

12

# EUROPEAN PATENT APPLICATION

21 Application number: 84400741.9

51 Int. Cl.<sup>3</sup>: D 06 N 7/00

22 Date of filing: 13.04.84

30 Priority: 13.04.83 US 484594

43 Date of publication of application:  
 21.11.84 Bulletin 84/47

84 Designated Contracting States:  
 AT BE CH DE FR GB IT LI LU NL SE

71 Applicant: CHEMICAL FABRICS CORPORATION  
 Water Street P.O. Box 476  
 North Bennington Vermont 05257(US)

72 Inventor: Effenberger, John A.  
 120 Elm Street  
 Bennington Vermont 05257(US)

72 Inventor: Keese, Frank M.  
 64 High Street  
 Hoosick Falls New York 12090(US)

74 Representative: Descourtieux, Philippe et al,  
 CABINET BEAU de LOMENIE 55 rue d'Amsterdam  
 F-75008 Paris(FR)

54 Novel reinforced fluoropolymer composite and method for making same.

57 A novel composite comprises a substrate having a coating matrix including an initial layer of a perfluoropolymer and an overcoat comprising a fluoroelastomer, a fluoroplastic, a fluoroelastomer/fluoroplastic blend, or a combination thereof. The perfluoropolymer in the initial layer may be a perfluoroplastic, a perfluoroelastomer, or blends thereof. In a separate embodiment, the novel composite includes a substrate coated solely with one or more layers of perfluoroelastomer alone or as a blend with a perfluoroplastic. Where the substrate is not susceptible to hydrogen fluoride corrosion, the composite may include solely one or more layers of a blend of a fluoroelastomer and a hydrogen-containing perfluoroplastic. Cross-linking accelerators may be used to cross-link one or more of the resins contained in the coating layers. Each composite may be topcoated with the layer or layers of a fluoroplastic, fluoroelastomer, and/or a blend thereof. The composite is flexible, exhibits good matrix cohesion and possesses substantial adhesion of the matrix to the material acting as the reinforcement or substrate. A method for making such a composite comprises the unique deployment of a perfluoropolymer directly onto the substrate in a relatively small amount sufficient to protect the substrate from chemical corrosion without impairing flexibility, followed by the application of the overcoat layer.

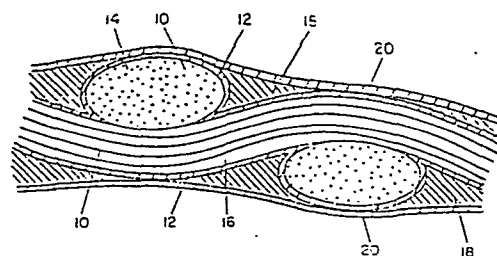


FIG. 1

Description

Novel Reinforced Fluoropolymer Composite  
And Method For Making Same

Background of the Invention

5        This is a continuation-in-part application of  
United States application Serial No. 484,594, filed  
on April 13, 1983.

10        This invention relates to new and useful fluoro-  
polymer composites comprising coated substrates. More  
particularly, the invention relates to a new fluoro-  
elastomer/fluoroplastic matrix useful as a coating in  
the manufacture of reinforced woven composites which  
are flexible, exhibit good matrix integrity, and pos-  
sess good adhesion or bonding of the coating matrix  
15        to the substrate. The invention includes composites  
which also have extraordinary chemical resistance,  
particularly at elevated temperatures and in humid  
environments. The invention further relates to a  
method of making such composites whereby the desirable  
20        high temperature, chemical inertness of fluoroplastic  
materials is combined with the desirable mechanical  
properties of fluoroelastomers in such a way as to  
maintain a desirable fabric-like flexibility.

25        Perhaps the most well-known subclass of fluoro-  
polymers are substances called "perfluoroplastics"  
which are generally recognized to have excellent elec-  
trical characteristics and physical properties, such  
as a low coefficient of friction, a low surface free  
energy (i.e., non-wetting to many organic fluids), and  
30        a very high degree of hydrophobicity. Fluoroplastics,  
and particularly perfluoroplastics (i.e., those fluoro-  
plastics which do not contain hydrogen), such as poly-  
tetrafluoroethylene (PTFE), fluoro (ethylene-propylene)  
copolymer (FEP) and copolymers of tetrafluoroethylene

and perfluoro-propyl vinyl ether (PFA), are resistant to a wide range of chemicals, even at elevated temperatures, making them particularly useful in a variety of industrial and domestic applications. However, due  
5 to the partially crystalline nature of these fluoroplastics, they exhibit a degree of stiffness or lack of compliance which is detrimental to the utilization of these desirable properties. This shortcoming is particularly noticeable and objectionable in a reinforced composite where some degree of flexibility,  
10 elasticity, and/or conformability is necessary.

The broad class of fluoropolymers also includes substances called "fluoroelastomers" which are not only elastomeric, but also possess, although to a  
15 lesser degree, the aforementioned physical and electrical properties of a fluoroplastic. Fluoroelastomers, including perfluoroelastomers, have the low flex modulus and conformability which fluoroplastics lack. The hydrogen-containing fluoroelastomers, however,  
20 do not maintain other advantageous physical properties associated with fluoropolymers over as broad a temperature range, or at as high a level, as do the perfluoroplastics. In other words, perfluoroplastics simply perform better over a wider temperature range.  
25 Moreover, the fluoroelastomers which contain hydrogen (i.e., which are partially fluorinated) generally degrade rapidly at higher temperatures resulting not only in the loss of physical integrity but also in the formation of hydrofluoric acid. Hydrofluoric  
30 acid is, of course, highly corrosive to most materials, including those normally used as reinforcing substrates for textile composites, and particularly to fiberglass substrates. For this reason, hydrogen-containing fluoroelastomer based composites presently  
35 used in high temperature environments require relatively frequent replacement. Notwithstanding these

drawbacks, fluoroelastomers containing hydrogen are considered excellent candidates for use in a variety of commercial applications requiring a lower flex modulus than that possessed by the stiffer fluoro-plastics.

In this regard, attempts have been made to employ reinforced fluoroelastomer composites where good thermo-chemical, as well as mechanical properties, i.e. low modulus, are required at higher temperatures.

One such application is in high temperature expansion joints which connect large duct sections in applications such as power plant systems. These ducts have in the past been joined at their section ends by metal bellows which, while basically chemically and thermally sound, provide minimal thermo-mechanical shock resistance under normal operating conditions, which can involve temperatures up to 550°F., or even 650°F. In an effort to improve the mechanical properties of metal expansion joints, the flexibility of an industrial fabric is desired, and fabric composites coated with fluoroelastomer based rubber compounds have been used.

These fabric composites have used various reinforcement materials, including fiberglass fabric, coated with a matrix containing a fluoroelastomer composition based on copolymers of hexafluoropropylene (HFP) and vinylidene fluoride ( $VF_2$ ) or terpolymers including HFP,  $VF_2$  and tetrafluoroethylene (TFE). The fluoroelastomer materials used all contain at least some hydrogen and, as such, are susceptible to the shortcomings associated with hydrofluoric acid elimination. Moreover, in order for the prior art fluoropolymer composites to be useful in high temperature, chemically corrosive applications, they customarily incorporate a relatively thick matrix of the fluoroelastomer based rubber, thereby increasing their

stiffness and potentially aggravating problems deriving from hydrofluoric acid formation and thermal embrittlement. In an effort to avoid these problems, composites using hydrogen-containing fluoroelastomer compounds are being reinforced with acid resistant alloys such as INCONEL, or high temperature synthetics, such as NOMEX and KEVLAR. None of these composites, however, offer the desired combination of thermal and chemical resistance with acceptable matrix integrity.

5 Even where chemically insusceptible substrates, such as PTFE, have been coated with fluoropolymers, such as in Westley, U.S. Patent No. 3,513,064, the resulting composites could only be achieved by selecting specific coating materials as limited by processing conditions, such that the composites possessed properties permitting use only in certain narrow applications.

10 In the hope of achieving an improved balance of fluoropolymer properties, prior attempts have been made to combine the respective good properties of fluoroplastic and fluoroelastomer materials in the manufacture of coated fabric. But these attempts have produced blends which either suffer the combined disadvantageous properties of the components or exhibit diminished good properties, particularly at higher temperatures, for example above about 500°F. A typical example of these prior attempts is found in U.S. Patent No. 3,019,206 to Robb.

20 While perfluoropolymers, whether thermoplastic or elastomeric, possess excellent thermal and chemical stability, it is difficult to form durable bonds between them and other materials due to their low surface free energy and chemical inertness. This difficulty is conventionally obviated by providing roughened surfaces to promote mechanical bonding, such as employing inorganic fillers or abraded surfaces.

Specific surface treatments, such as those based upon chemical etching, may also be employed. But none of these known techniques results in bonding which is particularly strong or durable under environmental stresses, such as ultraviolet or thermally induced oxidation.

Accordingly, it is an object of this invention to provide a fluoropolymer composite comprising a substrate coated with a fluoroelastomer/fluoroplastic matrix. The invention composite is flexible, exhibits good matrix cohesion, and possesses excellent adhesion of the matrix to the material acting as the reinforcement or substrate, while maintaining the low stiffness associated with a fluoroelastomer combined with, where desired, the superior high temperature performance of a fluoroplastic.

It is also an object of this invention to provide a fluoropolymer composite which is relatively light, but strong, and which is both chemically and thermally superior, particularly at elevated temperatures and under humid conditions, while ameliorating the polymer degradation problems that have heretofore arisen in the use of composites having a coating matrix based upon a hydrogen-containing fluoroelastomer.

It is a further object of this invention to provide a fluoropolymer composite having outstanding thermo-chemical properties for use as chemical liners, expansion joints, and life safety devices, such as escape hoods, escape chutes and chemically protective clothing.

It is yet another object of this invention to provide a composite having the combined advantages of perfluoroplastics and fluoroelastomers which can be used to make excellent plied constructions, including multiple biased-plied composites, as well as composites having a single coated face.

Summary Of The Invention

In accordance with the invention, a gradation of fluoropolymer layers is accomplished to form a coating matrix for application to a substrate in the manufacture of a novel composite. The fluoropolymer layers may include perfluoropolymer as well as hydrogen-containing fluoropolymer components which are deployed in a novel and unique way so as to combine as desired the respective advantageous properties of different fluoropolymer components. The hydrogen-containing fluoropolymer components include fluoroplastics, fluoroelastomers and blends of fluoroelastomers and fluoroplastics. The perfluoropolymer component or components are initially applied and provide a hydrogen-free interface such that a substrate material, which might otherwise be susceptible to the potential corrosive effects of hydrogen fluoride generated by any hydrogen-containing fluoropolymer component or otherwise, is shielded from such effects while the basic flexibility of the substrate is maintained. A fluoroplastic component may also comprise the topcoat or surface layer, or a part thereof, where the behavior of a thermoplastic, rather than an elastomer, is desired. Hydrogen-containing fluoroelastomer components are so deployed within the coating matrix so as to be isolated by the perfluoropolymer layer from a substrate potentially susceptible to HF corrosion, yet are so situated as to enhance the flexibility of the resulting composite membrane. When deployed as, or within, the top or surface coat, the fluoroelastomer component also functions to enhance the conformability of the composite and generally to endow the surface with rubber-like characteristics.

The novel reinforced composites according to the invention include a substrate, preferably a textile substrate, coated on one or both faces with a matrix comprising:

(A) an initial layer of a perfluorinated polymer, most preferably a perfluoroplastic, such as PTFE, or a perfluoroelastomer, such as KALREZ (DuPont), or blends thereof; and

5 (B) a further overcoat layer or layers of  
(1) a fluoroelastomer or perfluoroelastomer; (2) a  
fluoroplastic or perfluoroplastic; and/or (3) a blend  
of (i) a fluoroelastomer or perfluoroelastomer, and  
10 (ii) a fluoroplastic, preferably a perfluoroplastic,  
such as PTFE, wherein the fluoroelastomer or perfluoro-  
elastomer comprises about 10-90% by weight of the  
blend, preferably about 25 to 60% by weight.

In a separate embodiment of the invention, the  
novel composites will include a substrate coated solely  
15 with one or more layers of perfluoroelastomer alone  
or as a blend with a perfluoroplastic. Moreover, where  
the substrate is not susceptible to HF corrosion, the  
composite may include solely one or more layers of a  
blend of hydrogen-containing fluoroelastomer and a  
20 perfluoroplastic.

