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(54) Title: LOW TEMPERATURE CURE REPELLENTS

(57) **Abstract:** An improved method for treating fibrous substrates with a copolymer containing a fluorinated acrylate or fluorinated methacrylate to provide water repellency and alcohol repellency wherein the improvement comprises contacting the substrate with a composition of particular fluorinated copolymers followed by drying or curing without heating.

TITLE OF INVENTION

LOW TEMPERATURE CURE REPELLENTS

FIELD OF THE INVENTION

The present invention relates to an improved method of treating fibrous substrates to provide water repellency and alcohol repellency with fluorinated (meth)acrylate copolymers which dry and cure at ambient temperature without oven curing at elevated temperature.

BACKGROUND OF THE INVENTION

Various fluorinated polymer compositions are known to be useful as treating agents to provide surface effects to substrates. Most commercially available fluorinated polymers useful as treating agents for imparting repellency to substrates require oven drying and curing at about 140 °C to provide the desired repellency properties. These commercially available fluorinated polymers usually contain a perfluoroalkyl chain containing predominantly eight or more carbon atoms.

Poly(fluoroalkylacrylate)s containing perfluoroalkyl groups having less than six carbon atoms usually have poor dynamic water repellency. Koji Honda et al., "Molecular Aggregation Structure and Surface Properties of poly(fluoroalkylacrylate) Thin Films" Macromolecules (2005), 38(13), 5699-5705 teach that for perfluoroalkyl chains of greater than 8 carbons, orientation of the perfluoroalkyl groups, designated R_f groups, is maintained in a parallel configuration while for such chains having less than 6 carbons, reorientation occurs. This reorientation decreases surface properties such as contact angle. Thus shorter chain perfluoroalkyls have traditionally not been successful commercially.

Drying and curing of a treated substrate contributes to developing optimum performance of water/alcohol repellency. The curing process allows melt spreading of the repellent and orientation of the fluorochemical polymer. The drying and curing usually requires high temperature heat curing, according to Charles L. Strickler, in "Fluorochemical Repellent Finishes for Nonwovens", Journal of Industrial Fabrics (1984), 3(2), 10-18.

U.S. Patent 7,008,993 describes a composition for providing alcohol and water repellency comprising: (a) a cationic fluoroacrylate copolymer with a glass transition temperature near ambient temperature; (b) a cationic fluoroacrylate copolymer with a glass transition temperature of about 80 °C. to about 100 °C.; (c) a nonionic hydrophilic softener; and (d) an inorganic additive. The above composition does not provide sufficient low surface tension to treat a nonwoven fabric such as a polypropylene nonwoven or a polyethylene nonwoven.

It is desirable to have a method for providing water repellency and alcohol repellency to fibrous substrates which employs drying and curing at ambient temperature without oven curing at elevated temperature. Such a method requires less energy. It is desirable to have such a method which is particularly effective for nonwoven substrates which have a low glass transition temperature. The present invention provides such a method.

SUMMARY OF THE INVENTION

The present invention comprises a method for treating fibrous substrates with a copolymer containing a fluorinated acrylate or fluorinated methacrylate to provide water repellency and alcohol repellency wherein the improvement comprises contacting the substrate with a composition comprising repeating units in any sequence of Formula 1, Formula 2, Formula 3, or Formula 4, followed by drying or curing without heating, wherein

A. Formula 1 is

$$[R_f\text{-}X\text{-}Y\text{-}C(O)\text{-}CH\text{-}CH_2]_k\text{–}[R_f\text{-}X\text{-}Y\text{-}C(O)\text{-}CT\text{-}CH_2]_a\text{–}[CCl_2\text{-}CH_2]_b\text{-}[R^1\text{-}Y\text{-}C(O)\text{-}CZ\text{-}CH_2]_p\text{-} \qquad \text{Formula 1}$$

wherein

R_f is a straight or branched perfluoroalkyl group having 6 carbon atoms, or a mixture thereof, which is optionally interrupted by at least one oxygen atom,

X is an organic divalent linking group having from about 1 to about 20 carbon atoms, optionally containing a triazole, oxygen, nitrogen, or sulfur, or a combination thereof,

Y is O, S or N(R) wherein R is H or C_1 to C_{20} alkyl, T is a straight or branched alkyl group having from about 1 to about 4 carbon atoms, or halide,

k is a positive integer,

a is a zero or positive integer,

b is a zero or positive integer,

p is zero or a positive integer, and

Z is H, a straight, branched or cyclic alkyl group having from about 1 to about 10 carbon atoms, or halide,

R^1 is H, C_nH_{2n+1}, C_nH_{2n-1}, C_mH_{2m}-CH(O)CH_2, $[CH_2CH_2O]_iR^2$, $[CH_2CH(CH_3)O]_iR^2$, $[C_mH_{2m}]N(R^2)_2$,

n is from about 8 to about 40,

m is 1 to about 40,

each R^2 is independently H, CH_2OH or C_sH_{2s+1},

s is 0 to about 40, and

i is 1 to about 200,

provided that

1) the repeating unit of $[R_f$-X-Y-C(O)-CH-$CH_2]_k$– in Formula 1 is present at a minimum of about 7% by weight,

2) the total of repeating units $[R_f$-X-Y-C(O)-CH-$CH_2]_k$ + $[R_f$-X-Y-C(O)-CT-$CH_2]_a$ + $[CCl_2$-$CH_2]_b$ is present at a minimum of about 70% by weight, and

3) the total of all repeating units, $[R_f$-X-Y-C(O)-CH-$CH_2]_k$ + $[R_f$-X-Y-C(O)-CT-$CH_2]_a$ + $[CCl_2$-$CH_2]_b$ + $[R^1$-Y-C(O)-CZ-$CH_2]_p$ + optional monomers, is 100% by weight;

B. Formula 2 is

$[R_f$-X-Y-C(O)-C(CH_3)-$CH_2]_a$–$[CCl_2$-$CH_2]_b$–$[CH_3(CH_2)_3CH(C_2H_5)CH_2$-O-C(O)-CH-$CH_2]_q$–$[R^1$-Y-C(O)-CZ-$CH_2]_p$-

wherein

R_f, X, Y, Z, R^1, a, b, and p are each as defined in Formula 1, and

q is a positive integer,

provided that

1) the repeating unit of -$[R_f$-X-Y-C(O)-C(CH_3)-$CH_2]_a$– in Formula 2 is present at about 48% by weight,

2) the repeating units -$[CCl_2-CH_2]_b$- and the repeating unit -$[CH_3(CH_2)_3CH(C_2H_5)CH_2-O-C(O)-CH-CH_2]_q$– in Formula 2 are each present at about 24% by weight, and

3) the total of all repeating units, $[R_f-X-Y-C(O)-C(CH_3)-CH_2]_a + [CCl_2-CH_2]_b + [CH_3(CH_2)_3CH(C_2H_5)CH_2-O-C(O)-CH-CH_2]_q + [R^1-Y-C(O)-CZ-CH_2]_p$- is 100% by weight;

C. Formula 3 is

$[R_f-X-Y-C(O)-C(CH_3)-CH_2]_a–[CCl_2-CH_2]_b–[CH_3(CH_2)_{17}-O-C(O)-C(CH_3)-CH_2]_q–[CH_3(CH_2)_{17}-O-C(O)-CH-CH_2]_t–[R^1-Y-C(O)-CZ-CH_2]_p$-

wherein

R_f, X, Y, Z, R^1, a, b, and p are each defined as in Formula 1,

q is a positive integer, and

t is a positive integer,

provided that

1) the repeating unit of -$[R_f-X-Y-C(O)-C(CH_3)-CH_2]_a$– in Formula 3 is present at about 48% by weight,

2) the repeating unit -$[CCl_2-CH_2]_b$-, is present at about 24% by weight,

3) the repeating unit –$[CH_3(CH_2)_{17}-O-C(O)-C(CH_3)-CH_2]_q$– and the repeating unit –$[CH_3(CH_2)_{17}-O-C(O)-CH-CH_2]_t$– of Formula 3 are each present at about 12% by weight, and

4) the total of all repeating units, $[R_f-X-Y-C(O)-C(CH_3)-CH_2]_a + [CCl_2-CH_2]_b$ + –$[CH_3(CH_2)_{17}-O-C(O)-C(CH_3)-CH_2]_q + [CH_3(CH_2)_{17}-O-C(O)-CH-CH_2]_t + [R^1-Y-C(O)-CZ-CH_2]_p$-, is 100% by weight; and

D. Formula 4 is

$[R_f-X-Y-C(O)-CH-CH_2]_k–[R_f-X-Y-C(O)-C(CH_3)-CH_2]_a–[CH_3(CH_2)_{17}-O-C(O)-C(CH_3)-CH_2]_q–[CH_3(CH_2)_{17}-O-C(O)-CH-CH_2]_t–[CH_3(CH_2)_3CH(C_2H_5)CH_2-O-C(O)-CH-CH_2]_u–[CH_3(CH_2)_3CH(C_2H_5)CH_2-O-C(O)-C(CH_3)-CH_2]_v–[R^1-Y-C(O)-CZ-CH_2]_p$-

wherein

R_f, X, Y, Z and R^1, k, a, p are each defined as in Formula 1,

q is a positive integer,

t is a positive integer,

u is a positive integer, and

v is a positive integer,

provided that

1) the repeating unit $[R_f\text{-}X\text{-}Y\text{-}C(O)\text{-}CH\text{-}CH_2]_k$– and the repeating unit $-[R_f\text{-}X\text{-}Y\text{-}C(O)\text{-}C(CH_3)\text{-}CH_2]_a$– in Formula 4 are each present at about 32% by weight,

2) the repeating unit $-[CH_3(CH_2)_{17}\text{-}O\text{-}C(O)\text{-}C(CH_3)\text{-}CH_2]_q$–, the repeating unit $-[CH_3(CH_2)_{17}\text{-}O\text{-}C(O)\text{-}CH\text{-}CH_2]_t$–, the repeating unit $-[CH_3(CH_2)_3CH(C_2H_5)CH_2\text{-}O\text{-}C(O)\text{-}CH\text{-}CH_2]_u$ –, and the repeating unit $-[CH_3(CH_2)_3CH(C_2H_5)CH_2\text{-}O\text{-}C(O)\text{-}C(CH_3)\text{-}CH_2]_v$ – of Formula 4 are each present at about 8% by weight, and

3) the total of all repeating units, $[R_f\text{-}X\text{-}Y\text{-}C(O)\text{-}CH\text{-}CH_2]_k + [R_f\text{-}X\text{-}Y\text{-}C(O)\text{-}C(CH_3)\text{-}CH_2]_a + [CH_3(CH_2)_{17}\text{-}O\text{-}C(O)\text{-}C(CH_3)\text{-}CH_2]_q + [CH_3(CH_2)_{17}\text{-}O\text{-}C(O)\text{-}CH\text{-}CH_2]_t + [CH_3(CH_2)_3CH(C_2H_5)CH_2\text{-}O\text{-}C(O)\text{-}CH\text{-}CH_2]_u + [CH_3(CH_2)_3CH(C_2H_5)CH_2\text{-}O\text{-}C(O)\text{-}C(CH_3)\text{-}CH_2]_v + [R^1\text{-}Y\text{-}C(O)\text{-}CZ\text{-}CH_2]_p$-, is 100% by weight.

The present invention further comprises a substrate treated in accordance with the above method.

DETAILED DESCRIPTION OF THE INVENTION

All trademarks are denoted herein by capitalization. In all instances herein, the term "(meth)acrylate" is used to denote either or both acrylate or methacrylate.

The term of "ambient temperature" is used herein to mean a temperature of from about 15 °C to about 25 °C.

The present invention comprises an improved method of treating fibrous substrates, in particular nonwoven substrates having a low glass transition temperature, with a fluorinated (meth)acrylate copolymer to impart water repellency and alcohol repellency. In the improved method of the present invention the treated substrates are air dried and cured at ambient temperature.

The minimum thermal property of polymers to make good fibers and fabrics is a melting temperature, Tm, above ambient temperature; or else the polymer would not have the structural integrity to form fibers and fabrics. If the fabric reaches a temperature near or above its Tm during drying or curing, the fabric will lose many of its properties, such as air permeability, handle, and tensile strength. Between the glass transition temperature, Tg, and the Tm, the polymer fiber or fabric can be mechanically stressed to induce useful properties, such as bulk, creases, dimensional strength, uniformity and other properties. Drying or curing at temperatures approaching the Tm risks losing these beneficial properties imparted to the fiber or fabric in earlier processing. Examples of Tg and Tm for various polymers are listed below.

Polymer	Glass transition temperature (Tg)	Melting point (Tm)
Poly-ethylene	-125C	137C
Poly-isobutylene	-73C	44C
Poly-propylene	-13C	176C
Poly-vinyl chloride	-18C	200C
Nylon-6	52C	223C
Nylon-66	50C	265C
Polyester (PET)	69C	270C
Polystyrene	100C	240C

This data is from J. Brandup, E. H. Immergut, "Polymer Handbook", Chapter III, p.1-193, Wiley-Interscience, New York, 1975. Further explanation is found in G. Odian, "Principles of Polymerization", Wiley-Interscience, New York, 1981, p.29-36

The method of the present invention is particularly suitable for treating polymers having a Tg near ambient temperature, especially polypropylene nonwoven fabrics and polyethylene nonwoven fabrics.

The fluorinated (meth)acrylate copolymers used in the present invention comprise repeating units in any sequence of Formula 1, Formula 2, Formula 3, and Formula 4, as defined below. The polymer sequence includes random, statistical, block, multiblock, gradient, or alternating. The weight percentages given herein for each of Formula 1, Formula 2, Formula 3 and Formula 4 are by weight of the copolymer.

Formula 1 is

$[R_f\text{-}X\text{-}Y\text{-}C(O)\text{-}CH\text{-}CH_2]_k\text{–}[R_f\text{-}X\text{-}Y\text{-}C(O)\text{-}CT\text{-}CH_2]_a\text{–}[CCl_2\text{-}CH_2]_b\text{-}[R^1\text{-}Y\text{-}C(O)\text{-}CZ\text{-}CH_2]_p\text{-}$

wherein

R_f is a straight or branched perfluoroalkyl group having 6 carbon atoms, which is optionally interrupted by at least one oxygen atom, or a mixture of the straight or branched perfluoroalkyl groups having 6 carbon atoms,

X is an organic divalent linking group having from about 1 to about 20 carbon atoms, optionally containing a triazole, oxygen, nitrogen, or sulfur, or a combination thereof,

Y is O, S or N(R) wherein R is H or a straight, branched or cyclic C_1 to C_{20} alkyl group,

T is a straight or branched alkyl group having from about 1 to about 4 carbon atoms, or halide,

k is a positive integer,

a is a zero or positive integer,

b is a zero or positive integer,

p is zero or a positive integer, and

Z is H, a straight, branched or cyclic alkyl group having from about 1 to about 10 carbon atoms, or halide,

R^1 is H, C_nH_{2n+1}, C_nH_{2n-1}, $C_mH_{2m}\text{-}CH(O)CH_2$, $[CH_2CH_2O]_iR^2$, $[CH_2CH(CH_3)O]_iR^2$, $[C_mH_{2m}]N(R^2)_2$,

n is from about 8 to about 40,

m is 1 to about 40,

R^2 is H, CH_2OH or C_sH_{2s+1},

s is 0 to about 40, and

i is 1 to about 200,

provided that

1) the repeating unit of $[R_f\text{-}X\text{-}Y\text{-}C(O)\text{-}CH\text{-}CH_2]_k\text{–}$ in Formula 1 is present at a minimum of about 7% by weight,

2) the total of repeating units $[R_f\text{-}X\text{-}Y\text{-}C(O)\text{-}CH\text{-}CH_2]_k$ + $[R_f\text{-}X\text{-}Y\text{-}C(O)\text{-}CT\text{-}CH_2]_a$ + $[CCl_2\text{-}CH_2]_b$ is present at a minimum of about 70% by weight, and

3) the total of all repeating units, $[R_f\text{-}X\text{-}Y\text{-}C(O)\text{-}CH\text{-}CH_2]_k + [R_f\text{-}X\text{-}Y\text{-}C(O)\text{-}CT\text{-}CH_2]_a + [CCl_2\text{-}CH_2]_b + [R^1\text{-}Y\text{-}C(O)\text{-}CZ\text{-}CH_2]_p$, plus any other optional monomers, is 100%.

