(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 1 754 547 A2

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
21.02.2007 Bulletin 2007/08

(21) Application number: **06075643.4**

(22) Date of filing: **26.10.1999**

(51) Int Cl.:
B05D 7/08 $^{(2006.01)}$
B05D 7/12 $^{(2006.01)}$
B05D 7/24 $^{(2006.01)}$
C14C 11/00 $^{(2006.01)}$
D06M 14/00 $^{(2006.01)}$
D06M 15/256 $^{(2006.01)}$
D21H 19/16 $^{(2006.01)}$

(84) Designated Contracting States:
DE ES FR GB IT NL

(30) Priority: **27.10.1998 US 105798 P**
30.09.1999 US 409173
30.09.1999 US 409207

(62) Document number(s) of the earlier application(s) in accordance with Art. 76 EPC:
99970953.8 / 1 124 647

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Remarks:
This application was filed on 20 - 03 - 2006 as a divisional application to the application mentioned under INID code 62.

(54) In situ fluoropolymer polymerization into porous substrates

(57) The present invention relates to in situ polymerization of fluoropolymer into porous substrates, to improve resistance to wear, tear and creep, decay, and degradation by wetting, staining and warping, and to improve durability while maintaining the appearance of the substrate.

Printed by Jouve, 75001 PARIS (FR)

Description

FIELD OF THE INVENTION

[0001] This invention relates to the polymerization of fluoropolymers into porous substrates. The fluoropolymer/substrate network that results is present on the surface of the substrate and is also deposited into the substrate at appreciable depths. Depending upon the proportion of fluoropolymer relative to substrate, the fluoropolymer may provide a protective coating for the substrate and/or the substrate may improve the physical properties of the fluoropolymer.

TECHNICAL BACKGROUND OF THE INVENTION

[0002] Porous materials have a host of uses. Common uses for leather and porous polyurethane are to produce clothing and furniture. Common uses for wood include use as a building material and for the production of furniture. Polyimide compositions are known to have unique performance characteristics, which make them suitable for uses in the form of bushings, seals, electrical insulators, compressor vanes, brake linings, and others as described in U.S. Patent No. 5,789,523. Para-oriented aromatic polyamides (para-aramids) are used to make fiber substrates that are useful for wear resistant applications.

[0003] All of the porous materials described may degrade and decay over time by staining, wetting, warping, tearing or wearing. It is desirable to treat porous materials to improve resistance to wear, tear, creep, decay, and degradation by wetting, staining and warping, and to improve durability while maintaining the appearance of the materials.

[0004] For many years, textiles have been chemically treated to improve water and oil repellency. Different applications are commercially available to protect different kinds of substrates from oil and water staining. For example, Scotchgard® brand protector for fabrics sold by the 3M Company, and Teflon® Fabric Protector sold by E. I. du Pont de Nemours and Company, are available to consumers for use with textiles and fabrics. The use of granular fluoro-compounds is also discussed in Japanese Patent 05318413. The invention involves a method whereby a raw wood material is impregnated with fluorinated microparticles having a diameter of 5 microns and a compound which changes to insoluble cured resin.

[0005] There are several references which have used fluoro-compounds in wood to enhance the properties of wood. For example, U.S. Patent No. 3,962,171 discusses a protective coating composition. The composition is used for painted and unpainted metal, plastic and wood surfaces. The method comprises preparing a mixture of a solution of 20 parts of granular polytetrafluoroethylene in Freon®. The composition is sprayed onto an acrylic painted surface, dried and wiped to form a transparent coating.

[0006] The use of granular fluoro-compounds is also discussed in Japanese Patent 05318413. The invention involves a method whereby a raw wood material is impregnated with fluorinated microparticles having a diameter of 5 microns and a compound which changes to insoluble cured resin. The compound is cured to fix the microparticles with the resin. The uses and advantages listed in the abstract include use as building materials, woody appearance, contamination resistance, and moisture and water resistance. The invention does not teach polymerization of a fluoro-compound into the wood as the present invention does.

[0007] Other references include the treatment of microporous materials with fluoroacrylate to achieve permanent water and oil repellency. For example, U.S. Patent No. 5,156,780 teaches a method for treating microporous substrates to achieve water and oil repellency while maintaining porosity. In the '780 method, the substrates are impregnated with a solution of monomer in a carrier solvent. The carrier solvent is first substantially removed from the substrate for the express purpose of leaving the monomer as a thin conformal coating on all internal and external substrate surfaces. In this manner, the monomer is converted to polymer and the polymer does not block the pores or restrict flow in subsequent use as a filtration membrane.

[0008] If enough fluoromonomer is polymerized into a porous structure, a point is reached at which there is more fluoropolymer than substrate and the composition can be considered a filled fluoropolymer. Fluoropolymers such as PTFE are commonly filled with substances such as glass fibers, graphite, asbestos, and powdered metals (Kirk-Othmer Encyclopedia of Chemical Technology, Fourth Edition, Volume 11, John Wiley and Sons, New York, pages 626 and 630). The filler is generally added for the purpose of improving some property of the fluoropolymer, such as creep or hardness.

[0009] Most often, filled fluoropolymers are made by physically mixing the fluoropolymer with the filler or by coagulating an aqueous fluoropolymer emulsion on the filler, but such methods have their problems. Adhesion of fluoropolymer to filler can be quite poor, particularly if the fluoropolymer does not wet the filler and penetrate its pores and finer surface features. Fluoropolymer melts can be very stiff, making mixing/dispersion poor and nonuniform. Mechanical mixing can degrade some fillers, for example by breaking fine fibers. It is desirable to polymerize fluoromonomer onto the surface and into the pores of a substrate to achieve intimate fluoropolymer/substrate interpenetration and dispersion with minimal mechanical stress.

[0010] It is desirable to treat porous substrates, such as wood, wood by-products, aramids, polyimides, porous polyurethane, and leather compositions, such that the porous substrate is more resistant to degradation, especially by staining, warping and wetting.

SUMMARY OF THE INVENTION

[0011] Disclosed in this invention is a process for preparing a fluoropolymer/substrate composition, comprising:

in the case of gaseous fluoromonomer

(a) contacting a porous substrate with a solution comprising an initiator dissolved in a suitable solvent;
(b) exposing said substrate and said initiator to gaseous fluoromonomer under polymerization temperature and pressure conditions wherein the fluoromonomer polymerizes into said substrate;

wherein said polymerized gaseous fluoromonomer partially or completely fills and blocks the pores in the substrate; or in the case of liquid fluoromonomer

(a) preparing a solution comprising initiator and liquid fluoromonomer;
(b) contacting a porous substrate with said solution; and
(c) polymerizing the liquid fluoromonomer under polymerization temperature and pressure conditions wherein the fluoromonomer polymerizes into said substrate, optionally in the presence of gaseous fluoromonomer;

wherein said polymerized liquid fluoromonomer partially or completely fills and blocks the pores in the substrate.

[0012] Also disclosed is a composition of matter made by a process for preparing a fluoropolymer/substrate composition wherein said process, comprises:

in the case of gaseous fluoromonomer

(a) contacting a porous substrate with a solution comprising an initiator dissolved in a suitable solvent;
(b) exposing said substrate and said initiator to gaseous fluoromonomer under polymerization temperature and pressure conditions wherein the fluoromonomer polymerizes into said substrate;

wherein said polymerized gaseous fluoromonomer partially or completely fills and blocks the pores in the substrate; or in the case of liquid fluoromonomer

(a) preparing a solution comprising initiator and liquid fluoromonomer;
(b) contacting a porous substrate with said solution; and
(c) polymerizing the liquid fluoromonomer under polymerization temperature and pressure conditions wherein the fluoromonomer polymerizes into said substrate, optionally in the presence of gaseous fluoromonomer;

wherein said polymerized liquid fluoromonomer partially or completely fills and blocks the pores in the substrate.

[0013] A further disclosure of the present invention is a composition of matter, comprising: a porous substrate wherein said substrate is an open pore structure having a surface and interconnecting pores throughout the substrate; and polymerized fluoropolymer, wherein said fluoropolymer is present within and on the surface of said substrate, and wherein the amount of fluoropolymer present in said composition is, in the case of a non-wood substrate, from about 0.1 percent to about 300 percent of the weight of said non-wood substrate, and in the case of a wood substrate, from about 0.1 to about 150 percent of the weight of said wood substrate.

[0014] Also disclosed is the use of these compositions as filler materials for other polymers.

BRIEF DESCRIPTION OF THE DRAWINGS

[0015]

Figure 1 is a depiction of a block of redwood as described in Example 2 in the present invention.
Figure 2 is a depiction of the cross sectioning and electron microscopy scanning of a block of redwood as described in Example 2 in the present invention.
Figure 3 is a depiction of a block of oak as described in Example 3 in the present invention.

Figures 4 is a depiction of the cross sectioning and electron microscopy scanning of a block of oak as described in Example 3 in the present invention.

DETAILED DESCRIPTION OF THE INVENTION

[0016] The present invention discloses a fluoropolymer/substrate composition. The presence of fluoropolymer in the composition provides a protective material for the substrate and may also add aesthetic qualities to the substrate. A further advantage of the fluoropolymer/substrate composition is that the physical properties of the fluoropolymer are improved.

[0017] The present invention also discloses a method for in-situ fluoropolymer polymerization into porous substrates. The method produces a fluoropolymer/substrate composition wherein the presence of fluoropolymer adds aesthetic quality to some substrates, enhances some of the porous substrates, or functions as a protective material for other porous substrates. The method used leaves the initiator and the initiator carrier solvent in the substrate during polymerization and uses undiluted monomer or, in its preferred embodiment, gaseous monomer, to penetrate and block all pores to the greatest depth possible. The object of the present invention is to provide a method for treating the substrate such that the presence of the fluoropolymer/substrate composition decreases or eliminates penetration of agents that cause degradation so as to increase the substrate's resistance to wetting by oil and water, reduce warping and staining by oil, water, and other common materials, and to improve durability. The fluoropolymer/substrate composition improves resistance to wear, tear, creep and decay.

[0018] The disclosed fluoropolymer/substrate compositions that result have properties that give them a variety of utilities. For example, when the preferred fluoromonomer, TFE, is used in the process for wood substrates, a PTFE/wood composition results and the wood is protected by the presence of the PTFE. PTFE polymerized into the wood increases the wood's resistance to wetting by oil and water, reduces staining by oil and water, decreases warpage and improves durability. These properties make the composition attractive for building materials. The method disclosed herein for preparing intimately interpenetrated fluoropolymer/substrate compositions improves the functional lifetime and/or the appearance of the substrates.

[0019] Coating the surface and blocking the pores of a substrate with fluoropolymer prevents or slows degradation by wetting and penetration of the substrate by agents such as water, acids, bases, foodstuffs, and cosmetics, thereby preventing staining, warping, and unwanted chemical or physical property changes in the substrate. As a case in point, the Ultrasuede®/PTFE composition of Example 15 below wets less readily than untreated Ultrasuede®. Coating the surface and blocking the pores of a substrate with fluoropolymer can also slow mechanical degradation by such means as abrasion, creep, or tearing. As a case in point, the polyimide/PTFE composition of Example 8A abraded 8X more slowly than untreated polyimide.

[0020] Going further, once the volume of polymerized fluoropolymer exceeds that of the substrate or once the fluoropolymer/substrate network has been blended into pure fluoropolymer, the substrate can then be considered as dispersed in the fluoropolymer for the purpose of modifying fluoropolymer properties. These compositions are commonly referred to as "filled fluoropolymers". For example, intimately interpenetrated porous polyimide or aramid particulates can be added to poly(tetrafluoroethylene) to potentially decrease PTFE creep. In a process disclosed in the present invention, the fluoromonomer is polymerized both on the surfaces and into the pores of a substrate to achieve intimate fluoropolymer/substrate interpenetration and dispersion. By using this method, the filled fluoropolymer is prepared with minimal mechanical stress. This process reduces degradation, and thereby, offers a solution to the problem of degradation that occurs with mechanical mixing.

[0021] By "porous substrate" is meant any solid material penetrated throughout with interconnecting pores of a size such as to allow absorption of liquid initiator solution and monomer. The porous substrates can take any form including microscopic particulates, microscopic fibers, coarse particulates, pulp, fibrids, chunks, blocks, uncompressed, partially or fully compressed parts, sheets, films, membranes, and coatings. Porous substrates are not meant to include materials such as cloth where the only mechanism of fluoropolymer entrainment is gross entrapment between separate fibers rather than subsurface penetration into a substrate's pores. This process works with any porous substrate that does not inhibit fluoromonomer polymerization. Substrates not inhibiting polymerization include wood (including wood by-products such as paper), p-aramid fibers, molded polyimide parts, porous polyurethane and leather. By "wood" we mean raw lumber as well as more processed forms of wood and its by-products including wood veneer, wood chips, sawdust, paper, and cardboard. Whether a substrate will inhibit polymerization must be determined empirically substrate by substrate and may vary for the same substrate, depending upon prior finishing and treatment.

[0022] The inventive process involves in situ polymerization of fluoromonomer into substrates. Polymerization temperatures range from about 0°C to about 300°C, for non-wood substrates, preferably from about 0°C to about 100°C for all disclosed substrates, most preferably from about 5°C to about 30°C for all disclosed substrates. For those substrates that retain their rigid pore structures at high temperatures and do not thermally decompose, polymerizations can be run at temperatures up to about 300°C.