In other embodiments of the invention, the basic  
coating matrix will comprise elements A and B as set  
forth above having a multitude of fluoropolymer coat-  
ing layers all strategically deployed to achieve the  
25 desired properties. In those embodiments wherein a  
substrate is coated with a matrix on only one face,  
the substrate may be adhered to a different substrate  
on its other face. Each composite according to the  
invention may be topcoated with a layer or layers of  
30 a fluoroelastomer, fluoroplastic and/or a blend of a  
fluoroplastic and fluoroelastomer which may be differ-  
ent in composition from any overcoat blend.

In addition, relatively small amounts of cross-  
linking accelerators, such as triallyl isocyanurate,  
35 triallyl imidazole, and the like, may be used to  
cross-link one or more of the resins contained in the



coating layers, as desired, by use of high energy electrons or actinic irradiation.

5 The composites made in accordance with various embodiments of the invention are characterized by good matrix cohesion and adhesion between the substrate and the fluoropolymer matrix. Composites may also be prepared which possess extraordinary resistance to thermal and/or chemical degradation and accomodation to thermo-mechanical shock. Invention  
10 composites require much less coverage, i.e. reduced coating thickness, than similar prior art composites so as to provide a lighter and/or thinner, yet stronger product.

Any suitable reinforcement material capable of  
15 withstanding processing temperatures may be employed as a substrate. Examples include, inter alia, glass, fiberglass, ceramics, graphite (carbon), PBI (polybenzimidazole), PTFE, polyaramides, such as KEVLAR and NOMEX, metal wire, polyolefins such as TYVEK,  
20 polyesters such as REEMAY, polyamides, polyimides, novoloid phenolic fibers, thermoplastics such as KYNAR, TEFZEL, and KYNOL, polyether sulfones, polyether imides, polyether ketones, cotton, cloth and other natural as well as synthetic textiles. The  
25 substrate may comprise a yarn, filament, monofilament or any other fibrous material either as such or assembled as a textile, or any woven, non-woven, knitted, matted, felted, etc. material. Depending upon the nature of the substrate and the intended end use of  
30 the composite, the reinforcement or substrate is impregnated, either initially or simultaneously with the initial polymer layer, with a suitable lubricant or saturant, such as methylphenyl silicone oil, graphite, a highly fluorinated fluid, such as FLUOROLUBE  
35 or KRYTOX, and the like, and may include a coupling agent. The lubricant or saturant performs three functions vis-a-vis the reinforcing substrate:

(1) As a lubricant, it protects the substrate from self-abrasion by maintaining the mobility of the reinforcing elements;

5 (2) As a saturant, it inhibits extensive penetration of the initial polymer coat into the substrate which could reduce flexibility; and

10 (3) In a finished product, it remains in the substrate to inhibit wicking of moisture or other degrading chemicals through the substrate. The lubricant or saturant may either be applied separately as an initial pass or in combination with the first application of perfluoropolymer component.

15 The invention also encompasses a novel method of making invention composites which provides for the unique deployment of the various coating layers comprising the matrix, as heretofore described, particularly so as to minimize the deleterious effects of any hydrogen fluoride generated by a hydrogen-containing fluoroelastomer or fluoroplastic component  
20 and to maintain good overall composite flexibility. As such, the method results in the achievement of an improved product having a low modulus of stiffness and good chemical resistance applicable over a broad range of temperatures for a variety of end uses.

25 Detailed Description

The initial layer, described as element A above, is applied so as to minimize the stiffness of the final composite and to maximize adhesion of the matrix to the substrate. The application of the layer A may  
30 be accomplished in one or more passes and, preferably, any openings in an assembled substrate will remain substantially open in order to enhance flexibility, particularly where any additional overcoat layer or layers according to element B are contemplated. In  
35 instances where the substrate to be employed is an

assembled, fibrous material, the initial coating layer may be applied to the elements of the material (e.g. filament or yarn) prior to their assembly, by e.g. dip coating, impregnating or by extrusion coating. There-  
5 after, such materials may be assembled by weaving, knitting, felting, matting, etc.

In those embodiments which include both a hydrogen-containing fluoropolymer and a chemically-susceptible substrate, such as one which is susceptible to HF, the  
10 perfluorinated initial layer should be sufficient to substantially protect the reinforcing substrate, and in particular, a fiberglass substrate, from chemicals such as hydrogen fluoride which may be encountered. Again, depending on the substrate, additional thin  
15 layers of perfluoropolymer may be applied to insure that the reinforcement has an adequate protective layer. With the proper selection, application, and deployment of the coating layers, the penetration of aggressive chemicals such as hydrogen fluoride is  
20 impeded by the protective hydrogen-free perfluoropolymer interface, while flexibility is maintained.

The initial coating is then covered with a layer or layers of a fluoroplastic, fluoroelastomer, a fluoroelastomer/fluoroplastic blend or any combination thereof, as element B described above. Prefer-  
25 ably, this portion of the matrix includes a layer or layers of a blend containing the fluoroelastomer in such proportions so as to impart the desired balance of fluoropolymer properties to the composite. For  
30 example, where a composite having more pronounced elastomeric properties is desired, increased proportions of the fluoroelastomer are used in the blend. It has been found that through the combination of the layer A and the layer B, particularly employing the  
35 . fluoroelastomer/fluoroplastic blend according to the invention, adequate cohesion within the matrix itself

as well as matrix to substrate adhesion is often achieved by thermal means alone without any prior physical or chemical treatment of the substrate or individual matrix layers and without the use of adhesion promoters. Through the use of the invention matrix and the particular deployment of the layers thereof vis-a-vis each other and the substrate in accordance with the invention method, the ability to maintain an adequate degree of adhesion is achieved, while maintaining flexibility and the desired properties of the different fluoropolymer components of the matrix. This same feature allows for the selection of a top coat or surface layer having the attributes of a fluoroplastic or a fluoroelastomer, or any combination thereof, as may be desired.

Accordingly, once the initial and overcoat layers have been deployed, a topcoat of either a fluoroplastic or any additional fluoroelastomer layer may thereafter be applied. A surface coat of a perfluoroplastic, such as PTFE, or a perfluoroelastomer, such as KALREZ, or the fluoropolymer blend coatings containing copolymers of perfluorinated polyvinyl ether described in U.S. Patent No. 4,252,859 to Concannon et al., imparts better thermal properties and chemical resistance than, for example, the embodiment having a hydrogen-containing fluoroelastomer or blend thereof.

Coating layers of the invention matrix may be applied by dip coating from an aqueous dispersion, but any conventional method, such as spraying, dipping, and flow coating, from aqueous or solvent dispersion, calendering, laminating and the like, may be employed to form the coating, as is well-known in the art.

The term "fluoroplastic" as used herein shall encompass both hydrogen-containing fluoroplastics and hydrogen-free perfluoroplastics, unless otherwise indicated. Fluoroplastic means polymers of general

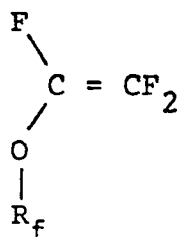
paraffinic structure which have some or all of the hydrogen replaced by fluorine, including inter alia polytetrafluoroethylene (PTFE), fluorinated ethylene propylene (FEP) copolymer, perfluoroalkoxy (PFA) resin, polychlorotrifluoroethylene (PCTFE) and its copolymers with TFE or  $\text{VF}_2$ , ethylene-chlorotrifluoroethylene (ECTFE) copolymer and its modifications, ethylene-tetrafluoroethylene (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 optionally one or more other compounds containing ethylenic unsaturation. The fluorinated monomer may be a perfluorinated mono-olefin, for example hexafluoropropylene or tetrafluoroethylene, or a partially fluorinated monoolefin which may contain other substituents, e.g. chlorine or perfluoroalkoxy, for example vinylidene fluoride, pentafluoropropylene, chlorotetrafluoroethyl and perfluoroalkyl vinyl ethers, e.g. perfluoro (methyl vinyl ether) or (propyl vinyl ether); 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.

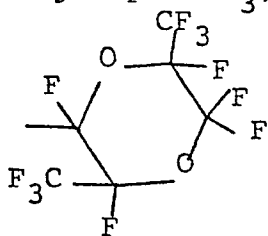
Any fluoropolymer component may contain a functional group such as carboxyl, and sulfonic acid and salts thereof, halogen as well as a reactive hydrogen on an alkyl side chain.

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



in which  $\text{R}_f$  is a perfluoroalkyl or perfluoro (cyclo-oxa alkyl) moiety. Particularly preferred are the perfluorovinyl ethers in which  $\text{R}_f$  is selected from the groups  $-\text{CF}_3$ ,  $-\text{C}_3\text{F}_7$ ,



, or  $-\text{CF}_2\text{CFOCF}_2\text{CF}_2\text{SO}_2\text{X}$ .

$\text{CF}_3\text{n}$

where  $n = 1-4$  and  $\text{X} = \text{H}, \text{Na}, \text{K}$  or  $\text{F}$ . Particularly contemplated is KALREZ is a copolymer including TFE and perfluoromethylvinyl ether (PMVE).

If desired, and as 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.

10       The deployment of the various matrix layers upon the substrate in accordance with the invention is essentially accomplished by a method which comprises the steps of:

15           1. If necessary or desired, removing the sizes or finishes from the substrate material, for example, in the instance of woven fiberglass, by heat cleaning the substrate or scouring a woven synthetic fabric.

20           2. Applying, as an initial layer to one or both faces of the substrate, a perfluoropolymer, preferably a perfluoroplastic such as PTFE or a perfluoroelastomer, such as KALREZ, or blends thereof. As heretofore noted, in one embodiment of the invention one or more layers of perfluoroelastomer, or a blend thereof as previously disclosed, may simply be applied to the substrate to prepare a composite. As hereinbefore discussed, a suitable saturant or lubricating agent, preferably methylphenyl silicone oil, typically in a mixture containing 2-14 parts by weight lubricant, may also be applied to the substrate either initially or simultaneously with the perfluoropolymer. In instances where sufficient flexibility otherwise exists, a coupling agent may be used to enhance the adhesion of the matrix to the substrate, as desired. As previously set

25

30

35

forth, the initial coating is applied so to minimize the stiffness of the composite and which may be a relatively light application depending upon the weight and openness of the substrate.

5 As indicated above, where the substrate is coated on only one face, the other face of the substrate may be adhered to a different substrate material.

3. Applying, in one or more layers, as an overcoat to the initial layer, a fluoroplastic, a fluoroelastomer, a blend of a fluoroelastomer and a fluoroplastic, preferably a perfluoroplastic, such as PTFE, or any combination thereof.

10 Where a fluoroelastomer/fluoroplastic blend is used, either alone or as a layer on top of a

15 fluoroelastomer layer, the blend should contain about 10-90% by weight of the fluoroelastomer component, preferably 25-60% by weight.

4. If desired, applying a topcoat of either a fluoroplastic, again preferably a perfluoroplastic such as PTFE or its melt-fabricable copolymers of TFE or a topcoat of an additional layer of a fluoroelastomer, preferably a perfluoroelastomer, or fluoroelastomer/fluoroplastic blend.

20 5. Optionally, applying a surface coating of a fluoroplastic in greater thicknesses by extruding or laminating a melt processible film such as PTFE, FEP or PFA, or a fluoroelastomer such as VITON, AFLAS, or KALREZ.

25 Moreover, it is clearly an advantage that the  
30 composites of the present invention may be produced, if so desired, by aqueous dispersion techniques. The process may be carried out under the conditions by which the cohesiveness of the matrix and adhesion to the substrate is thermally achieved. A preferred  
35 process for the manufacture of invention composites comprises an initial application of a perfluoropolymer



from a latex or dispersion to a suitably prepared substrate at temperatures leading to fusing or consolidation of the applied polymer. Following this initial coat, an overcoat comprising a fluoroelastomer, a fluoroplastic, or blends of fluoroelastomer and fluoroplastic derived from a latex or dispersion blend, is applied in such a manner as to dry the coating, but not to exceed the upper temperature limits of its most thermally labile component. The resulting, partially consolidated coating layers may then be subjected to more modest heat under pressure to further consolidate or strengthen the applied coating. Calendering is a convenient process to achieve this result. The topcoat is then applied at a temperature required to fuse the component with the highest melting point in order to complete consolidation with minimal heat exposure for the most thermally labile components. A latex is often available for this operation. Optionally, an uppermost coating may be applied by extrusion coating, calendering, or laminating the polymeric components on to the previously consolidated coating. Extrusion coating is most desirable when a foamed topcoat is desired.

It should be understood that in any embodiment according to the invention, the uppermost or surface layer may be applied as a foam to enhance compressibility or to increase thickness at low density.