In the Formula 1 copolymer the repeating unit $[R_f\text{-}X\text{-}Y\text{-}C(O)\text{-}CT\text{-}CH_2]_a$ is present at a minimum of 7% by weight and can range up to 100% by weight, preferably from about 7% to about 97% by weight of the copolymer, more preferably from about 7% to about 50% by weight of the copolymer. In Formula 1 the total of repeating units $[R_f\text{-}X\text{-}Y\text{-}C(O)\text{-}CH\text{-}CH_2]_k + [R_f\text{-}X\text{-}Y\text{-}C(O)\text{-}CT\text{-}CH_2]_a + [CCl_2\text{-}CH_2]_b$ is present at a minimum about 70% by weight. This total of repeating units $[R_f\text{-}X\text{-}Y\text{-}C(O)\text{-}CH\text{-}CH_2]_k + [R_f\text{-}X\text{-}Y\text{-}C(O)\text{-}CT\text{-}CH_2]_a + [CCl_2\text{-}CH_2]_b$ is present at a range of from about 70% to 100% by weight of the copolymer used in the present invention. Preferably this total is present at from about 70% to about 90% by weight, more preferably from about 70% to 80% by weight. The total of all repeating units in Formula 1, plus any other optional monomers is 100% by weight.

Formula 2 is $[R_f\text{-}X\text{-}Y\text{-}C(O)\text{-}C(CH_3)\text{-}CH_2]_a\text{–}[CCl_2\text{-}CH_2]_b\text{–}[CH_3(CH_2)_3CH(C_2H_5)CH_2\text{-}O\text{-}C(O)\text{-}CH\text{-}CH_2]_q\text{–}[R^1\text{-}Y\text{-}C(O)\text{-}CZ\text{-}CH_2]_p\text{-}$
wherein

R_f, X, Y, Z, R^1, a, b, and p are each as defined in Formula 1, and

q is a positive integer,

provided that

1) the repeating unit of $\text{-}[R_f\text{-}X\text{-}Y\text{-}C(O)\text{-}C(CH_3)\text{-}CH_2]_a\text{–}$ in Formula 2 is present at about 48% by weight,

2) the repeating unit $\text{-}[CCl_2\text{-}CH_2]_b\text{-}$ and the repeating unit $\text{-}[CH_3(CH_2)_3CH(C_2H_5)CH_2\text{-}O\text{-}C(O)\text{-}CH\text{-}CH_2]_q\text{–}$ in Formula 2 are each present at about 24% by weight, and

3) the total of all repeating units, $[R_f\text{-}X\text{-}Y\text{-}C(O)\text{-}C(CH_3)\text{-}CH_2]_a + [CCl_2\text{-}CH_2]_b + [CH_3(CH_2)_3CH(C_2H_5)CH_2\text{-}O\text{-}C(O)\text{-}CH\text{-}CH_2]_q + [R^1\text{-}Y\text{-}C(O)\text{-}CZ\text{-}CH_2]_p\text{-}$ is 100% by weight.

Formula 3 is

$[R_f\text{-}X\text{-}Y\text{-}C(O)\text{-}C(CH_3)\text{-}CH_2]_a\text{–}[CCl_2\text{-}CH_2]_b\text{–}[CH_3(CH_2)_{17}\text{-}O\text{-}C(O)\text{-}C(CH_3)\text{-}CH_2]_q\text{–}[CH_3(CH_2)_{17}\text{-}O\text{-}C(O)\text{-}CH\text{-}CH_2]_r\text{–}[R^1\text{-}Y\text{-}C(O)\text{-}CZ\text{-}CH_2]_p\text{-}$

wherein

R_f, X, Y, Z, R^1, a, b, and p are each defined as in Formula 1,

q is a positive integer, and

t is a positive integer,

provided that

1) the repeating unit of $-[R_f-X-Y-C(O)-C(CH_3)-CH_2]_a-$ in Formula 3 is present at about 48% by weight,

2) the repeating unit $-[CCl_2-CH_2]_b-$, is present at about 24% by weight,

3) the repeating unit $-[CH_3(CH_2)_{17}-O-C(O)-C(CH_3)-CH_2]_q-$ and the repeating unit $-[CH_3(CH_2)_{17}-O-C(O)-CH-CH_2]_t-$ of Formula 3 are each present at about 12% by weight, and

4) the total of all repeating units, $[R_f-X-Y-C(O)-C(CH_3)-CH_2]_a + [CCl_2-CH_2]_b + -[CH_3(CH_2)_{17}-O-C(O)-C(CH_3)-CH_2]_q + [CH_3(CH_2)_{17}-O-C(O)-CH-CH_2]_t + [R^1-Y-C(O)-CZ-CH_2]_p-$, is 100% by weight.

Formula 4 is

$[R_f-X-Y-C(O)-CH-CH_2]_k-[R_f-X-Y-C(O)-C(CH_3)-CH_2]_a-[CH_3(CH_2)_{17}-O-C(O)-C(CH_3)-CH_2]_q-[CH_3(CH_2)_{17}-O-C(O)-CH-CH_2]_t-[CH_3(CH_2)_3CH(C_2H_5)CH_2-O-C(O)-CH-CH_2]_u-[CH_3(CH_2)_3CH(C_2H_5)CH_2-O-C(O)-C(CH_3)-CH_2]_v-[R^1-Y-C(O)-CZ-CH_2]_p-$

wherein

R_f, X, Y, Z and R^1, k, a, p are each defined as in Formula 1,

q is a positive integer,

t is a positive integer,

u is a positive integer, and

v is a positive integer,

provided that

1) the repeating unit $[R_f-X-Y-C(O)-CH-CH_2]_k-$ and the repeating unit $-[R_f-X-Y-C(O)-C(CH_3)-CH_2]_a-$ in Formula 4 are each present at about 32% by weight,

2) the repeating unit $-[CH_3(CH_2)_{17}-O-C(O)-C(CH_3)-CH_2]_q-$, the repeating unit $-[CH_3(CH_2)_{17}-O-C(O)-CH-CH_2]_t-$, the repeating unit $-[CH_3(CH_2)_3CH(C_2H_5)CH_2-O-C(O)-CH-CH_2]_u-$, and the repeating unit

–[$CH_3(CH_2)_3CH(C_2H_5)CH_2$-O-C(O)-C($CH_3$)-$CH_2$]$_v$ – of Formula 4 are each present at about 8% by weight, and

3) the total of all repeating units, [R_f-X-Y-C(O)-CH-CH_2]$_k$ + [R_f-X-Y-C(O)-C(CH_3)-CH_2]$_a$ + [$CH_3(CH_2)_{17}$-O-C(O)-C(CH_3)-CH_2]$_q$ + [$CH_3(CH_2)_{17}$-O-C(O)-CH-CH_2]$_t$ + [$CH_3(CH_2)_3CH(C_2H_5)CH_2$-O-C(O)-CH-$CH_2$]$_u$ + [$CH_3(CH_2)_3CH(C_2H_5)CH_2$-O-C(O)-C($CH_3$)-$CH_2$]$_v$ + [R^1-Y-C(O)-CZ-CH_2]$_p$-, is 100% by weight.

In each of Formula 1 to 4, R_f is preferably a straight or branched perfluoroalkyl group having 6 carbon atoms, which is optionally interrupted by at least one oxygen atom, or a mixture of the straight or branched perfluoroalkyl groups having 6 carbon atoms. More preferably R_f is a straight or branched C_6F_{13}-, or a mixture thereof. Most preferably R_f is $CF_3(CF_2)_5$.

In Formula 1 to 4, the subscripts k, a, b, p, q, t, u, and v are each independently from 1 to about 10,000, more preferably from about 5 to about 2000, or a mixture thereof.

Examples of suitable linking groups X in Formula 1 to 4 include straight chain, branched chain or cyclic alkylene, phenyl, arylene, aralkylene, sulfonyl, sulfoxy, sulfonamido, carbonamido, carbonyloxy, urethanylene, ureylene, and combinations thereof such as sulfonamidoalkylene.

Examples of preferred groups Y in Formula 1 to 4 are O, S or N(R) wherein R is H or C_1 to C_4 alkyl.

The copolymers used in the present invention are prepared by polymerization of fluorinated (meth)acrylate monomers with other monomers as detailed below.

The copolymers of Formula 1 used in the present invention comprise monomers copolymerized in the following percentages by weight relative to the copolymer product:

(a) from about 7% to about 100% of Formula 5, or a mixture thereof

R_f-X-Y-C(O)-CH=CH_2 Formula 5

wherein

R_f, X and Y are defined as in Formula 1 above;

(b) from about 0% to about 93% of Formula 6, or a mixture of thereof:

R_f-X-Y-C(O)-CT=CH_2 Formula 6

wherein

R_f, X, Y and T are defined as in Formula 1 above;

c) from about 0% to about 93% of vinylidene chloride;

d) from about 0% to about 30% of Formula 7, or a mixture thereof:

$$R^1\text{-Y-C(O)-CZ-CH}_2 \qquad \text{Formula 7}$$

wherein

Y, R^1, and Z are each as defined as above in Formula 1; and

e) from about 0% to about 93% of an additional optional monomer. Thus the copolymer of Formula 1 can comprise repeating units derived from 100% of Formula 5; a mixture of Formula 5 and Formula 6; a mixture of Formula 5 and vinylidene chloride; a mixture of Formula 5 and Formula 7; a mixture of Formula 5 and an optional monomer; a mixture of Formula 5 and any two of Formula 6, Formula 7, vinylidene chloride, and an optional monomer; a mixture of Formula 5 and any three of Formula 6, Formula 7, vinylidene chloride, and an optional monomer; or a mixture of Formula 5, Formula 6, Formula 7, vinylidene chloride and an optional monomer. For any such mixture the weight percent of all repeating units adds up to 100%.

The copolymers of Formula 2 used in the present invention comprise monomers copolymerized in the following percentages by weight relative to the copolymer product:

(a) about 48% of Formula 8

$$R_f\text{-X-Y-C(O)-C(CH}_3\text{)=CH}_2 \qquad \text{Formula 8}$$

wherein

R_f, X and Y are defined as in Formula 1 above;

(b) about 24% of vinylidene chloride;

(c) about 24% of 2-ethylhexyl acrylate; and

(d) about 4% of Formula 7 as defined above.

The copolymers of Formula 3 used in the present invention comprise monomers copolymerized in the following percentages by weight relative to the copolymer product:

(a) about 48% of Formula 8

R_f-X-Y-C(O)-C(CH_3)=CH_2 Formula 8

wherein

R_f, X and Y are defined as in Formula 1 above;

(b) about 24% of vinylidene chloride;

(c) about 12% of stearyl methacrylate;

(d) about 12% of stearyl acrylate; and

(e) about 4% of Formula 7 as defined above.

The copolymers of Formula 4 used in the present invention comprise monomers copolymerized in the following percentages by weight relative to the copolymer product:

(a) about 32% of Formula 5 as defined above, or a mixture thereof,

(b) about 32% of Formula 8 as defined above, or a mixture of thereof,

(c) about 8% of stearyl methacrylate,

(d) about 8% of stearyl acrylate,

(e) about 8% of 2-ethylhexyl acrylate,

(f) about 8% of 2-ethylhexyl methacrylate, and

(g) about 4% of Formula 7 as defined above, or a mixture thereof.

In Formula 5 and Formula 8, R_f is preferably a straight or branched perfluoroalkyl group having 6 carbon atoms, or a mixture thereof, more preferably a straight or branched C_6F_{13}-, or a mixture thereof, most preferably $CF_3(CF_2)_5$-. Examples of Formula 5 suitable for use in the present invention are:

$CF_3(CF_2)_5$-CH_2CH_2-OC(O)-CH=CH_2,

C_6F_{13}-CH_2CH_2-OC(O)-CH=CH_2,

C_6F_{13}-R^2-SC(O)-CH=CH_2,

C_6F_{13}-R^2-OC(O)-CH=CH_2,

C_6F_{13}-SO_2-N(R^1)-R^2-OC(O)-CH=CH_2,

C_6F_{13}-CO-N(R^1)-R^2-OC(O)-CH=CH_2,

C_6F_{13}-CH_2CH(OR^3)CH-OC(O)-CH=CH_2,

C_6F_{13}-R^2-SO_2-N(R^1)-OC(O)-CH=CH_2,

C_6F_{13}-R^2-O-CON(R^1)-R^2-OC(O)-CH=CH_2,

wherein

R^1 is H or C_1-C_4 alkyl;

R^2 is C_1-C_{10} alkylene; and

R^3 is H or C_1-C_4 acyl.

Examples of suitable Formula 6 suitable for use in the present invention are:

$CF_3(CF_2)_5.CH_2CH_2$-OC(O)-$C(CH_3)=CH_2$,
$C_6F_{13}.CH_2CH_2$-OC(O)-$C(CH_3)=CH_2$,
C_6F_{13}-R^2-SC(O)-$C(CH_3)=CH_2$,
C_6F_{13}-R^2-OC(O)-$C(CH_3)=CH_2$,
C_6F_{13}-SO_2-N(R^1)-R^2-OC(O)-$C(CH_3)=CH_2$,
C_6F_{13}-CO-N(R^1)-R^2-OC(O)-$C(CH_3)=CH_2$,
C_6F_{13}-$CH_2CH(OR^3)CH$-OC(O)-$C(CH_3)=CH_2$,
C_6F_{13}-R^2-SO_2-N(R^1)-OC(O)-$C(CH_3)=CH_2$,
C_6F_{13}-R^2-O-CON(R^1)-R^2-OC(O)-$C(CH_3)=CH_2$,

wherein

R^1 is H or C_1-C_4 alkyl;
R^2 is C_1-C_{10} alkylene; and
R^3 is H or C_1-C_4 acyl.

Examples of Formula 8 suitable for use in the present invention are:

$CF_3(CF_2)_5.CH_2CH_2$-OC(O)-$C(CH_3)=CH_2$,
$C_6F_{13}.CH_2CH_2$-OC(O)-$C(CH_3)=CH_2$,
C_6F_{13}-R^2-SC(O)-$C(CH_3)=CH_2$,
C_6F_{13}-R^2-OC(O)-$C(CH_3)=CH_2$,
C_6F_{13}-SO_2-N(R^1)-R^2-OC(O)-$C(CH_3)=CH_2$,
C_6F_{13}-CO-N(R^1)-R^2-OC(O)-$C(CH_3)=CH_2$,
C_6F_{13}-$CH_2CH(OR^3)CH$-OC(O)-$C(CH_3)=CH_2$,
C_6F_{13}-R^2-SO_2-N(R^1)-OC(O)-$C(CH_3)=CH_2$,
C_6F_{13}-R^2-O-CON(R^1)-R^2-OC(O)-$C(CH_3)=CH_2$,

wherein

R^1 is H or C_1-C_4 alkyl;
R^2 is C_1-C_{10} alkylene; and
R^3 is H or C_1-C_4 acyl.

The nonfluorinated (meth)acrylate monomers as of Formula 7 suitable for the use in the method of the present invention comprise alkyl (meth)acrylates in which the alkyl group is a straight or branched chain containing 8 to 40 carbon atoms, or mixtures thereof. The preferred alkyl group for the alkyl (meth)acrylates containing 8 to 20 carbon atoms. The alkyl (meth)acrylates (linear or branched) are exemplified by, but not limited to, alkyl(meth)acrylates where the alkyl group is octyl, 2- ethylhexyl, decyl, isodecyl, lauryl, cetyl, or stearyl. The preferred examples are 2-ethylhexyl acrylate, lauryl acrylate and stearyl acrylate.