[0023] Polymerization pressures may vary. For gaseous monomers, pressures are generally from about 7 psia to about 500 psia. In the case of liquid monomers, such as 4,5-difluoro-2,2-bis(trifluoromethyl)-1,3-dioxole (PDD) or perfluoro (2-methylene-4-methyl-1,3-dioxolane) (PMD), the reaction is generally carried out under atmospheric pressure unless copolymers with TFE or other gaseous monomers are desired. In the absence of a pure gaseous monomer phase, oxygen should be excluded and an inert atmosphere, such as nitrogen, provided.

[0024] The process of the present invention uses fluoromonomer in either the gaseous or liquid state. Gaseous monomers include tetrafluoroethylene (TFE), trifluoroethylene, vinylidene fluoride, chlorotrifluoroethylene, hexafluoroisobutylene and perfluoro methyl vinyl ether. Liquid monomers include PDD, PMD and perfluoro propyl vinyl ether. These monomers may be homopolymerized or copolymerized to make compositions known to those skilled in the art. Examples include tetrafluoroethylene homopolymer, tetrafluoroethylene/4,5-difluoro-2,2-bis(trifluoromethyl)-1,3-dioxole copolymer, and tetrafluoroethylene/perfluoro (2-methylene-4-methyl-1,3-dioxolane) copolymer.

[0025] In the case of liquid fluoromonomer, such as PDD and PMD, the carrier solvent can be the monomer or the monomer containing a small amount of initiator solution (for example, hexafluoropropylene oxide dimer peroxide (DP) $\underline{1}$ $CF_3CF_2CF_2OCF(CF_3)(C{=}O)OO(C{=}O)CF(CF_3)OCF_2CF_2CF_3$ $\underline{1}$, DP in a Freon® solvent).

[0026] For an active monomer such as TFE, polymerization often deposits about 0.1 to 10 wt. % PTFE in the substrate at atmospheric pressure. Higher TFE pressures yield higher weight gains. When higher pressures are used, standard barricading must be employed to protect against TFE deflagration and runaway polymerization.

[0027] The process invention disclosed herein works for most organic initiators commonly used for fluoroolefin polymerizations, including, but not limited to, diacylperoxides, peroxides, azos and peroxydicarbonates. The preferred initiator is DP. DP has a half-life of about 4 hours at 20°C which means that DP lasts long enough for a polymerization run to be set up at room temperature without excessive initiator loss and yet DP still reacts fast enough at room temperature for polymerizations to run to completion fairly quickly. Preferred run times are from about 4 to about 24 hours.

[0028] In the preferred embodiment of this invention, the initiator is first synthesized in any solvent that is compatible with fluoroolefin polymerization and the initiator solution then absorbed into the substrate. Suitable solvents comprise chlorofluorocarbons such as Freon® 113 ($CFCl_2CF_2Cl$), hydrofluorocarbons, such as Vertrel® XF (HFC-43-10mee; 2,3-dihydroperfluoropentane) specialty fluid, perfluorocarbons, such as perfluorohexane, perfluoroethers, such as Fluorinert® FC-75 sold by 3M Company, perfluoroamines, such as Fluorinert® FC 40, and perfluorodialkylsulfides, such as $CF_3CF_2CF_2CF_2SCF_2CF_2CF_2CF_2CF_3$. The preferred solvents for DP are Vertrel® XF and Freon® E1 ($CF_3CF_2CF_2OCFHCF_3$).

[0029] In this invention, the preferred initiator solution comprises a solution of DP in Vertrel® XF ($CF_3CFHCFHCF_2CF_3$). It is further preferred that the fluoromonomer is tetrafluoroethylene. TFE polymerizes to form PTFE.

[0030] In the preferred embodiment of the process where the substrate is wood, the wood is soaked in a solution of free radical initiator. The preferred initiator when wood is used as a substrate is DP. The wood is then removed from the initiator solution and the free liquid is allowed to drain away. By "free liquid" is meant solution that is not absorbed by the substrate during soaking. The initiator-soaked wood is then placed in an apparatus suitable for polymerization. The apparatus is filled with gas phase fluoromonomer, and the polymerization allowed to run. The polymerization apparatus can be a simple plastic bag for atmospheric pressure polymerization or an autoclave for polymerization at pressures up to several hundred psi.

[0031] When a preferred substrate is used, the porous aramid or polyimide is immersed for about 1 minute in a 0.1 to 0.2 M solution of DP in $CF_3CFHCFHCF_2CF_3$ solvent. The excess solvent is filtered off or is drained from the aramid or polyimide, and the still damp polymer placed in a container with 1 atmosphere pressure of tetrafluoroethylene gas until the substrate has gained preferably 5 to 20% of its weight by polymerization of the tetrafluoroethylene to poly (tetrafluoroethylene).

[0032] The preferred aramids are poly(p-phenylene terephthalamide) (hereinafter "PPD-T") fibers and poly(m-phenylene isophthalamide)(hereinafter "MPD-I") in the form of fiber, particles, pulp or fibrids, that are dried or never-dried. Examples of preferred aramids are poly(p-phenylene terephthalamide) fibers sold by the DuPont Company under the tradename "Kevlar®", and poly(m-phenylene isophthalamide) sold by the DuPont Company under the tradename "Nomex®".

[0033] A "never-dried aramid" means an aramid coagulated from a solution by contact with a non-solvent (usually an aqueous bath of some sort, such as water or an aqueous solution). When contacted with the non-solvent, the polymer coagulates and most of the solvent is removed from the aramid. The aramid has an open sponge-like structure, which usually contains about 150-200% by weight of the aramid of non-solvent (again, usually water). It is this open sponge-like structure, which has imbibed the non-solvent, which is referred to herein as "never-dried aramid".

[0034] By PPD-T is meant the homopolymer resulting from mole-for-mole polymerization of p-phenylenediamine and terephthaloyl chloride and, also, copolymers resulting from incorporation of small amounts of other aromatic diamine with the p-phenylene diamine and of small amounts of other aromatic diacid chloride with the terephthaloyl chloride. Examples of other acceptable aromatic diamines include m-phenylene diamine, 4,4'-diphenyldiamine, 3,3'-diphenyldiamine, 3,4'-diphenyldiamine, 4,4'-oxydiphenyldiamine, 3,3'-oxydiphenyldiamine, 3,4'-oxydiphenyldiamine, 4,4'-sulfonyldiphenyldiamine, 3,3'-sulfonyldiphenyldiamine, 3,4'-sulfonyldiphenyldiamine, and the like. Examples of other acceptable aromatic diacid chlorides include 2,6-naphthalenedicarboxylic acid chloride, isophthaloyl chloride, 4,4'-oxydibenzoyl chloride, 3,3'-oxydibenzoyl chloride, 3,4'-oxydibenzoyl chloride, 4,4'-sulfonyldibenzoyl chloride, 3,3'-sulfonyldibenzoyl chloride, 3,4'-sulfonyldibenzoyl chloride, 4,4'-dibenzoyl chloride, 3,3'-dibenzoyl chloride, 3,4'-dibenzoyl chloride, and the like. As a general rule, other aromatic diamines and other aromatic diacid chlorides can be used in amounts up to as much as about 10 mole percent of the p-phenylene diamine or the terephthaloyl chloride, or perhaps slightly higher, provided only the other diamines and diacid chlorides have no reactive groups which interfere with the polymerization reaction.

[0035] By MPD-I is meant the homopolymer resulting from mole-for-mole polymerization of m-phenylenediamine and isophthaloyl chloride and, also, copolymers resulting from incorporation of small amounts of other aromatic diamine with the m-phenylene diamine and of small amounts of other aromatic diacid chloride with the isophthaloyl chloride. Examples of other acceptable aromatic diamines include p-phenylene diamine, 4,4'-diphenyldiamine, 3,3'-diphenyldiamine, 3,4'-diphenyldiamine, 4,4'-oxydiphenyldiamine, 3,3'-oxydiphenyldiamine, 3,4'-oxydiphenyldiamine, 4,4'-sulfonyldiphenyldiamine, 3,3'-sulfonyldiphenyldiamine, 3,4'-sulfonyldiphenyldiamine, and the like. Examples of other acceptable aromatic diacid chlorides include 2,6-naphthalenedicarboxylic acid chloride, terephthaloyl chloride, 4,4'-oxydibenzoyl chloride, 3,3'-oxydibenzoyl chloride, 3,4'-oxydibenzoyl chloride, 4,4'-sulfonyldibenzoyl chloride, 3,3'-sulfonyldibenzoyl chloride, 3,4'-sulfonyldibenzoyl chloride, 4,4'-dibenzoyl chloride, 3,3'-dibenzoyl chloride, 3,4'-dibenzoyl chloride, and the like. As a general rule, other aromatic diamines and other aromatic diacid chlorides can be used in amounts up to as much as about 10 mole percent of the m-phenylene diamine or the isophthaloyl chloride, or perhaps slightly higher, provided only the other diamines and diacid chlorides have no reactive groups which interfere with the polymerization reaction.

[0036] Substrates specifically exemplified for the present invention include wood, molded polyimide parts, porous polyimide powder (or polyimide particulate), porous para-aramids such as poly(para-phenylene terephthalamide) [PPD-T] in the forms of powder, pulp and/or fiber, and porous meta-aramids, such as poly(m-phenylene isophthalamide) [MPD-I] in the forms of powder, fibers or fibrids, porous polyurethane, and leather (pigskin and cowskin).

[0037] The present invention also provides a fluoropolymer/substrate composition wherein the substrates are open structures with interconnecting pores throughout their bulk and the level of fluoropolymer in the fluoropolymer/substrate composition is about 0.1% to about 300%, for non-wood substrates, and about 0.1 to about 150% for wood substrates, of the weight of the substrate. Substrates useful in this invention include wood, paper, leather, porous polyurethane, and aramids and polyimides that have been precipitated as porous particulates or porous fibers and then left wet, dried, or molded only so far as to preserve enough porosity for subsequent penetration by fluoromonomer and initiator. Preferred substrates are porous aramid, polyimide particulates and polyimide parts.

EXAMPLES

EXAMPLE 1

POLYMERIZATION OF (PTFE) INTO DIFFERENT WOODS DECREASED WATER ABSORPTION, INCREASED DURABILITY

A. Polymerization of TFE into wood

[0038] A saw was used to cut samples of cedar, cherry, oak, pine, poplar, redwood, and walnut into cubes which measured roughly 0.75 inches on a side. Using glass jars, three cubes of each wood were soaked for 1 hour in ~50 ml of 0.185 M hexafluoropropylene oxide dimer peroxide (1, DP) at -15°C
$CF_3CF_2CF_2OCF(CF_3)(C{=}O)OO(C{=}O)CF(CF_3)OCF_2CF_2CF_3$ 1, DP
in Freon® E1 ($CF_3CF_2CF_2OCFHCF_3$). Each group of three cubes was air dried for about 30 seconds and then transferred to a 400 ml autoclave. In all cases the autoclave was chilled, evacuated, and filled with tetrafluoroethylene (TFE) gas. Fifty grams of TFE gas were charged in the case of cedar, cherry, pine, poplar, and redwood, but only 25 g were charged in the case of oak and walnut. The wood cubes were recovered, dried for 16 hours under pump vacuum, scraped with a spatula to remove loose polymer from the surface, and put under pump vacuum again until, after several days, a constant weight was achieved. Averaged over the three cubes of each wood type, weight gains from TFE polymerized into the wood as PTFE ranged from 14 to 95% as shown in Chart 1 below, wherein the woods are listed in order of decreasing sample weight and density. Most often, the less dense the starting wood, the greater the weight of PTFE deposited into the wood.

TABLE 1

PTFE Weight Gains for Different Woods, Averaged over 3 Cubes

Wood Type	Grams TFE Loaded to Autoclave	Average Cube Wt. Before	Average Cube Wt. After	Average Wt. Gain PTFE	Weight Gain As A Percent
Oak	25 g*	5.25 g	6.01 g	0.76 g	14.5%
Walnut	25 g*	4.53 g	5.45 g	0.92 g	20.3%
Cherry	50 g	4.34 g	5.63 g	1.29 g	29.7%
Poplar	50 g	4.08 g	5.65 g	1.56 g	38.2%
Pine	50 g	4.02 g	5.73 g	1.71 g	42.5%
Cedar	50 g	2.81 g	4.23 g	1.42 g	50.5%
Redwood	50 g	2.09 g	4.08 g	1.99 g	95.2%

*Strong exotherm and charring of the wood observed with 50 g TFE

B. Effect of PTFE on Water Absorption

[0039] For each wood type, cedar, cherry, oak, pine, poplar, redwood, and walnut, three cubes 0.75" on a side were assembled:

Cube #1:	A cube from part A above containing polymerized PTFE
Cube #2:	A cube from part A above containing polymerized PTFE, the surface of which has been lightly sanded to remove most visible traces of PTFE. In the discussion that follows these lightly sanded cubes are referred to as "PTFE/wood blocks".
Cube #3:	A cube untreated except that it has been put under pump vacuum overnight to mimic the final devolatilization step of part A above. In the discussion that follows the blocks that were not chemically treated are referred to as the "control" blocks.

[0040] For each wood type, all three cubes were simultaneously immersed in distilled water in the same glass jar. In every case the control block showed an immediate darkening when immersed in water whereas the PTFE/wood blocks retained much of their natural color and appearance. The cubes were then periodically withdrawn, patted damp dry, weighed to determine the amount of water absorbed, and reimmersed in the water. A comparison of water absorption data of the control and PTFE/wood blocks after 600 cumulative hours of immersion in water is shown in Chart 2.

