(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
16 October 2008 (16.10.2008)

PCT

(10) International Publication Number
WO 2008/122517 A2

(51) International Patent Classification:
A61Q 17/04 (2006.01)

(21) International Application Number:
PCT/EP2008/053603

(22) International Filing Date: 27 March 2008 (27.03.2008)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/922,025 5 April 2007 (05.04.2007) US

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(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL, NO, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *without international search report and to be republished upon receipt of that report*

WO 2008/122517 A2

(54) Title: SUNSCREEN AND PERSONAL CARE COMPOSITIONS COMPRISING A RANDOM TERPOLYMER

(57) Abstract: Topically applicable, water-resistant cosmetic or dermatological compositions well suited for the UV-photoprotection of human skin and/or hair comprising an effective UV-photoprotecting amount of: (a) at least one UV screening agent; (b) at least one random terpolymer; and, optionally (c) other cosmetically acceptable ingredients. The present invention also relates to personal care compositions comprising at least one random terpolymer and other cosmetically acceptable ingredients.

SUNSCREEN AND PERSONAL CARE COMPOSITIONS COMPRISING A RANDOM TERPOLYMER

Field of the Invention

This application claims benefit under 35 USC 119(e) of U.S. Provisional app. No. 60/922,025, filed on April 5, 2007, which is incorporated herein by reference.

Topically applicable, water-resistant cosmetic or dermatological compositions well suited for the UV-photoprotection of human skin and/or hair comprising an effective UV-photoprotecting amount of: (a) at least one UV screening agent; and, (b) at least one random terpolymer; and, optionally, (c) other cosmetically acceptable ingredients.

Background of the Invention

Sunscreen compositions are applied to the skin to protect the skin from the sun's ultraviolet rays that can lead to erythema, a reddening of the skin also known as sunburn. Sunlight or ultraviolet radiation in the UV-B range has a wavelength of 290 nm to 320 nm and is known to be the primary cause of sunburn. Ultraviolet rays at a wavelength of 320 nm to 400 nm, known as UV-A radiation, produces tanning of the skin. However, in the process of doing so, the UV-A rays can damage or harm the skin.

Besides the immediate malady of sunburn, excessive sunlight exposure can lead to skin disorders. For instance, prolonged and constant exposure to the sun may lead to actinic keratoses and carcinomas. Another long-term effect is premature aging of the skin. This condition is characterized by skin that is wrinkled, cracked and has lost its elasticity.

As stated above, sunscreens are typically formulated with the goal of inhibiting skin damage from the sun's rays. The sunscreen composition filters or blocks the harmful UV-A and UV-B rays that can damage and harm the skin. It is believed that sunscreen agents accomplish this by absorbing the UV-A and/or UV-B rays.

Typically, the above-described UV-B filters are combined with the above-described UV-A filters in a solution with other lipophilic or oily ingredients and solvents to form an oil phase. The solvents are used to dissolve the sunscreen actives into the oil phase. Typically, but not necessarily, the oil phase is dispersed with the help of emulsifiers and stabilizers into an

aqueous solution composed primarily of water, to make an emulsion, which becomes the final sunscreen composition.

A wide variety of cosmetic compositions intended for the photoprotection (UV-A and/or UV-B) of the skin are also known to this art.

US 5,204,090 discloses waterproof sunscreens comprising a water insoluble film forming polymer, which is incorporated herein by reference.

US 5,653,965 discloses film forming polymers for a sunscreen spray, which is incorporated herein by reference.

US 5,487,886 discloses acrylic polymers for sunscreen formulations, which is incorporated herein by reference.

US 5,145,669 discloses water proof sunscreens containing crosslinked copolymer of maleic anhydride, which is incorporated herein by reference.

US 4,663,157 discloses a copolymer of ethylene and acrylic acid for use in sunscreen compositions, which is incorporated herein by reference.

US 2006/0008427 discloses a photo-protective composition that contains a synergistic combination of a least one sunscreen agent and at least one caroteniod, which is incorporated herein by reference.

US 7,108,860 discloses a cosmetic composition that contains at least two rheology modifiying agents, which is incorporated herein by reference.

US 7,014,842 discloses a sunscreen composition comprising one or more photoactive compounds and one or more optimization agents, which is incorporated herein by reference.

US 6,409,998 discloses a UV-photoprotecting emulsion comprising micronized insoluble screening agents and associative polymers, which is incorporated herein by reference.

US 2004/0126339 discloses a sunscreen composition that includes a mixture of a skin bonding polymer and at least one sunscreen active ingredient, which is incorporated herein by reference.

US 6,312,672 discloses waterproof sunscreen compositions which include polymers of isoprene, butadiene, and/or styrene, which is incorporated herein by reference.

US 2004/0091434 discloses a topically applicable photostable sunscreen composition containing at least one dibenzoylmethane UV-sunscreen and an effective amount of at least one amphiphilic block copolymer, which is incorporated herein by reference.

US 2003/0021847 discloses a composition for retaining active ingredients in personal care compositions based on one or more polymers having a network structure in an oil phase, which is incorporated herein by reference.

US 2002/0076390 discloses a composition for nails, skin and hair in the form of an aqueous emulsion or dispersion, which is incorporated herein by reference.

US 5,688,858 discloses a polymer suitable as a dispersant, which is incorporated herein by reference.

US 2006/0104923 discloses a sunscreen composition containing fluorinated alkyl ethers, which is incorporated herein by reference.

These anti-sun or sunscreen compositions are quite often provided in the form of an emulsion, of the oil-in-water (O/W) type (namely, a cosmetically and/or dermatologically acceptable carrier comprising an aqueous dispersing continuous phase and a fatty dispersed discontinuous phase) or of the water-in-oil (W/O) type (dispersed aqueous phase in a continuous fatty phase), which contains, at various concentrations, one or more lipophilic conventional organic UV-screening agents and/or inorganic nanopigments of metal oxides, which are suited for selectively absorbing the harmful UV radiation, these screening agents (and the quantities thereof) being selected according to the desired sun protection factor (the sun protection factor (SPF) being mathematically expressed by the ratio of the irradiation time required to attain the erythematogenic threshold with the UV-screening agent to the time

required to attain the erythematogenic threshold in the absence of UV-screening agent). In such emulsions, the hydrophilic screening agents are present in the aqueous phase and the lipophilic screening agents are present in the fatty phase.

The oil-in-water emulsions are, in general, more accepted by the consumer than the water-in-oil emulsions because, in particular, of their pleasant feel (similar to water) and their presentation in the form of a non-oily cream or milk; however, they also more readily lose their UV protection efficacy as soon as they come into contact with water. Indeed, the hydrophilic screening agents tend to disappear in water, upon washing in the sea or in a swimming pool, under the shower or when engaged in water sports; thus, anti-sun or sunscreen compositions containing same, whether alone or combined with lipophilic screening agents, no longer provide the desired initial protection as soon as the substrate (skin or hair) to which they have been applied is contacted with water.

Anti-sun (sunscreen) compositions exhibiting improved resistance to water have been formulated as water-in-oil emulsions. Indeed, a hydrophilic screening agent is more stable to water in a water-in-oil emulsion than in an oil-in-water emulsion. However, as indicated above, such compositions are not yet completely satisfactory since they promote, after application, a fat-like impression which is particularly unpleasant for the user.

Thus, serious need continues to exist for anti-sun or sunscreen compositions which impart to the skin and/or the hair effective solar protection which is stable over time and resistant to water (stability to water) and the cosmetic performance of which presents features that would be comparable to those obtained with conventional oil/water emulsions.

Summary of the Invention

It is now surprisingly and unexpectedly determined that specific sunscreen compositions containing at least one UV-screening agent and at least one random terpolymer not only provide anti-sun compositions whose cosmetic performance features are comparable to those generally associated with a conventional sunscreen composition formulated as an oil/water emulsion, but also exhibit good stability as well as enhanced stability to water.

Therefore, a first aspect of the present invention is directed to a sunscreen composition comprising at least one sunscreen agent, at least one random terpolymer of formula (I), and other cosmetically acceptable ingredients.

A second aspect of the present invention is directed to a method of preparing a sunscreen composition comprising mixing together at least one sunscreen agent, at least one random terpolymer of formula (I) and, optionally, other cosmetically acceptable ingredients.

A third aspect of the present invention is directed to a method of increasing the sun protection factor of a sunscreen composition wherein said method comprises incorporating into said compositions an effective amount of at least one random terpolymer according to formula (I).

A fourth aspect of the present invention is directed to a method of improved UV protection of mammalian hair and/or skin from the damaging effects of UV radiation wherein said method comprises applying to said skin and/or said hair an effective amount of a sunscreen composition comprising at least one sunscreen agent, at least one random terpolymer of formula (I), and, optionally, other cosmetically acceptable ingredients.

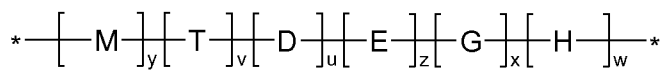
A fifth aspect of the present invention is directed to a cosmetic or dermatological composition comprising a random terpolymer of formula (I) and other cosmetically acceptable ingredients.

Detailed Description of the Invention

The present invention provides a sunscreen composition comprising:

(a) at least one UV screening agent;

(b) at least one random terpolymer of formula

(I)  , wherein

u, v, w, x, y, and z represent the percentage by weight that each repeating unit or derived monomer is contained within the terpolymer;

u, v, w, x, y, and z add up to total 100 weight percent relative to the total weight of the terpolymer;

y is from about 0 to about 40% by weight of the terpolymer;

v is from about 5% to about 75% by weight of the terpolymer;

u is from about 5% to about 80% by weight of the terpolymer;

z is from about 0% to about 60% by weight of the terpolymer;

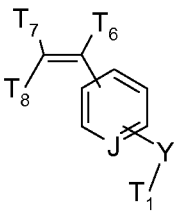
x is from about 1% to about 50% by weight of the terpolymer;

w is from about 0% to about 50% by weight of the terpolymer;

* is a terminal group, for example, a catalyst residue;

M, T, D, E, G, and H are covalently bonded to each other;

M is derived from at least one monomer of formula

(II) , wherein

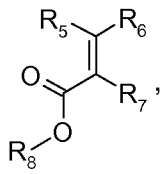
T_6, T_7, and T_8 are C_1-C_4alkyl or hydrogen;

Y is a direct bond, –O-, -S-, -N(H)- or –N(T_1)-;

T_1 is hydrogen or C_1-C_4alkyl; and

J is a nitrogen or carbon atom;

T, D, and E are independently derived from at least one monomer of formula

(III) , wherein

R_5, R_6 and R_7 may be the same or different and represent hydrogen or C_1-C_{22}alkyl;

R_8 is C_1-C_{30} lkyl, C_6-C_{15}cycloalkyl, or C_6-C_{15}aryl; said substituted alkyl, said cycloalkyl or said aryl may also be substituted by one or more –OH and/or NH_2-groups; or said alkyl or said cycloalkyl may be interrupted by one or more –O- groups and/or –N(H)- groups;

G is derived from at least one monomer comprising a heterocyclic group having at least one basic ring nitrogen atom or to which such a heterocyclic group is attached following polymerization;