The following additives may be included in the process for making the matrix composition: a surface active agent such as an anionic active agent or a non-ionic active agent; a creaming agent such as sodium or ammonium alginate; a viscosity-controlling agent or a thickener such as methyl cellulose or ethyl cellulose; a wetting agent such as a fluorinated alkyl-carboxylic acid, an organic solvent, or sulfonic acid; or a film former.

The achievement of the remarkable properties of the invention composites is further explained and illustrated below with reference to the accompanying drawings in which:

5        FIGS. 1 and 1A show enlarged schematic side view sections of woven composites by which several embodiments according to the invention are shown and illustrated.

10        FIG. 2 is an enlarged schematic plan view of a cross-section of an open weave fiberglass composite coated according to an embodiment of the invention.

15        FIG. 3 is a chart showing the relationship between tensile strength retained and time of exposure of the Example 2 invention composite to elevated temperatures in air.

FIG. 4 is a chart showing the relationship between tensile strength retained and time of exposure of the Example 2 invention composite immersed in 2N sulfuric acid at its boiling point.

20        In FIG. 1, the previously assembled (woven) yarn 10, having first been treated with silicone oil, is coated with a fluoropolymer initial coating layer 12 which completely covers both the warp 14 and fill 16 of the yarn 10. The layer 12 is then covered with  
25        an overcoat layer 18 comprising a blend of fluoroelastomer and fluoroplastic. The resulting composite may be further coated with an optional fluoroplastic or fluoroelastomer topcoat 20 as shown.

30        FIG. 1A shows a side view section of a woven composite wherein initial coating layer 12 is applied to the yarn prior to assembly (weaving) and completely surrounds and jackets the yarn 10. Such a composite may have enhanced flexibility, depending on the nature of coating layer 12.

35        FIG. 2 shows the deployment of the various layers of a coating matrix according to one embodiment of

the invention wherein the substrate is woven. An enlarged section of a plain woven substrate is shown wherein both the warp 14 and fill 16 of the yarn 10 are initially coated with a light layer of lubricant (not shown) and fluoropolymer 22. The layer 22 is displayed in such a way as to cover and protect the yarn 10, while leaving the openings 24 in the woven substrate free and clear so as not to substantially diminish the overall flexibility of the final composite. To the initially coated substrate is then applied an overcoat layer 26 of a fluoroelastomer/fluoroplastic blend according to the invention which covers the yarn 10, including the warp 14 and fill 16, as well as the openings 24 which, when filled with the more elastic blend layer 26, imparts a lower flex modulus to the resulting composite.

The invention and its advantages are also illustrated by the following examples. The examples illustrate composites employing a variety of substrates and coating matrices contemplated by the invention. The test procedures used for the chemical and physical testing and property determinations for the composites prepared according to the invention and the controls are identified below:

PROPERTY		TEST PROCEDURE
Weight (oz/sq yd)		FED STD 191-5041
Thickness (ins)		FED STD 191-5030
5	Tensile Strength (lbs/in)	Warp Fill FED STD 191-5102
	Tensile after fold (lbs/in) (or Flex Fold)	Warp Fill BIRDAIR LP-78*
10	Trapezoidal Tear (lbs)	Warp Fill FED STD 191-5136
	Coating Adhesion (lbs/in)	Dry Wet BIRDAIR LP-62**
15	Rack Elongation (%)	Warp Fill BIRDAIR LP-59***
	Flexural Rigidity (mg.cm)	ASTM D-1388
20	Dielectric Strength (volts)	ASTM D-902
	Porosity, SCF per hour per sq. ft. at 9 in H2O pressure	ASTM D-737
Hot Air Exposure, Hot Acid Exposure (%)		****

- 5       \* This is a comparative flex-fold test whereby a rectangular test specimen (long dimension parallel to warp yarns in the "warp test" and parallel to filling yarns in "fill test") is folded at its center, rolled with a weighted roller, ten times, and tested as per G.S.A. 171 #5102. The test values are compared with tensile values for an unfolded specimen. Fold resistance is reported as percent of strength retained after the fold. (In the exam-  
10       ples which follow, the results are expressed in actual tensile strength after folding, and the percent retention is not calculated.)
- 15       \*\* This test measures the adherance of the coating matrix to a substrate by subjecting a specimen (prepared from two pieces of the sample composite joined face to face as in making a production type joint or seam) to an Instron Tester, Model 1130, whereby the pieces forming the specimen are separated for a specified length (3") at a specified  
20       rate of strain (2"/min.). The average reading during separation is deemed the adhesion value in lbs./in.
- 25       \*\*\* This test relates to elongation or stretch characteristics under the continuous static loads experienced in actual applications. A cut rectangle (long dimension parallel to warp yarns for "warp" tests and parallel to filling yarns for "fill" tests) is attached to a rack and a 6 oz. weight at either end. A predetermined distance (10 inch) is  
30       marked off on the specimen and the 6 oz. weight is replaced with a specified load. After one minute, the change in distance between the "10 inch" marks is recorded. The same measurement is repeated at 1, 2, 4, 12 and 24 hour intervals to provide data  
35       for a plot of stretch vs. time. "Initial Stretch" is defined as per cent increase in length. Stretch is calculated using a scale graduated in 10ths and 100ths of an inch, each .1" increase over 10" gage marks equals 1% stretch.
- 40       \*\*\*\* These tests measure the tensile strength retained by materials exposed to hot air or hot sulfuric acid for various lengths of time. A number of cut rectangles are suspended in the indicated environ-  
45       ments. At the stated intervals, specimens are removed and tensile strength measured. The results are reported as percent tensile strength retained after exposure.

EXAMPLE 1

In accordance with a preferred embodiment of this invention, an 18 oz. per sq. yd. fiberglass substrate, Chemfab style no. 15227, was heat cleaned to remove residual sizing. A combination of PTFE (TE-3313 obtained from DuPont as an aqueous dispersion, 60% solids,) and methylphenyl silicone oil (ET-4327 obtained from Dow Corning as an aqueous emulsion, 35% solids,) was then applied to the surface of the substrate by dipping, drying and fusing in a two zone coating tower with drying zone temperatures of approximately 200-350°F. and a baking or sintering zone temperature of 700°F. The coating contained 93 parts PTFE, 7 parts methylphenyl silicone. The combination was applied as a very light undercoat, 5 oz./sq. yd., to avoid undesired stiffness. Only the yarns in the substrate were coated, the windows remaining substantially open.

A second coating, totaling approximately 20 oz/yd.<sup>2</sup>, was applied from a blend of VITON B fluoroelastomer (VTR-5307 obtained from DuPont as a terpolymer latex, 60-65% solids) and PTFE (TE-3313). The coating was applied in several passes, by dipping, drying, and baking in a two zone tower with drying temperatures of 200-350°F. and a baking zone temperature of only 500°F. The blend, designated FMK-4-10-B, comprised 60 percent PTFE and 40 percent terpolymer fluoroelastomer, by weight.

The material was completed by calendering the coated fabric with a 300°F. calender followed by a final dry pass through the coating tower to fuse or sinter the coating, with the baking zone at 700°F.

EXAMPLE 2

In accordance with the procedure of Example 1, a composite was prepared on a heat cleaned glass cloth

substrate (Chemfab Style No. 122, 32 oz/sq. yd) using  
the same primer coat composition to a weight of 40-41  
oz/sq. yd. and the same blend to a weight of 54-56  
oz/sq. yd. In addition, a topcoat of PTFE was applied  
5 in several passes through TE-3313, to bring the total  
composite weight to approximately 60-62 oz./sq. yd.  
In this example the PTFE topcoat was applied following  
the application of the blend, which was not calen-  
dered beforehand, by dipping, drying, and baking at  
10 590°F. The resulting material was calendered and  
processed through the tower, dry, with baking zone at  
700°F. to sinter or fuse the coating. The so-called  
dry-fused composite was given a final coat of PTFE by  
dipping in TE-3313, drying, and fusing at 700°F. The  
15 composite was .046" thick, had tensiles in lbs./in.  
of 1400/1375 warp to fill, flex-fold in lbs./in. of  
1400/1356 warp to fill, and tear strength in lbs. of  
231/295 warp and fill. The coating adhesion was  
measured at 23 lbs./in. and the porosity was .013.  
20 SCF/hr./ft.<sup>2</sup>

Four additional composites were manufactured in  
accordance with the method of Example 2, using glass  
cloth reinforcements of lighter weights and propor-  
tionately lighter builds of the various matrix compo-  
25 nents, as illustrated in the following table:

	Ex. 2A	Ex. 2B	Ex. 2C	Ex. 2D
Reinforcement Style No.	15227	128	116	1080
5 Reinforcement Weight*	18	6.1	3.2	1.45
Undercoat Weight	5	1.5	1.0	2.5
Blend Coat Weight	11	4.5	3.3	1.8
10 PTFE topcoat Weight	9	1.0	0.5	1.4
Total Weight	43	13.1	8.0	6.8

\* All weights in oz./sq.yd.



These composites were tested as indicated in Table I below:

TABLE I

		Ex. 1	Ex. 2	Ex. 2A	Ex. 2B	Ex. 2C	Ex.
Weight (oz/yd <sup>2</sup> )		46.8	60	42.1	13.1	8.0	6.
Thickness (ins)		.035	.046	.034	.009	.006	.0
Tensile (lbs/in)	Warp	1055	1400	983	217	177	1
	Fill	900	1375	935	186	164	1
Flex-Fold (lbs/in)	Warp	960	1400	944	213	183	
	Fill	645	1356	888	130	173	1
Tear (lbs)	Warp	106	231	105	16.0	10.0	7
	Fill	116	295	128	16.2	10.0	6
Coating Adhesion		Dry	16.5	23	21.6	3.9	5.12 3
Rack Elongation At 60 lb/in (%) Warp		Tensile Stress		Not Tested	2.0	2.2	Not Tested
Rack Elongation At 60 lb/in (%) Fill		Tensile Stress		Not Tested	5.5	7.8	Not Tested
Flexural Rigidity (mg cm)		Warp	Not Tested	193,000	110,000		Not Tested
Porosity (SCF/hr/ft <sup>2</sup> )		0.00	0.013	0.008			Not Tested

Additionally, Example 2A was tested after 9 months service in an expansion joint at an electrical power generating station. The material in service showed considerably less degradation than conventional joints based on fluoroelastomer.

EXAMPLES 3-8

Six additional composites were manufactured in accordance with the method of Examples 1 and 2, except that the ratio of the fluoroelastomer/PTFE blend was varied as follows:

TABLE II

	Ex. 3	Ex. 4	Ex. 5	Ex. 6	Ex. 7	Ex. 8
307 (Formula Wt.*)	16	40	53	64	96	120
13 ( " )	150	125	117	100	67	42
307 (Component Wt.**)	10	25	33	40	60	75
13 ( " )	90	75	67	60	40	25

pts by weight of ingredient used, in concentration  
plied by manufacturers.

pts by weight of component supplied by ingredient.

These compositions were tested as indicated in Table III below:

TABLE III

Property	Units	Ex. 3	Ex. 4	Ex. 5	Ex. 6	Ex. 7	Ex.
Blend Ratio	wt. % elas./ wt. % PTFE	10/90	25/75	33/67	40/60	60/40	75/2
Weight	oz/yd. <sup>2</sup>	46.9	44.4	45.0	44.9	43.9	43.4
Thickness	in.	.038	.036	.037	.036	.036	.035
Tensile strength							
warp	lbs./in.	1200	1205	1087	1190	1010	1055
fill		395	745	562	645	700	675
Tear strength							
warp	lbs.	113	120	118	132	109	118
fill		86	147	142	147	106	119
Flex-fold strength							
warp	lbs/in	945	840	not	1095	990	960
fill		450	730	run	710	755	715
Coating Adhesion	lbs./in.	17.3	16.5	17.0	18.3	19.3	15.5
Dielectric strength (2 in. electrode)	volts	5500	5300	4700	5200	5500	4500
Porosity at SCF/hr/ 9" water pressure	ft. <sup>2</sup>	.000	.011	.000	.011	.000	.067
Flexural rigidity	mg.cm	135900	122200	112300	112000	99300	61500

Preparation of Controls

A control A composite was prepared using Chemfab style 15227 glass cloth (18 oz./yd.<sup>2</sup>) which was heat cleaned to remove residual sizings. This substrate was then coated to 41 oz./sq. yd. with a blend of (a) a fluoroelastomer (L-6517 obtained from 3M and being a copolymer latex, 55% solids), and (b) PTFE (Teflon 30B from DuPont) in an 80/20 (PTFE/fluoroelastomer) ratio, by weight. The coating was applied in several passes at processing temperatures of 400°F. Control B is simply a portion of Control A baked under dry fuse conditions as are the invention composites. Control C is, in turn, a portion of Control B having a fused top coat of PTFE (TE-3313) in an amount of approximately 1.25 oz./sq. yd.

