a first layer of film principally comprising PTFE;

(b) a second layer comprising an impregnated non-woven substrate laminated to said first layer;

(c) a third layer comprising a barrier laminated to said second layer; and

(d) a fourth layer, laminated to said third layer, comprising a woven glass substrate coated with a fluoropolymer.

18. The laminate of claim 17 in which the barrier layer comprises one or more fluoropolymers.

19. The laminate of claim 17 in which the barrier layer comprises polyamide (nylon), ethylene/vinyl alcohol (EVAL), polyester or polyvinylidene chloride (PVDC) or its copolymers.

20. The laminate of claim 17 in which the barrier layer comprises a metal foil, a glass film or other inorganic barrier layer.

21. The laminate of claim 17 in which the barrier layer is laminated with a melt bondable adhesive.

22. The laminate of claim 17 in which the lamination is accomplished using a melt bondable adhesive.

23. The laminate of claim 17 in which the lamination is accomplished via a process which uses PTFE as a thermally activated pressure sensitive adhesive.

24. The laminate of claim 17 further comprising a fifth layer comprising a fluoropolymer-containing film adhered to the fourth layer.

25. The laminate of claim 17 in which the first layer of film comprises one or more layers in which the principal component is consolidated polytetrafluoroethylene, fluorinated ethylene propylene, perfluoroalkoxy resin or other melt processable fluoropolymer such as polyvinylfluoride, polychlorotrifluoroethylene, ethylene-chlorotrifluoroethylene, ethylene-tetrafluoroethylene or fluoroelastomer, and having a layer of partially fused tetrafluoroethylene, fluorinated ethylene-propylene, perfluoroalkoxy resin or other melt processable fluoropolymer on at least one side thereof to achieve adhesion; a non-woven material is adhered to the first layer and comprises a non-woven substrate coated with fluoropolymer, fluoroelastomer, silicone, alloy or blend thereof; the barrier-containing film is adhered to the non-woven material and comprises a film of one or more layers in which the principal component of one or more of the layers is consolidated polytetrafluoroethylene, fluorinated ethylene propylene, perfluoroalkoxy resin or other melt processable fluoropolymer such as polyvinylfluoride, polychlorotrifluoroethylene, ethylene-chlorotrifluoroethylene, ethylene-tetrafluoroethylene or fluoroelastomer, and having a layer of partially fused tetrafluoroethylene, fluorinated ethylene-propylene, perfluoroalkoxy resin or other melt processable fluoropolymer on at least one side thereof to achieve adhesion and; a fourth layer adhered to said third layer comprising a woven glass substrate coated with

fluoropolymer, fluoroelastomer, silicone, alloy or blend thereof.

26. The laminate of claim 25 further comprising a fifth layer adhered to said fourth layer and comprising a film of one or more layers in which the principal component is consolidated polytetrafluoroethylene, fluorinated ethylene propylene, perfluoroalkoxy resin or other melt processable fluoropolymer such as polyvinylfluoride, polychlorotrifluoroethylene, ethylene-chlorotrifluoroethylene, ethylene-tetrafluoroethylene or fluoroelastomer, and having a layer of partially fused tetrafluoroethylene, fluorinated ethylene-propylene, perfluoroalkoxy resin or other melt processable fluoropolymer on at least one side thereof to achieve adhesion.

27. The laminate of claim 25 in which the first and fifth layers contain an outside layer of melt bondable fluoropolymer to facilitate seaming and fabrication of the various articles.

28. The laminate of claim 17 which is produced by a manufacturing operation which assembles the layers in a sequence other than that delineated.

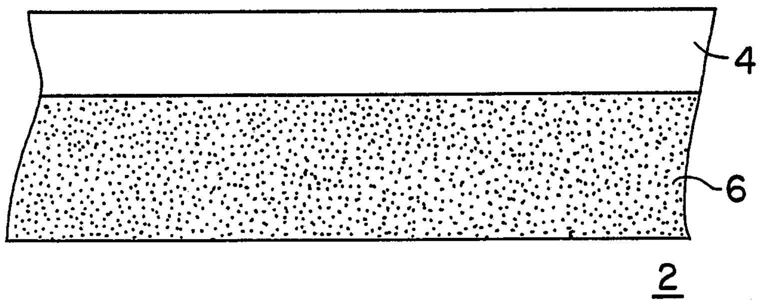


FIG. 1

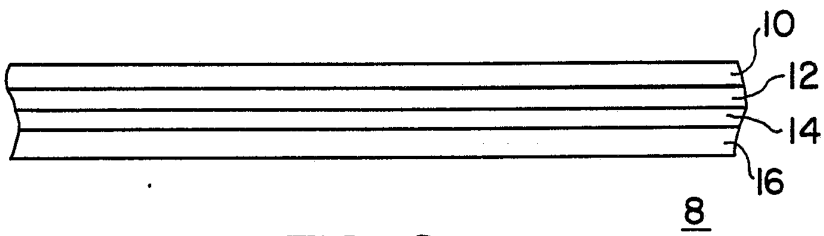


FIG. 2

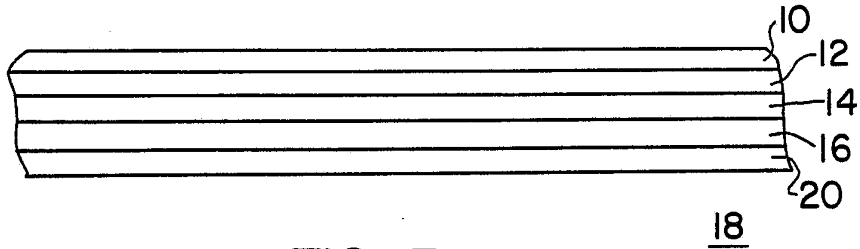


FIG. 3