TABLE 2

Affect of PTFE on Water Absorption After 600 Hours of Immersion

Wood	Starting Wood Density	ML H_2O Absorbed/ML of Wood (Control)	ML PTFE/ ML of Wood (PTFE/ wood)	ML H_2O/ ML of Wood (PTFE/ Wood)	(ML PTFE + ML H_2O/ ML Wood (PTFE/wood)
Oak	0.76 g/ml	0.60 ml	0.048 ml	0.52 ml	0.57 ml
Walnut	0.66 g/ml	0.58 ml	0.058 ml	0.38 ml	0.44 ml
Cherry	0.63 g/ml	0.64 ml	0.081 ml	0.42 ml	0.50 ml
Poplar	0.59 g/ml	0.71 ml	0.098 ml	0.35 ml	0.45 ml
Pine	0.58 g/ml	0.63 ml	0.11 ml	0.32 ml	0.43 ml
Cedar	0.41 g/ml	0.51 ml	0.089 ml	0.42 ml	0.51 ml
Redwood	0.30 g/ml	0.52 ml	0.13 ml	0.20 ml	0.33 ml

[0041] All starting cubes measured about 1.90 cm on a side for a net volume of about 6.9 ml each. Densities were calculated, as shown in column 2, from the average weights in Chart 1. The weight of the water absorbed over the course of 600 hours of immersion divided by the volume of the wood sample (6.9 ml), gave the volume of water absorbed per milliliter of wood in the control blocks, as shown in column 3. There was little correlation between wood density and the volume of water absorbed. For example, although redwood was calculated to have less than half the density of oak, redwood absorbed slightly less water. Using the weight gains from Chart 1 and an assumption of about 2.3 g/ml for the PTFE, the volume of PTFE deposited per ml of wood in the PTFE/wood cubes was calculated, as shown in column 4. The weight of water absorbed by the PTFE/wood blocks over 600 hours of immersion was divided by 6.9 to calculate the volume of water absorbed per ml of wood in the PTFE/wood blocks (column 5). Wood samples that contained PTFE absorbed 13 to 62% less water (column 5) than the same wood cubes without PTFE (column 3). With the exception of cedar, the combined volume of PTFE and of water in the PTFE/wood blocks (column 6) was less than the volume of water absorbed by the control blocks (column 3). That is, in all cases but cedar, the PTFE did more than just fill void space that would otherwise be filled by water.

C. Effect of Repetitive Polymerization.

[0042] Three cubes of poplar 0.75" on a side and with an average weight of 3.7942 grams were soaked for 15 minutes at -15°C in 0.16 M DP in Freon® E1 which had been previously filtered through a 0.45 μ filter. The soaked blocks, the average weight of which increased to 5.6650 grams in the soaking process, were briefly air dried and charged to a stainless steel autoclave. The autoclave was chilled, evacuated and further charged with 50 g of TFE. The autoclave was heated for 4 hours at 40°C. The cubes were recovered, lightly sanded to remove loose surface polymer, and dried at room temperature overnight with pump vacuum. The average cube weight was brought to 5.4960 g, which was a 45% weight increase compared to the starting weight.

[0043] The cubes were soaked a second time for 15 minutes in -15°C 0.16 M DP solution. The average weight of the cubes was 5.7628 g. The cubes were reloaded into the 400 ml autoclave with 25 g of TFE. The autoclave was heated for 4 hours at 40°C. The cubes were recovered, lightly sanded, and dried under pump vacuum overnight. The average weight was brought to 6.383 g.

[0044] The cubes were soaked a third time in DP, reacted with 25 g TFE in a 400 ml autoclave tube, recovered, lightly sanded, and dried for 3 days at room temperature under pump vacuum. The average weight was brought to 6.4953 g, which was a 71.2% weight gain compared to the start.

[0045] One of the cubes was immersed in water along with an untreated poplar control cube. Once again weight gain was followed as a function of cumulative immersion time. Chart 3 compares the 600-hour water absorption results for the poplar cubes prepared in part C of this Example to the poplar cubes of part B of this Example. While the poplar cube exposed to three polymerization cycles contained almost twice as much PTFE as the cube exposed to a single polymerization cycle, no difference was detected in the amount of water absorbed after 600 hours.

TABLE 3

Affect of PTFE on Water Absorption After 600 Hours of Immersion

Wood	Starting Wood Density	ML H_2O Absorbed/ ML of Wood (Control)	ML PTFE/ ML of Wood (PTFE/ wood)	ML H_2O/ ML of Wood (PTFE/ wood)	(ML PTFE + ML H_2O)/ ML Wood (PTFE/wood)
Poplar, 1X	0.59 g/ml	0.71 ml	0.098 ml	0.28 ml	0.38 ml
Poplar, 3X	0.55 g/ml	0.83 ml	0.17 ml	0.28 ml	0.45 ml

D. Resistance to Prolonged Water Exposure

[0046] The soaking experiments described in part B of this Example were continued for 8 to 9 months at room temperature. After the wood cubes were removed from the water, the surfaces were wiped damp dry with a tissue. The PTFE containing wood samples were uniformly less darkened and less "wet" looking as recorded in the Chart 4 below.

TABLE 4

Effect of Prolonged Water Exposure

Wood	Appearance of Water	Appearance of Untreated Wood	Appearance of PTFE/Wood
Oak	Yellow with black solids (fungi?)	Dark brown to black	Tan, more like starting wood

(continued)

TABLE 4

Effect of Prolonged Water Exposure

Wood	Appearance of Water	Appearance of Untreated Wood	Appearance of PTFE/Wood
Walnut	Orange with black solids (fungi?)	Black	Brown with occasional black spots
Cherry	Yellow with black solids (fungi?)	Dark brown	Tan with occasional dark spots
Poplar	Pale yellow with black solids (fungi?)	Medium brown	Blonde, more like starting wood
Pine	Colorless	Light brown	Blonde, more like starting wood
Cedar	Yellow with black solids (fungi?)	Dark brown	Tan, much like starting wood
Redwood	Yellow with white solids	Dark brown	Tan, much like starting wood

EXAMPLE 2

EVIDENCE FOR PTFE PENETRATION INCHES DEEP INTO REDWOOD

[0047] The experiments below establish that TFE polymerizes in wood at least inches below the wood surface and that, while deposition along the grain may be mildly favored, penetration occurs in other directions as well. Gaseous monomer, such as TFE, penetrates wood particularly easily.

A. Evidence for Deep Penetration

[0048] Two redwood blocks were cut so as to detect anisotropy in the penetration and polymerization of TFE. The first block measuring 10.8 cm X 2.6 cm X 1.8 cm was cut so that the grain of the wood ran in the 10.8 cm direction. It is referred to hereinafter as the "lengthwise" block. A second block measuring 11.0 cm X 2.7 cm X 1.8 cm was cut so that the grain of the wood ran in the 2.7 cm direction. It is referred to as the "crossgrain" block. It is supposed that if TFE can penetrate wood substrates only along the direction of the grain of the wood, then TFE must travel 5.4 cm to get to the center of the lengthwise block but only 1.35 cm to get to the center of the crossgrain block. The two blocks could thus differ greatly in PTFE weight gain and how any PTFE is distributed spatially. Each block was weighed and then soaked for 1 hour at -15°C in 0.16 M DP in Freon® E1. The blocks were briefly air dried and then transferred to separate 400 ml stainless steel autoclaves. Each tube was charged with 50 g of TFE and heated for four hours at 40°C. The blocks were recovered, lightly sanded to remove loose PTFE from the surface, dried for at least 4 days under pump vacuum, and reweighed. The lengthwise block increased in weight from 17.9 g to 30.3 g for a 69% weight gain. The crossgrain block increased in weight from 16.0 g to 28.7 g for a 79% weight gain. The volume of PTFE picked up per ml of wood was 0.103 ml of PTFE for the crossgrain sample and 0.108 ml for the lengthwise sample. These results are likely the same within experimental error and are not much different from the 0.13 ml of PTFE per ml of wood reported above for the much smaller redwood cubes in Example 1. This experiment provided the first indication that grain direction did not dominate deposition, that PTFE deposition is not limited primarily to the wood surface, and that sample size did not dramatically affect results up to dimensions of several inches.

[0049] Untreated wood contains no fluorine while PTFE is 76% by weight fluorine. Thus, the concentration of PTFE in a treated wood sample is proportional to the wood's fluorine content. As illustrated in Figure 1, the crossgrain sample (block 10 of Figure 1) was sawed in half creating two new blocks (blocks 12 and 13 of Figure 1), each measuring roughly 5.5 cm X 2.7 cm X 1.8 cm. The cut wood sample exposed the interior of the original block as two new faces. One of the two new block faces was scanned across its full width with the beam of an electron microscope set to a 50 micron spot size (scans #2 - #7). The electron microscope was operated in energy dispersive mode so as to give an output signal proportional to the fluorine content of the wood. In this way microscopic variations in relative fluorine concentration (y axis) could be plotted across the full width of the wood block (x axis).

[0050] Scan #3 was in the direction of the wood grain (the 2.7 cm dimension) while scan #6 was perpendicular to the grain (the 1.8 cm direction). The scans showed choppy alternation between areas of high and low fluorine concentration which was attributed to random areas of cellulose, void and PTFE that were crossed by the beam during the scan. While high fluorine concentrations were observed throughout the bulk of the wood, fluorine concentrations were noticeably higher toward the surface of the wood in scans #3 and #6.

[0051] A similar analysis was then done on the lengthwise block. As shown in Figure 2, the block (block 20 of Figure 2) was first cut in half to create two new faces (blocks 21 and 22 of Figure 2). One of the new faces was scanned with the beam of an electron microscope in energy dispersive mode to measure relative fluorine concentration as shown by the direction of the arrows in Figure 2. Three scans were performed in the 1.8 cm direction (scans #9, #10, and #11) and three scans were performed in the 2.6 cm direction (scans #12, #13, and #14). All six scans performed were perpendicular to the wood grain. High and low fluorine concentrations alternated irregularly across the full width of all six scans. There was no discemable preference for fluorine at the surface. One of the two 5.4 cm X 2.6 cm X 1.8 cm blocks created by the first cut was cut into half again. Two additional blocks were created (blocks 23 and 24 of Figure 2) that measured ~5.4 cm X 2.6 cm X 0.9 cm. The fresh cut face of one of the blocks was scanned three times along the grain of the wood, traveling each time the 5.4 cm distance from what had been the center of the original block to an outside end (scans #CE 15, #CE 16, and #CE 17). The fluorine concentrations increased 10 to 20 times from the center to the outer face of the block. Fluorine concentrations measured much lower at the center of the block for scan #CE16, than when scanned end on as in scans #9 through #14 of Figure 2. Combustion analysis was used to resolve the inconsistency.

[0052] Three small wood chips were cut from the end of the block where electron microscopy had shown high concentrations and three small wood chips from the end of the block (i.e., the deep interior of the original block before the block was cut in the first instance) where electron microscopy had shown 10 to 20 times lower concentrations in Figure 2 scans #CE15, #CE16, and #CE17, and one small wood chip was cut from the middle of the face. The weight percents of fluorine found by combustion analysis for all seven wood chips are provided in Figure 2. The fluorine content varied from an average of 30 wt % in the deep interior of the block to an average of 44 wt % at the outer end of the block. Electron microscopy had shown the correct trend but in an exaggerated fashion. The exaggeration is attributed to the effects of wood morphology and angle of viewing on PTFE content. This example provides a basis for concluding that there is a mild preference for TFE polymerization along the direction of the wood grain and that penetration occurs easily to depths of at least 5.4 cm.

B. Morphology of PTFE Deposits within the Wood

[0053] As shown in Figure 2, the redwood "lengthwise block" was cut into three pieces. A piece measuring ~5.4 cm X 2.6 cm X 0.9 cm and weighing about 4.5 g was digested chemically by heating it to reflux with 10 ml of concentrated sulfuric acid. Additional sulfuric acid was added to reduce the wood to an oily black residue. The carbon responsible for the black color was then burned away by the gradual addition of concentrated nitric acid. The residue was diluted with water, filtered, and dried. A white fibrous PTFE deposit was recovered. The residue accounted for 35.6% of starting sample weight, which was similar to the fluorine levels measured by combustion analysis. At 100X to 20,000X magnification, electron microscopy detected rod shaped structures 20μ-60μ across and of indefinite length. At 20,000X magnifications, the rods showed a spongy fine structure. Such spongy morphology is often seen when TFE is polymerized in the gas phase. Perhaps the void spaces in wood function as microscopic gas phase polymerization reactors for TFE. In this invention, the polymerization appears to have filled the pores in the wood substrates with spongy PTFE deposits rather than having deposited the PTFE as a conformal coating on the walls of the pores.

EXAMPLE 3

EVIDENCE FOR PTFE PENETRATION INCHES DEEP INTO OAK

[0054] Two oak blocks were cut so as to detect anisotropy in the penetration and polymerization of TFE. The first block which measured 12.1 cm X 2.5 cm X 1.9 cm, was cut so that the grain of the wood ran in the 12.1 cm direction. It will be referred to hereafter as the "lengthwise" block in this Example (block 40 of Figure 4). A second block which measured 2.1 cm X 2.5 cm X 1.9 cm was cut so that the grain of the wood ran in the 2.5 cm direction. It will be referred to hereafter as the "crossgrain" block in this Example (block 30 of Figure 3). To the extent that the TFE gas can penetrate the wood only along the direction of the grain, the TFE must travel 6.05 cm to get to the center of the lengthwise block but only 1.25 cm to get to the center of the crossgrain block. The two blocks could thus differ greatly in PTFE weight gain and how any PTFE is distributed spatially.