Examples of other nonfluorinated (meth)acrylate monomers as of Formula 7 suitable for the use in the present invention include N-methylol (meth)acrylates, hydroxyalkyl (meth)acrylates, alkyloxy(meth)acrylates, glycidyl (meth)acrylates, stearyl acrylate, aminoalkyl methacrylate hydrochloride, acrylamide, alkyl acrylamide. Wherein, N-methylol monomers are exemplified by, but not limited to N- methylolacrylamide and N-methylolmethacrylamide. The hydroxyalkyl (meth)acrylates have alkyl chain lengths in the range between 2 and 4 carbon atoms, and are exemplified by 2-hydroxyethyl acrylate, and 2- hydroxyethyl methacrylate. The alkyloxy(meth)acrylates also have alkyl chain lengths in the range between 2 and 4 carbon atoms, and contain between 1 and 12 oxyalkylene units per molecule, preferably between 4 and 10 oxyalkylene units per molecule, and most preferably between 6 and 8 oxyalkylene units per molecule.

Other suitable additional optional monomers for use in the preparation of the copolymers of Formula 1 include vinyl acetate, vinyl stearate, alkyl vinyl sulfone, styrene, vinyl benzoic acid, alkyl vinyl ether, maleic anhydride, vinyl chloride, and other olefin.

The fluorinated (meth)acrylate copolymers of Formula 1, 2, 3 or 4 used in this invention are prepared in organic solvent or water with one or more surfactants by free radical initiated polymerization of a mixture of fluorinated (meth)acrylate of Formula 5, 6 and/or 8, as appropriate, with the other monomers as listed above for each. The fluorinated copolymers used in this invention are made by agitating the monomers described above in organic solvent or water with one or more surfactants in a suitable reaction vessel which is equipped with an agitation device and an external heating and cooling device. A free radical initiator is added and the temperature raised to from about 20° to about 70° C. The polymerization initiator is exemplified by 2,2'-azobis(2-amidinopropane dihydrochloride or 2,2'-azobis(isobutyramidine) dihydrochloride. These initiators are sold by E. I. du Pont de Nemours and Company, Wilmington, Delaware, commercially under the name of "VAZO". An example of a suitable polymerization regulator or chain transfer agent is dodecylmercaptan. Suitable organic solvents useful in the preparation of the copolymers of Formula 1, 2, 3 or 4 used in the method of the present invention include tetrahydrofuran, acetone, methyl isobutyl ketone, isopropanol, ethyl acetate, and mixtures thereof. Tetrahydrofuran is preferred. The reaction is conducted under an inert gas, such as nitrogen, to the exclusion of oxygen. The polymer is isolated by precipitation, and optionally purified by for example, recrystallization. The solvent is removed by evaporation, or the solution is retained for dilution and application to the substrate. The product of the reaction is a fluorinated (meth)acrylate copolymer of Formula 1, 2, 3 or 4.

The resulting fluorinated (meth)acrylate copolymer of Formula 1, 2, 3 or 4 then can be diluted with water, or further dispersed or dissolved in a solvent selected from the groups comprising simple alcohols and ketones that are suitable as the solvent for final application to substrates (hereinafter the "application solvent"). Alternatively, an aqueous dispersion, made by conventional methods with surfactants, is prepared by removing solvents by evaporation and the use of emulsification or homogenization procedures known to those skilled in the art. Such solvent-free emulsions are preferred to minimize flammability and volatile organic compounds (VOC) concerns. The final product for application to a substrate is a dispersion (if water based) or a solution (if a solvent other than water is used) of the fluorinated (meth)acrylate copolymer of Formula 1, 2, 3 or 4.

In the improved method of the present invention water repellency and alcohol repellency are provided to a fibrous substrate by contacting the fluorinated (meth)acrylate copolymer solution or dispersion of Formula 1, 2, 3 or 4 with the substrate. Suitable substrates include fibrous substrates, particularly nonwoven substrates as defined below.

The fluorinated (meth)acrylate copolymer solution or dispersion of Formula 1, 2 3 or 4 is contacted with the substrate by any suitable method. Such methods are known to those skilled in the art, and include for example, application by foam, nip, pad, kiss-roll, spray, dipping, immersion, brush, roller, sponge, mat, and similar conventional techniques. The fluorinated (meth)acrylate copolymer solution or dispersion of Formula 1, 2, 3 or 4 is applied to the substrate as such, or in combination with other optional textile finishes or surface treating agents.

Such optional additional components include treating agents or finishes to achieve additional surface effects, or additives commonly used with such agents or finishes. Such additional components comprise compounds or compositions that provide surface effects such as no iron, easy to iron, shrinkage control, wrinkle free, permanent press, moisture control, softness, strength, anti-slip, anti-static, anti-snag, anti-pill, stain repellency, stain release, alcohol repellency, alcohol release, water repellency, alcohol repellency, odor control, antimicrobial, sun protection, cleanability and similar effects. One or more of such treating agents or finishes can be applied to the substrate before, after, or simultaneously with the copolymer of the present invention. Such optional components are typically blended into the treatment bath.

Other additives commonly used with such treating agents or finishes can also be present such as surfactants, pH adjusters, cross linkers, wetting agents, wax extenders, and other additives known by those skilled in the art. Suitable surfactants include anionic, cationic, nonionic, N-oxides and amphoteric surfactants. Examples of such additives include processing aids, foaming agents, lubricants, anti-stains, and the like. Such additives are typically blended with the treatment bath

Application rates for the fluorinated (meth)acrylate copolymer solution or dispersion of Formula 1, 2, 3 or 4 used in the present invention depend on the substrate porosity and is an amount to provide the desired fluorine content in the treated substrate. A treated fibrous substrate typically has a fluorine content of from about 100 μg/g to about 10,000 μg/g by weight. Preferably the fluorine content is from about 1,000 μg/g to about 4,000 μg/g.

Optionally, nonfluorinated extender compositions are also included in the application composition to potentially increase fluorine efficiency. Examples of such optional additional extender polymer compositions are those disclosed in co-pending US Provisional Application 60/607,612, filed September 7, 2004 (CH2996), and in US Serial number 11/175680 filed July 6, 2005 (CH3048).

The present invention further comprises substrates treated with the fluorinated (meth)acrylate copolymer solution or dispersion of Formula 1, 2, 3 or 4 using the method of the present invention. Suitable substrates include fibrous substrates. The fibrous substrates include woven, knit, and nonwoven fabrics or other textiles. In particular, the fluorinated (meth)acrylate copolymer solution or dispersion of Formula 1, 2, 3 or 4 used in the method of the present invention is suitable for providing excellent water repellency and alcohol repellency to woven, knit, and nonwoven fabrics, in particular those made from polyolefin fibers such as polypropylene, polyethylene, and low melting polymer blends, fibers made therefrom, and blends containing these fibers. The present invention is particularly suitable for polypropylene fabrics or polyethylene fabrics, and most particularly to polypropylene nonwoven fabrics or polyethylene nonwoven fabrics. The types of nonwoven fabrics include spun-bonded, melt-blown, and laminates containing either type of nonwoven structure. The types of nonwovens are described in the "Encyclopedia of Textile Finishing", Rouette, Hans-Karl, 2001 Springer - Verlag, ISBN: 3540654909. Such nonwovens typically have a low glass transition temperature, and thus when conventional treating processes are employed with a heated curing step, the nonwoven softens during heating. Thus the improved method of the present invention permits providing surface effects to nonwovens without this disadvantage. The fluorinated (meth)acrylate copolymer solution or dispersion of Formula 1, 2 3 or 4 used in the method of the present invention provides excellent water and alcohol repellency to substrates treated therewith.

The fluorinated (meth)acrylate copolymer compositions used in the present invention are useful to provide excellent water repellency and alcohol repellency to treated substrates with air drying or curing at ambient temperature. Elevated temperatures are not required to obtain effective repellency. The fluorinated (meth)acrylate copolymers used in the method of the present invention allow for the use of shorter fluoroalkyl groups containing, for example, 6 carbon atoms while conventional commercially available (meth)acrylates typically show poor alcohol repellency and water repellency performance if the fluoroalkyl groups contain less than 8 carbon atoms.

TEST METHODS

Test Method 1

The fabric was treated with the copolymer dispersion for emulsion padding application using a pad bath (dipping) process. The fluorinated (meth)acrylate copolymer of Formula 1, 2 ,3 or 4 was applied to spunbonded meltblown spunbonded polypropylene (SMS PP) nonwoven fabric manufactured by Kimberly-Clark (Roswell, GA) with a fabric weight of 76 grams/square meter. After application, the fabric was allowed to air dry and cure. The fabric was tested for water repellency and alcohol repellency using Test Methods 2 as described below.

Test Method 2 - Water/alcohol Repellency

The water/alcohol repellency of a treated substrate was measured according to INDA Standard Test for Water/Alcohol Repellency Test Method, IST 80.6-92. The test determines the resistance of a treated substrate to wetting by aqueous liquids. Three drops of water-alcohol mixtures of varying surface tensions are placed on the substrate and the extent of surface wetting is determined visually.

The composition of water repellency test liquids is shown in table 1.

Table 1. Alcohol/Water Repellency Test Liquids

Water Repellency Rating Number	Volume % Isopropyl Alcohol	Volume % Distilled Water
0	0	100
1	10	90
2	20	80
3	30	70
4	40	60
5	50	50
6	60	40
7	70	30
8	80	20
9	90	10
10	100	0

Three drops of Test Liquid 1 were placed on the treated substrate. If no liquid penetration or partial absorption (appearance of a darker wet patch on the substrate) was observed after 5 minutes, the test was repeated with Test Liquid 2. The test was repeated with Test Liquid 3 and progressively higher Test Liquid numbers until liquid penetration (appearance of a darker wet patch on the substrate) was observed. The test result was the highest Test Liquid number that did not penetrate into the substrate. Higher scores indicate greater repellency.

EXAMPLES

For all Tables in the Examples section, measured fluorine is the weight ratio of fluorine to the weight of the entire treated fabric unless specified otherwise. All chemicals used in the following were reagent grade and were obtained from Sigma-Aldrich (St. Louis, MO) unless otherwise specified,

Example 1

Into a plastic beaker were combined 200 grams of deionized water, 4.0 grams of Mazer MAPEG 600MS polyalkylene glycol esters from Mazer Chemicals, Inc., Gurnee, Illinois, 6.0 grams of AVITEX surface active agents from E. I. du Pont de Nemours and Company, Wilmington, DE, 7.1 grams of $CF_3(CF_2)_5CH_2CH_2OC(O)CHCH_2$ which is available from E. I. du Pont de Nemours and Company, Wilmington, DE, 7.1 grams of $CF_3(CF_2)_5CH_2CH_2$-$OC(O)C(CH_3)CH_2$ which is available from E. I. du Pont de Nemours and Company, Wilmington, DE, 1.0 grams of poly(ethylene glycol) methacrylate having an average of 8 ethoxy groups (8EO-MA) available by the product name of BLEMMER 350, as a co-monomer, from NOF-America, White Plains, NY, 7.1 grams of stearyl methacrylate from Sigma-Aldrich, Milwaukee, WI, 1.0 grams of hydroxymethyl acrylamide from Sigma-Aldrich, Milwaukee, WI, 0.50 grams of hydroxy ethyl methacrylate from Sigma-Aldrich, Milwaukee, WI, 0.25 grams of dodecyl mercaptan from Sigma-Aldrich, Milwaukee, WI, 10.0 grams of hexylene glycol Sigma-Aldrich, Milwaukee, WI, and 0.10 grams of sulfamic acid from Sigma-Aldrich, Milwaukee, WI. The reaction mixture was heated to 55°C and emulsified in a sonicator twice for two minutes until a uniform milky white emulsion resulted. The solution was charged to a 500 mL flask equipped a nitrogen blanket, condenser, overhead stirrer and temperature probe, set to nitrogen sparging, and stirred at 170 rpm. When the temperature had dropped below about 30°C the flask was switched to nitrogen blanket and 14.3 grams of vinylidene chloride(VDC) from Sigma-Aldrich, Milwaukee, WI with 10.0 grams of deionized water were added. The solution was stirred for 15 minutes. After 15 minutes 0.50 grams of VAZO-50 initiator in 10.0 grams of deionized water was added. The reaction mixture was then heated to 50°C over 30 min. The solution was stirred for 8 hours at 50°C. The solution was then cooled to room temperature and then filtered into a small necked bottle using gravity filtration through a milk filter to give an emulsion copolymer with 13.2% solids by weight and 3.2% fluorine by weight.

Spunbonded meltblown spunbonded polypropylene fabric (SMS PP) was treated with the copolymer in accordance with Test Method 1. The amount of fluorinated copolymer dispersion used in the pad bath was calculated to achieve a fluorine level on fabric of approximately 1200 micrograms per gram fluorine by weight. In addition to the fluorinated copolymer emulsion prepared as described above, the pad bath contained 0.15% by weight of ZELEC TY potassium butyl phosphate from E. I. du Pont de Nemours and Company, Wilmington, DE and 0.6% of n-hexanol from Sigma-Aldrich, Milwaukee, WI. After pad application of the fluorinated copolymer emulsion prepared as described above with a total bath wet pick up of approximately 140%, the nonwoven SMS PP fabric was either air dried or dried and cured in an oven until the fabric reached 140 °C. and remained at that temperature for 3 minutes. The fabric was allowed to "rest" after treatment and cure. The nonwoven SMS PP fabric was tested for water repellency and alcohol repellency using Test Method 2. The results are in Table 2.

Table 2

Example	Air Dry/Cure at ambient temperature	140 °C. Dry/Cure
1	8	9
Untreated	2	2

The data in Table 2 shows that the method of the present invention provided excellent water repellency and alcohol repellency on SMS PP nonwoven fabrics with air drying at ambient temperature which was substantially equivalent to use of drying at an elevated temperature.

Examples 2-27 and Comparative Examples A-P

For each of Examples 2 to 27 and Comparative Examples A to P the copolymers were prepared using the monomers listed in Table 3 by weight percent in the copolymer, and using the procedure of Example 1. The resulting copolymers from Examples 2-27 and from Comparative Examples A-P were each applied using Test Method 1 to nonwoven spunbonded meltblown spunbonded polypropylene (SMS PP) fabrics. The treated fabrics were tested for water/alcohol repellency according to Test method 2. The results are in Table 5.

The Comparative Examples provided copolymer compositions that are outside of Formula 1, 2, 3 or 4 and did not provide ambient temperature cure repellency. For Comparative Examples A, F, J, K, L, M, and O, no repeating unit of $[R_f\text{-}X\text{-}Y\text{-}C(O)\text{-}CH\text{-}CH_2]_k$ or of $-[R_f\text{-}X\text{-}Y\text{-}C(O)\text{-}C(CH_3)\text{-}CH_2]_a$ is present. For Comparative Examples B, C, D, G, H, I, and P, the total of $[R_f\text{-}X\text{-}Y\text{-}C(O)\text{-}CH\text{-}CH_2]_k + [R_f\text{-}X\text{-}Y\text{-}C(O)\text{-}CT\text{-}CH_2]_a + [CCl_2\text{-}CH_2]_b$ is less than 70% by weight. For Comparative Example E, R^1 is C_4H_9, a shorter chain length than required in Formula 1, 2, 3 or 4. For Comparative Example N, R^1 is C_6H_{11}, a shorter chain length than required in Formula 1, 2, 3 or 4.