H is derived from at least one monomer selected from the group consisting of toluene diisocyanate (all isomers), 4,4'-diphenylmethane diisocyanate, tolidine diisocyanate, dianisidine diisocyanate, m-xylylene diisocyanate, p-phenylene diisocyanate, m-phenylene diisocyanate, 1-chloro-2,4-phenylene diisocyanate, 3,3'-dimethyl-4,4'-bisphenylene diisocyanate, 4,4'-bis(2-methylisocyanatophenyl)methane, 4,4'-bisphenylene diiso-

cyanate, 4,4'-bis(2-methoxyisocyanatophenyl)methane, 1-nitrophenyl-3,5-diisocyanate, 4,4'-diisocyanatodiphenyl ether, 3,3'-dichloro-4,4'-diisocyanatodiphenyl ether, 3,3'-dichloro-4,4'-diisocyanatodiphenyl methane, 4,4'-diisocyanatodibenzyl, 3,3'-dimethoxy-4,4'-diisocyanatodiphenyl, 2,2'-dimethyl-4,4'-diisocyanatodiphenyl, 2,2'-dichloro-5,5'-dimethoxy-4,4'-diisocyanatodiphenyl, 3,3'-dichloro-4,4'-diisocyanatodiphenyl, 1,2-naphthalene diisocyanate, 4-chloro-1,2-naphthalene diisocyanate, 4-methyl-1,2-naphthalene diisocyanate, 1,5-naphthalene diisocyanate, 1,6-naphthalene diisocyanate, 1,7-naphthalene diisocyanate, 1,8-naphthalene diisocyanate, 4-chloro-1,8-naphthalene diisocyanate, 2,3-naphthalene diisocyanate, 2,7-naphthalene diisocyanate, 1,8-dinitro-2,7-naphthalene diisocyanate, 1-methyl-2,4-naphthalene diisocyanate, 1-methyl-5,7-naphthalene diisocyanate, 6-methyl-1,3-naphthalene diisocyanate, 7-methyl-1,3-naphthalene diisocyanate, 1,2-ethane diisocyanate, 1,3-propane diisocyanate, 1,4-butane diisocyanate, 2-chloropropane-1,3-diisocyanate, pentamethylene diisocyanate, propylene-1,2-diisocyanate, 1,8-octane diisocyanate, 1,10-decane diisocyanate, 1,12-dodecane diisocyanate, 1,16-hexadecane diisocyanate 1,3- and 1,4-cyclohexane diisocyanate, 1,6-hexamethylene diisocyanate, 2,2,4- and 2,4,4-trimethylhexamethylene diisocyanate, diisocyanates or a mixture thereof dimer acid derived diisocyanate obtained from dimerized linoleic acid, 4,4'-dicyclohexylmethane diisocyanate, isophorone diisocyanate, 3-isocyanatomethyl-3,5,5-trimethylcyclohexyl diisocyanate, lysine methyl ester diisocyanate, bis(2-isocyanatoethyl) fumarate bis(2-isocyanatoethyl) carbonate, m-tetramethylxylylene diisocyanate, and acrylonitrile; and

(c) other cosmetically acceptable ingredients,

with the proviso that T, D, and E are different from each other.

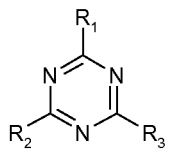
UV screening agents of component (a) useful in the present invention include organic sunscreens and/or inorganic sunscreens which are preferably active in the UV-A and/or UV-B regions (UV absorbers), and are soluble in water or in fats or insoluble in, e.g., cosmetic solvents commonly used. Typically, the compositions of the present invention contain combinations of one or more sunscreen agents. Additionally, the compositions of the present invention contain combinations of two or more sunscreen agents. The combination of sunscreen agents of component (a) can be, for example: two or more inorganic sunscreen agents; two or more organic soluble sunscreen agents; two or more organic micronized or micronizable sunscreen agents; and/or mixtures thereof.

Representative inorganic sunscreens of component (a) include pigments, or alternatively nanopigments (mean size of the primary particles: generally between 5 nm and 100 nm, preferably between 10 nm and 50 nm) formed from coated or uncoated metal oxides, such as, for example, titanium oxide (amorphous or crystalline in the rutile and/or anatase form), iron oxide, zinc oxide, zirconium oxide or cerium oxide nanopigments, which are all known in the art as UV sunscreens. Conventional coating agents are, furthermore, alumina and/or aluminium stearate. Such nanopigments formed from coated or uncoated metal oxides are disclosed in particular in EP 518 772 and EP 518 773.

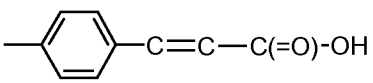
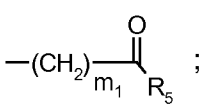
The organic sunscreens of component (a) may be soluble (non-micronized) or insoluble (micronized or micronizable) in the sunscreen composition of the instant invention.

Suitable insoluble (micronized or micronizable) organic sunscreens or UV absorbers of component (a) may be, e.g. a triazine, a benzotriazole, a benzophenone, a vinyl group-containing amide, a cinnamic acid amide or a sulfonated benzimidazole UV absorber.

A preferred class of triazine compounds is that having the formula

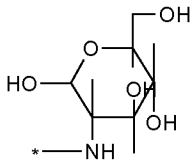
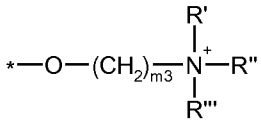
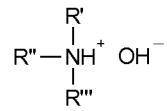
(1)  , wherein

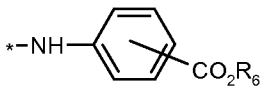
R_1, R_2 and R_3, independently from each other, are hydrogen; hydroxy; C_1-C_3alkoxy; NH_2; NHR_4; $N(R_4)_2$; OR_4; C_6-C_{12}aryl; phenoxy; anilino; pyrrolo; in which the respective phenyl, phenoxy, anilino or pyrrolo moieties are not substituted or substituted by one, two or three substitutents selected from OH, carboxy, CO-NH_2, C_1-C_{12}alkyl, C_1-C_{12}alkoxy, a methylidenecamphor group, a group $-(CH=CH)_mC(=O)-OR_4$, a group

 or the corresponding alkali metal, ammonium, mono-, di- or tri-C_1-C_4alkylammonium, mono-, di- or tri-C_2-C_4alkanolammonium salts, or the C_1-C_3alkyl esters thereof or by a radical of formula (1a)  ;

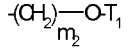
R_4 is C_1-C_5alkyl;

R_5 is hydroxy; C_1-C_5alkyl that is unsubstituted or substituted by one or more OH groups; C_1-C_5alkoxy; amino; mono- or di-C_1-C_5alkylamino; M; a radical of formula

(1b)  ; (1c)  ; (1d)  ; or

(1e)  ;

R', R" and R"' independently of the other are C_1-C_{14}alkyl that is unsubstituted or substituted by one or more OH groups;

R_6 is hydrogen; M; C_1-C_5alkyl; or a radical of the formula  ;

M is a metal cation;

T_1 is hydrogen; or C_1-C_8alkyl;

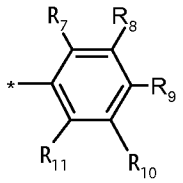
m is 0 or 1;

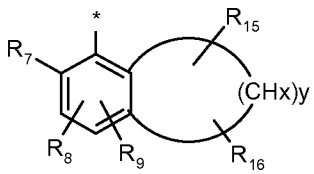
m_1 is from 1 to 5;

m_2 is from 1 to 4; and

m_3 is from 2 to 14.

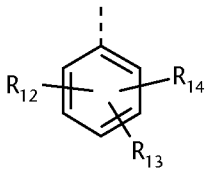
Preferred compounds of formula (1) are those, wherein

R_1, R_2 and R_3 independently from each other are a radical of formula (1f)  ; or

(1g) 

R_7 and R_{11} independently from each other are hydrogen; C_1-C_{18}alkyl; or C_6-C_{12}aryl;

R_8, R_9 and R_{10}, independently from each other, are hydrogen; or a radical of formula

(1h)  , wherein, in formula (1f), at least one of the radicals R_8, R_9 and R_{10} are a radical of formula (1h);

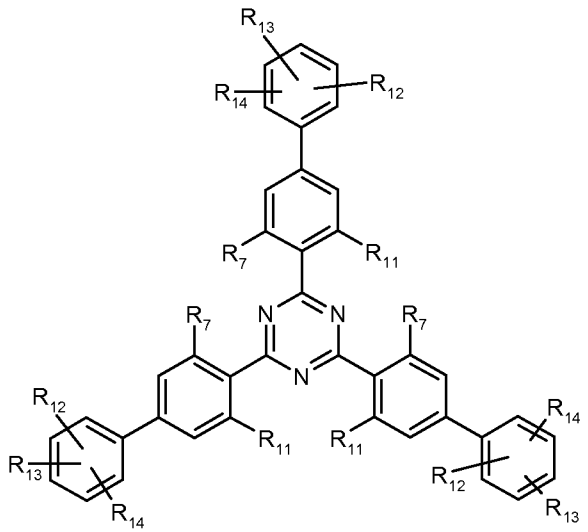
R_{12}, R_{13}, R_{14}, R_{15} and R_{16} independently from each other are hydrogen; hydroxy; halogen; C_1-C_{18}alkyl; C_1-C_{18}alkoxy; C_6-C_{12}aryl; biphenylyl; C_6-C_{12}aryloxy; C_1-C_{18}alkylthio; carboxy; -COOM; C_1-C_{18}-alkylcarboxyl; aminocarbonyl; or mono- or di-C_1-C_{18}alkylamino; C_1-C_{10}acylamino; -COOH;

M is an alkali metal ion;

x is 1 or 2; and

y is a number from 2 to 10.

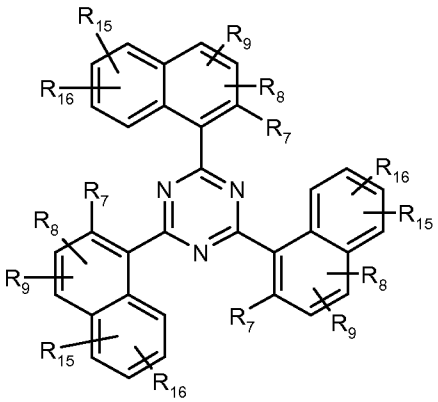
Most preferred triazine derivatives are compounds of formula

(2)  , wherein

R_7, R_{11}, R_{12}, R_{13} und R_{14} are defined as in formula (1f), (1g) or (1h), and most preferably compound of formula (2), wherein

$R_{7\ and}$ R_{11} are hydrogen.