[0055] Each block was weighed and then soaked for 1 hour at -15°C in 0.16 M DP in Freon® E1. The blocks were briefly air dried and then transferred to separate 400 ml stainless steel autoclaves. Each tube was charged with 25 g of TFE and heated for four hours at 40°C. The blocks were recovered, lightly sanded to remove loose PTFE from the surface, dried for at least 4 days under pump vacuum, and reweighed. The lengthwise block increased in weight from 44.36 to 47.98 g for an 8.1% weight gain. The crossgrain block increased in weight from 42.54 g to 49.81 g, or a 17.1 % weight gain. The crossgrain sample picked up 0.05 ml of PTFE/ml of oak and the lengthwise sample picked up 0.03 ml of PTFE/ml of oak. This compares to 0.048 ml of PTFE per ml of oak in the case of the 0.75" oak cubes of Example

1. The ~2X greater deposition of PTFE in the crossgrain block suggested a mild preference for penetration in the direction along the wood's conductive tissues by which food and nutrients travel.

[0056] Cross section experiments were done next. The crossgrain sample was cut in half to create two new blocks (blocks 31 and 32 of Figure 3). Each block measured roughly 6.05 cm X 2.5 cm X 1.9 cm. A 50 μ spot size was used to scan one of the new faces by electron microscopy. The scans were performed in energy dispersive mode to measure relative fluorine concentrations in the direction of the arrows as shown in Figure 3.

[0057] Scans #19, #20, and #21 shown in Figure 3 were in the direction of the wood grain (the 2.5 cm dimension) while scans #22, #23 and #24 were perpendicular to the grain (the 1.9 cm direction). All six scans showed choppy alternation between areas of high and low fluorine concentration which was attributed to the random crossing of areas of cellulose, void, and PTFE by the electron microscope beam. High PTFE concentrations occurred throughout the wood and were not clustered near the surface.

[0058] A similar analysis was then done on the lengthwise block. The block was first cut in half to create two new faces (blocks 41 and 42 of Figure 4). One of the new faces was scanned by electron microscope in energy dispersive mode measuring relative fluorine concentration in the direction of the arrows in Figure 4 below.

[0059] Three scans were performed in the 2.5 cm direction as indicated by the arrows #26, #27, #28 of Figure 4 and three scans were performed in the 1.9 cm direction, indicated by the arrows #29, #30, and #31 of Figure 4. All six scans were performed perpendicular to the wood grain. High and low fluorine concentrations alternated irregularly across the full width of all six scans. There was no discernable preference for fluorine at the surface. One of the two 6.05 cm X 2.5 cm X 1.9 cm blocks that was created by the first cut was cut in half again to create two more blocks (blocks 43 and 44 of Figure 4). The blocks measured ~6.05 cm X 2.5 cm X 0.95 cm each. The fresh cut face of one was scanned three times along the grain of the wood, traveling each time the ~6.05 cm distance from what had been the center of the original block to an outside end, as indicated in arrows #CE32, #CE33, and #CE34 of Figure 4. While the scans indicated by arrows #CE32, #CE33, and #CE34 showed very little fluorine towards the center of the block, high fluorine concentrations were detected at the center of the block in scans #26 to #31 of Figure 4. As in the redwood block of Example 2, the same dependence of fluorine concentration upon scan direction was seen and elemental analysis was used to support the higher fluorine concentrations. It was concluded that there was a mild preference for TFE polymerization along the direction of the wood grain and that penetration easily occurred to depths of at least 6 cm.

EXAMPLE 4

PROTECTION OF WOOD

A. High Pressure Process

[0060] A 3.8 cm X 8.6 cm rectangle was cut from each of the six types of wood in a package of Band-it® Real Wood Variety Veneer (Cloverdale Company, Inc., P. O. Box 400, Cloverdale, VA 24077). While the exact identities of the woods were unknown, their visual appearance suggested common woods such as walnut, pine, maple, and redwood. All six rectangles were notched so as to enable later identification and weighed and then soaked for one hour at -15°C in 0.175 M DP in Freon® E1. The strips were briefly air dried and loaded into a pre-chilled 400 ml autoclave along with 50 g tetrafluoroethylene gas. As the autoclave was warmed towards 40°C, pressure peaked at 261 psi at 20.7°C and then decreased to 74 psi at 38.5°C at the end of the run, about four hours later. All six strips became heavily coated with PTFE. Loose PTFE was removed from the surface and residual volatiles were removed. The surface of the wood still appeared white. Weight gains of 38%, 66%, 70%, 89%, 97%, and 145% were observed for the six different types of wood samples. The samples that showed weight gains of 38%, 66%, 97%, and 145% were sanded to return the wood to a reasonably natural surface appearance. Those samples were then spotted with Lea & Perrins® Worcestershire Sauce, Pathmark® Yellow Mustard, and Pathmark® Tomato Ketchup. After 5 to 10 minutes, the wood samples were wiped clean with a tissue and any residual moisture was allowed to air dry. No stains were readily apparent to the eye. The original starting woods that were not treated with TFE were stained by Worcestershire Sauce, Mustard, and Ketchup under the same conditions. The samples were compared to the starting woods. The wood/PTFE compositions prepared in this example were more resistant to staining, more easily cleaned, and more durable.

B. Low Pressure Process

[0061] A 30 mm X 40 mm rectangle was cut from each of the six types of wood in a package of Band-it® Real Wood Variety Veneer (Cloverdale Company, Inc., P. O. Box 400, Cloverdale, VA 24077). While the exact identities of the woods were unknown, their visual appearance suggested common woods such as walnut, pine, maple, and redwood. All six rectangles were notched so as to enable later identification and weighed. The strips were soaked for one hour at -15°C in 0.165 M DP in $CF_3CFHCFHCF_2CF_3$, briefly air dried, loaded into a 20.3 cm X 25.4 cm zip lock polyethylene bag (Brandywine Bag Co., part number 301630) equipped with a polypropylene gas inlet valve, and the bag was clamped shut. The bag was taped to a rectangular wire frame attached in turn to an ordinary laboratory stirrer motor. The bag was evacuated/purged three with N_2 and two times with TFE and then inflated loosely with TFE gas. For the next ~18 hours the bag and its contents were slowly tumbled using the stirrer motor mounted in a horizontal position. The wood strips were unchanged in visual appearance. The strips were devolatilized for 72 hours under pump vacuum and re-weighed. The strips had a weight gains of 0.9 wt % to 7 wt % as shown in Chart 5, column 2. Drops of water were placed on the wood and advancing contact angles measured about 10 minutes later. Advancing contact angles were uniformly high, 120° to 127° (Chart 5, column 3), indicative of PTFE at the surface. The behavior of the untreated control samples containing no polymerized PTFE was markedly different. While reasonably high contact angles of 90 to 122° were observed for the untreated control wood samples initially (Chart 5, column 5), these contact angles could be observed only briefly because the water droplets started to spread out over the surface after only about 15 seconds to 2 minutes (Chart 5, column 6). The PTFE treated and the control samples were next submerged in water at room temperature and then air dried to observe what effect the PTFE treatment had on warpage.

[0062] Before any exposure to water, PTFE, or other chemicals, the Band-it® Real Wood Variety Veneer starts off with a slight curvature, the decorative wood surface being on the convex side. Under immersion conditions, both the PTFE and control samples wet through with water. PTFE treated samples remained reasonably flat after 375 minutes of water immersion. After air drying overnight, five out of six of the untreated control samples noticeably curled back on themselves creating semicircular or even tubular shapes (Chart 5, column 7) while the PTFE treated samples varied from slight curling to flattening (Chart 5, column 4). Three of the untreated control samples also showed mild water staining while none of the PTFE treated samples showed any visible water marks.

TABLE 5

Water Contact Angles and Warpage for Low Pressure Polymerization Samples

	Wood with Polymerized PTFE			Untreated Wood Controls		
Wood	PTFE Weight Gain	Contact Angle with H_2O	Immerse in H_2O Then Dry Overnight	Initial Contact Angle	Time for Wetting	Immerse in H_2O Then Dry Overnight
#1	0.9%	120°	Slight Flattening	110°	~2 min	No Effect on Shape, Slight Stain
#2	2%	123°	Curled to Semicircle	110°	~2 min	Nearly Tubular, Slight Stain
#3	3%	127°	Flattened	122°	~2 min	Slight Curling
#4	4%	127°	Slight Curling	115°	~2 min	Slight Curling, Slight Stain
#5	5%	122°	Slight Flattening	105°	~15 sec	Nearly Tubular
#6	7%	122°	Flattened	90°	~15 sec	Slight Curling

[0063] In a final test, a drop of Squibb mineral oil 1 to 3 mm in diameter was placed on all the control and PTFE treated samples. The mineral oil immediately wetted and spread out over the surface of the control samples leaving a large oily mark. In contrast the mineral oil beaded up on the PTFE treated samples. After waiting 10 to 15 minutes, the oil droplet was wiped off the PTFE treated samples leaving an oily mark visible only where the oil droplet had contacted the wood. Both the control and PTFE treated samples were then repeatedly rinsed with Freon® 113 (CF_2ClCCl_2F) and air dried. All the untreated samples still showed a faint patch of darker wood 20 mm to 40 mm in maximum dimension where the oil had been. Of the PTFE treated woods, only wood #6 showed a faintly darker patch 8 mm in diameter where the oil had been.

[0064] TFE polymerized into the wood makes the wood harder to wet by oil and water, less subject to staining by oil and water, and less subject to warpage when wetted and then dried.

EXAMPLE 5

LIQUID PHASE PERFLUOROMONOMER

A. In Wood Under Inert Atmosphere

[0065] Ajar was chilled to about -15°C and 25 ml of PMD and 2 ml of ~0.16 M DP in $CF_3CF_2CFHCFHCF_3$ solvent were added. A cube of redwood ~1.9 cm on a side weighing 2.46 g was immersed in the solution contained in the jar for about 1 hour at -15°C. The redwood cube was removed, allowed to drain and then transferred to a 20.32 cm X 25.4 cm zip lock polyethylene bag (Brandywine Bag Co., part number 301630) equipped with a polypropylene gas inlet valve. The bag was clamped shut, inflated and evacuated 3 times with nitrogen, and allowed to sit over the weekend. The cube was removed and a few pieces of white polymer rubbed off its surface with a spatula. After devolatilizing for 9 days under pump vacuum at room temperature, the cube weighed 4.45 g for a 81% weight gain. One side of the cube was lightly sanded revealing an attractive brown surface slightly darker in appearance. A drop of water placed on the surface remained there for about two hours until it evaporated. A drop of water placed on an untreated redwood cube wet the surface within a minute and took about 30 minutes to soak into the cube, having spread out into a visibly large wet area on the cube.

B. In Wood Under TFE Atmosphere

[0066] A cube of redwood, ~1.9 cm on a side and weighing 2.27 g was immersed in the PMD/DP solution left over from part A of this Example for 1 hour at -15°C. The redwood cube was removed, allowed to drain and then transferred to a 20.32 cm X 25.4 cm zip lock polyethylene bag (Brandywine Bag Co., part number 301630) equipped with a polypropylene gas inlet valve. The bag was clamped shut, inflated and evacuated three times with nitrogen, inflated and evacuated three times with TFE, loosely inflated with TFE, and allowed to sit over a three days. The cube was removed along with 2.9 g of PTFE. Most of the PTFE removed was loose but some of it was scraped off of the redwood cube. After devolatilizing for 9 days under pump vacuum at room temperature, the cube weighed 4.51 g for a 99 percent weight gain. One side of the cube was light sanded revealing an attractive silvery brown surface darker in appearance than at the start. A drop of water placed on the surface remained on the surface of the cube for about two hours until it evaporated. A drop of water placed on an untreated redwood cube wet the surface of the cube within a minute and took about 30 minutes to soak into the cube, having spread out into a visibly large wet area on the cube.

EXAMPLE 6

PENETRATION AND DEPOSITION OF FLUOROPOLYMER

[0067] Lumber is most often cut with the wood grain running lengthwise. For monomer and initiator to thoroughly penetrate a long board, much of this penetration must either occur perpendicular to the wood grain or else monomer and initiator must be able to enter at the ends and travel rapidly down the wood grain. The experiments below show that significant penetration and PTFE deposition occurs perpendicular to the wood grain.

A. PTFE Deposition Perpendicular to Wood Grain

[0068] A block of pine measuring 14.5 cm X 2.6 cm X 1.9 cm and with the grain running lengthwise was cut roughly in half creating two new blocks: Block A measuring ~7.0 X 2.6 X 1.9 cm and weighing 16.1 g and Block B measuring ~7.4 X 2.6 X 1.9 cm and weighing 17.2 g. Using Epoxy-Patch® cement (Hysol Engineering Adhesives, The Dexter Corporation, Seabrook, NH) 2.6 X 1.9 cm patches of aluminum foil (Reynolds Wrap®, Reynolds Metal Company, Richmond, Virginia) were glued to the far ends of Block A. After 3 days of drying, Block A (plus foil) weighed 16.5 g. The purpose of the aluminum foil was to block entry and travel by initiator and monomer in the direction of the wood grain to test for ease of perpendicular penetration. Blocks A and B were immersed for 1 hour at -15°C in ~0.16 M DP in $CF_3CF_2CF_2OCFHCF_3$ solvent. The blocks were removed, briefly drained, chilled on dry ice, and loaded into a chilled (less than -20°C) 400 ml autoclave. The autoclave was evacuated and loaded with 50 g of TFE. After four hours at 40°C, the wood blocks were recovered, trace loose PTFE wiped off the surface with a tissue, and the blocks were dried under pump vacuum for 3 days. Block A weighed 23.9 g for a 46% weight gain and Block B weighed 25.0 g for a 45% weight gain. Thus, PTFE deposition was not particularly dependent upon the direction of the wood grain; or upon which wood surfaces (end grain or non-end grain) were exposed to initiator and TFE.