The results of physical tests of these contents are set forth below in Table IV

TABLE IV

5	<u>Property</u>	<u>Units</u>	<u>Control</u>		
			<u>A</u>	<u>B</u>	<u>C</u>
	(number of high temperature bake passes)		(none)	(1)	(2)
	Weight	oz/yd <sup>2</sup>	41.0	41.0	41.4
	Thickness	in.	.030	.032	.032
10	Tensile strength				
	warp	lbs/in.	935	843	753
	fill		818	660	750
15	Tear strength				
	warp	lbs.	131	97	94
	fill		130	91	89
	Coating Adhesion	lbs/in.	1.0*	1.0*	1.0*

20 \* very poor seal; coating is squeezed out of joint

EXAMPLES 9 A-C

A comparison was made using samples of the composites prepared in accordance with Examples 1 and 2, but using different commercially available fluoroelastomers. The first composite, 9A, was prepared essentially as was the composite of Example 6. Composite 9B was made in essentially the same manner, but substituting the L-6517 fluoroelastomer (a 3M copolymer latex, 55% solids). Similarly, composite 9C was prepared by substituting yet another 3M fluoroelastomer (L-6546, a terpolymer latex containing 60% solids) for the DuPont VTR 5307.

The results of the physical tests conducted with these composites are reported in Table V below:

TABLE V

Examples				
5	PROPERTIES	9A	9B	9C
	Weight (oz/yd )	44.5	44.4	45.0
	Thickness (ins)	.037	.037	.036
	Tensile (lbs./in.) comp	1190	1236	1267
10	fill	590	803	927
	Flex Fold (lbs./in.) comp	940	870	880
	fill	605	975	835
	Tear (lbs) comp	129	109	133
15	fill	117	149	141
	Porosity (SCF/hr./ft <sup>2</sup> )	.000	.000	.000
20	Coating Adhesion (lbs/in.)	18.2	15.2	13.3

EXAMPLE 10 A-C

Composite 10A was prepared using Style 15227 glass cloth (18 oz./sq. yd.) which was first heat cleaned to remove residual sizings. A combination of  
5 PTFE (TE3313) and methyl phenyl silicone oil (Dow Corning) was then applied to the substrate surface in an amount of 5 oz./sq. yd. A second coating of a blend of 3M fluoroelastomer (L-6517) and FEP resin -  
10 (DuPont TE-9503 aqueous dispersion, 55% solids) in a 40/60 ratio was then applied in several passes in an amount of 8 oz./sq. yd. The composite was finished with a top-coat of PTFE (TE-3313) in an amount of 5 oz./sq. yd. to yield a composite weight of 36 oz./sq. yd. A second composite 10B was prepared by substitut-  
15 ing a 40/60 blend of 3M L-6546 fluoroelastomer and DuPont TE-9503, and a third composite 10C was similarly prepared using a 40/60 blend of DuPont VTR5307 and TE-9503.



The results of physical tests with these composites is set forth in Table VI below:

TABLE VI

		<u>Samples</u>		
5	<u>Property</u>	<u>10 A</u>	<u>10 B</u>	<u>10 C</u>
	Weight (oz/yd <sup>2</sup> )	36.1	36.9	37.6
	Thickness (ins)	.034	.036	.034
	Tensile (lbs./in.)			
10	Warp	1028	1126	882
	Fill	522	590	360
	Flex-Fold (lbs./in.)			
	Warp	709	765	823
	Fill	578	620	343
	Tear (lbs.)			
15	Warp	108	110	95
	Fill	94	137	67
	Coating Adhesion			
	Dry	8.3	5.1	6.3
	Wet			
20	Porosity (SCF/hr./ft <sup>2</sup> )	.084	.033	.134
	Flexural Rigidity (mg.cm)	85,700	132,600	not run

EXAMPLE 11 A-C

5 Composites using reinforcements other than glass were prepared as indicated in Table VII. Composites 11A, 11B, and 11C were made in accordance with the method employed in the Example 2, using a three component matrix consisting of the PTFE-silicone oil primer, the intermediate blend component, and the PTFE topcoat.

TABLE VII

	Ex. 11A	Ex. 11B	Ex. 11C
Reinforcement Material	aramid Kevlar	aramid Nomex	graphite
5 Weaver Style No.	Chemfab 100-20	Chemfab 100-10TCN	Fiberite W-134
Reinforcement Weight*	6.6	2.8	5.8
10 PTFE-silicone oil primer weight	2.5	4.3	2.6
Blend weight	7.5	9.1	6.3
PTFE topcoat weight	1.4	2.0	0.9
15 Total weight	18.0	18.2	15.6

\* all weights in oz/yd<sup>2</sup>

The composites prepared in accordance with Example 11 were tested as indicated in Table VIII below.

TABLE VIII

5	EXAMPLE		11A	11B	11C
	Weight (oz/yd <sup>2</sup> )		17.8	18.8	15.4
	Thickness (ins)		.019	.020	.015
10	Tensile strength	Warp	661	73	403
		Fill	815	65	403
	Flex-Fold strength	Warp	639	79	118
		Fill	825	76	315
15	Tear (lbs) strength	Warp	84	5.3	40
		Fill	84	9.0	50
	Coating Adhesion	Dry	10.3	18.0	11.0

Hot Air and Hot Acid Exposure Test Results  
Tensile Strength (warp) Retained after Exposure (%)

	2N. sulfuric acid at b.p.			air at 450°F.			air at 525°F.		
	1wk	2wk	4wk	1wk	2wk	4wk	1wk	2wk	4wk
Ex. 1	69	57	nc*	95	99	nc	95	91	nc
2	80	57	54	100	95	89	92	72	75
2A	77	66	52	96	81	98	73	84	81
3	94	46	nc	100	98	nc	100	82	nc
4	98	46	nc	98	86	nc	95	84	nc
5	63	53	nc	99	100	nc	93	94	nc
6	100	56	nc	91	94	nc	95	86	nc
7	100	59	nc	96	100	nc	97	95	nc
8	94	48	nc	100	98	nc	99	92	nc
4A	32	26	nc	88	84	nc	77	68	nc
4B	61	35	nc	93	90	nc	94	79	nc
4C	56	25	nc	81	82	nc	73	69	nc
9A	74	56	46	100	94	90	91	79	80
9B	66	45	45	95	95	99	86	59	73
9C	55	33	41	91	91	95	84	59	67
10A	76	49	54	100	100	100	100	69	100
10B	73	53	51	100	88	100	96	82	90
10C	93	63	59	100	93	100	96	83	96

\* Test not complete as of date of filing

EXAMPLES 12 A-D

Four additional composites were manufactured in accordance with the method of Examples 1 and 2, however the lubricant/saturant was either (1) ET-4327 methyl-phenyl silicone oil emulsion applied in FMK-4-10-A (CHEMFAB internal designation for mixture of TE-3313 (DuPont) and ET-4327 (Dow Corning Corp.) containing approximately 93 percent by weight PTFE and 7 percent by weight silicone oil diluted with water to a specific gravity of 1.32); (2) ET-4327 methyl-phenyl silicone in an aqueous solution (mixture of 1 part by volume ET-4327 methyl-phenyl silicone oil emulsion, manufactured by Dow Corning, and 8 parts by volume tap water); (3) ET-4327 methyl-phenyl silicone in an aqueous solution, 1 part by volume:4 parts by volume tap water; or (4) a mixture of 9 pbw ET-4327 diluted with tap water, 1:8 by volume) and 1 pbw AQUADAG E colloidal graphite dispersion. With the exception of the material having the FMK-4-10-A initial fuse dip, a second fuse dip of TE-3313 (1.35 specific gravity) was applied following the application of the lubricant. The four compositions were then completed in accordance with the procedures of Examples 1 and 2.

The resulting materials were tested for weight; thickness; tensile, tear, and flex fold strength and coating adhesion; and MIT flex endurance. The results are shown in Table IX as follows:

TABLE IX

Lubricant/saturant	12A	12B	12C	12D
Composition	Silicone	Silicone	Silicone	Silicone-graphite
Applied from	FMK4-10A	1:8 sol.	1:4 sol.	9 pbw 2 1/2:5 sol 1 pbw Aquadag E
Pick-up (oz/yd <sup>2</sup> )	.4 (1)	.3 (2)	.7 (2)	.4 (3)
Weight (oz/yd <sup>2</sup> )	43	42	42	43
Thickness (in.)	.035	.035	.035	.034
Tensile (lbs/in.)				
strength	1095	1113	1060	1070
fill	970	907	910	1010
Tear (lbs.)				
strength	120	123	121	139
fill	119	132	135	159
Flex-fold (lbs/in.) (4)				
strength	715	920	930	985
fill	780	880	840	935
Coating adhesion (lbs/in.)	20	16	16	19
MIT Flex (5) (folds to failure x 10 <sup>3</sup> )				
warp	49	35	66	87
fill	44	44	54	83

## NOTES:

- (1) Calculated value based on 7% FMK4-10A pick-up.
- (2) Experimentally determined values.
- (3) Measured on actual run.
- (4) Rolled on 10X with 10 lb. roller.
- (5) MIT Folding Endurance Tester, 0.04 in. jaws, 5 lb. weight, No. 10 spring.

0125955

EXAMPLE 13

Composites using TE-5489 (low crystallinity, compliant, perfluorinated TFE copolymer obtained from DuPont) resin dispersion were prepared as follows.

- 5 In Example 13, Chemfab Style 116 glass was heat cleaned and given four fuse dips through the full strength TE-5489 (33% solids, 1.23 specific gravity, 9.5 cps). The 3.04 oz/yd<sup>2</sup> heat cleaned substrate picked up a total build of approximately 0.7 oz/yd<sup>2</sup>.  
10 Microscopic examination of the product revealed a resilient, uncracked and generally flaw-free coating encapsulating the yarns and well adhered to them.

EXAMPLE 14

- Example 14 was prepared by pouring 25 grams of  
15 TE-5489 on a 3 x 5 inch piece of heat cleaned and silicone treated 15227 glass cloth in a tray. The water was dried away in an air circulating oven at 75°C and the resulting fabric, saturated with the dried polymer, was molded in a .040 inch thick chase  
20 at approximately 400°F for ten minutes in a platen press. The resulting composite was extremely flexible and compliant, and the coating was strong and resilient and was resistant to scratching.

EXAMPLES 15 A-C

- 25 Examples 15A and 15B were prepared as follows. Following heat cleaning, two lengths of Chemfab Style 129 glass cloth (6.2 oz/yd<sup>2</sup>) (ECD 225 1/3, 38 x 40) were coated in multiple semifused dip passes through 50:50 (weight) blends of TE-5489 and commercially avail-  
30 able perfluorinated resin dispersions (as described below), followed by final dry fuse passes. Example 15A received 7 passes through such a blend made with TE-3313 which resulted in a 9.54 oz/yd<sup>2</sup> composite. Example 15B received 6 passes through a blend made



with TE-9503 thermally concentrated in the laboratory to 63% solids, and resulted in a 9.25 oz/yd<sup>2</sup> product. These examples were tested as shown below.

TABLE XI

5	<u>Property</u>	<u>Units</u>	<u>15A</u>	<u>15B</u>
	Weight	oz/yd	9.5	9.3
	Thickness	in.	.009	.009
	Dielectric strength	volts		
10	1/4" elec.		1700	1700
	2" elec.		1300	1300
	Strip Tensile strength	lbs/in		
	warp		308	325
	fill		315	348
15	Trap. tear strength	lbs		
	warp		20	22
	fill		26	22
	Coating adhesion	lbs/in.	7.1	4.4

20 Example 15C was prepared as follows. Following heat cleaning, Chemfab Style 15227 glass cloth (18 oz/yd<sup>2</sup>) (ECB 150 4/3, 18 x 19) was treated with  
 25 silicone oil by dipping the cloth in ET-4327 diluted 1:8 by volume with water, followed by drying and baking at 650°F. An initial coat of 50:50 (weight) blend of TE-3313 and TE-5489 was then applied by dipping, wiping with smooth bars, drying, and baking at 500°F. This initial coat weighed 5.1 oz/yd<sup>2</sup>. An overcoat of FMK-4-10-B was then applied in five successive semifuse  
 30 passes totaling 17.7 oz/yd<sup>2</sup>. A top coat of 1 oz/yd<sup>2</sup> of PTFE was applied in a single, unwiped semifused pass through TE-3313 at 1.30 specific gravity. The

material was then calendered and finally completed by fusing in a single dry fuse pass at 720°F.