Furthermore, triazine derivatives of formula

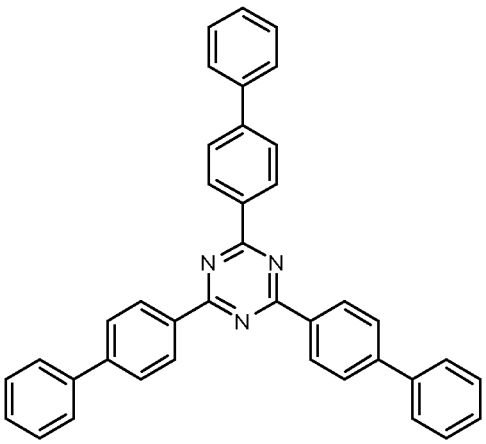
(3) 

are preferred, wherein

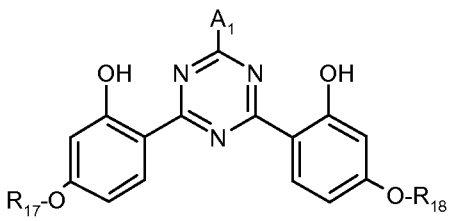
R_7, R_8, R_9, R_{15} and R_{16} are defined as in formula (1g), and most preferably compounds of formula (3), wherein

R_7, R_8, R_9, R_{15} and R_{16} are hydrogen; or, independently from each other, C_1-C_{18}alkyl.

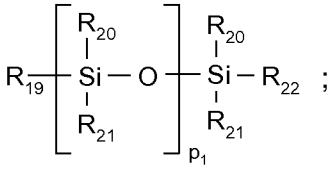
Most preferred as component (a) are triazine derivatives of formula

(4)  .

Further preferred triazine derivatives according to component (a) correspond to formula

(5)  , wherein

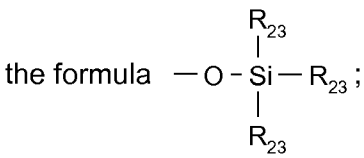
R_{17} and R_{18}, independently of one another, are C_1-C_{18}alkyl; C_2-C_{18}alkenyl; a radical of the formula $-CH_2-CH(-OH)-CH_2-O-T_1$; or a radical of the formula $-(CH_2)_{m_1}-O-(CH_2)_{m_2}-T_2$; a radical of the formula (5a)



;

R_{19} is a direct bond; a straight-chain or branched C_1-C_4alkylene radical or a radical of the formula $-C_{m_1}H_{2m_1}-$ or $-C_{m_1}H_{2m_1}-O-$;

R_{20}, R_{21} and R_{22}, independently of one another, are C_1-C_{18}alkyl; C_1-C_{18}alkoxy or a radical of the formula



;

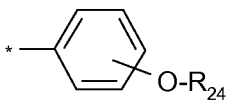
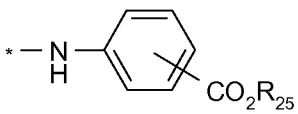
R_{23} is C_1-C_5alkyl;

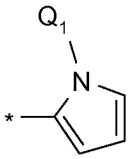
T_1 and T_2, independently from each other, are hydrogen; or C_1-C_8alkyl;

m_1, m_2 and m_3, independently of one another, are 1 to 4;

p_1 is 0; or a number from 1 to 5;

A_1 is a radical of the formula

(5b) , (5c)  ; or of the formula

(5d) 

R_{24} is hydrogen; C_1-C_{10}alkyl, $-(CH_2CHR_{26}-O)_{n_1}-R_{25}$; a $-CH_2-CH(-OH)-CH_2-O-T_1$; or radical of the formula $-(CH_2)_{m_1}-O-(CH_2)_{m_2}-T_2$

R_{25} is hydrogen; M; C_1-C_5alkyl; or a radical of the formula $-(CH_2)_{m_2}-O-T_1$;

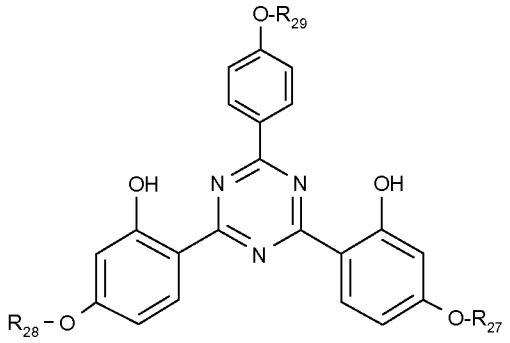
R_{26} is hydrogen; or methyl;

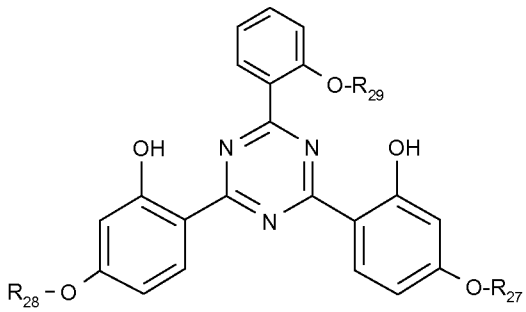
Q_1 C_1-C_{18}alkyl;

M is a metal cation; and

n_1 is 1-16.

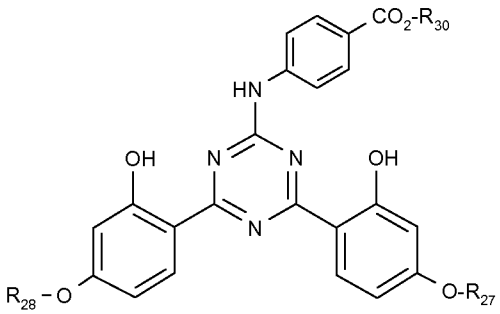
Further preferred triazine derivatives according to component are compounds of formulae

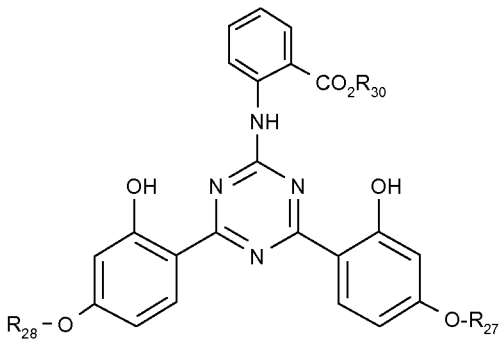
(5e) 

, (5f) 

,

the formula

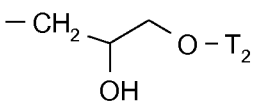
(5g) 

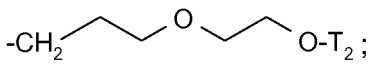
; (5h) 

in which

R_{27} and R_{28}, independently of one another, are C_3-C_{18}alkyl; or -CH_2-CH(-OH)-CH_2-O-T_1;

R_{30} is C_1-C_{10}alkyl or a radical of the formula

(5a$_1$) 

or the formula (5a$_2$) 

;

R_{30} is hydrogen; M; C_1-C_5alkyl; -NH-C_1-C_5alkyl, preferably -NH-tert.alkyl; or a radical of the formula -$(CH_2)_m$-O-T_2;

T_1 and T_2, independently of one another, are hydrogen; or C_1-C_5alkyl; and

m is 1 to 4.

Uppermost of interest are compounds of the formulae (5e) and (5f), in which

R_{27} and R_{28}, independently of one another, are C_3-C_{18}alkyl; or -CH_2-CH(-OH)-CH_2-O-T_1;

R_{29} is C_1-C_{10}alkyl;

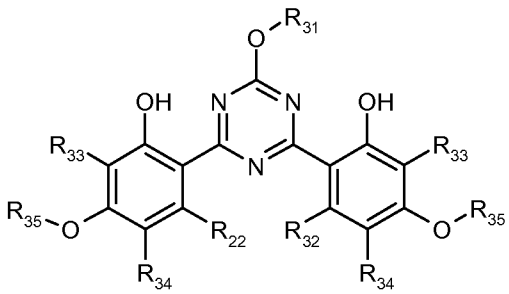
and compounds of the formulae (5g) and (5h), in which

R_{27} and R_{28}, independently of one another, are C_3-C_{18}alkyl or -CH_2-CH(-OH)-CH_2-O-T_1; and

T_1 is hydrogen; or C_1-C_5alkyl.

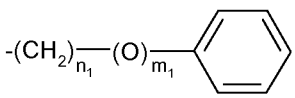
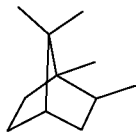
Very particularly preferred in this case are triazine compounds of the formula (5e) - (5h), in which R_{27} and R_{28} have the same meaning.

Furthermore, interesting triazines correspond to the formula

(6) 

in which

R_{31} is C_1-C_{30}alkyl; C_2-C_{30}alkenyl; unsubstituted or C_1-C_5alkyl-mono- or polysubstituted C_5-C_{12}cycloalkyl, C_1-C_5alkoxy-C_1-C_{12}alkyl; amino- C_1-C_{12}alkyl; C_1-C_5monoalkylamino-C_1-C_{12}alkyl; C_1-C_5dialkylamino-C_1-C_{12}alkyl; a radical of the

formula (6a)  ; or (6b)  ;

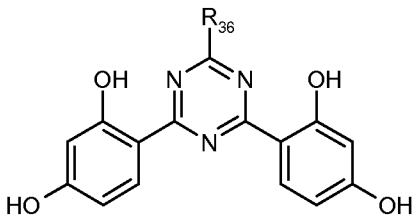
R_{32}, R_{33} and R_{34}, independently of one another, are hydrogen;, hydroxyl; C_1-C_{30}alkyl; or C_2-C_{30}alkenyl;

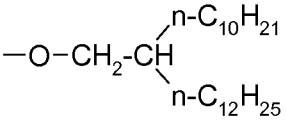
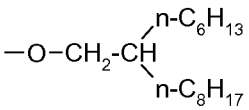
R_{35} is hydrogen; or C_1-C_5alkyl;

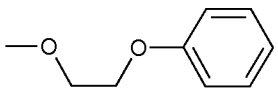
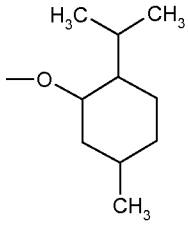
m_1 is 0 or 1; and

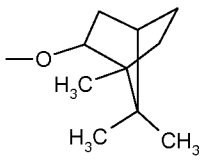
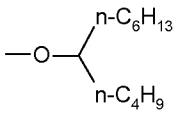
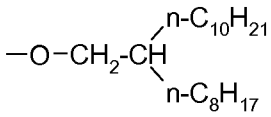
n_1 is 1 to 5.