EXAMPLE 7

TFE POLYMERIZATION INTO AS-MOLDED POLYIMIDE PARTS

A. Preparation of molded polyimide test bars with variable porosity

[0069] Polyimide resin powder used in the following Examples 1, 2 and 3 was prepared from pyromellitic dianhydride and 4,4'-oxydianiline, according to the procedures of U.S. Patent No. 3,179,614 or U.S. Patent No. 4,622,384. Polyimide powder samples weighing 2.1 to 2.5 g were cold pressed at room temperature into tensile bars. These tensile bars were dogbone shaped, measuring 90 mm long by 5 mm to 10 mm wide. In order to vary the porosity of the tensile bars, six different compressive forces were used, 10,000 psi, 20,000 psi, 30,000 psi, 40,000 psi, 50,000 psi, and 100,000 psi, the resulting bars being called the 10K, 20K, 30K, 40K, 50K, and 100K bars respectively. After pressing, the bars had thicknesses typically running from 2.7 to 3.3 mm. When the bars were dried overnight in a 75°C oven, they lost 1 to 3% of their weight. Pore volumes for dried polyimide powder starting material and dried tensile bars measured by nitrogen porosimetry are shown in the Table 6 below.

TABLE 6

Sample	Pore Volume for Pores 17 to 3000Å
Starting Powder	0.18 cc/g
10 K Bar	0.09 cc/g
20 K Bar	0.050 cc/g
30 K Bar	0.01 cc/g
40 K Bar	0.002 cc/g
50 K Bar	nil
100 K Bar	nil

B. Atmospheric Pressure TFE Polymerization Tensile Tests

[0070] One each of a 10K, a 50K, and a 100K bar were soaked at -15°C in initiator solution, a ~0.14 M DP 1 solution in Vertrel® XF solvent ($CF_3CFHCFHCF_2CF_3$). After 3 hours, the bars were pulled from the initiator solution, excess initiator solution allowed to drain, and then loaded into a 6 X 9" ziplock polyethylene bag equipped with a gas inlet valve. The bag was evacuated and filled 3X with N_2 and then 3X with tetrafluoroethylene (TFE). The bag was inflated with TFE and allowed to stand -20 hours overnight at room temperature. The next morning the three test bars were recovered and loose white PTFE powder was wiped off the surface. After 4 days of devolatilization under pump vacuum, the bars were reweighed with the weight changes shown in the table below. The bars were further compressed to 100,000 psi at room temperature. These bars were then finished by heating to 405°C for three hours. Tensile tests on these bars are also shown in the table below versus control polyimide bars containing no PTFE. Fluorine analyses on the broken remains of the bars are shown in Table 7 below.

TABLE 7

Sample	Nominal PTFE Weight Gain	PSI at Break	% Elongation at Break	Weight % Fluorine by Combustion Analysis
Control		11,500	10.9	-
10K	6.5 wt %	Broke when compressed	-	2.0% F
50K	-0.5 wt %	11,400	9.1	0.71% F
100K	-0.6 wt %	11,000	11.3	0.17% F

The apparent weight losses for the 50K and 100K bars needs comment. The starting polyimide powder and bars showed 1 to 3% weight loss when dried overnight at 75°C. The polyimide bars used here for TFE polymerizations were not dried before the TFE polymerization step but were devolatilized afterwards. The apparent weight change over the course of the experiment thus is the net result of volatiles loss and PTFE weight gain. Apparently volatiles loss is greater than PTFE weight gains for bars compressed at 50,000 and 100,000 psi.

C. High Pressure TFE Polymerization.

[0071] One each of a 10K, a 50K, and a 100K bar were soaked at -15°C in initiator solution, a ~0.15 M DP 1 solution in Vertrel® XF solvent ($CF_3CFHCFHCF_2CF_3$). After 30 minutes, the three bars were pulled from the initiator solution allowing excess initiator to drain away and then stored on dry ice until they could be loaded into a 400 ml autoclave prechilled to -20°C. The autoclave was evacuated and filled with 10 g of TFE. Polymerization was allowed to run overnight at room temperature, TFE pressure in the autoclave reaching a maximum of 111 psi at 16.3°C. The next morning, the test bars were recovered from a large volume of white PTFE fluff, using a tissue to wipe loose white PTFE off the surface. After 12 days of devolatilization under pump vacuum, the bars were analyzed for fluorine content by combustion analysis with the results shown in Table 8 below.

TABLE 8

Bar	Fluorine by Combustion Analysis
10K	13.97 wt % F
50K	0.93 wt % F
100K	0.51 wt % F

The fluorine contents are higher than observed when the TFE polymerization was run at atmospheric pressure in section B immediately above.

D. Atmospheric Pressure Polymerization

[0072] Groups of four to eight 20K, 30K, and 40K bars were soaked at -15°C in 20 to 30 ml of initiator solution, ~0.16 M DP 1 in Vertrel® XF solvent ($CF_3CFHCFHCF_2CF_3$). After 60 minutes, the bars were pulled from the initiator solution allowing excess initiator to drain away and then loaded into a 6 X 9" ziplock polyethylene bag equipped with a gas inlet valve. The bag was evacuated and filled 3X with N_2 and then 3X with tetrafluoroethylene (TFE). The bag was inflated with TFE and allowed to stand overnight at room temperature. The next morning the test bars were recovered, loose white PTFE powder wiped off the surface, and dried in a 75°C vacuum oven. Three bars from each set were further compressed at 100,000 psi at room temperature and then sintered by raising temperature at 1.5°C/min to 405°C and holding at 405°C for 3 hours. Tensile tests were performed and the broken fragments analyzed for fluorine content as shown in the table below. The data results in Table 9 below show that polymerization of TFE into an as-molded polyimide bar does not have a major effect on ultimate tensile properties.

TABLE 9

Test Bar	PSI at Break	Elongation at Break	Weight Percent Fluorine by Combustion Analysis	
			From Center of Bar	From End of Bar
20K	10,980	14.5%	0.79	0.59
20K	10,930	9.5%		
20K	10,676	8.5%		
30K	10,974	9.8%	0.49	0.14
30K	10,209	6.3%		
30K	11,335	7.8%		
40K	11,241	8.5%	0.66	0.56
40K	11,699	8.9%		
40K	11,312	8.1%		

EXAMPLE 8

POROUS POLYIMIDE POWDER, ATMOSPHERIC PRESSURE TFE POLYMERIZATION

A. Polyimide/PTFE Analyzing for 6.34% Fluorine

[0073] A 500-ml round-bottomed flask loaded with 15.59 g of polyimide powder and ~55 ml of Vertrel® XF was chilled overnight in a -15°C refrigerator. The next morning 5 ml of ~0.16 M DP in Vertrel® XF was added and then excess solvent was rapidly pulled off first using a rotary evaporator (~20 min) and then a vacuum pump (~13 min) so as to keep the reaction mixture cold by evaporative cooling. The polyimide powder, now impregnated with DP, was loaded into a 6 X 9" Ziplock® polyethylene bag equipped with a gas inlet valve. The bag was inflated and then evacuated 3X with N_2 and 3X with tetrafluoroethylene (TFE). The bag was inflated a final time with TFE and polymerization allowed to run until about half the TFE had been reacted as judged by visible deflation of the bag. This took about 72 minutes. The surface of the polyimide powder remained yellow indicating that the bulk of the PTFE polymerization was occurring within the pores of the particles rather than on the surface. The recovered polyimide powder weighed 19.33 g upon removal from the bag, 16.48 g after 147 minutes in a 75°C vacuum oven, and 16.38 g after continuing another -70 hours in the 75°C vacuum oven. Weight gain was 0.79 g or 5.1% relative to the weight of the starting polyimide powder. Combustion analysis on the product found 6.34 wt % fluorine. Finding 6.34 wt % fluorine versus a 5.1 wt % gain overall is, as observed with the test bars above, consistent with starting with a raw polyimide powder that had not been devolatilized.

[0074] Samples of this powder were compressed at 100,000 psi at room temperature into three tensile bars measuring 90 mm long by 5 mm to 10 mm wide (dogbone-shaped). These bars were then finished by heating to 405°C for three hours. In tensile tests these bars broke on average at 6,675 psi with 4.7% elongation. Combustion analysis on the broken pieces found 4.99 wt % fluorine.

[0075] The polyimide/PTFE composite made in this experiment was tested for resistance to wear using the method described in U.S. Patent No. 5,789,523, column 4, line 51. The powder was compressed at 100,000 psi into a disk 1" in diameter by about 0.25" thick. This disk was then heated to 405°C for three hours. After cooling to room temperature, the parts were machined to final dimensions for test specimens. The 0.25" (6.35 mm wide) contact surface of the wear/friction disk was machined to such a curvature that it conformed to the outer circumference of the 1.375" (34.9 mm) diameter X 0.375" (9.5 mm) wide metal mating ring. The disks were oven dried and maintained dry over desiccant until tested. Wear tests were performed using a Falex No. 1 Ring and Block Wear and Friction Tester. The equipment is described in ASTM Test method D2714. After weighing, the dry polyimide/PTFE disk was mounted against the rotating metal ring and loaded against it with the selected test pressure. Rotational velocity of the ring was set at the desired speed. No lubricant was used between the mating surfaces. The rings were SAE 4620 steel, Rc 58-63, 6-12 RMS. A new ring was used for each test. Test time was usually 24 hours, except when friction and wear were high, in which case the test was terminated early. At the end of the test time, the block was disconnected, weighed, and the wear calculated using the following calculation:

$$\text{Wear volume (cc/hr)} = \frac{\text{Weight Lost (grams)}}{\text{Material density(grams/cc) X Test duration (hours)}}$$

In this test the wear volume of the polyimide/PTFE sample was at least 8X less than for a polyimide sample free of PTFE.

B. Polyimide/PTFE Analyzing for 14.15% Fluorine

[0076] A 500-ml round-bottomed flask loaded with 15.82 g of polyimide powder and ~55 ml of Vertrel® XF was chilled for 1 hour in a -15°C refrigerator. About 5 ml of ~0.16 M DP in Vertrel® XF was added and then excess solvent was rapidly pulled off first using a rotary evaporator (10-15 min) and then a vacuum pump (~5 min) so as to keep the reaction mixture cold by evaporative cooling. The polyimide powder, now impregnated with DP was loaded into a 6 X 9" ziplock polyethylene bag equipped with a gas inlet valve. The bag was purged of air by inflating and evacuating the bag 3X with N_2 and 3X with tetrafluoroethylene (TFE). Polymerization was started by inflating the bag with TFE and allowing polymerization to deflate the bag over about a 2 hour period. The still yellow polyimide powder was dried overnight in an 88°C vacuum oven. Combustion analysis on the product found 14.15 wt % fluorine.

[0077] Samples of this powder were compressed at 100,000 psi at room temperature into three tensile bars measuring 90 mm long by 5 mm to 10 mm wide (dogbone-shaped). These bars were then heated from to 405°C for three hours.

In tensile tests these bars broke on average at 1,369 psi with 0.5% elongation. Combustion analysis on the broken pieces found 13.89 wt % fluorine.

C. Polyimide/PTFE Analyzing for 19.93% Fluorine

[0078] A 500-ml round-bottomed flask loaded with 15.51 g of polyimide powder and -55 ml of Vertrel® XF was chilled for 1 hour in a -15°C refrigerator. About 5 ml of ~0.16 M DP in Vertrel® XF was added and then excess solvent was rapidly pulled off first using a rotary evaporator (~15 min) and then a vacuum pump (~4 min) so as to keep the reaction mixture cold by evaporative cooling. The polyimide powder, now impregnated with DP, was loaded into a 6 X 9" ziplock polyethylene bag equipped with a gas inlet valve. The bag was purged of air by inflating and evacuating the bag 3X with N_2 and 3X with tetrafluoroethylene (TFE). Polymerization was started by repeatedly inflating the bag with TFE and allowing polymerization to deflate the bag twice, the defilations taking 40 minutes and overnight respectively. The still yellow polyimide powder was dried for ~4 days in a 75°C vacuum oven. Combustion analysis on the product found 19.93 wt % fluorine.

[0079] Samples of this powder were compressed at 100,000 psi at room temperature into three tensile bars measuring 90 mm long by 5 mm to 10 mm wide (dogbone-shaped). These bars were then heated to 405°C for three hours. In tensile tests these bars broke on average at 1,385 psi with 0.6% elongation. Combustion analysis on the broken pieces found 18.76 wt % fluorine.

D. Polyimide/PTFE Analyzing for 23.99% Fluorine

[0080] A 500-ml round-bottomed flask loaded with 15.66 g of polyimide powder and ~55 ml of Vertrel® XF was chilled overnight in a -15°C refrigerator. The next morning 5 ml of ~0.16 M DP in Vertrel® XF was added and then excess solvent was rapidly pulled off first using a rotary evaporator (~18 min) and then a vacuum pump (~9 min) so as to keep the reaction mixture cold by evaporative cooling. The polyimide powder, now impregnated with DP, was loaded into a 6 X 9" ziplock polyethylene bag equipped with a gas inlet valve. The bag was purged of air by repeatedly inflating and evacuating the bag 3X with N_2 and 3X with tetrafluoroethylene (TFE). Polymerization was started by repeatedly inflating the bag with TFE and allowing polymerization to deflate the bag three times, the defilations taking 55, 50, and 130 minutes respectively. The still yellow polyimide powder was dried overnight (~17 hrs) in a 75°C vacuum oven. Combustion analysis on the product found 23.99 wt % fluorine.