Table 3 - Monomers used in Copolymerization

Monomer*	A	B	VDC	D	E	F	G	H	I
Formula	5	6	-	7	7	7	7	7	7
Example									
2	19%	19%	39%	19%					4%
3	7%	18%	50%	21%					4%
4	38%	24%	30%					C_{12} 4%	4%
5	48%		24%	24%					4%
6	48%		24%		12%	12%			4%
7	24%	24%	24%	24%					4%
8	38%		38%	9%			10%		4%
9	38%		38%	19%					4%
10	48%		24%	12%			12%		4%

11	38%		48%		10%				4%
12	38%		38%		9%	10%			4%
13	44%		31%				22%		4%
14	58%		29%		10%				4%
15	48%		24%		24%				4%
16	19%		67%		10%				4%
17	13%	17%	40%					branched C_{13} 26%	4%
18	13%	17%	40%					C_{18}-C_{24} blend 26%	4%
19	32%		42%		22%				4%
20		48%	24%			24%			4%
21		48%	24%	12%	12%				4%
22	70%		10%	16%					4%
23	44%		31%			22%			4%
24	38%	24%	30%					branched C_{10} 4%	4%
25	32%	32%		8%	8%	8%	8%		4%
26	58%		19%	19%					4%
27	24%	26%	46%						4%
A		44%						C_{12} 52%	4%
B	48%			24%			24%		4%
C	64%						32%		4%
D	38%		29%		29%				4%
E	38%	24%	30%					C_4 4%	4%
F		64%				32%			4%
G	19%		48%		29%				4%
H	44%			52%					4%
I	44%				52%				4%
J		51%	24%				21%		4%
K		38%	38%				19%		4%
L		58%	19%	19%					4%
M		36%	36%				25%		4%
N	13%	17%	40%					cyclic C_6 26%	4%
O		48%	24%				24%		4%
P	19%		29%		48%				4%

* Monomer A - $CF_3(CF_2)_5CH_2CH_2OC(O)CHCH_2$
Monomer B - $CF_3(CF_2)_5CH_2CH_2OC(O)C(CH_3)CH_2$
Monomer VDC - vinylidene chloride
Monomer D - stearyl methacrylate
Monomer E - stearyl acrylate
Monomer F - 2-ethylhexyl acrylate
Monomer G - 2-ethylhexyl methacrylate
Monomer H – alkyl methacrylate
Monomer I – a mixture of 1.6% poly(ethylene glycol) methacrylate having an average of seven ethoxylates (7EO methacrylate), 1.0% hydroxyethyl methacrylate, 1.0% hydroxymethyl acrylamide, and 0.4% dodecyl mercaptan.

<u>Comparative Examples Q and R</u>

For each of Comparative Example Q and Comparative Example R, the procedure of Example 1 was employed, but using as the fluorochemical a perfluoroalkylethyl acrylate mixture of the formula $F(CF_2)_aCH_2CH_2OC(O)CHCH_2$, wherein a ranged from 4 to 12, and was predominately 6, 8, and 10. The typical mixture was as follows: 27% to 37% of a = 6, 28% to 32% of a = 8, 14% to 20% of a = 10, 8% to 13% of a = 12, and 3% to 6% of a = 14, available from E. I. du Pont de Nemours and Company, Wilmington, DE. Thus for Comparative Examples Q and R, the group R_f is a blend of C_6F_{13}, C_8F_{17}, $C_{10}F_{21}$, $C_{12}F_{25}$, $C_{14}F_{29}$, which is outside of Formula 1, 2, 3 or 4. The monomers used are listed in Table 4 by weight percent of the copolymer. The resulting copolymers were each applied using Test Method 1 to nonwoven spunbonded meltblown spunbonded polypropylene SMS PP fabrics. The treated fabrics were tested for water/alcohol repellency according to Test method 2. The results are in Table 5.

Table 4 - Monomers used in Copolymerization

Example No.	$F(CF_2)_aCH_2CH_2$-$OC(O)CHCH_2$	Stearyl methacrylate	Vinylidene chloride	I*
Comparative-Q	19%	29%	48%	4%
Comparative-R	59%	18%	18%	4%

*Monomer I was a mixture of 1.6% poly(ethylene glycol) methacrylate having an average of seven ethoxylates (7EO methacrylate), 1.0% hydroxyethyl methacrylate, 1.0% hydroxymethyl acrylamide, and 0.4% dodecyl mercaptan.

Table 5 - Water/Alcohol Repellency

Example	Repellency	Example	Repellency	Example	Repellency
2	8	17	6	Comparative-E	2
3	8	18	5	Comparative-F	2
4	8	19	5	Comparative-G	2
5	8	20	5	Comparative-H	2
6	8	21	5	Comparative-I	1
7	8	22	5	Comparative-J	1
8	8	23	5	Comparative-K	1
9	7	24	4	Comparative-L	1
10	7	25	4	Comparative-M	1
11	7	26	4	Comparative-N	1
12	7	27	3.5	Comparative-O	1
13	6	Comparative-A	3	Comparative-P	0
14	6	Comparative-B	3	Comparative-Q	1
15	6	Comparative-C	3	Comparative-R	1
16	6	Comparative-D	2	Untreated	2

In Table 5 Formula 1 is represented by Examples 1-19, 22-24, and 26-27. Formula 2 is represented by Example 20. Formula 3 is represented by Example 21. Formula 4 is represented by Example 25. The data in Table 5 shows that very high repellency was obtained in Examples 1 to 23, and moderate repellency in Examples 24 to 27. The Comparative Examples showed unacceptably low or no repellency.

CLAIMS

What is claimed is:

1. A method for treating fibrous substrates with a copolymer containing a fluorinated acrylate or fluorinated methacrylate to provide water repellency and alcohol repellency wherein the improvement comprises contacting the substrate with a composition comprising repeating units in any sequence of Formula 1, Formula 2, Formula 3, or Formula 4, followed by drying or curing without heating, wherein

A. Formula 1 is

$[R_f\text{-}X\text{-}Y\text{-}C(O)\text{-}CH\text{-}CH_2]_k\text{–}[R_f\text{-}X\text{-}Y\text{-}C(O)\text{-}CT\text{-}CH_2]_a\text{–}[CCl_2\text{-}CH_2]_b\text{-}[R^1\text{-}Y\text{-}C(O)\text{-}CZ\text{-}CH_2]_p\text{-}$ Formula 1

wherein

R_f is a straight or branched perfluoroalkyl group having 6 carbon atoms, or a mixture thereof, which is optionally interrupted by at least one oxygen atom,

X is an organic divalent linking group having from about 1 to about 20 carbon atoms, optionally containing a triazole, oxygen, nitrogen, or sulfur, or a combination thereof,

Y is O, S or N(R) wherein R is H or C_1 to C_{20} alkyl,

T is a straight or branched alkyl group having from about 1 to about 4 carbon atoms, or halide,

k is a positive integer,

a is a zero or positive integer,

b is a zero or positive integer,

p is zero or a positive integer, and

Z is H, a straight, branched or cyclic alkyl group having from about 1 to about 10 carbon atoms, or halide,

R^1 is H, C_nH_{2n+1}, C_nH_{2n-1}, $C_mH_{2m}\text{-}CH(O)CH_2$, $[CH_2CH_2O]_iR^2$, $[CH_2CH(CH_3)O]_iR^2$, $[C_mH_{2m}]N(R^2)_2$,

n is from about 8 to about 40,

m is 1 to about 40,

each R^2 is independently H, CH_2OH or C_sH_{2s+1}, s is 0 to about 40, and

i is 1 to about 200,

provided that

1) the repeating unit of $[R_f\text{-}X\text{-}Y\text{-}C(O)\text{-}CH\text{-}CH_2]_k$– in Formula 1 is present at a minimum of about 7% by weight,

2) the total of repeating units $[R_f\text{-}X\text{-}Y\text{-}C(O)\text{-}CH\text{-}CH_2]_k + [R_f\text{-}X\text{-}Y\text{-}C(O)\text{-}CT\text{-}CH_2]_a + [CCl_2\text{-}CH_2]_b$ is present at a minimum of about 70% by weight, and

3) the total of all repeating units, $[R_f\text{-}X\text{-}Y\text{-}C(O)\text{-}CH\text{-}CH_2]_k + [R_f\text{-}X\text{-}Y\text{-}C(O)\text{-}CT\text{-}CH_2]_a + [CCl_2\text{-}CH_2]_b + [R^1\text{-}Y\text{-}C(O)\text{-}CZ\text{-}CH_2]_p$ + optional monomers, is 100% by weight;

B. Formula 2 is

$[R_f\text{-}X\text{-}Y\text{-}C(O)\text{-}C(CH_3)\text{-}CH_2]_a\text{–}[CCl_2\text{-}CH_2]_b\text{–}[CH_3(CH_2)_3CH(C_2H_5)CH_2\text{-}O\text{-}C(O)\text{-}CH\text{-}CH_2]_q\text{–}[R^1\text{-}Y\text{-}C(O)\text{-}CZ\text{-}CH_2]_p$-

wherein

R_f, X, Y, Z, R^1, a, b, and p are each as defined in Formula 1, and

q is a positive integer,

provided that

1) the repeating unit of -$[R_f\text{-}X\text{-}Y\text{-}C(O)\text{-}C(CH_3)\text{-}CH_2]_a$– in Formula 2 is present at about 48% by weight,

2) the repeating unit -$[CCl_2\text{-}CH_2]_b$- and the repeating unit -$[CH_3(CH_2)_3CH(C_2H_5)CH_2\text{-}O\text{-}C(O)\text{-}CH\text{-}CH_2]_q$– in Formula 2 are each present at about 24% by weight, and

3) the total of all repeating unit, $[R_f\text{-}X\text{-}Y\text{-}C(O)\text{-}C(CH_3)\text{-}CH_2]_a + [CCl_2\text{-}CH_2]_b + [CH_3(CH_2)_3CH(C_2H_5)CH_2\text{-}O\text{-}C(O)\text{-}CH\text{-}CH_2]_q + [R^1\text{-}Y\text{-}C(O)\text{-}CZ\text{-}CH_2]_p$- is 100% by weight;

C. Formula 3 is

$[R_f\text{-}X\text{-}Y\text{-}C(O)\text{-}C(CH_3)\text{-}CH_2]_a\text{–}[CCl_2\text{-}CH_2]_b\text{–}[CH_3(CH_2)_{17}\text{-}O\text{-}C(O)\text{-}C(CH_3)\text{-}CH_2]_q\text{–}[CH_3(CH_2)_{17}\text{-}O\text{-}C(O)\text{-}CH\text{-}CH_2]_r\text{–}[R^1\text{-}Y\text{-}C(O)\text{-}CZ\text{-}CH_2]_p$-

wherein

R_f, X, Y, Z, R^1, a, b, and p are each defined as in Formula 1, q is a positive integer, and

t is a positive integer,

provided that

1) the repeating unit of $-[R_f\text{-}X\text{-}Y\text{-}C(O)\text{-}C(CH_3)\text{-}CH_2]_a-$ in Formula 3 is present at about 48% by weight,

2) the repeating unit $-[CCl_2\text{-}CH_2]_b-$, is present at about 24% by weight,

3) the repeating unit $-[CH_3(CH_2)_{17}\text{-}O\text{-}C(O)\text{-}C(CH_3)\text{-}CH_2]_q-$ and the repeating unit $-[CH_3(CH_2)_{17}\text{-}O\text{-}C(O)\text{-}CH\text{-}CH_2]_t-$ of Formula 3 are each present at about 12% by weight, and

4) the total of all repeating units, $[R_f\text{-}X\text{-}Y\text{-}C(O)\text{-}C(CH_3)\text{-}CH_2]_a + [CCl_2\text{-}CH_2]_b + [CH_3(CH_2)_{17}\text{-}O\text{-}C(O)\text{-}C(CH_3)\text{-}CH_2]_q + [CH_3(CH_2)_{17}\text{-}O\text{-}C(O)\text{-}CH\text{-}CH_2]_t + [R^1\text{-}Y\text{-}C(O)\text{-}CZ\text{-}CH_2]_p-$, is 100% by weight; and

D. Formula 4 is

$[R_f\text{-}X\text{-}Y\text{-}C(O)\text{-}CH\text{-}CH_2]_k-[R_f\text{-}X\text{-}Y\text{-}C(O)\text{-}C(CH_3)\text{-}CH_2]_a-[CH_3(CH_2)_{17}\text{-}O\text{-}C(O)\text{-}C(CH_3)\text{-}CH_2]_q-[CH_3(CH_2)_{17}\text{-}O\text{-}C(O)\text{-}CH\text{-}CH_2]_t-[CH_3(CH_2)_3CH(C_2H_5)CH_2\text{-}O\text{-}C(O)\text{-}CH\text{-}CH_2]_u-[CH_3(CH_2)_3CH(C_2H_5)CH_2\text{-}O\text{-}C(O)\text{-}C(CH_3)\text{-}CH_2]_v-[R^1\text{-}Y\text{-}C(O)\text{-}CZ\text{-}CH_2]_p-$

wherein

R_f, X, Y, Z and R^1, k, a, p are each defined as in Formula 1,

q is a positive integer,

t is a positive integer,

u is a positive integer, and

v is a positive integer,

provided that

1) the repeating unit $[R_f\text{-}X\text{-}Y\text{-}C(O)\text{-}CH\text{-}CH_2]_k-$ and the repeating unit $-[R_f\text{-}X\text{-}Y\text{-}C(O)\text{-}C(CH_3)\text{-}CH_2]_a-$ in Formula 4 are each present at about 32% by weight,

2) the repeating unit $-[CH_3(CH_2)_{17}\text{-}O\text{-}C(O)\text{-}C(CH_3)\text{-}CH_2]_q-$, the repeating unit $-[CH_3(CH_2)_{17}\text{-}O\text{-}C(O)\text{-}CH\text{-}CH_2]_t-$, the repeating unit $-[CH_3(CH_2)_3CH(C_2H_5)CH_2\text{-}O\text{-}C(O)\text{-}CH\text{-}CH_2]_u-$, and the repeating unit $-[CH_3(CH_2)_3CH(C_2H_5)CH_2\text{-}O\text{-}C(O)\text{-}C(CH_3)\text{-}CH_2]_v-$ of Formula 4 are each present at about 8% by weight, and

3) the total of all repeating units, $[R_f\text{-}X\text{-}Y\text{-}C(O)\text{-}CH\text{-}CH_2]_k$ + $[R_f\text{-}X\text{-}Y\text{-}C(O)\text{-}C(CH_3)\text{-}CH_2]_a$ + $[CH_3(CH_2)_{17}\text{-}O\text{-}C(O)\text{-}C(CH_3)\text{-}CH_2]_q$ + $[CH_3(CH_2)_{17}\text{-}O\text{-}C(O)\text{-}CH\text{-}CH_2]_t$ + $[CH_3(CH_2)_3CH(C_2H_5)CH_2\text{-}O\text{-}C(O)\text{-}CH\text{-}CH_2]_u$ + $[CH_3(CH_2)_3CH(C_2H_5)CH_2\text{-}O\text{-}C(O)\text{-}C(CH_3)\text{-}CH_2]_v$ + $[R^1\text{-}Y\text{-}C(O)\text{-}CZ\text{-}CH_2]_{p\text{-}}$, is 100% by weight.

2. The method of claim 1 wherein the total of repeating units $[R_f\text{-}X\text{-}Y\text{-}C(O)\text{-}CH\text{-}CH_2]_k$ + $[R_f\text{-}X\text{-}Y\text{-}C(O)\text{-}CT\text{-}CH_2]_a$ + $[CCl_2\text{-}CH_2]_b$ is present at from about 70% to 100% by weight of the copolymer.

3. The method of claim 1 wherein the substrate, after treating, is air dried and cured at a temperature from about 15 °C to about 25 °C.

4. The method of claim 1 wherein R_f is a straight or branched C_6F_{13}-, or wherein R_f is $CF_3(CF_2)_5$-.

5. The method of claim 1 wherein k, a, b, p, q, t, u and v are each independently from about 5 to about 2,000, or a mixture thereof.

6. The method of claim 1 wherein the composition is applied in the presence of at least one of

A) an agent which provides a surface effect which is no iron, easy to iron, shrinkage control, wrinkle free, permanent press, moisture control, softness, strength, anti-slip, antistatic, anti-snag, anti-pill, stain repellency, stain release, alcohol repellency, alcohol release, water repellency, alcohol repellency, odor control, antimicrobial, or sun protection,

B) a surfactant, antioxidant, light fastness agent, color fastness agent, water, pH adjuster, cross linker, wetting agent, extender, foaming agent, processing aid, lubricant, blocked isocyanate, nonfluorinated and extenders, or

C) combinations thereof.

7. The method of claim 1 wherein the composition of Formula 1 further comprises repeating units from optional monomers, said monomers selected from the group consisting of vinyl acetate, vinyl stearate, alkyl vinyl sulfone, styrene, vinyl benzoic acid, alkyl vinyl ether, maleic anhydride, vinyl chloride, and other olefins.