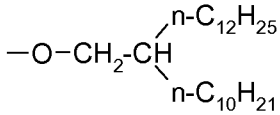
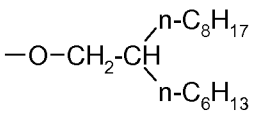
Preferred compounds correspond to the formula

(7)  , wherein

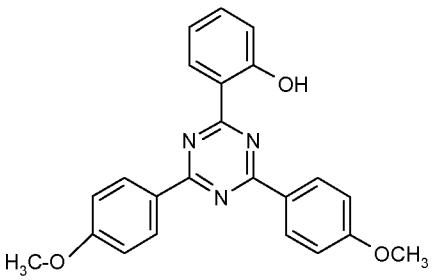
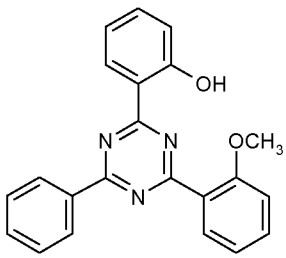
R_{36} is  ;-O-iso-$C_{18}H_{38}$;  -O-n-$C_{18}H_{37}$; or

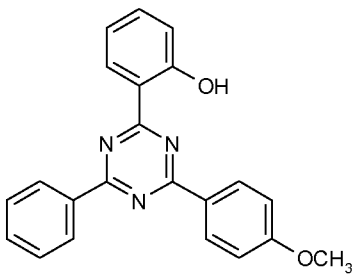
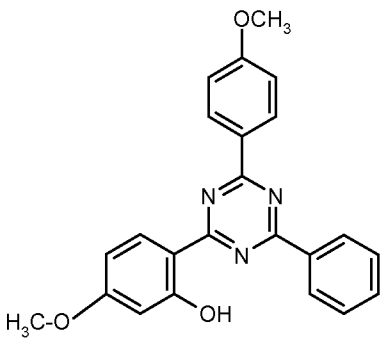
-O-2-ethylhexyl; -O-$(CH_2)_3$-$N(C_2H_5)_2$;;  ;  ;

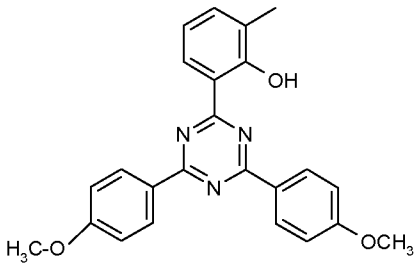
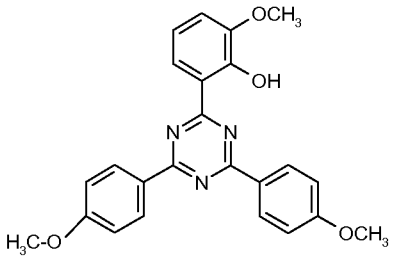
 ;  ; -O-n-$C_{18}H_{37}$;  ;

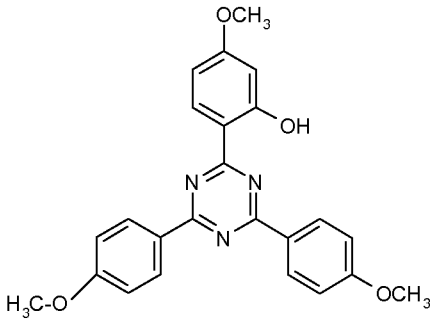
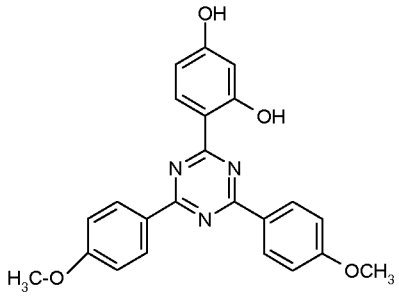
 ; or  .

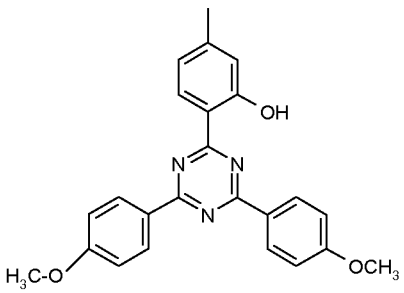
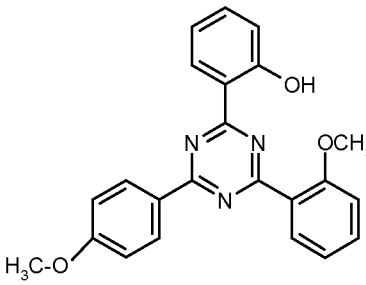
Further preferred triazine derivatives according to component (a) are those compounds having one of the formulae

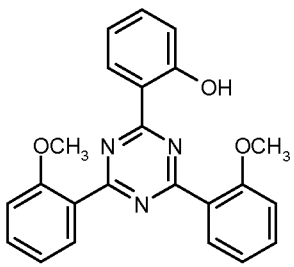
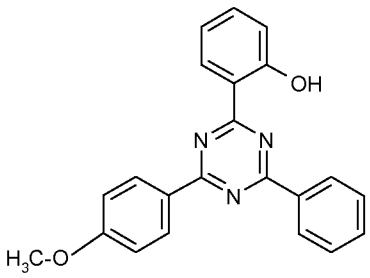
(8)  ; (9)  ;

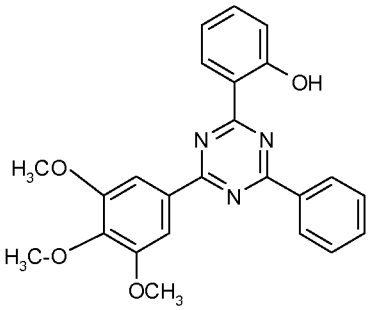
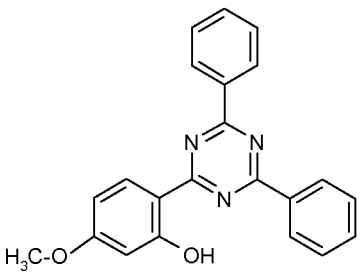
(10)  ; (11)  ;

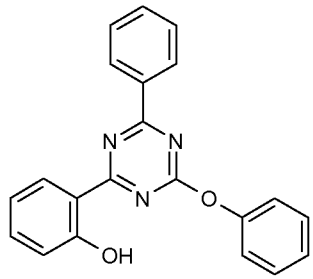
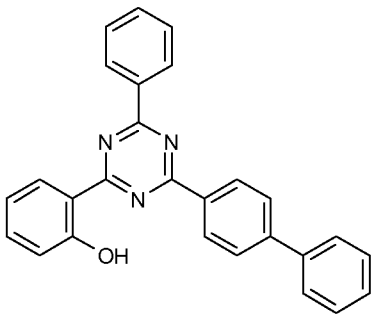
(12)  ; (13)  ;

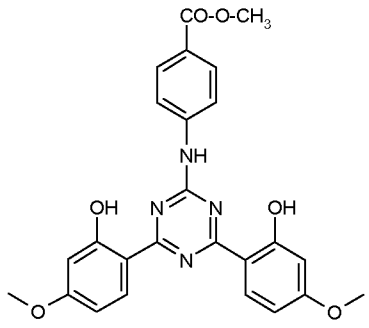
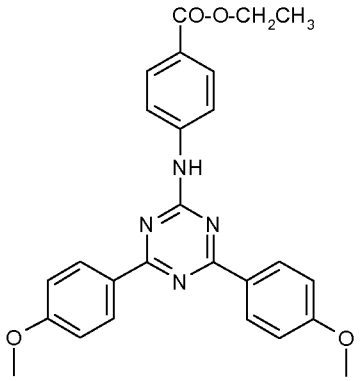
(14)  ; (15)  ;

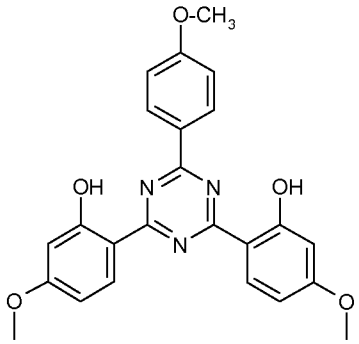
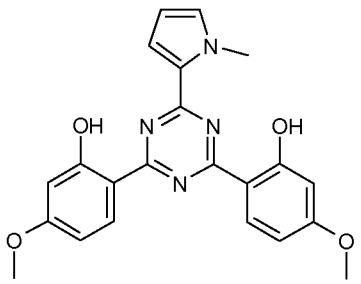
(16)  ; (17)  ;

(18)  ; (19)  ;

(20)  ; (21)  ;

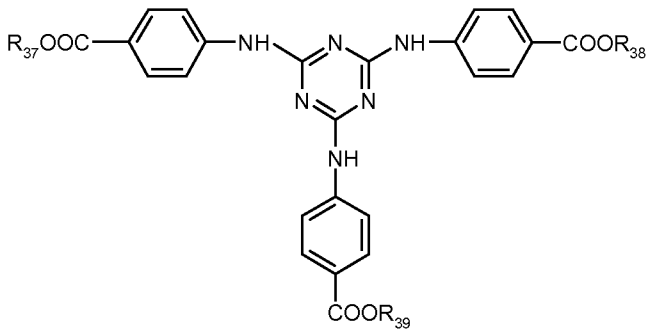
(22)  ; (23)  ;

(24)  ; (25)  ;

(26)  ; and (27)  ;

as well as 2,4,6-tris(diisobutyl-4'-aminobenzalmalonate)-s-triazine and 2,4-bis(diisobutyl-4-aminobenzalmalonate)-6-(4'-aminobenzylidenecamphor)-s-triazine.

Particularly preferred compounds of formula (1) are those having the formula:

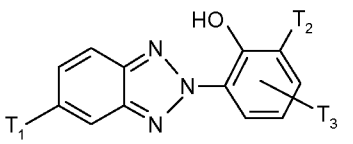
(28)  , wherein

R_{37}, R_{38} and R_{39}, independently from each other are hydrogen; an alkali metal; or an ammonium group $N^+(R_{40})_4$;

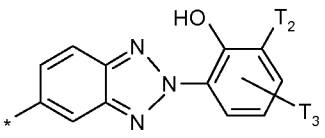
R_{40} is hydrogen; or an organic radical; C_1-C_3alkyl; or a polyoxyethylene radical which contains from 1 to 10 ethylene oxide units and the terminal OH group of which may be etherified by a C_1-C_3alcohol.

In relation to the compounds of formula (28), when R_{37}, R_{38} and R_{39} is an alkali metal it is preferably potassium or, especially sodium; when R_{37}, R_{38} and R_{39} is a group $N(R_{40})_4$ in which R_{30} has its previous significance, it is preferably a mono-, di- or tri-C_1-C_4alkylammonium salt, a mono-, di- or tri-C_2-C_4alkanolammonium salt or a C_1-C_3alkyl ester thereof; when R_{40} is a C_1-C_3alkyl group, it is preferably a C_1-C_2alkyl group, more preferably a methyl group; and when R_{30} is polyoxyethylene group, this preferably contains from 2-6 ethylene oxide units.

One preferred class of benzotriazole micronized organic UV absorbers is that having the formula

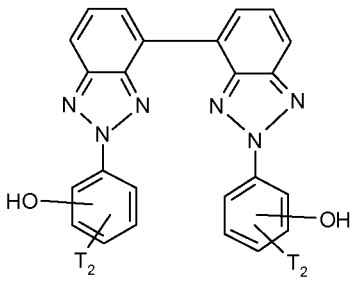
(29)  , wherein

T_1 is C_1-C_3alkyl or, preferably, hydrogen; or a radical of formula

(29a)  ; and

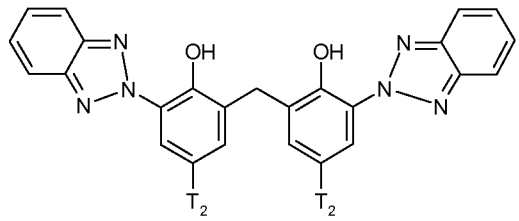
T_2 and T_3, independently from each other are C_1-C_{12}alkyl, preferably i-octyl; or C_1-C_4alkyl substituted by phenyl, preferably α,α-dimethylbenzyl.