[0081] Samples of this powder were compressed at 100,000 psi at room temperature into three tensile bars measuring 90 mm long by 5 mm to 10 mm wide (dogbone-shaped). These bars were then heated to 405°C for three hours. In tensile tests these bars broke on average at 1,688 psi with 0.9% elongation. Combustion analysis on the broken pieces found 24.26 wt % fluorine.

E. Polyimide/PTFE Analyzing for 27.77% Fluorine

[0082] A 500-ml round-bottomed flask loaded with 16.01 g of polyimide powder and ~55 ml of Vertrel® XF was chilled for 1 hour in a -15°C refrigerator. About 5 ml of ~0.16 M DP in Vertrel® XF was added and then excess solvent pulled off first using a rotary evaporator (~12 min) and then a vacuum pump (~7 min) so as to keep the reaction mixture cold by evaporative cooling. The polyimide powder, now impregnated with DP, was loaded into a 6 X 9" ziplock polyethylene bag equipped with a gas inlet valve. The bag was purged of air by inflating and evacuating the bag 3X with N_2 and 3X with tetrafluoroethylene (TFE). Polymerization was started by repeatedly inflating the bag with TFE and allowing polymerization to deflate the bag four times, the defilations taking 21, 23, 23, and 42 minutes respectively. The still yellow polyimide powder was dried overnight (~19 hrs) in a 75°C vacuum oven. Combustion analysis on the product found 27.77 wt % fluorine.

[0083] Samples of this powder were compressed at 100,000 psi at room temperature into three tensile bars measuring 90 mm long by 5 mm to 10 mm wide (dogbone-shaped). These bars were then heated to 405°C for three hours. In tensile tests these bars broke on average at 1442 psi with 0.6% elongation. Combustion analysis on the broken pieces found 26.32 wt % fluorine.

F. Polyimide/PTFE Analyzing for 37.94% Fluorine

[0084] A round-bottomed flask chilled to ~0°C was loaded with 16.6 g of polyimide powder, 40 ml of Vertrel® XF, and 10 ml of ~0.16 M DP in Vertrel® XF. Excess solvent was rapidly pulled off first using a rotary evaporator and then a pump so as to keep the reaction mixture cold by evaporative cooling. The polyimide powder, now impregnated with DP, was loaded into a 6 X 9" ziplock polyethylene bag equipped with a gas inlet valve. The bag was purged of air by inflating and evacuating the bag 3X with N_2 and 3X with tetrafluoroethylene (TFE). Polymerization was started by repeatedly inflating the bag with TFE and allowing polymerization to deflate the bag over an afternoon and then overnight. The next morning the polyimide powder was recovered. After three days of devolatilization under pump vacuum, combustion analysis on the product found 37.94 wt % fluorine.

[0085] Samples of this powder were compressed at 100,000 psi at room temperature into five tensile bars measuring 90 mm long by 5 mm to 10 mm wide (dogbone-shaped). These bars were then heated to 405°C for three hours. In tensile tests these bars broke on average at 733 psi with 0.4% elongation. Combustion analysis on the broken pieces found 31.85 wt % fluorine.

G. Summary of Results on Polyimide Powder with PTFE Polymerized into its Pores

[0086] Table 10 below summarizes the results for parts A through F above.

TABLE 10

Weight % Fluorine by Combustion Analysis			
Starting Polyimide/PTFE	After Bar Pressed and Heated	PSI at Break	Elongation at Break
6.34%	4.99%	6,675 psi	4.7%
14.15%	13.89%	1,369 psi	0.5%
19.93%	18.76%	1,385 psi	0.6%
23.99%	24.26%	1,688 psi	0.9%
27.77%	26.32%	1,442 psi	0.6%
37.94%	31.85%	733 psi	0.4%

EXAMPLE 9

POROUS POLYIMIDE, ATMOSPHERIC PRESSURE

TFE POLYMERIZATION; CO_2 AS CARRIER FOR INITIATOR

[0087] A 400-ml stainless steel autoclave was loaded first with 15.05 g of polyimide powder and then with a 100-g layer of dry ice on top. Five ml of ~0.16 M DP in Vertrel® XF was poured over the dry ice. The autoclave was sealed and its contents shaken without any provision for additional cooling. As soon as the contents of the autoclave reached 0°C, the CO_2 was vented. The polyimide powder was recovered and chilled on dry ice until it could be transferred to a 6 X 9" ziplock polyethylene bag equipped with a gas inlet valve. The bag was inflated and evacuated 3X with N_2 and 3X with tetrafluoroethylene (TFE). The bag was inflated a final time with TFE. Polymerization was allowed to run 132 minutes until about a quarter of the TFE had been reacted as judged from deflation of the bag. Drying for 21 hours in a 75°C vacuum oven gave 13.69 g of polyimide powder that analyzed for 2.49 wt % fluorine by combustion analysis.

EXAMPLE 10

POROUS POLY(P-PHENYLENE TEREPHTHALAMIDE) POWDER,

ATMOSPHERIC PRESSURE TFE POLYMERIZATION

[0088] Porous poly(p-phenylene terephthalamide) particulates were prepared by adding poly(p-phenylene terephthalamide) precipitate as made in N-methyl-pyrrolidinone/$CaCl_2$ to water, filtering, rinsing with water, and sucking dry on the filter. A 25.6 g sample of these poly(p-phenylene terephthalamide) particulates was soaked in 30 ml of 0.18 M HFPO dimer peroxide in Vertrel® XF at -15°C. After 15 minutes, the poly(p-phenylene terephthalamide) was separated by vacuum filtration, stopping filtration as soon as the liquid flow seemed near an end. The poly(p-phenylene terephthalamide), still damp with initiator solution, was transferred to a 6 X 9" ziplock polyethylene bag equipped with a gas inlet valve. The bag was evacuated and filled 3X with N_2 and 3X with TFE. The bag was inflated a final time with TFE and the polymerization allowed to run at room temperature. Over the next several hours the bag was reinflated four times with TFE. Before reinflation, the contents of the bag were shaken and/or squeezed lightly with finger pressure to break up nascent lumps. The polymerization was allowed to continue overnight at room temperature. The next morning the contents of the bag were poured out, avoiding as much as possible entrainment of white PTFE deposits attached to the walls of the bag. After two days under pump vacuum, the product consisting largely of yellow granules plus a few white PTFE flakes from the wall of the bag, weighed 32.9 g for a weight gain of 28%. Taking just the yellow granules, combustion analysis found 15.70 wt % fluorine.

EXAMPLE 11

POROUS POLY(P-PHENYLENE TEREPHTHALAMIDE) POWDER,

ATMOSPHERIC PRESSURE TFE POLYMERIZATION

A. Lower PTFE Loading

[0089] Porous poly(p-phenylene terephthalamide) particulates were prepared by adding poly(p-phenylene terephthalamide) precipitate as made in N-methyl-pyrrolidinone/$CaCl_2$ to water, filtering, rinsing with water, and sucking dry on the filter. These particulates were then dried overnight in a 150°C vacuum oven. A 36 mL sample of ~0.17 M HFPO dimer in Vertrel® XF at -15°C was added to 360 ml of room temperature Vertrel® XF with swirling for ~1 minute. This initiator solution was then added immediately to 218.1 g of dried poly(p-phenylene terephthalamide) in a large crystallizing dish. In order to ensure thorough mixing, the contents of the crystallizing dish were worked for 1 minute with a spatula. The resulting poly(p-phenylene terephthalamide) slurry was filtered using a Buchner funnel, the vaccuum being applied for ~1 minute so as to leave the poly(p-phenylene terephthalamide) still damp with initiator solution (weight 295 g). The poly(p-phenylene terephthalamide) was transferred to a 8 X 10" ziplock polyethylene bag equipped with a gas inlet valve. The bag was evacuated and filled 3X with N_2 and 3X with TFE. The bag was inflated a final time with TFE to a height of ~3.5 inches and the polymerization allowed to run at room temperature. As TFE polymerization proceeded the bag periodically deflated to a near vacuum and was then reinflated with TFE gas first 10 and again 18 minutes into the run. Throughout the run, the bag was noticeably warm to the touch. After the last deflation, 28 minutes into the run, the contents of the bag were transferred back to a large crystallizing dish. Residual volatiles were removed by first putting under pump vacuum overnight and then in a 150°C vacuum oven overnight. The product consisting largely of yellow granules, weighed 227.8 g for a weight gain of 4.4% and combustion analysis found 4.16 wt % fluorine or 5 wt % PTFE in reasonable agreement with the measured weight gain. It should be noted that when running with an oven dried poly (p-phenylene terephthalamide) sample and at much larger scale than in Example 4 above, no free PTFE particulates on the walls of the bag or mixed in with the poly(p-phenylene terephthalamide) were apparent to the eye.

B. Intermediate PTFE Loading

[0090] Porous poly(p-phenylene terephthalamide) particulates were prepared by adding poly(p-phenylene terephthalamide) precipitate as made in N-methyl-pyrrolidinone/$CaCl_2$ to water, filtering, rinsing with water, and sucking dry on the filter. These particulates were then dried overnight in a 150°C vacuum oven. A 36 mL sample of ~0.17 M HFPO dimer in Vertrel® XF at -15°C was added to 360 ml of room temperature Vertrel® XF with swirling. This initiator solution was then added immediately to 218 g of dried poly(p-phenylene terephthalamide) in a large crystallizing dish. In order to ensure thorough mixing the contents of the crystallizing dish were worked for 1 minute with a spatula. The resulting poly(p-phenylene terephthalamide) slurry was filtered using a Buchner funnel, the vacuum being applied for only 50 seconds so as to leave the poly(p-phenylene terephthalamide) still damp with initiator solution. The poly(p-phenylene terephthalamide) was transferred to an 8 X 10" ziplock polyethylene bag equipped with a gas inlet valve. The bag was evacuated and filled 3X with N_2 and 3X with TFE. The bag was inflated a final time with TFE and the polymerization allowed to run at room temperature. As TFE polymerization proceeded the bag periodically deflated to a near vacuum and was then reinflated -2 to 3" tall with TFE gas 8, 14, 25, 37, 46, 62, and 80 minutes into the run. During much of the run, the bag was noticeably warm to the touch. After the last deflation, 98 minutes into the run, the contents of the bag were transferred back to a large crystallizing dish. Residual volatiles were removed by first putting under pump vacuum overnight and then in a 150°C vacuum oven overnight. The product consisting largely of yellow granules, weighed 244 g for a weight gain of 12% and combustion analysis found 8.40 wt % fluorine or 11 wt % PTFE in reasonable agreement with the measured weight gain.

C. Higher PTFE Loading

[0091] Porous poly(p-phenylene terephthalamide) particulates were prepared by adding poly(p-phenylene terephthalamide) precipitate as made in N-methyl-pyrrolidinone/$CaCl_2$ to water, filtering, rinsing with water, and sucking dry on the filter. These particulates were then dried overnight in a 150°C vacuum oven. A 36 mL sample of ~0.17 M HFPO dimer in Vertrel® XF at -15°C was added to 360 ml of room temperature Vertrel® XF with swirling. This initiator solution was then added immediately to 217 g of dried poly(p-phenylene terephthalamide) in a large crystallizing dish. In order to ensure thorough mixing the contents of the crystallizing dish were worked for 1 minute with a spoon. The resulting poly(p-phenylene terephthalamide) slurry was filtered using a Buchner funnel, the vacuum being applied for only 50 seconds so as to leave the poly(p-phenylene terephthalamide) still damp with initiator solution. The poly(p-phenylene terephthalamide) was transferred to a 8 X 10" ziplock polyethylene bag equipped with a gas inlet valve. The bag was evacuated and filled 3X with N_2 and 3X with TFE. The bag was inflated a final time with TFE and the polymerization allowed to run at room temperature. As TFE polymerization proceeded the bag periodically deflated to a near vacuum and was then reinflated -2 to 4" tall with TFE gas 9, 18, 27, 40, 50, 57, 67, 81, 97, 110, 133, 161, 199, and 250 minutes into the run. During much of the run, the bag was noticeably warm to the touch. After the last deflation, 303 minutes into the run, the contents of the bag were transferred back to a large crystallizing dish. Residual volatiles were removed by first putting under pump vacuum overnight and then in a 150°C vacuum oven for 73 hours. The product consisting largely of yellow granules, weighed 261 g for a weight gain of 20% and combustion analysis found 12.33 wt % fluorine or 16 wt % PTFE in rough agreement with the measured weight gain.