8. The method of claim 1 wherein the composition is applied as an aqueous dispersion or solution.

9. A substrate treated in accordance with the method of claim 1.

10. The substrate of claim 9 which is woven, knit, or nonwoven fabric made from polyolefin fibers selected from the group consisting of polyethylene, polypropylene, and blends thereof, and wherein said nonwoven fabric is selected from the group consisting of spunbonded, meltblown, and laminates containing either spunbonded nonwoven or melt-blown nonwoven, or a combination thereof.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2007/020530

A. CLASSIFICATION OF SUBJECT MATTER
INV. D06M15/233 D06M15/248 D06M15/263 D06M15/277 D06M15/333

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
D06M

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 525 423 A (LYNN MICHAEL M [US] ET AL) 25 June 1985 (1985-06-25) column 2, line 22 - column 7, line 45	1-10
A	DATABASE WPI Week 200608 Derwent Publications Ltd., London, GB; AN 2006-079668 XP002475540 & WO 2006/001322 A (DAIKIN IND LTD) 5 January 2006 (2006-01-05) abstract	1-10
A	US 5 350 795 A (SMITH RICHARD S [US] ET AL) 27 September 1994 (1994-09-27) column 3, line 44 - column 8, line 28	1-10
A	EP 1 201 815 A (ASAHI GLASS CO LTD [JP]) 2 May 2002 (2002-05-02) paragraphs [0009] - [0032]; examples	1-10

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

* Special categories of cited documents :

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

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"&" document member of the same patent family

Date of the actual completion of the international search 9 April 2008	Date of mailing of the international search report 17/04/2008
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INTERNATIONAL SEARCH REPORT

Information on patent family members

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权利要求书 5 页 说明书 23 页

[54] 发明名称

低温固化排斥剂

[57] 摘要

本发明公开了一种使用包含氟化丙烯酸酯或氟化甲基丙烯酸酯的共聚物来处理纤维基底以提供拒水性和拒醇性的改良方法，其中所述改良包括使所述基底接触特定的氟化共聚物的组合物，然后在不加热的情况下干燥或固化。

1. 使用包含氟化丙烯酸酯或氟化甲基丙烯酸酯的共聚物来处理纤维基底以提供拒水性和拒醇性的方法，其中所述改良包括使所述基底接触组合物，然后在不加热的情况下干燥或固化，所述组合物包含式1、式2、式3或式4的任何序列的重复单元，其中

A. 式1为

$$[R_f\text{-}X\text{-}Y\text{-}C(O)\text{-}CH\text{-}CH_2]_k\text{-}[R_f\text{-}X\text{-}Y\text{-}C(O)\text{-}CT\text{-}CH_2]_a\text{-}[CCl_2\text{-}CH_2]_b\text{-}[R^1\text{-}Y\text{-}C(O)\text{-}CZ\text{-}CH_2]_p\text{-} \qquad \text{式 1}$$

其中

R_f为任选被至少一个氧原子间隔的具有6个碳原子的直链或支链的全氟烷基、或它们的混合物，

X为任选包含三唑、氧、氮、或硫、或它们的组合的具有约1至约20个碳原子的有机二价连接基团，

Y为O、S或N(R)，其中R为H或C_1至C_{20}烷基，

T为具有约1至约4个碳原子的直链或支链烷基、或卤化物，

k为正整数，

a为零或正整数，

b为零或正整数，

p为零或正整数，并且

Z为H、具有约1至约10个碳原子的直链、支链或环状烷基、或卤化物，

R^1为H、C_nH_{2n+1}、C_nH_{2n-1}、$C_mH_{2m}\text{-}CH(O)CH_2$、$[CH_2CH_2O]_iR^2$、$[CH_2CH(CH_3)O]_iR^2$、$[C_mH_{2m}]N(R^2)_2$，

n为约8至约40，

m为1至约40，

每个R^2独立地为H、CH_2OH或C_sH_{2s+1}，

s为0至约40，并且

i 为 1 至约 200，

前提条件是

1) 在式 1 中所述重复单元$[R_f-X-Y-C(O)-CH-CH_2]_k-$ 以至少约 7 重量% 的量存在，

2) 重复单元$[R_f-X-Y-C(O)-CH-CH_2]_k$ + $[R_f-X-Y-C(O)-CT-CH_2]_a$ + $[CCl_2-CH_2]_b$ 的总量以至少约 70 重量% 的量存在，以及

3) 所有重复单元 $[R_f-X-Y-C(O)-CH-CH_2]_k$ + $[R_f-X-Y-C(O)-CT-CH_2]_a$ + $[CCl_2-CH_2]_b$ + $[R^1-Y-C(O)-CZ-CH_2]_p$ + 任选单体的总量为 100 重量%；

B. 式 2 为

$$[R_f-X-Y-C(O)-C(CH_3)-CH_2]_a-[CCl_2-CH_2]_b-[CH_3(CH_2)_3CH(C_2H_5)CH_2-O-C(O)-CH-CH_2]_q-[R^1-Y-C(O)-CZ-CH_2]_p-$$

其中

R_f、X、Y、Z、R^1、a、b 和 p 分别如式 1 所定义，并且

q 为正整数，

前提条件是

1) 在式 2 中所述重复单元$-[R_f-X-Y-C(O)-C(CH_3)-CH_2]_a-$ 以约 48 重量% 的量存在，

2) 在式 2 中所述重复单元$-[CCl_2-CH_2]_b-$和所述重复单元 $-[CH_3(CH_2)_3CH(C_2H_5)CH_2-O-C(O)-CH-CH_2]_q-$ 各自以约 24 重量% 的量存在，以及

3) 所有重复单元 $[R_f-X-Y-C(O)-C(CH_3)-CH_2]_a$ + $[CCl_2-CH_2]_b$ + $[CH_3(CH_2)_3CH(C_2H_5)CH_2-O-C(O)-CH-CH_2]_q$ + $[R^1-Y-C(O)-CZ-CH_2]_p-$ 的总量为 100 重量%；

C. 式 3 为

$$[R_f-X-Y-C(O)-C(CH_3)-CH_2]_a-[CCl_2-CH_2]_b-[CH_3(CH_2)_{17}-O-C(O)-C(CH_3)-CH_2]_q-[CH_3(CH_2)_{17}-O-C(O)-CH-CH_2]_t-[R^1-Y-C(O)-CZ-CH_2]_p-$$

其中

R_f、X、Y、Z、R^1、a、b和p分别如式1所定义，

q为正整数，并且

t为正整数，

前提条件是

1) 在式3中所述重复单元$-[R_f-X-Y-C(O)-C(CH_3)-CH_2]_a-$以约48重量%的量存在，
2) 所述重复单元$-[CCl_2-CH_2]_b-$以约24重量%的量存在，
3) 式3的所述重复单元$-[CH_3(CH_2)_{17}-O-C(O)-C(CH_3)-CH_2]_q-$和所述重复单元$-[CH_3(CH_2)_{17}-O-C(O)-CH-CH_2]_t-$各自以约12重量%的量存在，以及
4) 所有重复单元$[R_f-X-Y-C(O)-C(CH_3)-CH_2]_a + [CCl_2-CH_2]_b + [CH_3(CH_2)_{17}-O-C(O)-C(CH_3)-CH_2]_q + [CH_3(CH_2)_{17}-O-C(O)-CH-CH_2]_t + [R^1-Y-C(O)-CZ-CH_2]_p-$的总量为100重量%；以及

D. 式4为

$$[R_f-X-Y-C(O)-CH-CH_2]_k-[R_f-X-Y-C(O)-C(CH_3)-CH_2]_a-[CH_3(CH_2)_{17}-O-C(O)-C(CH_3)-CH_2]_q-[CH_3(CH_2)_{17}-O-C(O)-CH-CH_2]_t-[CH_3(CH_2)_3CH(C_2H_5)CH_2-O-C(O)-CH-CH_2]_u-[CH_3(CH_2)_3CH(C_2H_5)CH_2-O-C(O)-C(CH_3)-CH_2]_v-[R^1-Y-C(O)-CZ-CH_2]_p-$$

其中

R_f、X、Y、Z、和R^1、k、a、p分别如式1所定义，

q为正整数，

t为正整数，

u为正整数，并且

v为正整数，

前提条件是

1) 在式 4 中所述重复单元$[R_f\text{-}X\text{-}Y\text{-}C(O)\text{-}CH\text{-}CH_2]_k$- 和所述重复单元-$[R_f\text{-}X\text{-}Y\text{-}C(O)\text{-}C(CH_3)\text{-}CH_2]_a$- 各自以约 32 重量% 的量存在，

2) 式 4 的所述重复单元 -$[CH_3(CH_2)_{17}\text{-}O\text{-}C(O)\text{-}C(CH_3)\text{-}CH_2]_q$-、所述重复单元 -$[CH_3(CH_2)_{17}\text{-}O\text{-}C(O)\text{-}CH\text{-}CH_2]_t$-、所述重复单元 -$[CH_3(CH_2)_3CH(C_2H_5)CH_2\text{-}O\text{-}C(O)\text{-}CH\text{-}CH_2]_u$-、和所述重复单元 -$[CH_3(CH_2)_3CH(C_2H_5)CH_2\text{-}O\text{-}C(O)\text{-}C(CH_3)\text{-}CH_2]_v$- 各自以约 8 重量% 的量存在，以及

3) 所有重复单元 $[R_f\text{-}X\text{-}Y\text{-}C(O)\text{-}CH\text{-}CH_2]_k$ + $[R_f\text{-}X\text{-}Y\text{-}C(O)\text{-}C(CH_3)\text{-}CH_2]_a$ + $[CH_3(CH_2)_{17}\text{-}O\text{-}C(O)\text{-}C(CH_3)\text{-}CH_2]_q$ + $[CH_3(CH_2)_{17}\text{-}O\text{-}C(O)\text{-}CH\text{-}CH_2]_t$ + $[CH_3(CH_2)_3CH(C_2H_5)CH_2\text{-}O\text{-}C(O)\text{-}CH\text{-}CH_2]_u$ + $[CH_3(CH_2)_3CH(C_2H_5)CH_2\text{-}O\text{-}C(O)\text{-}C(CH_3)\text{-}CH_2]_v$ + $[R^1\text{-}Y\text{-}C(O)\text{-}CZ\text{-}CH_2]_p$- 的总量为 100 重量%。

2. 权利要求 1 的方法，其中重复单元$[R_f\text{-}X\text{-}Y\text{-}C(O)\text{-}CH\text{-}CH_2]_k$ + $[R_f\text{-}X\text{-}Y\text{-}C(O)\text{-}CT\text{-}CH_2]_a$ + $[CCl_2\text{-}CH_2]_b$ 的总量占所述共聚物的约 70 重量% 至 100 重量%。

3. 权利要求 1 的方法，其中在处理后，在约 15℃至约 25℃的温度下，将所述基底风干和固化。

4. 权利要求 1 的方法，其中 R_f 为直链或支链的 C_6F_{13}-，或其中 R_f 为 $CF_3(CF_2)_5$-。

5. 权利要求 1 的方法，其中 k、a、b、p、q、t、u 和 v 各自独立地为约 5 至约 2,000，或它们的混合。

6. 权利要求 1 的方法，其中在至少一种以下物质的存在下施用所述组合物：

A) 提供表面功效的试剂，所述表面功效为免烫性、易烫性、收缩控制、抗皱、耐久定形、水分控制、柔软性、强度、防滑性、防静电性、防钩伤性、防起球、抗污性、去污性、拒醇性、释醇性、拒水性、拒醇性、气味控制、抗微生物性、或防晒性，

B) 表面活性剂、抗氧化剂、耐光剂、固色剂、水、pH 调节剂、交联剂、润湿剂、增充剂、发泡剂、加工助剂、润滑剂、嵌段异氰酸酯、非氟化增充剂，或

C) 它们的组合。

7. 权利要求 1 的方法，其中式 1 的所述组合物还包含来自任选单体的重复单元，所述单体选自乙酸乙烯酯、硬脂酸乙烯酯、烷基乙烯基砜、苯乙烯、乙烯基苯甲酸、烷基乙烯基醚、马来酸酐、氯乙烯、以及其它烯烃。

8. 权利要求 1 的方法，其中所述组合物作为水分散体或溶液进行施用。

9. 根据权利要求 1 的方法处理的基底。

10. 权利要求 9 的基底，所述基底为由聚烯烃纤维制成的织造织物、编织织物或非织造织物，所述聚烯烃纤维选自聚乙烯、聚丙烯、和它们的共混物，并且其中所述非织造织物选自纺粘非织造织物、熔喷非织造织物、以及包含纺粘非织造材料或熔喷非织造材料的层压体、或它们的组合。

低温固化排斥剂

发明领域

本发明涉及使用氟化（甲基）丙烯酸酯共聚物来处理纤维基底以提供拒水性和拒醇性的改良的方法，所述氟化（甲基）丙烯酸酯共聚物在环境温度下干燥和固化，而无需在高温下炉内固化。

发明背景

已知有多种氟化聚合物组合物可用作处理剂以向基底提供表面功效。可用作处理剂以向基底赋予排斥性的大多可商购获得的氟化聚合物需要在约140℃下炉内干燥和固化以提供所期望的排斥特性。这些可商购获得的氟化聚合物通常包含主要具有八个或更多个碳原子的全氟烷基链。

包含具有小于六个碳原子的全氟烷基的聚（氟化烷基丙烯酸酯）通常具有差的动力学拒水性。Koji Honda 等人在“Molecular Aggregation Structure and Surface Properties of poly(fluoroalkylacrylate) Thin Films”（“Macromolecules”，2005，38（13），第 5699 至 5705 页）中提出，对于具有大于 8 个碳的全氟烷基链，使由 R_f 基团代表的全氟烷基的取向保持平行构型，而对于具有小于 6 个碳的此类链而言，则发生重新取向。这种重新取向降低了表面特性如接触角。因此，较短链的全氟烷基传统上一直未获得商业成功。

干燥和固化所处理的基底有助于逐步获得最佳的拒水/拒醇性能。固化方法能够使排斥剂熔融铺展，并且能够使含氟化合物聚合物取向。根据 Charles L. Strickler 在“Fluorochemical Repellent Finishes for Nonwovens”（“Journal of Industrial Fabrics”，1984，3（2），10-18）中所述，干燥和固化通常需要高温热固化。

美国专利 7,008,993 描述了用于提供拒醇性和拒水性的组合物，所述组合物包含：（a）玻璃化转变温度接近环境温度的阳离子氟化丙烯酸酯共聚物；（b）玻璃化转变温度为约 80℃至约 100℃的阳离子氟化丙烯酸酯共

聚物；（c）非离子亲水性软化剂；和（d）无机添加剂。上述组合物不提供足够低的表面张力来处理非织造织物诸如聚丙烯非织造材料或聚乙烯非织造材料。

希望有一种可向纤维基底提供拒水性和拒醇性的方法，所述方法采用在环境温度下干燥和固化，而无需在高温下炉内固化。此方法需要较少的能量。希望有这样一种对于具有低玻璃化转变温度的非织造基底尤其有效的方法。本发明提供了此类方法。

发明简述

本发明包括使用包含氟化丙烯酸酯或氟化甲基丙烯酸酯的共聚物来处理纤维基底以提供拒水性和拒醇性的方法，其中改良包括使所述基底接触组合物，然后在不加热的情况下干燥或固化，所述组合物包含式 1、式 2、式 3、或式 4 的任何序列的重复单元，其中

A. 式 1 为

$$[R_f\text{-}X\text{-}Y\text{-}C(O)\text{-}CH\text{-}CH_2]_k\text{-}[R_f\text{-}X\text{-}Y\text{-}C(O)\text{-}CT\text{-}CH_2]_a\text{-}[CCl_2\text{-}CH_2]_b\text{-}[R^1\text{-}Y\text{-}C(O)\text{-}CZ\text{-}CH_2]_p\text{-}$$