The finished composite was softer than Examples 1 and 2. The coating, although not as glossy and feeling more compressible than the coatings of Examples 1 and 2, otherwise was as durable when the material was subjected to rough handling such as scraping and creasing. The warp tensile strength of this material was 863 lbs/in.; the coating adhesion strength was 8.9 lbs/in.

#### EXAMPLES 16 A-F

Example 16A was prepared by giving Chemfab Style 100-20 woven KEVLAR fabric (approximately 16 x 16 count, approximately 6.6 oz/yd<sup>2</sup>, yarn construction unknown) 2 wiped fuse dips through undiluted TE-5489 dispersion. Sintering zone temperatures were 550°F during both passes. The finished weight of the fabric was 8.9 oz/yd<sup>2</sup>.

Example 16B was made with the same reinforcement as Example 16A and was given a single fuse dip through TE-5489 under the same conditions as the initial operation on Example 16A, bringing its total weight to 7.90 oz/yd<sup>2</sup>. This was followed by three semifuse dips, wiped, through FMK-4-10-B, with baking zone at 500°F, which raised the total weight, in succession, to 11.4, 13.5, and 17.0 oz/yd<sup>2</sup>, respectively. The material was completed with a fuse pass at 700°F.

Example 16C was also made with the same reinforcement as Examples 16A and 16B, but in Example 16C the initial coat consisted of a blend of 50% by weight PTFE from TE-3313 and 50% by weight polymer from TE-5489, applied as a wiped fuse dip at 550°F. The total weight of the reinforcement and the initial coat thus applied was 8.4 oz/yd<sup>2</sup>. As an overcoat, 3 dips of FMK-4-10-B were applied and dry fused essentially as

they were in making Example 16B, yielding a finished product weighing 16.8 oz/yd<sup>2</sup>. The three products were tested as shown in the following table.

TABLE XII

5	<u>Property</u>	<u>Units</u>	<u>16A</u>	<u>16B</u>	<u>16C</u>
	Weight	oz/yd <sup>2</sup>	8.7	17.0	16.5
	Thickness	in.	.017	.019	.019
	Trap. tear strength	lbs.			
10	warp		NR*	88	70
	fill		NR *	NR	74
	Strip Tensile strength	lbs/in.			
15	warp		435	600	631
	fill		581	640	827
	Coating adhesion	lbs/in.	4.8	7.2	10.0

\* NR - no reading (yarns bunched)

20 A reinforcement for Examples 16D, E and F was made by heat cleaning Style No. W-134 woven graphite fabric (5.8 oz/yd<sup>2</sup>, approximately 12 x 12 count manufactured by Fiberite Corporation) by baking at 680°F. Example 16D was then made by giving the reinforcement two wiped fuse dips through TE-5489 dispersion at 550°F. The finished weight was 8.3 oz/yd<sup>2</sup>.

25 In making the composition of Example 16E, the heat cleaned graphite was given a silicone treatment by dipping the unwiped reinforcement through ET-4327, diluted 1:8 by volume with water, followed by drying and baking at 500°F. This was followed by a wiped

fuse dip through TE-5489 and baking at 550°F bringing the 6.0 oz/yd<sup>2</sup> silicone treated fabric to a total weight of 7.4 oz/yd<sup>2</sup>. Three additional wiped, semi-fused dips of FMK-4-10-B were applied and followed by baking at 500°F bringing the weight to 11.9, 13.6, and 15.7 oz/yd<sup>2</sup>, respectively, after each pass. A final bake was accomplished at 700°F.

Example 16F was made according to essentially the same procedure as Example 16E, using the silicone treated reinforcement, but with the 50:50 solids blend of TE-3313 and TE-5489 replacing the TE-5489 as the initial coat. The weight following this step was 7.8 oz/yd<sup>2</sup>. Three wiped, semifused dips of FMK-4-10-B were subsequently applied and dry fused as they were in making Example 16E, resulting in a finished weight of 15.5 oz/yd<sup>2</sup>. The three products were tested as shown in the following table.

TABLE XIII

	<u>Property</u>	<u>Units</u>	<u>16D</u>	<u>16E</u>	<u>16F</u>
20	Weight	oz/yd <sup>2</sup>	8.4	16.5	15.5
	Thickness	in.	.014	.017	.017
	Strip Tensile strength	lbs/in.			
	warp		363	443	360
25	fill		330	435	343
	Trap. tear strength	lbs.			
	warp		27	15	9.5
	fill		17	20	4.0
30	Coating adhesion	lbs/in.	6.6	8.0	11.4

EXAMPLES 17 A-M

Several examples incorporating a KALREZ latex obtained from DuPont and identified as 34045-133 were prepared by a laminating process which involved evaporating the dispersion to dryness to obtain a crumb, pressing the crumb to a film in a platen press and laminating the film to a substrate, also in a platen press. Example 17A was prepared by heat cleaning Style 15227 glass and giving the glass a silicone treatment by dipping through ET-4327 diluted 1:8 by volume with water followed by drying and baking. The treated substrate was then dipped through the KALREZ dispersion, unwiped, and baked at 500°F. The resulting composite weighed 20.8 oz/yd<sup>2</sup>.

Example 17B was prepared by giving a portion of the coated fabric of Example 17A four semifused passes through TE-3313, viscosified to approximately 150 cps while wiping with 40 mil wire wound bars. The resulting 36.2 oz/yd<sup>2</sup> material was pressed in a platen press for 1 minute at approximately 1,300 psi with platens heated to 325°F. The coated surfaces were protected by release sheets of CHEMFAB 100-10 TCGF (PTFE coated glass fabric) during the pressing. The material was then baked for 20 minutes in an air circulating oven at 525°F to remove residual surfactant. It was returned to the press, protected by clean aluminum foil on both sides, and sintered by pressing at minimum pressure (less than 15 psi), with platens heated to 720°F, for 5 minutes. The resulting material weighed approximately 35.5 oz/yd<sup>2</sup>.

Example 17C was prepared by giving a portion of the coated fabric of Example 17A five wiped passes through undiluted VTR-5307 fluoroelastomer latex. Each pass was dried and baked at approximately 300-450°F. The material was then baked in a 525°F air circulating oven for 20 min. to remove residual surfactant. The final weight was 32.2 oz/yd<sup>2</sup>.

Example 17D was prepared by giving a portion of coated fabric of Example 17A three semifuse passes wiped with 40 mil wire wound bars, through FMK-4-10-B, all passes at 10 in/min. The material, which at this point weighed 32.9 oz/yd<sup>2</sup>, was subsequently baked 20 minutes in a 525°F air circulating oven and fused in a platen press at less than 15 psi with 720°F platens for 5 minutes between sheets of clean aluminum foil.

In Example 17E, a KALREZ crumb was prepared by evaporating a quantity of KALREZ dispersion to dryness in an air circulating oven at 75-85°C. Ten grams of the crumb were placed between an approximately 18 x 18 inch piece of aluminum foil treated with silicone mold release (SPRITS SILICONE MOLD RELEASE, sold by Sprits of Melville, New York) on one side and a similar sized sheet of silicone resin coated glass fabric (available as SRC-5 from Oak Industries, Inc., Hoosick Falls, New York) on the other. The material was placed between smooth caul plates of 1/8" stainless steel and pressed for 5 minutes at 80 tons force on the platens at 550°F, following which the work was cooled under pressure. The result was a circular piece of KALREZ film approximately 8-10" in diameter and varying in thickness from .005 to .008 in.

The film was then folded over an edge of a portion of Example 17A in such a way that approximately equal semicircular areas of film were opposite each other on opposite sides of the Example 17A coated reinforcement. This sandwich was placed in the press between thicknesses of glass cloth serving as compression pads to force the film into the irregularities of the reinforcement. Aluminum foil, treated with a silicone mold release, was used between the film and compression pads. Stainless caul plates were used. The laminate was pressed for 5 minutes at 550°F employing a force of 10 tons on the platens, (approximately

400-500 lbs/in<sup>2</sup> on the 10 in. diameter semicircular composite). The composite was cooled under pressure.

5 The foil was easily stripped away to obtain the resulting semicircular laminated composite surrounded by the more lightly coated reinforcement. This material was again placed in the press between mold-release-treated aluminum foil sheets for 5 minutes with 5 tons force on the platens at 350°F to smooth out the fabric imprint which came through the foil from the compression pad. The completed smooth laminate was 0.028 to 10 0.029 inches thick near the center and 0.026 to 0.027 inches near the edges. Under the microscope, no voids were visible, either looking through the face of the fabric or at cut edges. Visually, it could not be 15 distinguished from dip coated material except for its complete lack of bubbles, pin holes and craters.

Similar laminated composites were made by the same technique as Example 17E, using Examples 17D, 17C and 17B as substrates. These were designated 20 Examples 17G, 17H, and 17J, respectively.

To facilitate comparisons, the compositions of Examples 17A-E and G, H and J are summarized in the following table.

TABLE XIV

<u>Example No.</u>		<u>17A</u>	<u>17B</u>	<u>17C</u>	<u>17D</u>
Reinforcement		15227	15227	15227	15227
1st matrix comp. (dip coat)		ET-4327	ET-4327	ET-4327	ET-4327
5	2nd matrix comp. (dip coat)	Kalrez	Kalrez	Kalrez	Kalrez
3rd matrix comp. (dip coat)		-	TE-3313	VTR-5307	FMK-4-10-B blend
Weight (oz/yd <sup>2</sup> )		20.8	35.5	32.2	32.9
10	(portions of the above materials were in turn laminated to produce the following:)				
<u>Laminate Exp. No.</u>		<u>17E</u>	<u>17J</u>	<u>17H</u>	<u>17G</u>
Laminated matrix comp.		Kalrez	Kalrez	Kalrez	Kalrez
Thickness (in.)		.027-.030	.037-.041	.030-.034	.033-.035

- 15                    Example 17K was prepared by placing a film made  
from KALREZ latex as described in the procedure for  
preparing Example 17E on one side of a piece of Chemfab  
Style 129 glass fabric which had been previously heat  
cleaned. The layup was protected on both sides by  
20 aluminum foil and placed in a platen press and pressed  
for one minute at 550°F using minimum obtainable force.  
The material which was removed from the press was a  
one-sided composite with the film well adhered to the  
reinforcement. A piece of the one-sided composite  
was coated on the bare glass side with contact adhe-  
25 sive (Armstrong "N-111 INDUSTRIAL ADHESIVE"). The  
same adhesive was also applied to one side of a swatch  
of polyester-cotton fabric. After drying, the two  
adhesive-coated materials were pressed together to  
30 form a two-ply fabric having one perfluoroelastomer  
face and one polyester-cotton face, such as would be  
suitable for a garment.



Example 17L was a graphite reinforced perfluoro-polymer composite which was prepared by using the Example 16D material as a substrate and making a laminate according to the techniques employed in producing Example 17E. As heretofore noted, the initial coating on the substrate was derived from TE-5489, a low crystallinity perfluoropolymer based dispersions. The resulting laminate was approximately 0.015 inches thick with a smooth, resilient matrix which appeared to thoroughly saturate the reinforcement.

Example 17M was a laminate prepared by bonding .005 inch thick PTFE skived film (available from Chemplast, Inc., Wayne, New Jersey) to both faces of a substrate of Example 17D, which in turn consisted of 15227 reinforcement, silicone treated with an initial coat of KALREZ followed by an overcoat of blended fluoroelastomer-PTFE (FMK4-10B). The laminate was pressed under the following conditions: platen temperature, 720°F; pressure, 10 tons force on a specimen measuring approximately 5 in. x 10 in.; time at temperature, 5 minutes; cooled under pressure to 500°F; and removed from press. The completed specimen was 0.035 to 0.037 inches thick. The PTFE appeared to be strongly adhered to the overcoat. There was no tendency toward separation even after repeated splitting off of small areas of the laminated overcoat and attempting to pull the layers apart.

#### EXAMPLES 19 A&B

Example 19A was prepared as follows: Chemfab Style 122 glass fabric was heat cleaned. A silicone oil lubricant/saturant and an initial coat of PTFE were then applied simultaneously in a single dip through a bath of FMK 4-10A followed by drying and baking. The prepared reinforcement was laminated between .012 inch sheets of uncured calendered sheet

stock identified as "Fluorel based Diak catalyzed  
fluoroelastomer compound suitable for flue duct  
applications" (Passaic Rubber Corporation, Clifton,  
N.J.) The rubber was brushed with acetone on the sides  
5 contacting the fabric before the material was laid-up  
and the sandwich was cured by pressing for 15 minutes  
between 350°F platens at approximately 250 to 300  
lbs/in.<sup>2</sup> (on specimen) and cooling under pressure  
to 200°F. The resulting reinforced rubber slab was  
10 approximately 0.14 inches thick and was very flexible  
with a good integrity.