A further preferred class of benzotriazole micronized organic UV absorbers corresponds to the formula

(30)  , wherein

T_2 has its previous significance.

A still further preferred class of benzotriazole micronized organic UV absorbers corresponds to the formula

(31)  , wherein

T_2 is hydrogen; C_1-C_{12}alkyl, preferably iso-octyl, or C_1-C_4alkyl substituted by phenyl, preferably α,α-dimethylbenzyl.

A preferred class of vinyl group-containing amide micronized organic UV absorbers corresponds to the formula:

(32) R_{41}-$(Y)_m$-CO-$C(R_{42})$=$C(R_{43})$-$N(R_{44})(R_{45})$, wherein

R_{41} is C_1-C_3alkyl, preferably C_1-C_2alkyl, or phenyl optionally substituted by one, two or three substituents selected from OH, C_1-C_3alkyl, C_1-C_3alkoxy or CO-OR_{46},

R_{46} C_1-C_3alkyl;

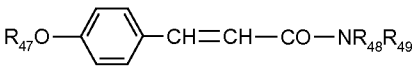
R_{42}, R_{43}, R_{44} and R_{45} are the same or different and each is C_1-C_3alkyl, preferably C_1-C_2alkyl; or hydrogen;

Y is -NH- ; or -O-; and

m is 0; or 1.

Preferred compounds of formula (32) are 4-methyl-3-penten-2-one, ethyl-3-methylamino-2-butenoate, 3-methylamino-1-phenyl-2-buten-1-one and 3-methylamino-1-phenyl-2-buten-1-one.

A preferred class of cinnamic acid amide micronized organic UV absorbers corresponds to the formula:

(33)  , wherein

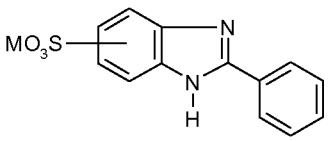
R_{47} is hydroxy or C_1-C_4alkoxy, preferably methoxy or ethoxy;

R_{48} is hydrogen or C_1-C_4alkyl, preferably methyl or ethyl; and

R_{49} is -$(CONH)_m$-phenyl in which m is 0 or 1 and the phenyl group is optionally substituted by one, two or three substituents selected from OH, C_1-C_3alkyl, C_1-C_3alkoxy or CO-$OR_{50;}$ and

R_{50} is C_1-C_4alkyl.

A preferred class of sulfonated benzimidazole micronized organic UV absorbers corresponds to the formula

(34)  , in which

M is hydrogen; or an alkali metal, preferably sodium, an alkaline earth metal, such as magnesium or calcium, or zinc.

Further preferred classes of micronized or micronizable UV absorbers used for the present invention are:

- p-aminobenzoic acid derivatives, typically 2-ethylhexyl-4-dimethylaminobenzoate
- salicylic acid derivatives, typically 2-ethylhexyl salicylate; homosalates; and isopropyl sylicylates;
- benzophenone derivatives, typically 2-hydroxy-4-methoxybenzophenone;
- dibenzoylmethane derivatives, typically 1-(4-tert-butylphenyl)-3-(4-methoxyphenyl)-propane-1,3-dione;
- diphenylacrylates, typically 2-ethylhexyl-2-cyano-3,3-diphenylacrylate and 3-(benzo-furanyl)-2-cyanoacrylate;

- 3-imidazol-4-yl-acrylic acid and 3-imidazol-4-yl-acrylate;
- benzofurane derivatives, preferably 2-(p-aminophenyl)benzofuran derivatives, disclosed in EP-A-582 189, US-A-5 338 539, US-A-5 518 713 and EP-A-613 893;
- polymeric UV absorbers, such as the benzylidenemalonate derivatives described, inter alia in EPA-709 080;
- cinnamic acid derivatives, typically the 2-ethylhexyl-4-methoxycinnamate or isoamylate or cinnamic acid derivatives disclosed, inter alia, in US-A-5 601 811 and WO 97/00851;
- camphor derivatives, typically 3-(4'-methyl)benzylidenebornan-2-one, 3-benzylidene-bornan-2-one, N-[2(and 4)-2-oxyborn-3-ylidenemethyl)benzyl]acrylamide polymer, 3-(4'-trimethylammonium)benzylidenebornan-2-one methylsulfate, 3,3'-(1,4-phenylenedimethine)-bis(7,7-dimethyl-2-oxobicyclo-[2.2.1]heptane-1-methanesulfonic acid) and the salts thereof, 3-(4'-sulfo)benzylidenebornan-2-one and the salts thereof;
- 2-phenylbenzimidazole-5-sulfonic acids and the salts thereof; and
- menthyl-o-aminobenzoate.

The micronized organic UV absorber, component (a), is preferably produced by the method described in GB-A-2303549, namely by a process which comprises grinding the corresponding organic UV absorber, in coarse particle form, in a grinding apparatus, in the presence of 1 to 50%, preferably 5 to 40% by weight, based on the micronized organic UV absorber, of an alkyl polyglucoside having the formula $C_nH_{2n+1}O(C_6H_{10}O_5)_xH$, in which n is an integer ranging from 8 to 16 and x is the mean polymerization level of the glucoside moiety ($C_6H_{10}O_5$) and ranges from 1.4 to 1.6, or an ester thereof.

Any known process suitable for the preparation of microparticles can be used for the preparation of the micronised UV absorbers, for example wet-milling, wet-kneading, spray-drying from a suitable solvent, by the expansion according to the RESS process (Rapid Expansion of Supercritical Solutions), by reprecipitation from suitable solvents, including supercritical fluids (GASR process = Gas Anti-Solvent Recrystallization / PCA process = Precipitation with Compressed Anti-solvents).

The micronized UV absorbers of component (a) so obtained usually have an average particle size from 0.02 to 2, preferably from 0.03 to 1.5, and more especially from 0.05 to 1.0 micrometer.

The micronizable UV absorbers according to component (a) can also be used as dry substrates in powder form.

The sunscreen composition according to the present invention may additionally contain one or more than one further non-micronized UV filter or UV absorbers as listed in Tables 1 and 2.

The non-micronized UV absorbers as described in Tables 1 and 2 below may be added to the sunscreen composition according to the present invention in amounts from 0.01 to 25 % based on weight. One or more of these UV absorbers can be used, *inter alia*, to improve the solubility or to increase UV absorption of the instant sunscreen composition.

Table 1. Suitable non-micronized UV filter substances which can be used according to the present invention
p-aminobenzoic acid derivatives, for example 4-dimethylaminobenzoic acid 2-ethylhexyl ester;
salicylic acid derivatives, for example salicylic acid 2-ethylhexyl ester;
benzophenone derivatives, for example 2-hydroxy-4-methoxybenzophenone and its 5-sulfonic acid derivative;
dibenzoylmethane derivatives, for example 1-(4-tert-butylphenyl)-3-(4-methoxyphenyl)-propane-1,3-dione;
diphenylacrylates, for example 2-ethylhexyl 2-cyano-3,3-diphenylacrylate, and 3-(benzo-furanyl) 2-cyanoacrylate;
3-imidazol-4-ylacrylic acid and esters;
benzofuran derivatives, especially 2-(p-aminophenyl)benzofuran derivatives, described in EP-A-582 189, US-A-5 338 539, US-A-5 518 713 and EP-A-613 893;
polymeric UV absorbers, for example the benzylidene malonate derivatives described in EP-A-709 080;
cinnamic acid derivatives, for example the 4-methoxycinnamic acid 2-ethylhexyl ester and isoamyl ester or cinnamic acid derivatives described in US-A-5 601 811 and WO 97/00851;
camphor derivatives, for example 3-(4'-methyl)benzylidene-bornan-2-one, 3-benzylidene-bornan-2-one, N-[2(and 4)-2-oxyborn-3-ylidene-methyl)-benzyl]acrylamide polymer, 3-(4'-trimethylammonium)-benzylidene-bornan-2-one methyl sulfate, 3,3'-(1,4-phenylenedimethine)-bis(7,7-dimethyl-2-oxo-bicyclo[2.2.1]heptane-1-methanesulfonic acid) and salts, 3-(4'-sulfo)benzylidene-bornan-2-one and salts; camphorbenzalkonium methosulfate;
hydroxyphenyltriazine compounds, for example 2-(4'-methoxyphenyl)-4,6-bis(2'-hydroxy-4'-n-octyloxyphenyl)-1,3,5-triazine; 2,4-bis{[4-(3-(2-propyloxy)-2-hydroxy-propyloxy)-2-hydroxy]-phenyl}-6-(4-methoxyphenyl)-1,3,5-triazine; 2,4-bis{[4-(2-ethyl-hexyloxy)-2-hydroxy]-phenyl}-6-[4-(2-methoxyethyl-carboxyl)-phenylamino]-1,3,5-triazine; 2,4-bis{[4-

Table 1. Suitable non-micronized UV filter substances which can be used according to the present invention
(tris(trimethylsilyloxy-silylpropyloxy)-2-hydroxy]-phenyl}-6-(4-methoxyphenyl)-1,3,5-triazine; 2,4-bis{[4-(2"-methylpropenyloxy)-2-hydroxy]-phenyl}-6-(4-methoxyphenyl)-1,3,5-triazine; 2,4-bis{[4-(1',1',1',3',5',5',5'-heptamethyltrisilyl-2"-methyl-propyloxy)-2-hydroxy]-phenyl}-6-(4-methoxyphenyl)-1,3,5-triazine; 2,4-bis{[4-(3-(2-propyloxy)-2-hydroxy-propyloxy)-2-hydroxy]-phenyl}-6-[4-ethylcarboxy)-phenylamino]-1,3,5-triazine;
benzotriazole compounds, for example 2,2'-methylene-bis(6-(2H-benzotriazol-2-yl)-4-(1,1,3,3-tetramethylbutyl)-phenol;
trianilino-s-triazine derivatives, for example 2,4,6-trianiline-(p-carbo-2'-ethyl-1'-oxy)-1,3,5-triazine and the UV absorbers disclosed in US-A-5 332 568, EP-A-517 104, EP-A-507 691, WO 93/17002 and EP-A-570 838;
2-phenylbenzimidazole-5-sulfonic acid and salts thereof;
menthyl o-aminobenzoates;
physical sunscreens coated or not as titanium dioxide, zinc oxide, iron oxides, mica, MnO, Fe_2O_3, Ce_2O_3, Al_2O_3, ZrO_2. (surface coatings: polymethylmethacrylate, methicone (methylhydrogenpolysiloxane as described in CAS 9004-73-3), dimethicone, isopropyl titanium triisostearate (as described in CAS 61417-49-0), metal soaps as magnesium stearate (as described in CAS 4086-70-8), perfluoroalcohol phosphate as C9-15 fluoroalcohol phosphate (as described in CAS 74499-44-8; JP 5-86984 , JP 4-330007)). The primary particle size is an average of 15nm–35nm and the particle size in dispersion is in the range of 100nm – 300nm.
aminohydroxy-benzophenone derivatives disclosed in DE 10011317, EP 1133980 and EP 1046391
phenyl-benzimidazole derivatives as disclosed in EP 1167358
the UV absorbers described in “Sunscreens”, Eds. N.J. Lowe, N.A.Shaath, Marcel Dekker, Inc. , New York and Basle or in Cosmetics & Toiletries (107), 50ff (1992) also can be used as additional UV protective substances.