式 1

其中

R_f 为任选被至少一个氧原子间隔的具有 6 个碳原子的直链或支链的全氟烷基、或它们的混合物，

X 为任选包含三唑、氧、氮、或硫、或它们的组合的具有约 1 至约 20 个碳原子的有机二价连接基团，

Y 为 O、S 或 N(R)，其中 R 为 H 或 C_1 至 C_{20} 烷基，

T 为具有约 1 至约 4 个碳原子的直链或支链烷基、或卤化物，

k 为正整数，

a 为零或正整数，

b 为零或正整数，

p 为零或正整数，并且

Z为H、具有约1至约10个碳原子的直链、支链或环状烷基、或卤化物，

R^1为H、C_nH_{2n+1}、C_nH_{2n-1}、C_mH_{2m}-CH(O)CH_2、$[CH_2CH_2O]_iR^2$、$[CH_2CH(CH_3)O]_iR^2$、$[C_mH_{2m}]N(R^2)_2$，

n为约8至约40，

m为1至约40，

每个R^2独立地为H、CH_2OH或C_sH_{2s+1}，

s为0至约40，并且

i为1至约200，

前提条件是

1) 式1中重复单元$[R_f$-X-Y-C(O)-CH-$CH_2]_k$- 以至少约7重量%的量存在，

2) 重复单元$[R_f$-X-Y-C(O)-CH-$CH_2]_k$ + $[R_f$-X-Y-C(O)-CT-$CH_2]_a$ + $[CCl_2$-$CH_2]_b$的总量以至少约70重量%的量存在，并且

3) 所有重复单元$[R_f$-X-Y-C(O)-CH-$CH_2]_k$ + $[R_f$-X-Y-C(O)-CT-$CH_2]_a$ + $[CCl_2$-$CH_2]_b$ + $[R^1$-Y-C(O)-CZ-$CH_2]_p$ + 任选单体的总量为100重量%；

B. 式2为

$[R_f$-X-Y-C(O)-C(CH_3)-$CH_2]_a$-$[CCl_2$-$CH_2]_b$-$[CH_3(CH_2)_3CH(C_2H_5)CH_2$-O-C(O)-CH-$CH_2]_q$-$[R^1$-Y-C(O)-CZ-$CH_2]_p$-

其中

R_f、X、Y、Z、R^1、a、b和p分别如式1所定义，并且

q为正整数，

前提条件是

1) 式2中重复单元-$[R_f$-X-Y-C(O)-C(CH_3)-$CH_2]_a$- 以约48重量%的量存在，

2) 式2中重复单元-$[CCl_2$-$CH_2]_b$-和重复单元

$-[CH_3(CH_2)_3CH(C_2H_5)CH_2-O-C(O)-CH-CH_2]_q-$ 各自以约 24 重量%的量存在，并且

3) 所有重复单元 $[R_f-X-Y-C(O)-C(CH_3)-CH_2]_a$ + $[CCl_2-CH_2]_b$ + $[CH_3(CH_2)_3CH(C_2H_5)CH_2-O-C(O)-CH-CH_2]_q$ + $[R^1-Y-C(O)-CZ-CH_2]_p-$ 的总量为 100 重量%；

C. 式 3 为

$$[R_f-X-Y-C(O)-C(CH_3)-CH_2]_a-[CCl_2-CH_2]_b-[CH_3(CH_2)_{17}-O-C(O)-C(CH_3)-CH_2]_q-[CH_3(CH_2)_{17}-O-C(O)-CH-CH_2]_t-[R^1-Y-C(O)-CZ-CH_2]_p-$$

其中

R_f、X、Y、Z、R^1、a、b 和 p 分别如式 1 所定义，

q 为正整数，并且

t 为正整数，

前提条件是

1) 式 3 中重复单元 $-[R_f-X-Y-C(O)-C(CH_3)-CH_2]_a-$ 以约 48 重量%的量存在，

2) 重复单元 $-[CCl_2-CH_2]_b-$ 以约 24 重量% 的量存在，

3) 式 3 中重复单元 $-[CH_3(CH_2)_{17}-O-C(O)-C(CH_3)-CH_2]_q-$ 和重复单元 $-[CH_3(CH_2)_{17}-O-C(O)-CH-CH_2]_t-$ 各自以约 12 重量% 的量存在，以及

4) 所有重复单元 $[R_f-X-Y-C(O)-C(CH_3)-CH_2]_a$ + $[CCl_2-CH_2]_b$ + $-[CH_3(CH_2)_{17}-O-C(O)-C(CH_3)-CH_2]_q$ + $[CH_3(CH_2)_{17}-O-C(O)-CH-CH_2]_t$ + $[R^1-Y-C(O)-CZ-CH_2]_p-$ 的总量为 100 重量%；并且

D. 式 4 为

$$[R_f-X-Y-C(O)-CH-CH_2]_k-[R_f-X-Y-C(O)-C(CH_3)-CH_2]_a-[CH_3(CH_2)_{17}-O-C(O)-C(CH_3)-CH_2]_q-[CH_3(CH_2)_{17}-O-C(O)-CH-CH_2]_t-[CH_3(CH_2)_3CH(C_2H_5)CH_2-O-C(O)-CH-CH_2]_u-[CH_3(CH_2)_3CH(C_2H_5)CH_2-O-C(O)-C(CH_3)-CH_2]_v-[R^1-Y-C(O)-CZ-CH_2]_p-$$

其中

$\mathrm{R_f}$、X、Y、Z、和$\mathrm{R^1}$、k、a、p分别如式1所定义，

q为正整数，

t为正整数，

u为正整数，并且

v为正整数，

前提条件是

1) 式4中重复单元$\mathrm{[R_f{-}X{-}Y{-}C(0){-}CH{-}CH_2]_k}$- 和重复单元-$\mathrm{[R_f{-}X{-}Y{-}C(0){-}C(CH_3){-}CH_2]_a}$- 各自以约32重量%的量存在，

2) 式4中重复单元-$\mathrm{[CH_3(CH_2)_{17}{-}O{-}C(0){-}C(CH_3){-}CH_2]_q}$-、重复单元-$\mathrm{[CH_3(CH_2)_{17}{-}O{-}C(0){-}CH{-}CH_2]_t}$-、重复单元-$\mathrm{[CH_3(CH_2)_3CH(C_2H_5)CH_2{-}O{-}C(0){-}CH{-}CH_2]_u}$-、和重复单元-$\mathrm{[CH_3(CH_2)_3CH(C_2H_5)CH_2{-}O{-}C(0){-}C(CH_3){-}CH_2]_v}$- 各自以约8重量%的量存在，以及

3) 所有重复单元$\mathrm{[R_f{-}X{-}Y{-}C(0){-}CH{-}CH_2]_k + [R_f{-}X{-}Y{-}C(0){-}C(CH_3){-}CH_2]_a + [CH_3(CH_2)_{17}{-}O{-}C(0){-}C(CH_3){-}CH_2]_q + [CH_3(CH_2)_{17}{-}O{-}C(0){-}CH{-}CH_2]_t + [CH_3(CH_2)_3CH(C_2H_5)CH_2{-}O{-}C(0){-}CH{-}CH_2]_u + [CH_3(CH_2)_3CH(C_2H_5)CH_2{-}O{-}C(0){-}C(CH_3){-}CH_2]_v + [R^1{-}Y{-}C(0){-}CZ{-}CH_2]_p}$-的总量为100重量%。

本发明还包括根据上述方法处理的基底。

发明详述

所有商标以大写字母标明。在本文所有情况下，术语“（甲基）丙烯酸酯”用于表示丙烯酸酯或甲基丙烯酸酯中的任一者或两者。

本文中，术语“环境温度”用于表示约15℃至约25℃的温度。

本发明包括使用氟化（甲基）丙烯酸酯共聚物来处理纤维基底尤其是具有低玻璃化转变温度的非织造基底，以赋予拒水性和拒醇性的改良方法。在本发明的改良方法中，在环境温度下将所处理的基底风干和固化。

为制得良好的纤维和织物，聚合物的最低热性质为高于环境温度的熔融温度Tm；否则聚合物将不具有形成纤维和织物的结构完整性。如果在干燥或固化期间织物达到接近或高于其Tm的温度，则所述织物将丧失其众多

特性，诸如透气性、处理性、以及拉伸强度。在玻璃化转变温度Tg和Tm之间，聚合物纤维或织物可被机械加压以产生可用的特性，诸如堆积性、折皱性、空间强度、均匀性以及其它特性。在接近Tm的温度下干燥或固化，则存在丧失早期处理时赋予纤维或织物的这些有益特性的风险。各种聚合物的Tg和Tm实例列于下文中。

聚合物	玻璃化转变温度(Tg)	熔点（Tm）
聚乙烯	-125C	137C
聚异丁烯	-73C	44C
聚丙烯	-13C	176C
聚氯乙烯	-18C	200C
尼龙-6	52C	223C
尼龙-66	50C	265C
聚酯（PET）	69C	270C
聚苯乙烯	100C	240C

该数据来自J. Brandup、E. H. Immergut的“Polymer Handbook”第III章第1至193页（Wiley-Interscience，New York，1975）。进一步说明可见于G. Odian的“Principles of Polymerization”（Wiley-Interscience，New York，1981，第29至36页）中。

本发明的方法尤其适用于处理Tg接近环境温度的聚合物，尤其是聚丙烯非织造织物和聚乙烯非织造织物。

如下文定义，用于本发明中的氟化（甲基）丙烯酸酯共聚物包含式1、式2、式3或式4的任何序列的重复单元。聚合物序列包括无规、统计、嵌段、多重嵌段、梯度、或交替。本文式1、式2、式3和式4分别给出的重量百分比均按所述共聚物的重量计。

式1为

$$[R_f\text{-}X\text{-}Y\text{-}C(O)\text{-}CH\text{-}CH_2]_k\text{-}[R_f\text{-}X\text{-}Y\text{-}C(O)\text{-}CT\text{-}CH_2]_a\text{-}[CCl_2\text{-}CH_2]_b\text{-}[R^1\text{-}Y\text{-}C(O)\text{-}CZ\text{-}CH_2]_p\text{-}$$

其中

R_f为任选被至少一个氧原子间隔的具有 6 个碳原子的直链或支链的全氟烷基，或具有 6 个碳原子的直链或支链的全氟烷基的混合物，

X 为任选包含三唑、氧、氮、或硫、或它们的组合的具有约 1 至约 20 个碳原子的有机二价连接基团，

Y 为 O、S 或 N(R)，其中 R 为 H 或直链、支链或环状 C_1至 C_{20}烷基，

T 为具有约 1 至约 4 个碳原子的直链或支链烷基、或卤化物，

k 为正整数，

a 为零或正整数，

b 为零或正整数，

p 为零或正整数，并且

Z 为 H、具有约 1 至约 10 个碳原子的直链、支链或环状烷基、或卤化物，

R^1 为 H、C_nH_{2n+1}、C_nH_{2n-1}、C_mH_{2m}-CH(O)CH$_2$、$[CH_2CH_2O]_iR^2$、$[CH_2CH(CH_3)O]_iR^2$、$[C_mH_{2m}]N(R^2)_2$，

n 为约 8 至约 40，

m 为 1 至约 40，

R^2为 H、CH_2OH 或 C_sH_{2s+1}.

s 为 0 至约 40，并且

i 为 1 至约 200，

前提条件是

1) 式 1 中重复单元$[R_f\text{-X-Y-C(O)-CH-CH}_2]_k$- 以至少约 7 重量% 的量存在，
2) 重复单元 $[R_f\text{-X-Y-C(O)-CH-CH}_2]_k$ + $[R_f\text{-X-Y-C(O)-CT-CH}_2]_a$ + $[CCl_2\text{-}CH_2]_b$的总量以至少约 70 重量% 的量存在，以及
3) 所有重复单元$[R_f\text{-X-Y-C(O)-CH-CH}_2]_k$ + $[R_f\text{-X-Y-C(O)-CT-CH}_2]_a$ + $[CCl_2\text{-}CH_2]_b$ + $[R^1\text{-Y-C(O)-CZ-CH}_2]_p$加上任何其它任选单体的总量为 100%。

在式 1 的共聚物中，重复单元$[R_f\text{-X-Y-C(O)-CT-CH}_2]_a$以至少 7 重量% 的量存在，并且在所述共聚物中的含量可最多 100 重量%，优选约 7 重量% 至约 97 重量%，更优选约 7 重量% 至约 50 重量% 的范围内。在式 1 中，重

复单元 $[R_f\text{-}X\text{-}Y\text{-}C(O)\text{-}CH\text{-}CH_2]_k$ + $[R_f\text{-}X\text{-}Y\text{-}C(O)\text{-}CT\text{-}CH_2]_a$ + $[CCl_2\text{-}CH_2]_b$ 的总量以至少约 70 重量% 的量存在。所有这些重复单元 $[R_f\text{-}X\text{-}Y\text{-}C(O)\text{-}CH\text{-}CH_2]_k$ + $[R_f\text{-}X\text{-}Y\text{-}C(O)\text{-}CT\text{-}CH_2]_a$ + $[CCl_2\text{-}CH_2]_b$ 在本发明所用共聚物中的含量在约 70 重量% 至 100 重量% 范围内。此总含量优选为约 70 重量% 至约 90 重量%，更优选约 70 重量% 至 80 重量%。式 1 中所有重复单元加上任何其它任选单体的总量为 100 重量%。

式 2 为 $[R_f\text{-}X\text{-}Y\text{-}C(O)\text{-}C(CH_3)\text{-}CH_2]_a\text{-}[CCl_2\text{-}CH_2]_b\text{-}[CH_3(CH_2)_3CH(C_2H_5)CH_2\text{-}O\text{-}C(O)\text{-}CH\text{-}CH_2]_q\text{-}[R^1\text{-}Y\text{-}C(O)\text{-}CZ\text{-}CH_2]_p\text{-}$

其中

R_f、X、Y、Z、R^1、a、b 和 p 分别如式 1 所定义，并且

q 为正整数，

前提条件是

1) 式 2 中重复单元 $\text{-}[R_f\text{-}X\text{-}Y\text{-}C(O)\text{-}C(CH_3)\text{-}CH_2]_a\text{-}$ 以约 48 重量% 的量存在，
2) 式 2 中重复单元 $\text{-}[CCl_2\text{-}CH_2]_b\text{-}$ 和重复单元 $\text{-}[CH_3(CH_2)_3CH(C_2H_5)CH_2\text{-}O\text{-}C(O)\text{-}CH\text{-}CH_2]_q\text{-}$ 各自以约 24 重量% 的量存在，以及
3) 所有重复单元 $[R_f\text{-}X\text{-}Y\text{-}C(O)\text{-}C(CH_3)\text{-}CH_2]_a$ + $[CCl_2\text{-}CH_2]_b$ + $[CH_3(CH_2)_3CH(C_2H_5)CH_2\text{-}O\text{-}C(O)\text{-}CH\text{-}CH_2]_q$ + $[R^1\text{-}Y\text{-}C(O)\text{-}CZ\text{-}CH_2]_p\text{-}$ 的总量为 100 重量%。

式 3 为

$[R_f\text{-}X\text{-}Y\text{-}C(O)\text{-}C(CH_3)\text{-}CH_2]_a\text{-}[CCl_2\text{-}CH_2]_b\text{-}[CH_3(CH_2)_{17}\text{-}O\text{-}C(O)\text{-}C(CH_3)\text{-}CH_2]_q\text{-}[CH_3(CH_2)_{17}\text{-}O\text{-}C(O)\text{-}CH\text{-}CH_2]_t\text{-}[R^1\text{-}Y\text{-}C(O)\text{-}CZ\text{-}CH_2]_p\text{-}$

其中

R_f、X、Y、Z、R^1、a、b 和 p 分别如式 1 所定义，

q 为正整数，并且

t 为正整数，

前提条件是

1) 式 3 中重复单元$-[R_f-X-Y-C(O)-C(CH_3)-CH_2]_a-$ 以约 48 重量% 的量存在，

2) 重复单元$-[CCl_2-CH_2]_b-$ 以约 24 重量% 的量存在，

3) 式 3 中重复单元$-[CH_3(CH_2)_{17}-O-C(O)-C(CH_3)-CH_2]_q-$ 和重复单元$-[CH_3(CH_2)_{17}-O-C(O)-CH-CH_2]_t-$ 各自以约 12 重量% 的量存在，以及