Example 19B was prepared according to the same  
procedures as those employed in the preparation of  
Example 19A except that the substrate used was 15227  
15 as the reinforcement and the rubber slabs were not  
brushed with acetone prior to lay-up. The resulting  
material was also 0.04 inches thick, appeared to be  
equally flexible when compared with Example 19A, and  
also possessed good integrity.

20 EXAMPLES 20 A&B

A KALREZ crumb containing 1.5 parts per hundred  
parts rubber of Triallylisocyanurate (TAIC) (manufac-  
tured by Nippon Kasei Chemical Company, Ltd., Tokyo,  
Japan and available in the United States from Mitsubishi  
25 International Corporation, New York, New York) was  
made by adding the necessary TAIC as a 5% solution in  
denatured ethanol to the KALREZ dispersion and evapo-  
rating the treated latex to dryness at about 90°C.  
The addition of TAIC in this manner did not appear to  
30 induce coagulation.

Two composites were made according to techniques  
identical with those used in preparing Examples 17E,  
G, H and J. One was made on Example 17A, designated  
. Example 20A, and one was made on Example 16A, designated  
35 Example 20B. Each of these composites was irradiated

with a 1 MeV electron beam to a total of 4, 8 and 16 megarads, respectively. The beam current employed was 5 milliamps. Determination of the dynamic modulus for the irradiated composites suggests that the radiation had induced cross-linking.

EXAMPLE 21

Composites manufactured in accordance with the method of Example 2 were plied and laminated in a platen press, with 0.005 inch FEP film as a melt adhesive between plies, using the following laminating conditions:

platen temperature : 670°F  
pressure : approximately 500 psi  
time at temperature : 6 min.

Four examples of 2 ply laminates were produced, differing in the relative orientation of the warp yarns in the plies. Examples were made with warp yarns parallel (0° skew), skewed 30°, skewed 45°, and perpendicular (90° skew).

Composites manufactured in accordance with Example 2A were also laminated, using pressing conditions similar to those described above, but with lower pressure, approximately 280 psi (45 tons force on 18 in. x 18 in. laminate). Ply warp yarn orientations of 0, 30, 45, and 90 degrees were employed in making these examples also.

The laminates were tested for strip tensile and trapezoidal tear strength. The results of these tests are reported in Table XVI below.

TABLE XVI

## Strip Tensile and Trapezoidal Tear Strength of 2 Ply Laminates

Ply Construction	Warp Yarn Orientation(deg)	Strip Tensile (lbs/in) <sup>1</sup>		Trapezoidal Tear (lbs/in)	
		Warp	Fill	Warp	Fill
Example 2	Single ply control	1265	1141	185	203
"	0	1895 <sup>2</sup>	1775 <sup>2</sup>	415	503
"	30	1306	1400	507	706
"	45	1265	1243	541	731
"	90	1438	1511	518	485
Example 2A	Single ply control	833	869	87	101
"	0	1468	1437	134	150
"	30	828	855	163	285
"	45	858	815	149	208
"	90	827	853	165	207

Notes: 1. Specimen width 2 inches; calculated breaking stress per inch of width shown in table

2. Specimens slipped in jaws with highest clamping pressure

0125955

EXAMPLE 22

A knit fiberglass fabric weighing approximately 5 oz/yd<sup>2</sup> was given an unwiped dip through Dow Corning ET-4327, which had been diluted 1:8 by volume with tap water dried and baked. The treated knit substrate was then given a single dip through KALREZ dispersion; dried; and baked at 700°F. The coated reinforcement was placed between layers of a film prepared from Kalrez and the sandwich, protected by aluminum foil treated with a silicone mold release, was pressed between platens 550°F at approximately 100 psi for 5 minutes and cooled under pressure. The resulting composite was soft and flexible.

EXAMPLE 23

In accordance with the method used in preparing Example 22, but with different laminating conditions (i.e., 720°F platen temperature, approximately 500 psi pressure, 3 minutes at temperature followed by cooling under pressure), a laminate was made with a film of FMK-4-10-B reinforced with knitted fiberglass fabric which had been primed with ET-4327 and dip coated in a Kalrez latex.

EXAMPLES 24 A-D

A series of four specimens similar to Example 2A was produced comparing PFA, FEP, and PTFE as topcoats and PFA and PTFE as the resin constituent of the perfluoropolymer/fluoroelastomer blend overcoat. The construction of the composites is summarized in the following table.

Example No.	<u>24A</u>	<u>24B</u>	<u>24C</u>	<u>24D</u>
Reinforcement	-----15227, Heat Cleaned-----			
Initial Layer	-----FMK-4-10-A-----			
Overcoat, layer 1	FMK-4-10-B	FMK-4-10-B	TE-335/ VTR 5307	FMK-4-10-B
Overcoat, layer 2	TE-3313*	TE-3313*	TE-3313*	TE-3313*
Topcoat	TE-335	TE-3313	TE-3313	TE-9503

NOTES: FMK-4-10-B is 60/40 weight blend of TE-3313 and VTR 5307

TE-335 is PFA (perfluoroalkoxy modified PTFE) dispersion  
(Du Pont)

TE-3313 is a PTFE dispersion.

TE-9503 is FEP dispersion (Du Pont)

\*Viscosified

All materials were processed in a manner similar to Example 2A. The initial layer was applied in an unwiped fuse dip. The overcoat layers were applied in multiple, wiped, semifuse dips to bring total fabric weight to approximately 40 oz/yd . The fabrics were calendered to consolidate the semifused layers, dry fused, and completed with single unwiped fuse dips through the topcoat dispersions.

Samples of the materials were tested for initial physical properties with results shown below.

TABLE XVII

<u>Property</u>	<u>Units</u>	<u>24A</u>	<u>24B</u>	<u>24C</u>	<u>24D</u>
Weight	oz/yd	40.9	40.9	44.4	40.7
Thickness	in.	.032	.032	.038	.032
Tensile	lbs/in				
warp		967	933	860	940
fill		853	875	720	730
Tear	lbs.				
warp		108	107	129	117
fill		131	122	121	135
flex fold	lbs/in				
warp		607	760	733	813
fill		873	793	600	773
Dielectric Strength,					
2" elec.	volts	3700	4000	3800	4000
MIT Flex	folds to				
warp	failure,				
	$\times 10^{-3}$	34	37	33	46
Coating Adhesion	lbs/in	15.5	14.2	12.3	14.2

20

EXAMPLES 25 A-C

25

Pieces of copper foil, .003 inches thick, etched on one side (available from Yates Industries, Inc., Bordentown, New Jersey; specify type "A" etch) were washed with soap and water, rinsed with distilled water, washed with reagent grade acetone, and air dried. The etched surface was treated with gamma-Aminopropyltriethoxysilane (available from Union

Carbide Corporation, New York, New York as A-1100) by dipping in a 1% aqueous solution and drying in an air circulating oven at 225°F. Laminates were made on the treated foil substrate as shown in the following table:

	<u>25A</u>	<u>25B</u>	<u>25C</u>
Initial coat layer	.005"FEP film*	TE-5489 film* (from solids)	FMK-4-10-B film* (from solids)
Overcoat layer	FMK-4-10-B film	no overcoat	no overcoat
Platen temperature (°F)	-----550-----		
Pressure on specimen (psi)	-----130-----		
Time at temperature (min)	-----5-----		
Laminate thickness (inches)	.0108	.0062	.0065

\* Each film was processed above the fusing temperature of the respective resins.

TE-5489 as supplied by DuPont contains a high temperature methyl-phenyl silicone oil. When the dispersion is dried to form a crumb and the crumb is pressed into a film in accordance with the method of Example 17E, the silicone oil saturates and coats the films and prevents adhesion to other components in hot pressed laminates. To remove this silicone, the cast film was chopped and washed in clean toluene in a Ross Mixer-Emulsifier, dried in an air circulated oven at 50°C, and re-pressed to a film. This was repeated four times and the resulting silicone-free film was used in making Example 25B.



The three examples are foils with durable, compressible polymeric coatings. Example 25B possessed a particularly soft yet resilient coating very firmly bonded to the copper surface. The coating can be gouged with a knife but shows no tendency to delaminate even in boiling water. Example 25C has a somewhat less resilient and softer coating than 25B, but appears equally resistant to delamination. Example 25A has coating characteristics similar to 25C, but was the most easily gouged of the three.

EXAMPLE 26

A piece of ordinary, 16 ga. cold rolled steel was abraded with 200 grit sandpaper on one side until the surface was bright and shiny and free of mill scale and rust. The surface was washed with reagent grade acetone, allowed to air dry, flooded with 6 normal sodium hydroxide solution, allowed to stand several minutes, washed with distilled water, and allowed to air dry. The surface was treated with silane and a polymer film comprised of resin derived from TE-5489 (silicone-free) was press laminated to it, in accordance with the method of Example 25B. The result was sheet steel with a soft, compressible, resilient coating; firmly bonded and when gouged with a knife showing no tendency toward delamination.

EXAMPLE 27

A piece of 1/8 inch window glass was washed with soap and water, washed with reagent grade acetone, immersed in 6 normal sodium hydroxide solution for several minutes, washed with distilled water, and allowed to air dry. The surface was silane treated and a film of silicone-free TE-5489 was press laminated to the glass substrate, essentially in accordance with the method of Examples 25B and 26, but using

very low pressure, less than 50 psi on specimen, and beginning with the platens at room temperature, raising them to 550°F over a period of approximately one half hour, and allowing them to air cool to room temperature over a period of several hours, thus avoiding thermal shock which might have broken the glass. The TE-5489 produced a resilient, .005 inch coating which did not delaminate in boiling water after 24 hrs. exposure.

10

EXAMPLE 28A

A thin extruded coating of PTFE was applied by paste extrusion to ECG 37 1/3 fiberglass yarn. The jacketed yarn thus produced was woven into an approximately 14 x 15 count plain woven fabric weighing approximately 35 oz./yd<sup>2</sup> (about 60% of which is represented PTFE). Overcoat layers were applied as follows: Cast films of FMK-4-10-B were laminated to both sides of this substrate in a platen press at a pressure of approximately 280 psi. Platen temperatures of 700°F. were maintained for 5 minutes, followed by cooling to approximately 150°F. over a period of about 15 minutes, also under pressure. The resulting product weighed 41 oz./yd.<sup>2</sup>, had excellent physical integrity, and was exceptionally flexible.

25

EXAMPLE 28B

A cast film of a 60/40 weight % blend of TE-3313 and fluoroelastomer (derived from L-9025) latex (obtained from 3M) was laminated to the substrate of Example 28A. The resulting product had a flexibility and integrity comparable to Example 28A.

30

EXAMPLE 28C

The woven substrate of Example 28A was given 8 semi-fuse passes through FMK-4-10-B followed by a

final dry fuse pass. This resulted in a material .044 in. thick and weighing 52.4 oz./yd<sup>2</sup>. The product had excellent integrity and was somewhat more flexible than Example 2A, even though it was 20 percent heavier and approximately 30 percent thicker. The material was subjected to physical testing with the following results:

Trapazoidal Tear Strength, Warp Direction 260 lbs.  
Elongation at 40 lbs./in. load, Warp Direction 4.5%

#### EXAMPLE 29

A substrate of Style 15227 glass cloth was heat cleaned and impregnated with ET 4327 methyl phenyl silicone emulsion. An initial layer of perfluoroelastomer was applied in a single fuse dip operation through DuPont's TE-5506 experimental low crystallinity perfluorinated polymer in aqueous dispersion having specific gravity of 1.39.

A blend containing 104 parts by weight of TE-3313 (57.7 percent PTFE solids) and 154 parts by weight of KALREZ latex (26 percent perfluoroelastomer solids) was prepared. The mixture was evaporated to dryness in an air circulating oven operating at 90°C and the resulting cake was chopped and washed several times in hot water in a Waring blender and again dried at 90°C to yield a coarse, flaked crumb. Using the technique employed in making Example 17E, the crumb was pressed into a film and the film was laminated to the substrate. The substrate weighed 24.7 oz./yd.<sup>2</sup>.

The film and the laminate were both pressed under the following conditions: platen temperature, 550°F.; force on platens, 20 tons (approximately 560 psi on film, 1100 psi on laminate); time at temperature, 3 min.

The resulting flexible product was approximately .040 in. thick, and exhibited good physical integrity, with a resilient, well-adhered, and tough coating.