Table 2: Suitable specific non-micronized UV filter substances and adjuvants which can be used according to the present invention

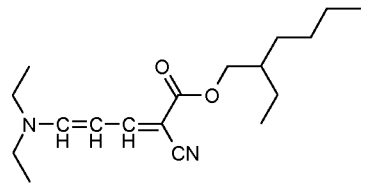
No.	Chemical Name	CAS No.
1	(+/-)-1,7,7-trimethyl-3-[(4-methylphenyl)methylene]bicyclo-[2.2.1]heptan-2-one; p-methyl benzylidene camphor	36861-47-9
2	1,7,7-trimethyl-3-(phenylmethylene)bicyclo[2.2.1]heptan-2-one; benzylidene camphor	15087-24-8
3	(2-Hydroxy-4-methoxyphenyl)(4-methylphenyl)methanone	1641-17-4
4	2,4-dihydroxybenzophenone	131-56-6
5	2,2',4,4'-tetrahydroxybenzophenone	131-55-5
6	2-Hydroxy-4-methoxy benzophenone;	131-57-7
7	2-Hydroxy-4-methoxy benzophenone-5-sulfonic acid	4065-45-6

Table 2: Suitable specific non-micronized UV filter substances and adjuvants which can be used according to the present invention

No.	Chemical Name	CAS No.
8	2,2'-dihydroxy-4,4'-dimethoxybenzophenone	131-54-4
9	2,2'-Dihydroxy-4-methoxybenzophenone	131-53-3
10	Alpha-(2-oxoborn-3-ylidene)toluene-4-sulphonic acid and its salts; Mexoryl SL	56039-58-8
11	1-[4-(1,1-dimethylethyl)phenyl]-3-(4-methoxyphenyl)propane-1,3-dione; avobenzone	70356-09-1
12	Methyl N,N,N-trimethyl-4-[(4,7,7-trimethyl-3-oxobicyclo[2,2,1]hept-2-ylidene)methyl]anilinium sulphate; Mexoryl SO	52793-97-2
22	3,3,5-Trimethyl cyclohexyl-2-hydroxy benzoate; homosalate	118-56-9
23	Isopentyl p-methoxycinnamate; isoamyl methoxy cinnamate	71617-10-2
27	Menthyl-o-aminobenzoate	134-09-8
28	Menthyl salicylate	89-46-3
29	2-Ethylhexyl 2-cyano,3,3-diphenylacrylate; octocrylene	6197-30-4
30	2- ethylhexyl 4- (dimethylamino)benzoate	21245-02-3
31	2- ethylhexyl 4- methoxycinnamate; octyl methoxy cinnamate	5466-77-3
32	2- ethylhexyl salicylate	118-60-5
33	Benzoic acid, 4, 4', 4"- (1, 3, 5- triazine- 2, 4, 6- triyltriimino)tris-, tris(2-ethylhexyl)ester; 2,4,6-Trianilino-(p-carbo-2'-ethylhexyl-1'-oxi)-1,3,5-triazine; octyl triazone	88122-99-0
34	4- aminobenzoic acid	150-13-0
35	Benzoic acid, 4-amino-, ethyl ester, polymer with oxirane	113010-52-9
38	2- phenyl- 1H- benzimidazole- 5- sulphonic acid; phenylbenzimidazolsulfonic acid	27503-81-7
39	2-Propenamide, N-[[4-[(4,7,7-trimethyl-3-oxobicyclo[2.2.1]hept-2-ylidene)methyl]phenyl]methyl]-, homopolymer	147897-12-9
40	Triethanolamine salicylate	2174-16-5
41	3, 3'-(1,4-phenylenedimethylene)bis[7, 7-dimethyl- 2-oxo-bicyclo[2.2.1]heptane-1 methanesulfonic acid]; Cibafast H	90457-82-2
42	Titanium dioxide	13463-67-7
44	Zinc oxide	1314-13-2
45	2,4-bis{[4-(2-ethylhexyloxy)-2-hydroxy]-phenyl}-6-(4-methoxyphenyl)-(1,3,5)-triazine; Tinosorb S	187393-00-6
46	1H-Benzimidazole-4,6-disulfonic acid, 2,2'-(1,4-phenylene)bis-, disodium salt	180898-37-7

Table 2: Suitable specific non-micronized UV filter substances and adjuvants which can be used according to the present invention

No.	Chemical Name	CAS No.
47	Benzoic acid, 4,4'-[[6-[[4-[[(1,1-dimethylethyl)amino]carbonyl]phenyl]amino]1,3,5-triazine-2,4-diyl]diimino]bis-, bis(2-ethylhexyl)ester; diethylhexyl butamido triazone; Uvasorb HEB	154702-15-5
48	Phenol, 2-(2H-benzotriazol-2-yl)-4-methyl-6-[2-methyl-3-[1,3,3,3-tetramethyl-1-[(trimethylsilyl)oxy]disiloxanyl]propyl]-; drometrizole trisiloxane; Mexoryl XL	155633-54-8
49	Dimethicodiethylbenzalmalonate; Polysilicone 15; Parsol SLX	207574-74-1
50	Benzenesulfonic acid, 3-(2H-benzotriazol-2-yl)-4-hydroxy-5-(1-methylpropyl)-, monosodium salt ; Tinogard HS	92484-48-5
51	Benzoic acid, 2-[4-(diethylamino)-2-hydroxybenzoyl]-, hexyl ester; Uvinul a plus	302776-68-7
52	1-Dodecanaminium, N-[3-[[4-(dimethylamino)benzoyl]amino]propyl]-N,N-dimethyl-, salt with 4-methylbenzenesulfonic acid (1:1); Escalol HP610	156679-41-3
53	1-Propanaminium, N,N,N-trimethyl-3-[(1-oxo-3-phenyl-2-propenyl)-amino]-, chloride	177190-98-6
54	1H-Benzimidazole-4,6-disulfonic acid, 2,2'-(1,4-phenylene)bis-	170864-82-1
55	1,3,5-Triazine, 2,4,6-tris(4-methoxyphenyl)-	7753-12-0
56	1,3,5-Triazine, 2,4,6-tris[4-[(2-ethylhexyl)oxy]phenyl]-	208114-14-1
57	1-Propanaminium, 3-[[3-[3-(2H-benzotriazol-2-yl)-5-(1,1-dimethylethyl)-4-hydroxyphenyl]-1-oxopropyl]amino]-N,N-diethyl-N-methyl-, methyl sulfate (salt)	340964-15-0
58	2-Propenoic acid, 3-(1H-imidazol-4-yl)-	104-98-3
59	Benzoic acid, 2-hydroxy-, [4-(1-methylethyl)phenyl]methyl ester	94134-93-7
60	1,2,3-Propanetriol, 1-(4-aminobenzoate); glyceryl PABA	136-44-7
61	Benzeneacetic acid, 3,4-dimethoxy-a-oxo-	4732-70-1
62	2-Propenoic acid, 2-cyano-3,3-diphenyl-, ethyl ester	5232-99-5
63	Anthralinic acid, p-menth-3-yl ester	134-09-8
64	2,2'-bis(1,4-phenylene)-1H-benzimidazole-4,6-disulphonic acid mono sodium salt or Disodium phenyl dibenzimidazole tetrasulfonate or Neoheliopan AP	349580-12-7,
65	1,3,5-Triazine-2,4,6-triamine, N,N'-bis[4-[5-(1,1-dimethylpropyl)-2-benzoxazolyl]phenyl]-N''-(2-ethylhexyl)- or Uvasorb K2A	288254-16-0
66	Merocyanine derivatives as described in WO 2004006878 and in IPCOM000022279D	

Table 2: Suitable specific non-micronized UV filter substances and adjuvants which can be used according to the present invention		
No.	Chemical Name	CAS No.
67		
68	sterols (cholesterol, lanosterol, phytosterols), as described in WO0341675	
69	mycosporines and/or mycosporine-like amino acids as described in WO2002039974, e.g. Helioguard 365 from Milbelle AG, isolated mycosporine like amino acids from the red alga porphyra umbilicalis (INCI: Porphyra Umbilicalis) that are encapsulated into liposomes,)	
70	alpha-lipoic-acid as described in DE 10229995	
71	synthetic organic polymers as described in EP 1371358, [0033]-[0041]	
72	phyllosilicates as described in EP 1371357 [0034]-[0037]	
73	silica compounds as described in EP1371356, [0033]-[0041]	
74	inorganic particles as described in DE10138496 [0043]-[0055]	
75	latex particles as described in DE10138496 [0027]-[0040]	
76	1H-Benzimidazole-4,6-disulfonic acid, 2,2'-(1,4-phenylene)bis-, disodium salt ; Bisimidazylate; Neo Heliopan APC	180898-37-7

The UV screening agent of component (a) is present in the sunscreen composition in amounts from about 0.01 weight% to about 50 weight% based on the weight of the total composition. Additionally, the UV screening agent of component (a) is present in the sunscreen composition in amounts from about 0.1 weight% to about 30 weight% based on the weight of the total composition. Typically, UV screening agent of component (a) is present in the sunscreen composition in amounts from about 1 weight% to about 20 weight% based on the weight of the total composition. Typically, UV screening agent of component (a) is present in the sunscreen composition in amounts from about 1 weight% to about 5 weight% based on the weight of the total composition.

Typically, sunscreen formulations contain compositions of several UVA, UVB or broad-spectrum sunscreen actives: organic that are oil or water soluble, inorganic or organic particulates.

The term “effective amount” means for example the amount necessary to achieve the desired effect.

For the random copolymers of component b) formula (I), u+v+w+x+y+z = 100 weight percent relative to the total weight of the terpolymer.

The random terpolymers of component (b) formula (I) according to the instant invention are derived from at least three different monomers. Another aspect of the instant invention is the random terpolymers of component (b) formula (I) are derived from at least four different monomers.

The random terpolymers of component (b) formula (I) can be used in conjunction with other polymers or copolymer in a sunscreen formulation; for example, the polymers listed in US 6,409,998 and/or in US 2006/0104923.

Another embodiment of the instant invention for component b) formula (I) is that y is from about 0.1% to about 35% by weight based on the total weight of the terpolymer. Another embodiment of the instant invention for component b) formula (I) is that y is from about 1% to about 30% by weight based on the total weight of the terpolymer. Another embodiment of the instant invention for component b) formula (I) is that y is from about 5% to about 20% by weight based on the total weight of the terpolymer.

Another embodiment of the instant invention for component b) formula (I) is that v is from about 5% to about 70% by weight based on the total weight of the terpolymer. Another embodiment of the instant invention for component b) formula (I) is that v is from about 5% to about 60% by weight based on the total weight of the terpolymer. Another embodiment of the instant invention for component b) formula (I) is that v is from about 10% to about 60% by weight based on the total weight of the terpolymer.