4) 所有重复单元 $[R_f-X-Y-C(O)-C(CH_3)-CH_2]_a + [CCl_2-CH_2]_b + -[CH_3(CH_2)_{17}-O-C(O)-C(CH_3)-CH_2]_q + [CH_3(CH_2)_{17}-O-C(O)-CH-CH_2]_t + [R^1-Y-C(O)-CZ-CH_2]_p-$ 的总量为 100 重量%。

式 4 为

$$[R_f-X-Y-C(O)-CH-CH_2]_k-[R_f-X-Y-C(O)-C(CH_3)-CH_2]_a-[CH_3(CH_2)_{17}-O-C(O)-C(CH_3)-CH_2]_q-[CH_3(CH_2)_{17}-O-C(O)-CH-CH_2]_t-[CH_3(CH_2)_3CH(C_2H_5)CH_2-O-C(O)-CH-CH_2]_u-[CH_3(CH_2)_3CH(C_2H_5)CH_2-O-C(O)-C(CH_3)-CH_2]_v-[R^1-Y-C(O)-CZ-CH_2]_p-$$

其中

R_f、X、Y、Z、和 R^1、k、a、p 分别如式 1 所定义，

q 为正整数，

t 为正整数，

u 为正整数，并且

v 为正整数，

前提条件是

1) 式 4 中重复单元 $[R_f-X-Y-C(O)-CH-CH_2]_k-$ 和重复单元$-[R_f-X-Y-C(O)-C(CH_3)-CH_2]_a-$ 各自以约 32 重量% 的量存在，

2) 式 4 中重复单元$-[CH_3(CH_2)_{17}-O-C(O)-C(CH_3)-CH_2]_q-$、重复单元$-[CH_3(CH_2)_{17}-O-C(O)-CH-CH_2]_t-$、重复单元$-[CH_3(CH_2)_3CH(C_2H_5)CH_2-O-C(O)-CH-CH_2]_u-$、和重复单元$-[CH_3(CH_2)_3CH(C_2H_5)CH_2-O-C(O)-C(CH_3)-CH_2]_v-$ 各自以约 8 重量% 的量存在，以及

3) 所有重复单元$[R_f\text{-}X\text{-}Y\text{-}C(O)\text{-}CH\text{-}CH_2]_k$ + $[R_f\text{-}X\text{-}Y\text{-}C(O)\text{-}C(CH_3)\text{-}CH_2]_a$ + $[CH_3(CH_2)_{17}\text{-}O\text{-}C(O)\text{-}C(CH_3)\text{-}CH_2]_q$ + $[CH_3(CH_2)_{17}\text{-}O\text{-}C(O)\text{-}CH\text{-}CH_2]_t$ + $[CH_3(CH_2)_3CH(C_2H_5)CH_2\text{-}O\text{-}C(O)\text{-}CH\text{-}CH_2]_u$ + $[CH_3(CH_2)_3CH(C_2H_5)CH_2\text{-}O\text{-}C(O)\text{-}C(CH_3)\text{-}CH_2]_v$ + $[R'\text{-}Y\text{-}C(O)\text{-}CZ\text{-}CH_2]_{p}$-的总量为100重量%。

在式1至4的每一个中，R_f优选为任选被至少一个氧原子间隔的具有6个碳原子的直链或支链的全氟烷基，或具有6个碳原子的直链或支链的全氟烷基的混合物。R_f更优选为直链或支链C_6F_{13}-，或其混合物。R_f最优选为$CF_3(CF_2)_5$。

在式1至4中，下标k、a、b、p、q、t、u和v各自独立地为1至约10,000，更优选约5至约2000，或它们的混合。

在式1至4中，合适的连接基团X的实例包括直链、支链或环状亚烷基、苯基、亚芳基、亚芳烷基、磺酰基、次磺酰基、磺酰胺基、碳酰胺基、羰氧基、亚尿烷基、亚脲基、以及它们的组合诸如磺酰胺亚烷基。

式1至4中优选基团Y的实例为O、S或N(R)，其中R为H或C_1至C_4烷基。

如下文所详述，通过氟化（甲基）丙烯酸酯单体与其它单体的聚合反应来制备用于本发明中的共聚物。

用于本发明中的式1的共聚物包含以下列关于共聚物产物的重量百分比共聚的单体：

(a) 约7%至约100%的式5，或它们的混合物

$$R_f\text{-}X\text{-}Y\text{-}C(O)\text{-}CH{=}CH_2 \qquad \text{式 5}$$

其中

R_f、X和Y如上文式1所定义；

(b) 约0%至约93%的式6，或它们的混合物：

$$R_f\text{-}X\text{-}Y\text{-}C(O)\text{-}CT{=}CH_2 \qquad \text{式 6}$$

其中

R_f、X、Y 和 T 如上文式 1 所定义；

(c) 约 0% 至约 93% 的偏二氯乙烯；

(d) 约 0% 至约 30% 的式 7，或它们的混合物：

$$R^1\text{-}Y\text{-}C(O)\text{-}CZ\text{-}CH_2 \qquad \text{式 7}$$

其中

Y、R^1 和 Z 分别如上文式 1 所定义；和

(e) 约 0% 至约 93% 的附加任选单体。因此式 1 的共聚物可包括重复单元，所述重复单元衍生自 100% 的式 5；式 5 与式 6 的混合物；式 5 与偏二氯乙烯的混合物；式 5 与式 7 的混合物；式 5 与任选单体的混合物；式 5 与式 6、式 7、偏二氯乙烯和任选单体中任何两者的混合物；式 5 与式 6、式 7、偏二氯乙烯和任选单体中任何三者的混合物；或者式 5、式 6、式 7、偏二氯乙烯和任选单体的混合物。对于任何此类混合物，所有重复单元的重量百分比合计达 100%。

用于本发明中的式 2 的共聚物包含以下列关于共聚物产物的重量百分比共聚的单体：

(a) 约 48% 的式 8

$$R_f\text{-}X\text{-}Y\text{-}C(O)\text{-}C(CH_3)\text{=}CH_2 \qquad \text{式 8}$$

其中

R_f、X 和 Y 如上文式 1 所定义；

(b) 约 24% 的偏二氯乙烯；

(c) 约 24% 的丙烯酸 2-乙基己酯；以及

(d) 约 4% 的如上定义的式 7。

用于本发明中的式 3 的共聚物包含以下列关于共聚物产物的重量百分比共聚的单体：

(a) 约 48% 的式 8

R_f-X-Y-C(O)-C(CH_3)=CH_2 式 8

其中

R_f、X 和 Y 如上文式 1 所定义；

(b) 约 24% 的偏二氯乙烯；

(c) 约 12% 的甲基丙烯酸硬脂基酯；

(d) 约 12% 的丙烯酸硬脂基酯；以及

(e) 约 4% 的如上定义的式 7。

用于本发明中的式 4 的共聚物包含以下列关于共聚物产物的重量百分比共聚的单体：

(a) 约 32% 的如上定义的式 5，或它们的混合物，

(b) 约 32% 的如上定义的式 8，或它们的混合物，

(c) 约 8% 的甲基丙烯酸硬脂基酯，

(d) 约 8% 的丙烯酸硬脂基酯，

(e) 约 8% 的丙烯酸 2-乙基己酯，

(f) 约 8% 的甲基丙烯酸 2-乙基己酯，和

(g) 约 4% 的如上定义的式 7，或它们的混合物。

在式 5 和式 8 中，R_f 优选为具有 6 个碳原子的直链或支链的全氟烷基，或它们的混合物，更优选为直链或支链 C_6F_{13}-，或它们的混合物，最优选 $CF_3(CF_2)_5$-。适用于本发明的式 5 的实例为：

$CF_3(CF_2)_5$-CH_2CH_2-OC(O)-CH=CH_2,

C_6F_{13}-CH_2CH_2-OC(O)-CH=CH_2,

C_6F_{13}-R^2-SC(O)-CH=CH_2,

C_6F_{13}-R^2-OC(O)-CH=CH_2,

C_6F_{13}-SO_2-N(R^1)-R^2-OC(O)-CH=CH_2,

C_6F_{13}-CO-N(R^1)-R^2-OC(O)-CH=CH_2,

C_6F_{13}-CH_2CH(OR^3)CH-OC(O)-CH=CH_2,

C_6F_{13}-R^2-SO_2-N(R^1)-OC(O)-CH=CH_2,

C_6F_{13}-R^2-O-CON(R^1)-R^2-OC(O)-CH=CH_2,

其中

R^1为 H 或 C_1-C_4烷基；

R^2为 C_1-C_{10}亚烷基；并且

R^3为 H 或 C_1-C_4酰基。

适用于本发明的合适式 6 的实例为：

$CF_3(CF_2)_5$-CH_2CH_2-OC(O)-C(CH_3)=CH_2,

C_6F_{13}-CH_2CH_2-OC(O)-C(CH_3)=CH_2,

C_6F_{13}-R^2-SC(O)-C(CH_3)=CH_2,

C_6F_{13}-R^2-OC(O)-C(CH_3)=CH_2,

C_6F_{13}-SO_2-N(R^1)-R^2-OC(O)-C(CH_3)=CH_2,

C_6F_{13}-CO-N(R^1)-R^2-OC(O)-C(CH_3)=CH_2,

C_6F_{13}-CH_2CH(OR^3)CH-OC(O)-C(CH_3)=CH_2,

C_6F_{13}-R^2-SO_2-N(R^1)-OC(O)-C(CH_3)=CH_2,

C_6F_{13}-R^2-O-CON(R^1)-R^2-OC(O)-C(CH_3)=CH_2,

其中

R^1为 H 或 C_1-C_4烷基；

R^2为 C_1-C_{10}亚烷基；以及

R^3为 H 或 C_1-C_4酰基。

适用于本发明的式 8 的实例为：

$CF_3(CF_2)_5$-CH_2CH_2-OC(O)-C(CH_3)=CH_2,

C_6F_{13}-CH_2CH_2-OC(O)-C(CH_3)=CH_2,

C_6F_{13}-R^2-SC(O)-C(CH_3)=CH_2,

C_6F_{13}-R^2-OC(O)-C(CH_3)=CH_2,

C_6F_{13}-SO_2-N(R^1)-R^2-OC(O)-C(CH_3)=CH_2,

C_6F_{13}-CO-N(R^1)-R^2-OC(O)-C(CH_3)=CH_2,

C_6F_{13}-CH_2CH(OR^3)CH-OC(O)-C(CH_3)=CH_2,

C_6F_{13}-R^2-SO_2-N(R^1)-OC(O)-C(CH_3)=CH_2,

C_6F_{13}-R^2-O-CON(R^1)-R^2-OC(O)-C(CH_3)=CH_2,

其中

R^1为 H 或 C_1-C_4烷基；

R^2为C_1-C_{10}亚烷基；以及

R^3为H或C_1-C_4酰基。

适用于本发明方法中的式7的非氟化（甲基）丙烯酸酯单体包括（甲基）丙烯酸烷基酯，其中所述烷基为包含8至40个碳原子的直链或支链、或它们的混合物。（甲基）丙烯酸烷基酯中优选的烷基包含8至20个碳原子。（甲基）丙烯酸烷基酯（直链或支链）的实例为但不限于（甲基）丙烯酸烷基酯，其中所述烷基为辛基、2-乙基己基、癸基、异癸基、月桂基、鲸蜡基、或硬脂基。优选的实例为丙烯酸2-乙基己酯、丙烯酸月桂酯和丙烯酸硬脂基酯。

适用于本发明的方法中的式7的其它非氟化（甲基）丙烯酸酯单体实例包括N-羟甲基（甲基）丙烯酸酯、（甲基）丙烯酸羟烷酯、烷氧基（甲基）丙烯酸酯、（甲基）丙烯酸缩水甘油酯、丙烯酸硬脂基酯、甲基丙烯酸氨烷基酯盐酸盐、丙烯酰胺、烷基丙烯酰胺。其中，N-羟甲基单体实例为但不限于N-羟甲基丙烯酰胺和N-羟甲基甲基丙烯酰胺。（甲基）丙烯酸羟烷酯具有2至4个碳原子范围内的烷基链长，并且实例为丙烯酸2-羟基乙酯和甲基丙烯酸2-羟基乙酯。烷氧基（甲基）丙烯酸酯也具有2至4个碳原子范围内的烷基链长，并且包含1至12个氧化烯单元每分子，优选4至10个氧化烯单元每分子，并且最优选6至8个氧化烯单元每分子。

可用于制备式1的共聚物的其它合适附加任选单体包括乙酸乙烯酯、硬脂酸乙烯酯、烷基乙烯基砜、苯乙烯、乙烯基苯甲酸、烷基乙烯基醚、马来酸酐、氯乙烯、以及其它烯烃。

可在含有一种或多种表面活性剂的有机溶剂或水中使式5、6和/或8的氟化（甲基）丙烯酸酯混合物（在适当情况下）与上文分别所列的其它单体经由自由基引发聚合反应，从而制得用于本发明中的式1、2、3或4的氟化（甲基）丙烯酸酯共聚物。通过在配备搅拌装置和外部加热和冷却装置的适当反应容器内，在含有一种或多种表面活性剂的有机溶剂或水中搅拌上述单体来制备用于本发明中的氟化共聚物。加入自由基引发剂，并且将温度升至约20℃至约70℃。聚合反应引发剂的实例为2,2’-偶氮二(2-脒基丙烷）二盐酸盐或2,2’-偶氮二（异丁基脒）二盐酸盐。这些引发剂以名称“VAZO”售自E.I. du Pont de Nemours and Company（Wilmington, Delaware）。

合适的聚合反应调节剂或链转移剂的实例为十二硫醇。本发明的方法中所用的适用于制备式1、2、3或4共聚物的有机溶剂包括四氢呋喃、丙酮、甲基异丁基酮、异丙醇、乙酸乙酯、以及它们的混合物。优选四氢呋喃。为排除掉氧，在惰性气体诸如氮气下实施所述反应。通过沉淀分离所述聚合物，并且任选通过例如重结晶进行纯化。通过蒸发除去溶剂，或者保留溶液，以稀释并且施用于基底。反应产物为式1、2、3或4的氟化（甲基）丙烯酸酯共聚物。

然后用水稀释式1、2、3或4的所得的氟化（甲基）丙烯酸酯共聚物，或进一步分散或溶解于溶剂中，所述溶剂选自适用于最终施用到基底上的简单的醇和酮（下文称为“施用溶剂”）。作为另外一种选择，由传统方法使用表面活性剂制得的水分散体可通过除去溶剂（通过蒸发）和使用本领域的技术人员已知的乳化或均化步骤来制备。优选这类不含溶剂的乳液，以最大程度地降低易燃性以及与挥发性有机化合物（VOC）相关的问题。施用到基底上的最终产物为式1、2、3或4的氟化（甲基）丙烯酸酯共聚物的分散体（如果基于水）或溶液（如果使用除水以外的溶剂）。

在本发明的改良的方法中，通过使式1、2、3或4的氟化（甲基）丙烯酸酯共聚物溶液或分散体接触基底来向纤维基底提供拒水性和拒醇性。合适的基底包括纤维基底，尤其是如下定义的非织造基底。

可经由任何合适的方法使式1、2、3或4的氟化（甲基）丙烯酸酯共聚物溶液或分散体接触所述基底。此类方法是本领域技术人员已知的，并且包括例如通过泡沫、钳夹、软垫、湿润辊、喷雾、浸渍、浸没、刷子、轧辊、海绵、小垫以及类似的常规方法来施用。可将式1、2、3或4的氟化（甲基）丙烯酸酯共聚物的分散体本身施用到所述基底上，或将其与其它任选的织物整理剂或表面处理剂组合施用到所述基底上。

此类任选附加的组分包括可获得附加表面功效的处理剂或整理剂，或通常与此类处理剂或整理剂一起使用的添加剂。此类附加组分包括可提供表面功效的化合物或组合物，所述表面功效诸如免烫性、易烫性、收缩控制、抗皱、耐久定形、水分控制、柔软性、强度、防滑性、防静电性、防钩伤性、防起球、抗污性、去污性、拒醇性、释醇性、拒水性、拒醇性、气味控制、抗微生物性、防晒性、可清洁性、以及类似的功效。可在施用本发明的