EXAMPLE 12

POLYMERIZATION OF PTFE IN POROUS POLY(P-PHENYLENE TEREPHTHALAMIDE) FIBERS

[0092] Never dried poly(p-phenylene terephthalamide) fibers, containing 30% to 70% by weight water, was first made ready for TFE polymerization by replacing the water in its pores with a solvent suitable for fluoroolefin polymerization. Thirty-five grams of never dried poly(p-phenylene terephthalamide) fibers were mixed in a jar with 50 ml of trifluoroacetic acid. After standing overnight, the contents of the jar were washed into a chromatography column using additional trifluoroacetic acid. Excess trifluoroacetic acid was drained off. Fifty ml of fresh trifluoroacetic acid were added to the top of the column and excess fluid again drained off, leaving the liquid level in the column about 3 cm above the poly(p-phenylene terephthalamide) layer. Over the following days, the poly(p-phenylene terephthalamide) in the chromatography column was washed in turn with 50 ml trifluoroacetic acid, 50 ml of Freon® E1 ($CF_3CF_2CF_2OCFHCF_3$), 50 ml Freon® E1, 50 ml Freon® E1, and 50 ml of chilled -0.03 M DP in Freon® E1. The cold DP solution was drained through the poly (p-phenylene terephthalamide) as rapidly as possible while low pressure nitrogen was applied to the top of the column towards the end for the purpose of expelling most unabsorbed fluid. In this operation the nitrogen flow was stopped before drying out of the poly(p-phenylene terephthalamide) particulates occurred. The poly(p-phenylene terephthalamide) having DP initiator in its pores was chilled on dry ice and transferred to a 400 ml autoclave pre-chilled to less than -20°C. The autoclave was evacuated and 25 g of TFE was added, raising pressure to -78 psi at -43°C. After shaking overnight at room temperature, pressure in the autoclave had decreased to 7 psi. Upon recovery and drying under pump vacuum, the poly(p-phenylene terephthalamide) weighed 38.3 g. The appearance of the composition after recovery was a mix of free flowing particulates and agglomerated particulates, and was cream colored. The poly(p-phenylene terephthalamide) was yellow in color prior to TFE polymerization. Examination by optical microscopy under cross polarizers showed bright, irregularly-shaped poly(p-phenylene terephthalamide) particles with dark PTFE deposits filling most of the pores. Little PTFE was visible at the surface of the poly(p-phenylene terephthalamide) particles. Most often, the dark PTFE areas were 50 microns to 200 microns in diameter. Combustion analysis of one of the agglomerated chunks showed 57.1% fluorine by weight.

EXAMPLE 13

POROUS POLY(M-PHENYLENE ISOPHTHALAMIDE) POWDER, ATMOSPHERIC PRESSURE TFE POLYMERIZATION

A. Intermediate PTFE Loading

[0093] Porous poly(m-phenylene isophthalamide) [MPD-I] particulates were prepared by precipitating MPD-I solution (in dimethylacetamide/$CaCl_2$) in water, washing with water and drying in vacuum at 100°C. A 4.83 g sample of these poly(m-phenylene isophthalamide) particulates was soaked at -15°C in 40 ml of CF_2ClCCl_2F containing 1.0 ml 0.16 M HFPO dimer peroxide in Vertrel® XF. After 15 minutes, the poly(m-phenylene isophthalamide) was separated by vacuum filtration, stopping filtration as soon as the liquid flow seemed near an end. The poly(m-phenylene isophthalamide), still damp with initiator solution, was transferred to a 6 X 9" ziplock polyethylene bag equipped with a gas inlet valve. The bag was evacuated and filled 3X with N_2 and 3X with TFE. The bag was inflated a final time with TFE and the polymerization allowed to run at room temperature. Most of the TFE reacted over the next 2.5 hours as seen in the near total deflation of the bag. The contents of the bag were poured out. After ~64 hours under pump vacuum, the product weighed 7.50 g (153% of starting weight) and consisted largely of white lumps not much different in visual appearance than at the start. Combustion analysis found 12.8 wt % fluorine.

B. Higher PTFE Loading

[0094] Porous poly(m-phenylene isophthalamide) [MPD-I] particulates were prepared by precipitating MPD-I solution (in dimethylacetamide/$CaCl_2$) in water, washing with water and drying in vacuum at 100°C.. A 6.5 g sample of these poly(m-phenylene isophthalamide) particulates was soaked at -15°C in 50 ml of 0.18 M HFPO dimer peroxide in Vertrel® XF. After 15 minutes, the poly(m-phenylene isophthalamide) was separated by vacuum filtration, stopping filtration as soon as the liquid flow seemed near an end. The poly(m-phenylene isophthalamide), still damp with initiator solution, was transferred to a 6 X 9" ziplock polyethylene bag equipped with a gas inlet valve. The bag was evacuated and filled 3X with N_2 and 3X with TFE. The bag was inflated a final time with TFE and the polymerization allowed to run at room temperature. Over the next 3 hours the bag deflated and was refilled with TFE five times. The contents of the bag were poured out. After four days under pump vacuum, the product weighed 20.5 g (315 % of starting weight) and consisted largely of white lumps not much different in visual appearance than at the start. Combustion analysis found 48.7 wt % fluorine.

EXAMPLE 14

POROUS POLY(M-PHENYLENE ISOPHTHALAMIDE) FIBRIDS,

ATMOSPHERIC PRESSURE TFE POLYMERIZATION

A. Intermediate PTFE Loading

[0095] Porous [poly(m-phenylene isophthalamide)] fibrids were prepared by precipitating MPD-I solution (in dimethylacetamide/$CaCl_2$) in water under shear, washing with water and drying in vacuum at 100°C. A 6.52 g sample of these poly(m-phenylene isophthalamide) fibrids was soaked at -15°C in 40 ml of CF_2ClCCl_2F containing 1.0 ml 0.16 M HFPO dimer peroxide in Vertrel® XF. After 15 minutes, the poly(m-phenylene isophthalamide) was separated by vacuum filtration, stopping filtration as soon as the liquid flow seemed near an end. The poly(m-phenylene isophthalamide), still damp with initiator solution, was transferred to a 6 X 9" ziplock polyethylene bag equipped with a gas inlet valve. The bag was evacuated and filled 3X with N_2 and 3X with TFE. The bag was inflated a final time with TFE and the polymerization allowed to run at room temperature. Most of the TFE reacted over the next 1.5 hours as seen in the near total deflation of the bag. The contents of the bag were poured out. After a weekend under pump vacuum, the product weighed 9.84 g (151% of starting weight) and consisted largely of flat white clumps of fibrids not much different in visual appearance than at the start. Combustion analysis found 40.5 wt % fluorine.

B. Higher PTFE Loading

[0096] Porous poly(m-phenylene isophthalamide) [MPD-I] particulates were prepared by precipitating MPD-I solution (in dimethylacetamide/$CaCl_2$) in water, washing with water and drying in vacuum at 100°C. A 6.5 g sample of these poly (m-phenylene isophthalamide) particulates was soaked at -15°C in 50 ml of 0.18 M HFPO dimer peroxide in Vertrel® XF. After 15 minutes, the poly(m-phenylene isophthalamide) was separated by vacuum filtration, stopping filtration as soon as the liquid flow seemed near an end. The poly(m-phenylene isophthalamide), still damp with initiator solution, was transferred to a 6 X 9" ziplock polyethylene bag equipped with a gas inlet valve. The bag was evacuated and filled 3X with N_2 and 3X with TFE. The bag was inflated a final time with TFE and the polymerization allowed to run at room temperature. Over the next 3 hours the bag deflated and was refilled with TFE five times. The contents of the bag were poured out. After four days under pump vacuum, the product weighed 18.1 g (278% of starting weight) and consisted largely of flat white clumps of particulates not much different in visual appearance than at the start. Combustion analysis found 55.3 wt % fluorine.

EXAMPLE 15

ULTRASUEDE®, ATMOSPHERIC PRESSURE TFE POLYMERIZATION

[0097] A rectangular sample of blue Ultrasuede® (a leather mimic believed to be a foamed polyurethane) weighing 2.1 g and measuring 7.6 cm X 8.2 cm X 0.09 cm thick, was immersed in a ~0.16 M solution of DP in Vertrel® XF maintained at -15°C. After 15 minutes, the Ultrasuede® was removed from the initiator solution and excess fluid allowed to drain for five or 10 seconds. The Ultrasuede® still wet with absorbed initiator was transferred to a 6 X 9" ziplock polyethylene bag provided with a gas inlet valve. The bag was sealed, evacuated and inflated 3X with N_2 and 3X with TFE. The bag was inflated a fourth time with TFE. Using an exterior clamp, all but a corner of the Ultrasuede® sample was held away from contact with the walls of the bag. The Ultrasuede® was recovered 23 hours later and devolatilized for 3 days under pump vacuum. While unchanged in appearance, the Ultrasuede® weighed 2.4 g, ~14% more than at the start. Combustion analysis found 6.00 wt % fluorine. A drop of distilled water placed on either side of the Ultrasuede® sample treated here took ~46 minutes to show initial wetting and never soaked into the Ultrasuede® prior to evaporation. For comparison purposes, an untreated Ultrasuede® sample was found to completely absorb a drop of water within about one minute on one side and to not be wetted at all by water on the reverse side (combustion analysis found 0.14 wt % F on the starting Ultrasuede® suggesting a fluorinated finish at the start).

EXAMPLE 16

PIGSKIN AND COWSKIN

[0098] A 5-cm square of commercial beige pigskin purchased at retail (chrome tanned split, one side suede, reverse side rough) weighing 1.69 g and measuring ~0.15 cm thick was immersed in a ~0.16 M solution of DP in Vertrel® XF maintained at -15°C. A 5 cm square of commercial black cowhide purchased at retail (chrome tanned split, suede both sides) weighing 2.09 g and measuring ~0.12 cm thick was immersed in a ~0.16 M solution of DP in Vertrel® XF maintained at -15°C. After 60 minutes, the two leather samples were removed from the initiator solution and excess fluid allowed to drain for five or 10 seconds. The leather samples still wet with absorbed initiator were transferred to a 6 X 9" ziplock polyethylene bag provided with a gas inlet valve. The bag was sealed, evacuated and inflated 3X with N_2 and 3X with TFE. The bag was inflated a fourth time and the bag and its contents tumbled overnight at room temperature. After recovery, the leather samples were devolatilized to constant weight under pump vacuum. The pigskin, slightly darkened in appearance, now weighed 1.86 g for a 10% weight gain and analyzed for 9.56 wt % F by combustion analysis. While unchanged in appearance, the cowskin weighed 2.25 g for a 5% weight gain and analyzed for 9.15 wt % F by combustion analysis. It should be noted that the starting pigskin and cowhide samples analyzed for 1.77 and 0.39 wt % F before the treatment described here.

Exemplary Embodiments

[0099]

1. A process for preparing a fluoropolymer/substrate composition, comprising:

   in the case of gaseous fluoromonomer

      (a) contacting a porous substrate with a solution comprising an initiator dissolved in a suitable solvent;
      (b) exposing said substrate and said initiator to gaseous fluoromonomer under polymerization temperature and pressure conditions wherein the fluoromonomer polymerizes into said substrate;

   wherein said polymerized gaseous fluoromonomer partially or completely fills and blocks the pores in the substrate; or in the case of liquid fluoromonomer

      (a) preparing a solution comprising initiator and liquid fluoromonomer;
      (b) contacting a porous substrate with said solution; and
      (c) polymerizing the liquid fluoromonomer under polymerization temperature and pressure conditions wherein the fluoromonomer polymerizes into said substrate, optionally in the presence of gaseous fluoromonomer;

   wherein said polymerized liquid fluoromonomer partially or completely fills and blocks the pores in the substrate.

2. The process of Claim 1 wherein the porous substrate is selected from the group consisting of paper, polyimide,

aramid, polyurethane, leather compositions, wood and wood-by-products.

3. The process of Claim 2 wherein the porous substrate is in a form selected from the group consisting of particulates, pulp, fibrids, fibers, and uncompressed, partially compressed, or fully compressed parts, sheets, films, membranes and coatings.

4. A process of Claim 1 wherein the fluoromonomer is selected from the group consisting of tetrafluoroethylene, trifluoroethylene, vinylidene fluoride, chlorotrifluoroethylene, 4,5-difluoro-2,2-bis(trifluoromethyl)-1,3-dioxole, and perfluoro (2-methylene-4-methyl-1,3-dioxolane), and optionally, further comprising at least one additional fluoromonomer selected from the group consisting of hexafluoroisobutylene, perfluoro methyl vinyl ether, and perfluoro propyl vinyl ether.

Claims

1. A composition of matter, comprising: a porous substrate wherein said substrate is an open pore structure having a surface and interconnecting pores throughout the substrate; and polymerized fluoropolymer, wherein said fluoropolymer is present within and on the surface of said substrate, and wherein the amount of fluoropolymer present in said composition is, in the case of a non-wood substrate, from about 0.1 percent to about 300 percent of the weight of said non-wood substrate, and in the case of a wood substrate, from about 0.1 to about 150 percent of the weight of said wood substrate.

2. The composition of Claim 1 wherein the non-wood substrate is selected from the group consisting of paper, molded polyimide parts, polyimide particulate, aramid, polyurethane and leather compositions.

3. The composition of Claim 1 wherein the wood substrate is selected from the group consisting of cedar, cherry, oak, pine, poplar, redwood, walnut, veneer and wood by-products.

4. The composition of Claim 2 wherein aramid is selected from the group consisting of porous poly(p-phenylene terephthalamide) and poly(p-phenylene terephthalamide) copolymers in particulate, pulp or fiber form; poly(m-phenylene isophthalamide) and poly(m-phenylene isophthalamide) copolymers in particulate, fibrid or fiber form.

5. The composition of Claim 2 or 3 wherein polyimide is in molded parts or powder form.

6. The composition of matter of Claim 1 in which the fluoropolymer is polytetrafluoroethylene.

7. A composition of Claim 2 or Claim 3 wherein the fluoropolymer is a homopolymer or copolymer of fluorinated and partially fluorinated olefins selected from the group consisting of tetrafluoroethylene, trifluoroethylene, vinylidene fluoride, vinyl fluoride, chlorotrifluoroethylene, hexafluoro-isobutylene, perfluoro methyl vinyl ether, perfluoro propyl vinyl ether, perfluoro (2-methylene-4-methyl)-1,3-dioxolane, 4,5 difluoro-2,2-bis (trifluoromethyl)-1,3-dioxole and hexafluoroisobutylene.