EXAMPLE 30

A film was prepared from TE 5489 derived solids treated to remove silicone oil as described in Example 17E. 10 grams of toluene-washed crumb were pressed in a platen press between pieces of aluminum foil treated with a silicone mold release. The platens were operated at 325°F under a force of 1 ton for one minute. Thereafter, the material was cooled under pressure.

The resulting film was placed on a piece of 100 percent polyester knit fabric, Style 5162, white, 1980 (manufactured by Armtex, Inc., Pilot Mountain, North Carolina) and pressed essentially as described in Example 17K, but with a platen temperature of 325°F and 10 tons of force on the platens for one minute.

A durable, flexible composite having a thickness of approximately .015 in. resulted. The knit reinforcement was thoroughly encapsulated by the perfluoroelastomer matrix.

EXAMPLE 31

Employing methods described in Example 30, 5 grams of TE 5489 solids were pressed into a film and laminated to one side of a piece of TYVEK spun-bonded polyolefin, Style 1056D (manufactured by DuPont). Platen temperatures of 240°F were employed to laminate the material and the work was pressed for 2 minutes with approximately 1 ton of force on the platens. After a 1 minute dwell at temperature and pressure, the material was cooled under pressure to about room temperature. The resulting laminate containing perfluoropolymer on one face (approximately .009 in. thick) was flexible and tough.

EXAMPLES 32 A&B

Employing methods similar to those described in Example 31, laminates of TE-5489 fluoroelastomer on

two styles of REEMAY spun-bonded polyester (manufactured by DuPont) were prepared. Example 32A included DuPont Style 2431 reinforcement and Example 32B contained DuPont Style 2024 reinforcement. In both  
5 examples, pressing conditions were as follows: platen temperature, 335°F.; force on platen, 2 tons; time at temperature, 2 minutes; and cooling under pressure. Composites so produced contained perfluoropolymer on one face and polymer on the other. Moreover, the  
10 composites were flexible and tough.

#### EXAMPLE 33

Example 33 was prepared by using the materials and techniques employed in making Example 30, but with reduced laminating pressure to obtain a composite  
15 with perfluoropolymer on one face of the Armtex Style No. 5162 polyester knit. Pressing conditions were: platen temperature, 335°F.; force on platen, 1-2 tons; time at temperature, 1 minute; and cooling under pressure.

20 The resulting laminated composite at .012 inches of thickness was noticeably more flexible and conformable than that of Example 30. The polymer matrix was firmly bonded to the reinforcement, showing no tendency toward delamination.

#### EXAMPLE 34

25 Employing the techniques used in making Example 33, a single faced laminate employing resin derived from TE-5489 was produced on a 50/50 polyester/cotton interlock fabric, 1.85 yield at 60 inch width (Style  
30 No. 443833 produced by Burlington Industries, New York, New York).

The resulting product was a durable, flexible and conformable laminate. The perfluoropolymer was firmly anchored to one side. The unlaminated side of  
35 the composite maintained its soft textile quality.

EXAMPLES 35 A&B

Examples 35 A&B were made using methods essentially similar to those used in making Examples 2A and 2B with the exception that Dupont VTR-5307 latex in the PTFE/fluoroelastomer latex blend was replaced with AFLAS TFE/propylene copolymer latex was obtained from Xenox, Inc., Houston, Texas. The blend was made by mixing 104 pbw of Dupont TE-3313 with 129 pbw of the AFLAS latex, thereby maintaining the 60/40 proportion of PTFE to fluoroelastomer. The composition of Examples 35 A&B is shown below:

	<u>Example 35A</u>	<u>Example 35B</u>
reinforcement component weight	15227 glass cloth 18 oz./yd. <sup>2</sup>	129 glass cloth* 6.6 oz./yd. <sup>2</sup>
reinforcement finish	silicone oil**	silicone oil**
initial layer	PTFE** 5 oz./yd. <sup>2</sup>	PTFE** 1.0 oz./yd. <sup>2</sup>
overcoat layer	AFLAS/PTFE 10.6 oz./yd. <sup>2</sup>	AFLAS/PTFE 2.6 oz./yd. <sup>2</sup>
topcoat	PTFE 1.2 oz./yd. <sup>2</sup>	PTFE 0.6 oz./yd. <sup>2</sup>

---

\* Style No. 129 glass cloth, ECD 225 1/3, plain weave, 38 x 40, 6.56 oz./yd.<sup>2</sup>, manufactured by Chemical Fabrics Corporation.

\*\* Reinforcement finish and initial layer applied simultaneously.

The physical properties of Examples 35 A&B are as follows:

<u>Property</u>	<u>Units</u>	<u>Example 35A</u>	<u>Example 35B</u>
weight	oz./yd. <sup>2</sup>	34.8	10.8
thickness	in.	.030	.009
strip tensile strength	lbs./in.		
warp		813	258
fill		907	332
trapezoidal tear strength	lbs.		
warp		93	19
fill		111	25
tensile strength after fold	lbs./in.		
warp		807	not
fill		960	tested
coating adhesion	lbs./in.	12.1	5.3

#### EXAMPLES 36A-C

Example 36A was prepared by the following procedure: ECB150 4/3 fiberglass yarn was treated with silicone oil and impregnated with TE-5506 low crystallinity perfluoropolymer (DuPont) in a single application using a mixture of TE-5506 and ET-4327 emulsion (Dow Corning), followed by drying and fusing. The bath was prepared by mixing 199 pbw of TE-5506 (50.3% solids) with 23 pbw of ET-4327 (35% solids) and was diluted with water to a specific gravity of 1.225. The proportion of perfluoropolymer to silicone polymer in the bath was 12.5 to 1, by weight.

The impregnated yarn prepared according to Example 36A was woven into a 14 x 14 count fabric weighing approximately 20 oz/yd<sup>2</sup>. The woven fabric was then baked at approximately 550°F for 1 minute and used in preparing Examples 36B and 36C as follows. Example 36B was prepared by applying to the fabric of

Example 36A an intermediate coating of PTFE/fluoro-elastomer blend, weighing approximately 13 oz/yd<sup>2</sup>, in 4 semifused passes through FMK 4-10-B. The coating was fused by baking for 1 minute at approximately 700°F and an overcoat of PTFE was applied from TE-3313 (DuPont) diluted to a specific gravity of 1.30. The final weight of the example was 34 oz/yd<sup>2</sup>.

Example 36C was prepared by applying to the fabric of Example 36A an intermediate coating of PTFE in 6 semifuse dip passes through TE-3313 at 1.485 specific gravity followed by calendering, dry fusing, and a final fuse dip through TE-3313 at 1.30 specific gravity. No overcoat layer was applied.

Examples 36B-C were subjected to physical testing and the following results were obtained:

<u>Test</u>	<u>Units</u>	<u>Example 36B</u>	<u>Example 36C</u>
weight	oz./yd. <sup>2</sup>	34.0	34.8
thickness	in.	.035	.033
tensile strength	lbs./in.		
warp		630	667
fill		590	515
tensile strength after fold	lbs./in.		
fill		575	455
trapezoidal tear strength	lbs.		
fill		93	95
coating adhesion	lbs./in.	9.7	10.7

While representative applications and embodiments of the invention have been described, those skilled in the art will recognize that many variations and modifications of such embodiments may be made without departing from the spirit of the invention, and it is intended to claim all such variations and modifications as fall within the true scope of the invention.



Claims

1. A composite which comprises a substrate coated  
with a matrix comprising:
  - 5           A) an initial layer of a perfluoropolymer  
            selected from the group comprising a  
            perfluoroplastic, a perfluoroelastomer,  
            a blend of perfluoroplastic and per-  
            fluoroelastomer, or any combination  
            thereof; and
  - 10          B) an overcoat layer of a fluoroelastomer, a  
            fluoroplastic, a fluoroelastomer/fluoro-  
            plastic blend, or any combination thereof.
2. A composite according to claim 1 wherein the  
15       initial layer comprises a perfluoropolymer and a  
      lubricating agent.
3. A composite according to claim 1 wherein the  
      substrate is treated with a coupling agent to  
      promote bonding.
4. A composite according to claim 1 wherein said  
20       overcoat layer comprises a blend of a fluoro-  
      elastomer and a fluoroplastic, wherein the fluoro-  
      elastomer comprises from about 10% to about 90%  
      by weight of the blend.
5. A composite according to claim 4 wherein said  
25       fluoroelastomer comprises from 25% to 60% by  
      weight of said blend.
6. A composite according to claim 4 wherein an  
      intermediate layer comprising a fluoroelastomer  
      is interposed between said initial layer and  
30       said overcoat layer.

7. A composite according to claim 1 having a topcoat selected from the group comprising a fluoroplastic, a fluoroelastomer, a fluoroplastic/fluoroelastomer blend or a combination thereof.
- 5 8. A composite according to claim 1 wherein resins in said layers are at least partially cross-linked.
9. A composite according to claim 1 wherein only one face of said substrate is coated with a matrix.
- 10 10. A composite according to claim 1 wherein said substrate is reinforcement material capable of withstanding composite formation temperatures.
11. A composite according to claim 10 wherein said substrate is a yarn, filament, monofilament, or  
15 other fibrous material.
12. A composite according to claim 10 wherein said substrate is a textile selected from the group comprising woven and non-woven materials.
13. A composite according to claims 1 or 12 wherein  
20 said substrate is selected from the group comprising glass, fiberglass, ceramics, graphite (carbon), polybenzimidazole, polyaramides, PTFE metal, polyolefins, polyesters, polyamides, copolymers of TFE, polyether sulfones, polyimides  
25 polyether ketones, polyethenimides, novoloid phenolic fibers, natural and synthetic textiles.
14. A composite according to claims 1 or 7 wherein said fluoroplastic comprises PTFE, PFA or FEP.

15. A composite according to claims 1 or 7 wherein said fluoroelastomer is selected from the group comprising copolymers of vinylidene fluoride and at least one other fluorinated monomer selected from the group comprising hexafluoropropylene; tetrafluoroethylene; chlorotrifluoroethylene; and pentafluoropropylene.
16. A composite according to claim 1 wherein said perfluoroplastic comprises PTFE, PFA or FEP.
17. A composite according to claim 1 wherein said perfluoroelastomer comprises a copolymer of TFE and perfluorovinylether such as PMVE or PPVE.
18. A composite according to claim 1 wherein any fluoropolymer component may contain a functional group selected from the group comprising carboxyl and sulfonic acid and salts thereof, halogen, and a reactive hydrogen on an alkyl side chain.
19. A composite which comprises a substrate coated with a layer comprising a perfluoroelastomer or a perfluoroelastomer/perfluoroplastic blend.
20. A composite which comprises a substrate which is insusceptible to the corrosive effects of hydrogen fluoride and which is coated with a matrix comprising a fluoroelastomer/perfluoroplastic blend.