共聚物之前、之后或同时，将一种或多种此类处理剂或整理剂施用到所述基底上。通常将此类任选组分共混到处理浴液中。

还可存在通常与此类处理剂或整理剂一起使用的其他添加剂，诸如表面活性剂、pH 调节剂、交联剂、润湿剂、蜡增充剂、以及本领域的技术人员已知的其他添加剂。合适的表面活性剂包括阴离子表面活性剂、阳离子表面活性剂、非离子表面活性剂、N-氧化物和两性表面活性剂。此类添加剂的实例包括加工助剂、发泡剂、润滑剂、防污剂等。通常将此类添加剂与处理浴液共混。

本发明所用的式 1、2、3 或 4 的氟化（甲基）丙烯酸酯共聚物溶液或分散体的施用速率取决于基底孔隙率，并且施用量为在被处理基底中提供所期望的氟含量。被处理的纤维基底通常具有按重量计约 100μg/g 至约 10,000μg/g 的氟含量。氟含量优选为约 1,000μg/g 至约 4,000μg/g。

任选地，施用组合物中还包含非氟化增充剂组合物以潜在增加氟效率。此类任选的附加增充剂聚合物组合物的实例为 2004 年 9 月 7 日提交的共同未决的美国临时申请 60/607,612（CH2996）和 2005 年 7 月 6 日提交的美国系列号 11/175680（CH3048）中公开的那些。

本发明还包括采用本发明的方法使用式 1、2、3 或 4 的氟化（甲基）丙烯酸酯共聚物溶液或分散体处理的基底。合适的基底包括纤维质基底。所述纤维基底包括织造织物、编织织物和非织造织物或其它纺织物。具体地讲，用于本发明方法中的式 1、2、3 或 4 的氟化（甲基）丙烯酸酯共聚物溶液或分散体适于将卓越的拒水性和拒醇性提供给织造织物、编织织物、和非织造织物，尤其是由聚烯烃纤维诸如聚丙烯、聚乙烯以及低熔融共混聚合物制得的那些，由其制得的纤维，以及包含这些纤维的共混物。本发明尤其适用于聚丙烯织物或聚乙烯织物，并且最适用于聚丙烯非织造织物或聚乙烯非织造织物。非织造织物的类型包括纺粘型、熔喷型以及包含任一类型非织造结构的层压体。非织造材料的类型描述于“Encyclopedia of Textile Finishing”（Rouette，Hans-Karl，2001，Springer - Verlag，ISBN: 3540654909）中。此类非织造材料通常具有低玻璃化转变温度，因此当采用带有热固化步骤的常规处理过程时，非织造材料会在加热期间软化。因此，本发明的改良方法能够向非织造材料提供表面功效，而无此缺点。用

于本发明方法中的式1、2、3或4的氟化（甲基）丙烯酸酯共聚物溶液或分散体可向其所处理的基底提供卓越的拒水性和拒醇性。

用于本发明的方法中的氟化（甲基）丙烯酸酯共聚物组合物可用于向在环境温度下风干或固化处理的基底提供卓越的拒水性和拒醇性。无需以高温来获得有效的排斥性。用于本发明的方法中的氟化（甲基）丙烯酸酯共聚物能够使用包含例如6个碳原子的较短链氟代烷基，而如果氟代烷基包含小于8个碳原子，则可商购获得的常规（甲基）丙烯酸酯通常显示出差的拒醇性和拒水性。

测试方法

测试方法1

采用浸轧浴（浸渍）方法使用供乳液浸轧施用的共聚物分散体来处理所述织物。将式1、2、3或4的氟化（甲基）丙烯酸酯共聚物施用到由Kimberly-Clark（Roswell，GA）制造的织物重76克/平方米的纺粘-熔喷-纺粘聚丙烯（SMS PP）非织造织物上。施用后，使织物风干并且固化。采用下文所述测试方法2来测定织物的拒水性和拒醇性。

测试方法2 – 拒水性/拒醇性

根据拒水性/拒醇性测试方法IST 80.6-92中所用的INDA标准测试来测定所处理基底的拒水性/拒醇性。所述测试确定所处理的基底对于含水液体润湿性的抵抗力。将三滴具有不同表面张力的水醇混合物置于基底上，目测确定表面润湿的程度。

拒水性测试液体的组成示于表1中。

表1：拒水性/拒醇性测试液体

拒水性等级编号	体积%异丙醇	体积%蒸馏水
0	0	100
1	10	90
2	20	80
3	30	70
4	40	60
5	50	50
6	60	40
7	70	30

8	80	20
9	90	10
10	100	0

将三滴测试液体 1 置于处理过的基底上。如果在 5 分钟后未观察到液体渗透或部分吸收（基底上出现较深的湿斑），则用测试液体 2 重复测试。用测试液体 3 重复测试，并且逐渐使用更高的测试液体编号，直到观察到液体渗入（基底上出现较深的湿斑）。测试结果为不会渗入基底的测试液体的最高编号。值越高表明拒水性越强。

实施例

除非另外指明，对于实施例部分的所有列表来讲，所测的氟为氟与所处理的整个织物重量的重量比率。除非另外指明，下面所用的所有化学制品均为试剂等级，并且均得自 Sigma-Aldrich（St. Louis, MO）。

实施例 1

在塑性烧杯中，混合 200 克去离子水、4.0 克得自 Mazer Chemicals, Inc.（Gurnee, Illinois）的 Mazer MAPEG 600MS 聚亚烷基二醇酯、6.0 克得自 E. I. du Pont de Nemours and Company（Wilmington, DE）的 AVITEX 表面活性剂、7.1 克得自 E. I. du Pont de Nemours and Company（Wilmington, DE）的 $CF_3(CF_2)_5CH_2CH_2OC(O)CHCH_2$、7.1 克得自 E. I. du Pont de Nemours and Company（Wilmington, DE）的 $CF_3(CF_2)_5CH_2CH_2OC(O)C(CH_3)CH_2$、1.0 克作为共聚单体以产品名 BLEMMER 350 得自 NOF-America（White Plains, NY）的具有平均 8 个乙氧基的聚（乙二醇）甲基丙烯酸酯（8EO-MA）、7.1 克得自 Sigma-Aldrich（Milwaukee, WI）的甲基丙烯酸硬脂基酯、1.0 克得自 Sigma-Aldrich（Milwaukee, WI）的羟甲基丙烯酰胺、0.50 克得自 Sigma-Aldrich（Milwaukee, WI）的甲基丙烯酸羟乙酯、0.25 克得自 Sigma-Aldrich（Milwaukee, WI）的十二硫醇、10.0 克得自 Sigma-Aldrich（Milwaukee, WI）的己二醇、和 0.10 克得自 Sigma-Aldrich（Milwaukee, WI）的氨基磺酸。将反应混合物加热至 55℃，并且在超声波破碎仪中乳化两次，每次两分钟，直至获得均匀的乳白色乳液。将所述溶液加入到配备氮气层、冷凝器、顶置式搅拌器和温度探针的 500mL 烧瓶中，开始氮气鼓泡，并且在 170rpm 下搅拌。当温度降至约 30℃以下时，

将烧瓶切换到氮气层，并且加入 14.3 克得自 Sigma-Aldrich（Milwaukee，WI）的偏二氯乙烯（VDC）和 10.0 克去离子水。将所述溶液搅拌 15 分钟。15 分钟后，加入 0.50 克 VAZO-50 引发剂的 10.0 克去离子水溶液。然后在 30 分钟内，将反应混合物加热至 50℃。将所述溶液在 50℃下搅拌 8 小时。然后使溶液冷却至室温，接着采用重力过滤，通过滤乳器过滤到细颈瓶中，获得具有 13.2 重量% 固体和 3.2 重量% 氟的乳液共聚物。

根据测试方法 1，用所述共聚物处理纺粘-熔喷-纺粘聚丙烯织物（SMS PP）。计算用于浸轧浴中的氟化共聚物分散体的量，以在织物上获得按重量计约 1200 微克/克氟的氟含量。除了如上所述制备的氟化共聚物乳液以外，所述浸轧浴还包含 0.15 重量% 得自 E.I.du Pont de Nemours and Company（Wilmington，DE）的 ZELEC TY 丁基磷酸钾和 0.6% 得自 Sigma-Aldrich（Milwaukee，WI）的正己醇。在浸轧施用如上所述制得的氟化共聚物乳液（浴液总湿吸收为约 140%）后，使所述非织造 SMS PP 织物风干，或在烘箱中干燥和固化，直至织物达到 140℃，并且在该温度下保持 3 分钟。处理和固化后，使织物“静置”。采用测试方法 2，测定非织造 SMS PP 织物的拒水性和拒醇性。结果示于表 2 中。

表 2

实施例	在环境温度下风干/固化	140 ℃风干/固化
1	8	9
未处理过的	2	2

表 2 中的数据显示，本发明的方法在环境温度下风干的 SMS PP 非织造织物上提供了卓越的拒水性和拒醇性，这基本上与采用高温干燥相当。

实施例 2 至 27 和比较实施例 A 至 P

对于实施例 2 至 27 和比较实施例 A 至 P 中的每一个，使用表 3 中按共聚物中重量百分比列出的单体，并且采用实施例 1 中的方法，来制备所述共聚物。使用测试方法 1，分别将得自实施例 2 至 27 和得自比较实施例 A 至 P 的共聚物施用到非织造纺粘-熔喷-纺粘聚丙烯（SMS PP）织物上。根据测试方法 2，测定所处理织物的拒水性/拒醇性。结果示于表 5 中。

比较实施例提供了不在式 1、2、3 或 4 之内的共聚物组合物，并且不提供环境温度固化排斥性。对于比较实施例 A、F、J、K、L、M 和 O，不存在重复单元$[R_f\text{-}X\text{-}Y\text{-}C(O)\text{-}CH\text{-}CH_2]_k$或$-[R_f\text{-}X\text{-}Y\text{-}C(O)\text{-}C(CH_3)\text{-}CH_2]_a$。对于比较实施例 B、C、D、G、H、I 和 P，$[R_f\text{-}X\text{-}Y\text{-}C(O)\text{-}CH\text{-}CH_2]_k$ + $[R_f\text{-}X\text{-}Y\text{-}C(O)\text{-}CT\text{-}CH_2]_a$ + $[CCl_2\text{-}CH_2]_b$总量小于 70 重量%。对于比较实施例 E，R^1为 C_4H_9，其链长比式 1、2、3 或 4 中所需的更短。对于比较实施例 N，R^1为 C_6H_{11}，其链长比式 1、2、3 或 4 中所需的更短。

表 3 – 用于共聚反应中的单体

单体*	A	B	VDC	D	E	F	G	H	I
化学式	5	6	–	7	7	7	7	7	7
实施例									
2	19%	19%	39%	19%					4%
3	7%	18%	50%	21%					4%
4	38%	24%	30%					C_{12} 4%	4%
5	48%		24%	24%					4%
6	48%		24%		12%	12%			4%
7	24%	24%	24%	24%					4%
8	38%		38%	9%			10%		4%
9	38%		38%	19%					4%
10	48%		24%	12%			12%		4%
11	38%		48%		10%				4%
12	38%		38%		9%	10%			4%
13	44%		31%				22%		4%
14	58%		29%		10%				4%
15	48%		24%		24%				4%
16	19%		67%		10%				4%
17	13%	17%	40%					支链的 C_{13} 26%	4%
18	13%	17%	40%					C_{18}-C_{24}共混物 26%	4%
19	32%		42%		22%				4%
20		48%	24%			24%			4%
21		48%	24%	12%	12%				4%
22	70%		10%	16%					4%
23	44%		31%			22%			4%
24	38%	24%	30%					支链 C_{10} 4%	4%
25	32%	32%		8%	8%	8%	8%		4%
26	58%		19%	19%					4%
27	24%	26%	46%						4%

A		44%						C_{12} 52%	4%
B	48%			24%			24%		4%
C	64%						32%		4%
D	38%		29%		29%				4%
E	38%	24%	30%					C_4 4%	4%
F		64%				32%			4%
G	19%		48%		29%				4%
H	44%			52%					4%
I	44%				52%				4%
J		51%	24%				21%		4%
K		38%	38%				19%		4%
L		58%	19%	19%					4%
M		36%	36%				25%		4%
N	13%	17%	40%					环状 C_6 26%	4%
O		48%	24%				24%		4%
P	19%		29%		48%				4%

* 单体 A – $CF_3(CF_2)_5CH_2CH_2OC(O)CHCH_2$

单体 B – $CF_3(CF_2)_5CH_2CH_2OC(O)C(CH_3)CH_2$

单体 VDC – 偏二氯乙烯

单体 D – 甲基丙烯酸硬脂基酯

单体 E – 丙烯酸硬脂基酯

单体 F – 丙烯酸 2-乙基己酯

单体 G – 甲基丙烯酸 2-乙基己酯

单体 H – 甲基丙烯酸烷基酯

单体 I – 1.6% 具有平均七个乙氧基化物的聚（乙二醇）甲基丙烯酸酯（7EO 甲基丙烯酸酯）、1.0% 甲基丙烯酸羟乙酯、1.0% 羟甲基丙烯酰胺和 0.4% 十二硫醇的混合物。

比较实施例 Q 和 R

对于比较实施例 Q 和比较实施例 R 中的每一个，采用实施例 1 中的方法，但是使用式 $F(CF_2)_aCH_2CH_2OC(O)CHCH_2$ 的丙烯酸全氟烷基乙酯混合物作为含氟化合物，其中 a 在 4 至 12 的范围内，并且主要为 6、8 和 10。典型的混合物如下：27% 至 37% 的 a = 6，28% 至 32% 的 a = 8，14% 至 20% 的 a

= 10，8% 至 13% 的 a = 12，并且 3% 至 6% 的 a = 14，得自 E. I. du Pont de Nemours and Company（Wilmington，DE）。因此，对于比较实施例 Q 和 R 来讲，基团 R_f 为 C_6F_{13}、C_8F_{17}、$C_{10}F_{21}$、$C_{12}F_{25}$、$C_{14}F_{29}$ 的共混物，其不在式 1、2、3 或 4 之内。所用单体按占所述共聚物的重量百分比列于表 4 中。使用测试方法 1，分别将所得共聚物施用到非织造纺粘-熔喷-纺粘聚丙烯 SMS PP 织物上。根据测试方法 2 来测定所处理织物的拒水性/拒醇性。结果示于表 5 中。

表 4 - 用于共聚反应中的单体

实施例编号	$F(CF_2)_aCH_2CH_2$-OC(O)CHCH$_2$	甲基丙烯酸硬脂基酯	偏二氯乙烯	I*
比较实施例-Q	19%	29%	48%	4%
比较实施例-R	59%	18%	18%	4%

* 单体 I 为 1.6% 具有平均七个乙氧基化物的聚（乙二醇）甲基丙烯酸酯（7EO 甲基丙烯酸酯）、1.0% 甲基丙烯酸羟乙酯、1.0% 羟甲基丙烯酰胺和 0.4% 十二硫醇的混合物。

表 5 - 拒水性/拒醇性

实施例	排斥性	实施例	排斥性	实施例	排斥性
2	8	17	6	比较实施例-E	2
3	8	18	5	比较实施例-F	2
4	8	19	5	比较实施例-G	2
5	8	20	5	比较实施例-H	2
6	8	21	5	比较实施例-I	1
7	8	22	5	比较实施例-J	1
8	8	23	5	比较实施例-K	1
9	7	24	4	比较实施例-L	1
10	7	25	4	比较实施例-M	1
11	7	26	4	比较实施例-N	1
12	7	27	3.5	比较实施例-O	1
13	6	比较实施例-A	3	比较实施例-P	0
14	6	比较实施例-B	3	比较实施例-Q	1
15	6	比较实施例-C	3	比较实施例-R	1
16	6	比较实施例-D	2	未处理的	2

在表5中，式1由实施例1至19、22至24、和26至27来代表。式2由实施例20代表。式3由实施例21代表。式4由实施例25代表。表5中的数据显示，在实施例1至23中获得了非常高的排斥性，而在实施例24至27中获得了中等程度的排斥性。比较实施例显示出不可接受的低排斥性或无排斥性。