8. A composition of matter comprising 1 to 99% by weight of the composition of Claim 2 when added as tiller to 1 to 99% by weight of fluoropolymer.

9. A composition of matter comprising 1 to 99% by weight of the composition of Claim 5 when added as filler to 1 to 99% by weight of polyimide or aramid.

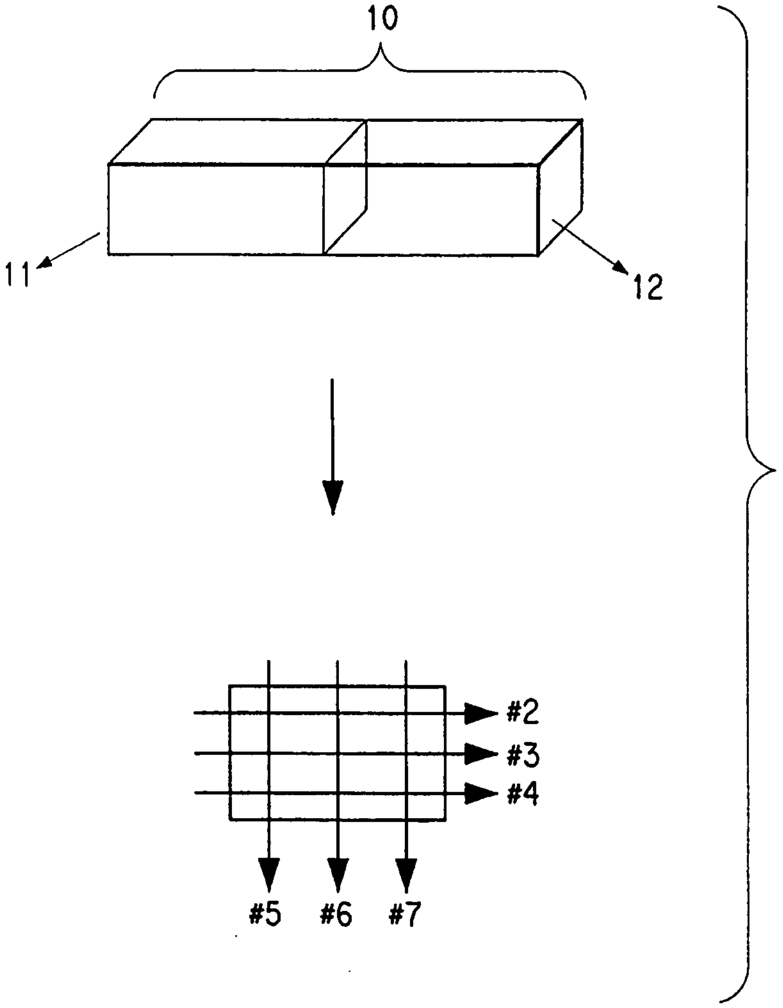
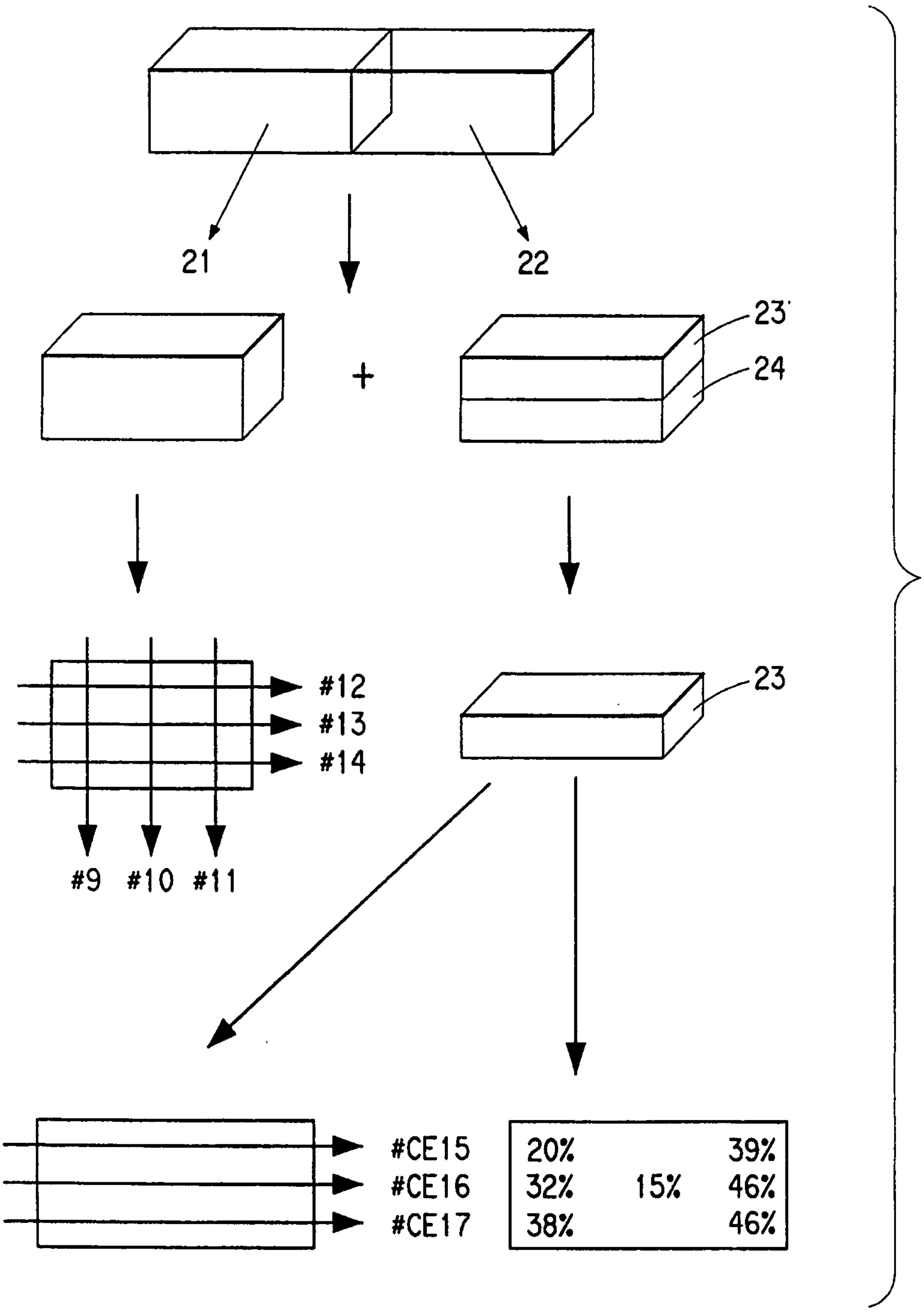


FIG.1

FIG.2



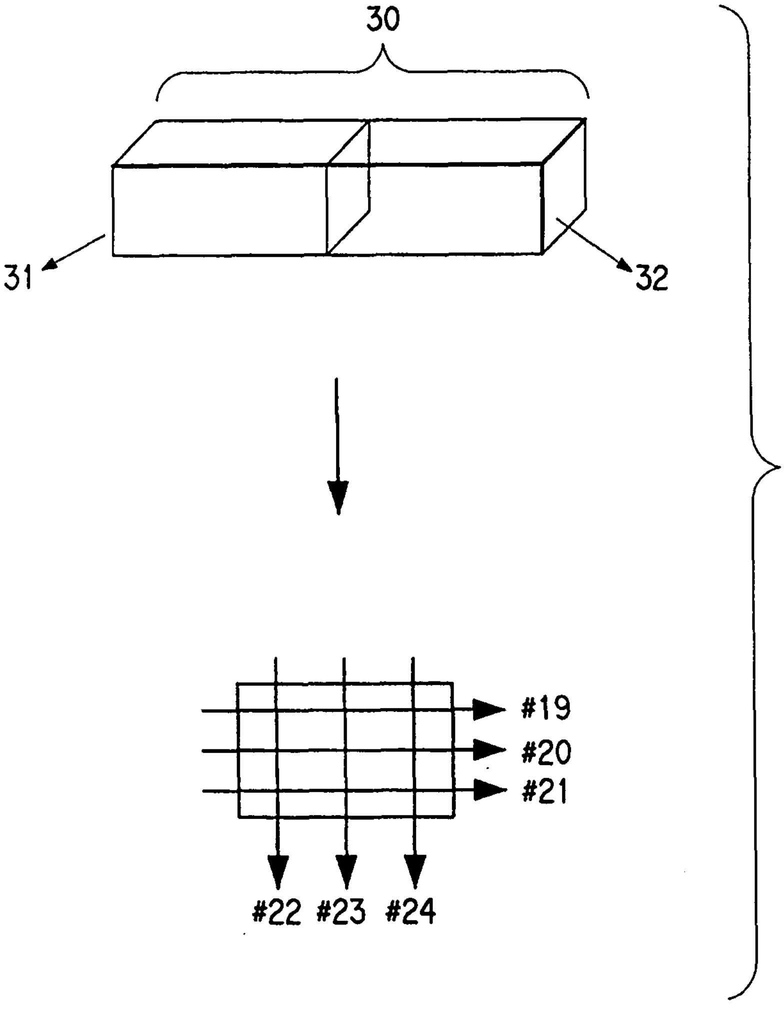
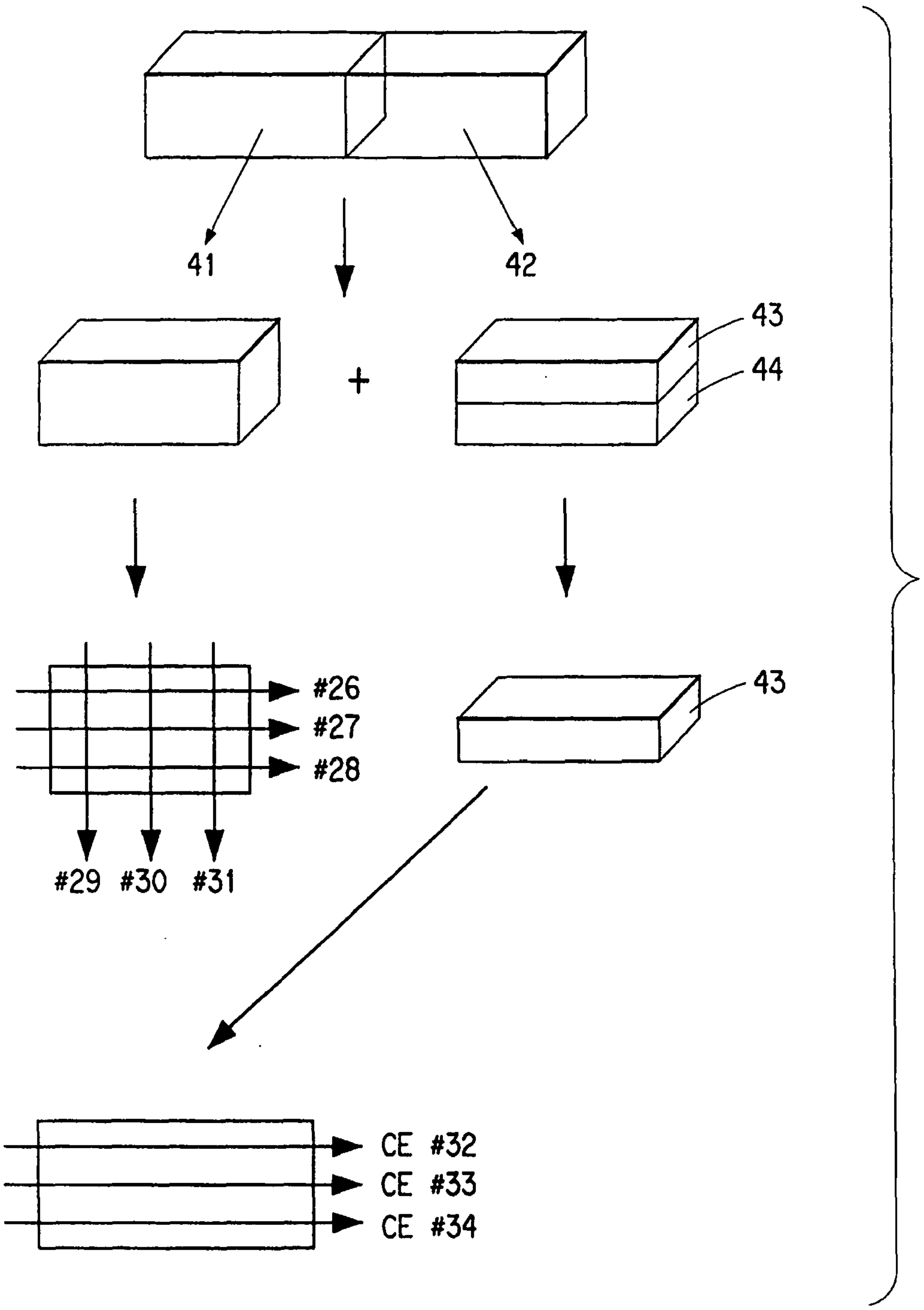


FIG.3

FIG.4



REFERENCES CITED IN THE DESCRIPTION

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- JP 05318413 B **[0004] [0006]**
- US 3962171 A **[0005]**
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