Another embodiment of the instant invention for component b) formula (I) is that u is from about 5% to about 75% by weight based on the total weight of the terpolymer. Another embodiment of the instant invention for component b) formula (I) is that u is from about 5% to about 65% by weight based on the total weight of the terpolymer. Another embodiment of the

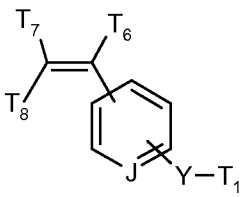
instant invention for component b) formula (I) is that u is from about 5% to about 60% by weight based on the total weight of the terpolymer.

Another embodiment of the instant invention for component b) formula (I) is that z is from about 0.1% to about 50% by weight based on the total weight of the terpolymer. Another embodiment of the instant invention for component b) formula (I) is that z is from about 1% to about 50% by weight based on the total weight of the terpolymer. Another embodiment of the instant invention for component b) formula (I) is that z is from about 1% to about 40% by weight based on the total weight of the terpolymer.

Another embodiment of the instant invention for component b) formula (I) is that x is from about 1% to about 40% by weight based on the total weight of the terpolymer. Another embodiment of the instant invention for component b) formula (I) is that x is from about 1% to about 30% by weight based on the total weight of the terpolymer. Another embodiment of the instant invention for component b) formula (I) is that x is from about 5% to about 25% by weight based on the total weight of the terpolymer.

Another embodiment of the instant invention for component b) formula (I) is that w is from about 0.1% to about 45% by weight based on the total weight of the terpolymer. Another embodiment of the instant invention for component b) formula (I) is that w is from about 1% to about 40% by weight based on the total weight of the terpolymer. Another embodiment of the instant invention for component b) formula (I) is that w is from about 5% to about 30% by weight based on the total weight of the terpolymer.

Another embodiment of the instant invention for component b) formula (I) is that M is derived from at least one monomer of formula

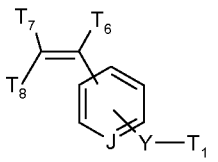
(II)  , wherein

T_6, T_7, and T_8 are methyl, ethyl or hydrogen; Y is a direct bond;

T_1 is hydrogen or C1-C4 alkyl; and

J is a carbon atom.

Another embodiment of the instant invention for component b) formula (I) is that M is derived from at least one monomer of formula

(II)  , wherein

T_6, T_7, and T_8 are methyl or hydrogen;

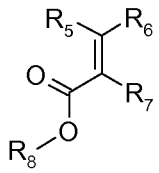
Y is a direct bond;

T_1 is hydrogen, methyl, or ethyl; and

J is a carbon atom.

Another embodiment of the instant invention for component b) formula (I) is that M is derived from at least one monomer selected from the group consisting of styrene, alpha-methyl-styrene, 2-vinyltoluene, 3-vinyltoluene, 4-vinyltoluene, ethylvinylbenzene and mixtures thereof.

Another embodiment of the instant invention for component b) formula (I) is T, D, and E are independently derived from at least one monomer of formula

(III)  , wherein

R_5, R_6 and R_7 may be the same or different and represent hydrogen or C_1-C_{12} alkyl;

R_8 is C_1-C_{18}alkyl, or C_6-C_{15}cycloalkyl; said substituted alkyl, or said cycloalkyl may also be substituted by one or more –OH and/or NH_2-groups; said alkyl or said cycloalkyl may be interrupted by one or more –O- groups and/or –N(H)- groups.

Another embodiment of the instant invention for component b) formula (I) is T, D, and E are independently derived from at least one monomer selected from the group consisting of methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, butyl (meth)acrylate, isobutyl (meth)acrylate, hexyl (meth)acrylate, cyclohexyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, octyl (meth)acrylate, decyl (meth)acrylate, dodecyl (meth)acrylate, dimethyl aminoethyl (meth)acrylate, isobornyl (meth)acrylate, stearyl (meth)acrylate, behenyl

(meth)acrylate, polypropylene glycol mono(meth)acrylate, glycidyl (meth)acrylate, polyethylene glycol mono(meth)acrylate, EO-PO-mono(meth)acrylate and mixtures thereof. The parentheses indicate that the monomers of formula (III) are esters based on either methacrylic acid or acrylic acid.

Another embodiment of the instant invention is random terpolymers of component (b) formula (I) that consist of a polymer chain having attached thereto a monomer derived from G containing heterocyclic groups with basic nitrogen atoms. Such a chain can be obtained either by polymerizing-in compounds containing both a vinyl and such a heterocyclic group, or by later attaching a heterocyclic group to the polymer chain containing corresponding reactive groups.

Preferred are heterocyclic groups with basic nitrogen groups having a pKa value of 2 to 14, more in particular 5 to 14 and most preferably 5 to 12. These pKa values relate to the measurement thereof at 25C in a 0.01 molar concentration in water. These basic groups impart to the random terpolymers according to the invention a basicity. These basic groups allow the random terpolymers to form organic and/or inorganic salts too. The random terpolymers can therefore be used in the form of such salts.

These salts are obtained by neutralization of the polymer with organic acids, e.g., aromatic acids having not more than 25 carbon atoms or aliphatic and cycloaliphatic acids having not more than 22 carbon atoms. Preference is given to salts of the polymer with organic monocarboxylic acids. Inorganic acids are, for example, hydrochloric acid, hydrobromic acid, sulfurous acid, sulfuric acid, and the like.

Suitable compounds of component b formula (I) G to be polymerized-in are selected from the group consisting of vinylimidazole, 2-vinylpyridine, 4-vinylpyridine, 2-methyl-N-vinylimidazole, vinylpyrrolidone, vinylcarbazole and mixtures thereof.

Suitable compounds containing at least one basic nitrogen atom and capable of being attached to a polymer chain of formula (I) G are described in, among others, EP-A 154,678.

Suitable compounds containing at least one basic nitrogen atom and capable of being attached to a polymer chain of formula (I) G are selected from the group consisting of 1-(2-

hydroxyethyl)-pyrrolidine, 2-(1-pyrrolidyl)-ethylamine, 2-(1-piperidyl)-ethylamine, 1-(2-hydroxyethyl)-piperidine, 1-(2-aminopropyl)-piperidine, N-(2-hydroxyethyl)-hexamethylen-imine, 4-(2-hydroxyethyl)-morpholine, 2-(4-morpholinyl)-ethylamine, 4-(3-aminopropyl)-morpholine, 1-(2-hydroxyethyl)-piperazine, 1-(2-aminoethyl)-piperazine, 1-(2-hydroxyethyl)-2-alkylimidazoline, 1-(3-aminopropyl)-imidazole, (2-aminoethyl)-pyridine, (2-hydroxyethyl)-pyridine, (3-hydroxypropyl)-pyridine, (hydroxymethyl)-pyridine, N-methyl-2-hydroxy-methyl-piperidine, 1-(2-hydroxyethyl)-imidazole, 2-amino-6-methoxybenzothiazole, 4-aminomethyl-pyridine, 4-amino-2-methoxypyrimidine, 2-mercaptopyrimidine, 2-mercapto-benzimidazole, 3-mercapto-1,2,4-triazole, 3-amino-1,2,4-triazole, 2-isopropyl-imidazole, 2-ethyl-imidazole, 4-methyl-imidazole, 2-methyl-imidazole, 2-ethyl-4-methyl-imidazole, 2-phenyl-imidazole, 4-nitro-imidazole and mixtures thereof.

Another embodiment of the instant invention for component b) formula (I) H is derived from at least one monomer selected from the group consisting of toluene diisocyanate (all isomers), 4,4'-diphenylmethane diisocyanate, tolidine diisocyanate, dianisidine diisocyanate, m-xylylene diisocyanate, p-phenylene diisocyanate, m-phenylene diisocyanate, 1-chloro-2,4-phenylene diisocyanate, 3,3'-dimethyl-4,4'-bisphenylene diisocyanate, 4,4'-bisphenylene diisocyanate, 4,4'-bis(2-methoxyisocyanatophenyl)methane, 4,4'-diisocyanatodiphenyl ether, 3,3'-dichloro-4,4'-diisocyanatodiphenyl ether, 3,3'-dichloro-4,4'-diisocyanatodiphenyl methane, 4,4'-diisocyanatodibenzyl, 3,3'-dimethoxy-4,4'-diisocyanatodiphenyl, 2,2'-dimethyl-4,4'-diisocyanatodiphenyl, 2,2'-dichloro-5,5'-dimethoxy-4,4'-diisocyanatodiphenyl, 3,3'-dichloro-4,4'-diisocyanatodiphenyl, 1,2-ethane diisocyanate, 1,3-propane diisocyanate, 1,4-butane diisocyanate, 2-chloropropane-1,3-diisocyanate, pentamethylene diisocyanate, propylene-1,2-diisocyanate, 1,8-octane diisocyanate, 1,10-decane diisocyanate, 1,12-dodecane diisocyanate, 1,16-hexadecane diisocyanate 1,3- and 1,4-cyclohexane diisocyanate, 1,6-hexamethylene diisocyanate, 2,2,4- and 2,4,4-trimethylhexamethylene diisocyanate, diisocyanates or a mixture thereof dimer acid derived diisocyanate obtained from dimerized linoleic acid, 4,4'-dicyclohexylmethane diisocyanate, isophorone diisocyanate, 3-isocyanatomethyl-3,5,5-trimethylcyclohexyl diisocyanate, lysine methyl ester diisocyanate, m-tetramethylxylylene diisocyanate and mixtures thereof.

Another embodiment of the instant invention for component b) formula (I) is that H is derived from at least one monomer selected from the group consisting of toluene diisocyanate, 4,4'-diphenylmethane diisocyanate, tolidine diisocyanate, m-xylylene diisocyanate, p-phenylene

diisocyanate, m-phenylene diisocyanate, 1-chloro-2,4-phenylene diisocyanate, 3,3'-dimethyl-4,4'-bisphenylene diisocyanate, 4,4'-bisphenylene diisocyanate, 4,4'-bis(2-methoxyisocyanatophenyl)methane, 4,4'-diisocyanatodiphenyl ether, 4,4'-diisocyanatodibenzyl, 3,3'-dimethoxy-4,4'-diisocyanatodiphenyl, 2,2'-dimethyl-4,4'-diisocyanatodiphenyl, 2,2'-dichloro-5,5'-dimethoxy-4,4'-diisocyanatodiphenyl, 3,3'-dichloro-4,4'-diisocyanatodiphenyl, 1,3-propane diisocyanate, 1,4-butane diisocyanate, 2-chloropropane-1,3-diisocyanate, pentamethylene diisocyanate, propylene-1,2-diisocyanate, 1,8-octane diisocyanate, 1,10-decane diisocyanate, 1,12-dodecane diisocyanate, 1,16-hexadecane diisocyanate 1,3- and 1,4-cyclohexane diisocyanate, 1,6-hexamethylene diisocyanate, 2,2,4- and 2,4,4-trimethylhexamethylene diisocyanate, 4,4'-dicyclohexylmethane diisocyanate, isophorone diisocyanate, 3-isocyanatomethyl-3,5,5-trimethylcyclohexyl diisocyanate, lysine methyl ester diisocyanate, m-tetramethylxylylene diisocyanate and mixtures thereof.