21. A method for the manufacture of a composite including a substrate coated with a matrix, wherein the said matrix is formed by a gradation of fluoropolymer layers, which comprises the steps of:
- 5
- i) first applying an initial layer comprising a perfluoropolymer in an amount sufficient to substantially shield the substrate from chemical corrosion without impairing flexibility;
- 10
- ii) thereafter applying to said initial layer an overcoat layer comprising a fluoroelastomer, a fluoroplastic, a fluoroelastomer/fluoroplastic blend, or
- 15
- a combination thereof.
22. A method according to claim 21 wherein said initial layer comprises a perfluoropolymer, a lubricating agent, and a coupling agent.
23. A method according to claim 21 wherein the outermost layer is applied as a foam.
- 20

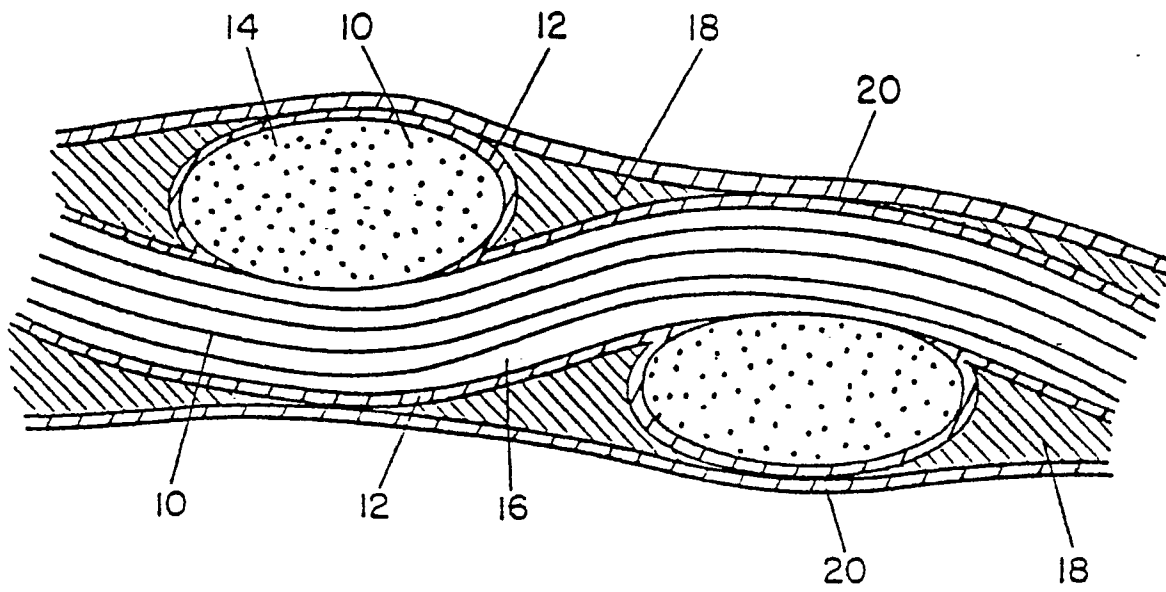


FIG. 1

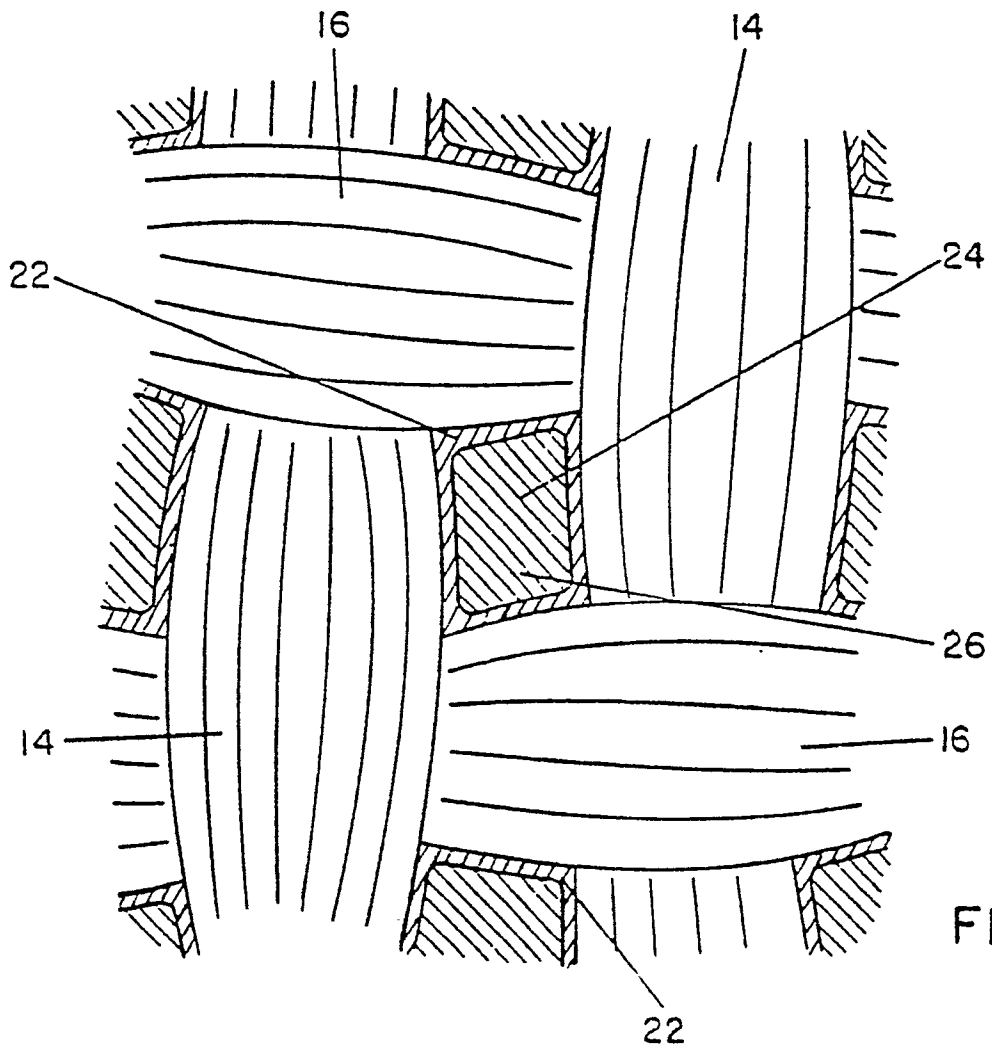


FIG. 2

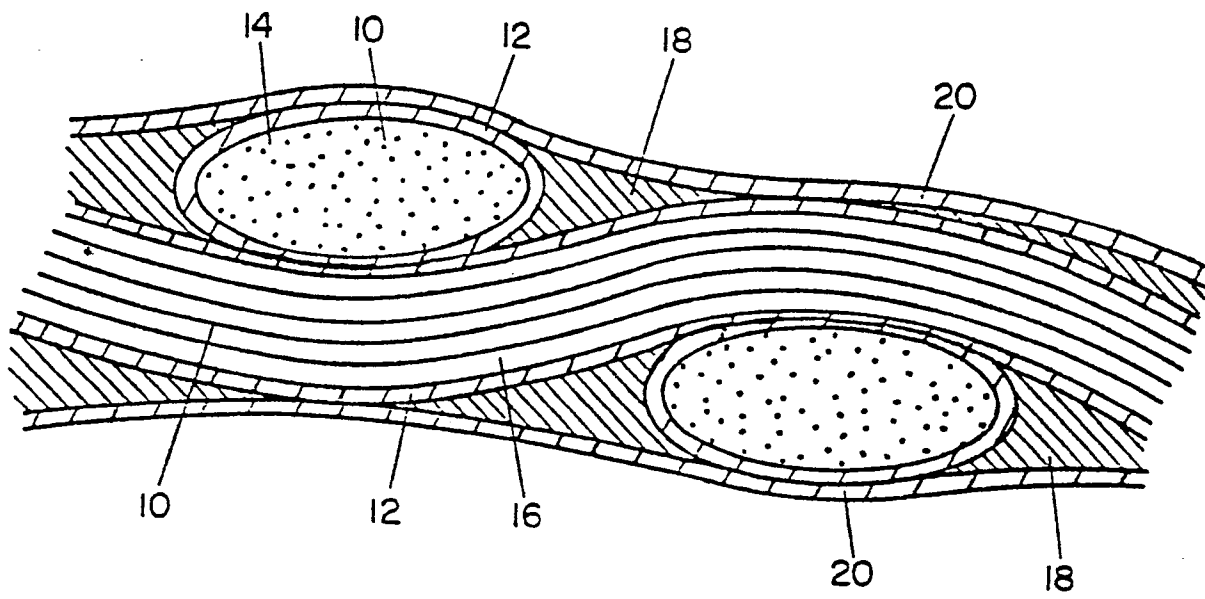


FIG. 1A

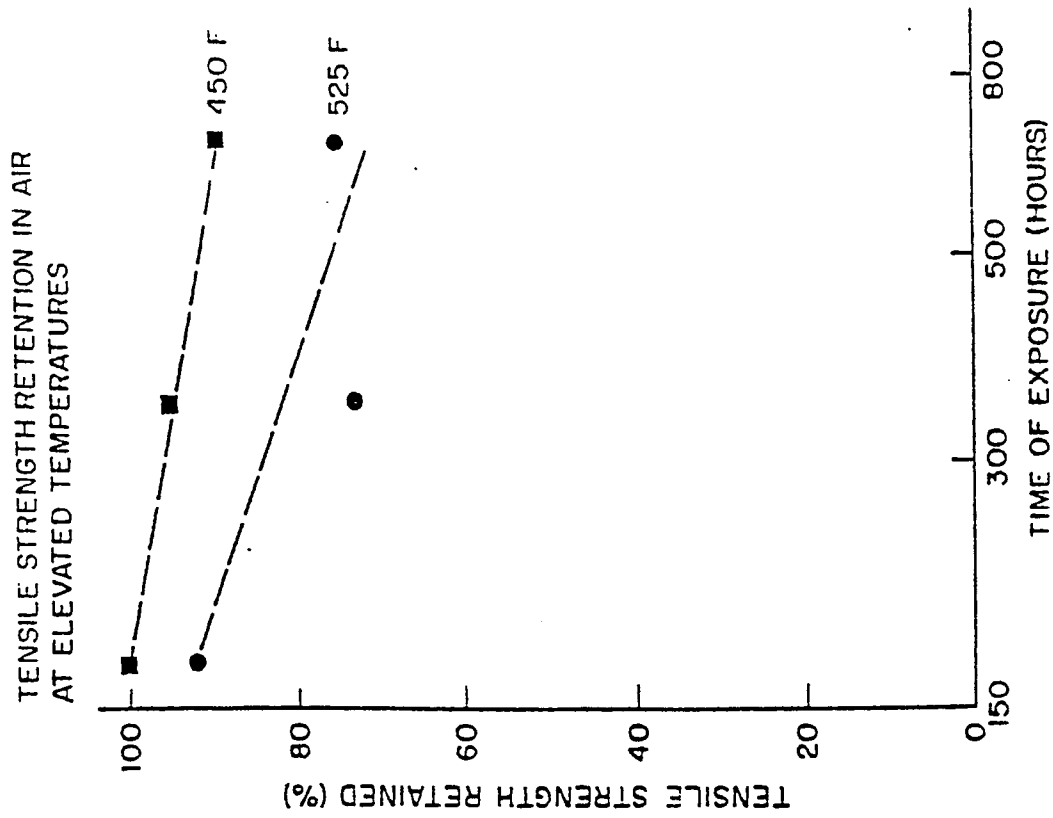


FIG. 3

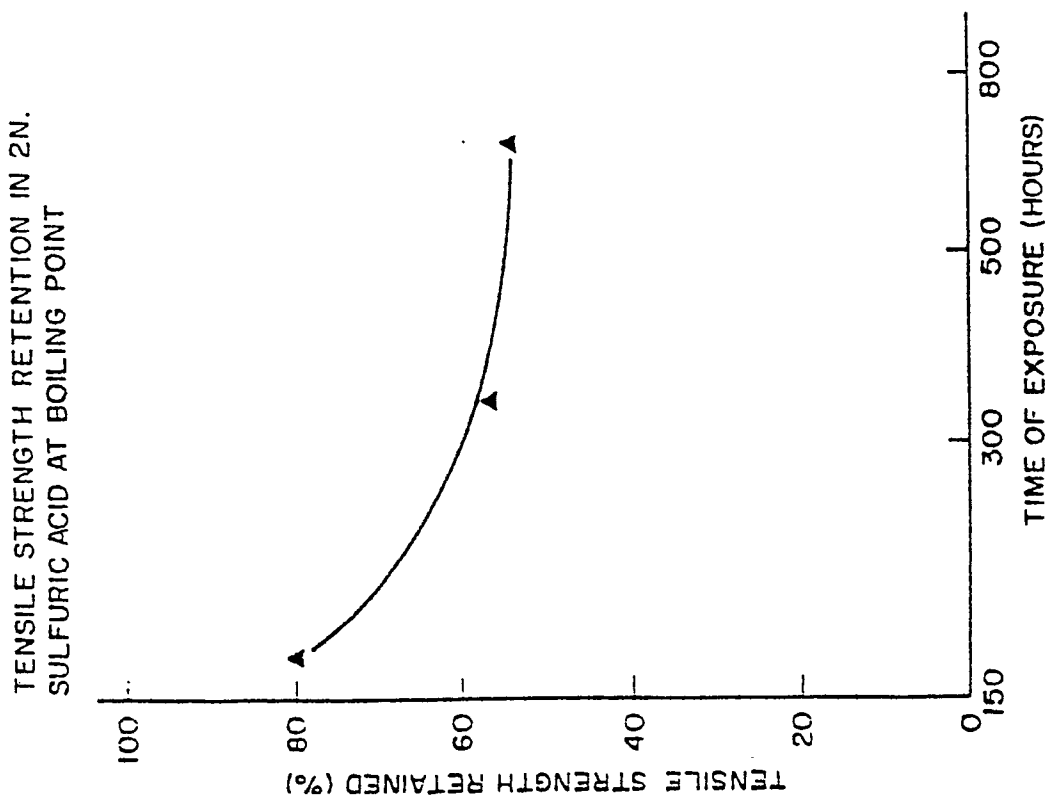


FIG 4