The random terpolymers of formula (I) according to the instant invention maybe be crosslinked by multifunctional monomers. These multifunctional monomers are selected from the group consisting of divinyl benzene, trivinylbenzene, divinyltoluene, divinylpyridine, divinylnaphthalene divinylxylene, ethyleneglycol di(meth)acrylate, trimethylolpropane tri(meth)acrylate, diethyleneglycol divinyl ether, trivinylcyclohexane, allyl (meth)acrylate, diethyleneglycol di(meth)acrylate, propyleneglycol di(meth)acrylate, 2,2-dimethylpropane-1,3-di(meth)acrylate, 1,3-butylene glycol di(meth)acrylate, 1,4-butanediol di(meth)acrylate, 1,6-hexanediol di(meth)acrylate, tripropylene glycol di(meth)acrylate, triethylene glycol di(meth)acrylate, tetraethylene glycol di(meth)acrylate, polyethylene glycol di(meth)acrylates, polyethylene glycol 200 di(meth)acrylate, polyethylene glycol 600 di(meth)acrylate, ethoxylated bisphenol A di(meth)acrylate, poly(butanediol) di(meth)acrylate, pentaerythritol tri(meth)acrylate, trimethylolpropane triethoxy tri(meth)acrylate, glyceryl propoxy tri(meth)acrylate, pentaerythritol tetra(meth)acrylate, dipentaerythritol monohydroxypenta(meth)acrylate, divinyl silane, trivinyl silane, dimethyl divinyl silane, divinyl methyl silane, methyl trivinyl silane, diphenyl divinyl silane, divinyl phenyl silane, trivinyl phenyl silane, divinyl methyl phenyl silane, tetravinyl silane, dimethyl vinyl disiloxane, poly(methyl vinyl siloxane), poly(vinyl hydro siloxane), poly(phenyl vinyl siloxane), and mixtures thereof.

The weight-average molecular weight of the random terpolymer of component (b) formula (I) exhibits a weight-average molecular weight of about 500 Daltons to about 1,000,000 Daltons.

In another aspect of the instant invention, the weight-average molecular weight of the random terpolymer of component (b) formula (I) exhibits a weight-average molecular weight of about 500 Daltons to about 500,000 Daltons. In yet another aspect of the instant invention, the weight-average molecular weight of the random terpolymer of component (b) formula (I) exhibits a weight-average molecular weight of about 500 Daltons to about 100,000 Daltons. In still another aspect of the instant invention, the weight-average molecular weight of the random terpolymer of component (b) formula (I) exhibits a weight-average molecular weight of about 1000 Daltons to about 75,000 Daltons.

The random terpolymer of component (b) formula (I) is present in the sunscreen composition in amounts from about 0.01 weight% to about 50 weight% based on the weight of the total composition. In another aspect of the instant invention, the random terpolymer of component (b) formula (I) is present in the sunscreen composition in amounts from about 0.1 weight% to about 25 weight% based on the weight of the total composition. In still another aspect of the instant invention, the random terpolymer of component (b) formula (I) is present in the sunscreen composition in amounts from about 0.1 weight% to about 10 weight% based on the weight of the total composition.

Another embodiment of the instant invention are random terpolymers of component (b) formula (I) that contain less than 250 ppm of residual monomers. Another embodiment of the instant invention are random terpolymers of component (b) formula (I) that contain less than 200 ppm of residual monomers. Another embodiment of the instant invention are random terpolymers of component (b) formula (I) that contain less than 100 ppm of residual monomers. Another embodiment of the instant invention are random terpolymers of component (b) formula (I) that contain less than 50 ppm of residual monomers. Another embodiment of the instant invention are random terpolymers of component (b) formula (I) that contain less than 5 ppm of residual monomers.

The random terpolymers of formula (I) according to the instant invention are water-dispersible and can be distributed throughout the aqueous phase or the oil phase of the instant compositions or formulations.

The random terpolymers of component (b) formula (I) can be prepared in the conventional manner, e.g., by mass or solution polymerization. The polymerization in a solvent is preferred

in view of the controllability of the polymerization and the viscosity of the final product. Suitable solvents are DMSO, THF, DMF, ethyl, propyl, butyl, acetate, benzene, toluene, xylene, N-butanol, isobutanol, isopropanol, MEK, MIBK, acetone, etc.

The monomers are preferably polymerized using a radical reaction, by addition of peroxides, optionally in the presence of redox systems.

The polymerization time of the random terpolymer of component (b) formula (I) depends on the temperature and the desired final product properties but is preferably within the range of from 0.5 to 10 hours at temperatures ranging from about 50C to about 190C. The polymerization can be carried out continuously, discontinuously or semicontinuously. If it is preferred to obtain a polymer chain having random distribution of monomers, all of the monomers together will be preferably added to the reaction mixture. This may be done in one portion or in the course of time.

On the basis of the reactivity of the monomers, which is known, a skilled artisan can control the polymerization so as to obtain the desired distribution.

The sunscreen compositions according to the invention may also contain agents for tanning and/or for artificial tanning of the skin (self-tanning agents), such as, for example, dihydroxyacetone (DHA).

The sunscreen compositions according to the invention may also contain agents for lightening or brightening of the skin, such as, for example, kojic acid, or arbutin.

The compositions of the invention may further comprise, cosmetically acceptable ingredients and adjuvants selected, in particular, from among fatty substances, organic solvents, thickeners, demulcents, opacifiers, colorants, effect pigments, stabilizers, emollients, antifoaming agents, moisturizing agents, antioxidants, vitamins, peptides, amino acids, botanical extracts, particulates, perfumes, preservatives, polymers, fillers, sequestrants, propellants, alkalinizing or acidifying agents or any other ingredient customarily formulated into cosmetics, in particular for the production of anti-sun/sunscreen compositions.

The fatty substances may be an oil or a wax or mixtures thereof, and they also comprise fatty acids, fatty alcohols and esters of fatty acids. The oils may be selected from among animal, vegetable, mineral or synthetic oils and, in particular, from among liquid paraffin, paraffin oil, silicone oils, volatile or otherwise, isoparaffins, polyolefins, fluorinated or perfluorinated oils. Likewise, the waxes may be animal, fossil, vegetable, mineral or synthetic waxes which are also known per se.

Exemplary organic solvents include the lower alcohols and polyols.

Of course, one skilled in this art will take care to select this or these optional additional compounds and/or their quantities such that the advantageous properties, in particular the resistance to water, the stability, which are intrinsically associated with the sunscreen compositions in accordance with the invention are not, or not substantially, altered by the addition(s) envisaged.

The sunscreen compositions of the invention may be formulated according to techniques well known to this art, in particular those suited for the preparation of emulsions of the oil-in-water or water-in-oil type.

The subject sunscreen compositions may be provided, in particular, in the form of a simple or complex (O/W, W/O, O/W/O or W/O/W) emulsion such as a cream, a milk, a gel or a gel cream, of a powder, a lotion, an ointment, a solid stick and may optionally be packaged as an aerosol and provided in the form of a foam, mousse or spray.

When an emulsion is provided, the aqueous phase thereof may comprise a nonionic vesicular dispersion prepared according to known techniques (Bangham, Standish and Watkins, J. Mol. Biol., 13, 238 (1965), FR-2,315,991 and FR-2,416,008).

The sunscreen compositions according to the invention may be formulated for protecting the human epidermis or the hair against the damaging effects of ultraviolet radiation, as an anti-sun composition or as a makeup product.

When the sunscreen compositions according to the invention are formulated for protecting the human epidermis against UV rays, or as anti-sun/sunscreen compositions, same may be

provided in the form of a suspension or a dispersion in solvents or fatty substances, in the form of a nonionic vesicular dispersion or, alternatively, in the form of an emulsion, preferably of the oil-in-water type, such as a cream or a milk, in the form of an ointment, a gel, a gel cream, a solid stick, a powder, a stick, an aerosol foam or a spray.

When the sunscreen compositions according to the invention are formulated for protecting the hair against UV rays, same may be provided in the form of a shampoo, a body wash, a lotion, a gel, an alcohol-based system, an emulsion, a nonionic vesicular dispersion and may constitute, for example, a rinse-off composition to be applied before or after shampooing, before or after dyeing or bleaching, before, during or after permanent-waving or hair straightening, a hair-styling or treatment lotion or gel, a lotion or gel for blow drying or hair setting, a composition for permanent waving or straightening, dyeing or bleaching the hair.

When the subject compositions are formulated as makeup products for the eyelashes, the eyebrows or the skin, such as a treatment cream for the epidermis, foundation, lipstick, eyeshadow, blusher, mascara or eyeliner, same may be provided in a solid or pasty, anhydrous or aqueous form, such as oil-in-water or water-in-oil emulsions, nonionic vesicular dispersions or alternatively suspensions.

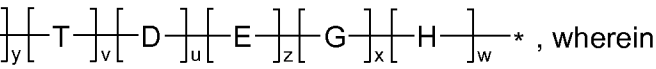
For example, for the anti-sun formulations in accordance with the invention which have a carrier, vehicle or diluent of the oil-in-water emulsion type, the aqueous phase (comprising in particular the hydrophilic screening agents), generally constitutes from 50% to 95% by weight, preferably from 70% to 90% by weight, relative to the total weight of the formulation, the oily phase (comprising in particular the lipophilic screening agents), from 5% to 50% by weight, preferably from 10% to 30% by weight, relative to the total weight of the formulation, and the (co)emulsifier(s) from 0.5% to 20% by weight, preferably from 2% to 10% by weight, also relative to the total weight of the formulation.

As indicated above, the present invention thus features formulating the subject emulsions for the production of cosmetic compositions for protecting the skin and/or the hair against ultraviolet radiation, in particular solar radiation.

The sunscreen composition of the instant invention may further comprise a fragrance. The term "perfume" or "fragrance" as used herein refers to odoriferous materials which are able

to provide a pleasing fragrance to fabrics, and encompasses conventional materials commonly used in cosmetic compositions to counteract a malodor in such compositions and/or provide a pleasing fragrance thereto. The perfumes are preferably in the liquid state at ambient temperature, although solid perfumes are also useful, particularly cyclodextrin/-perfume inclusion complexes for controlled release. Included among the perfumes contemplated for use herein are materials such as aldehydes, ketones, esters and the like which are conventionally employed to impart a pleasing fragrance to liquid and solid personal care or cosmetic compositions. Naturally occurring plant and animal oils are also commonly used as components of perfumes. Accordingly, the perfumes useful for the present invention may have relatively simple compositions or may comprise complex mixtures of natural and synthetic chemical components, all of which are intended to provide a pleasant odor or fragrance when applied to fabrics. The perfumes used in personal care or cosmetic compositions are generally selected to meet the normal requirements of odor, stability, price and commercial availability. The term "fragrance" is often used herein to signify a perfume itself, rather than the aroma imparted by such perfume.

The present invention is directed to a method of increasing the sun protection factor of a sunscreen composition wherein said method comprises incorporating into said composition an effective amount of at least one random terpolymer according to formula

(I)  , wherein

u, v, w, x, y, and z represent the percentage by weight that each repeating unit or derived monomer is contained within the terpolymer;

u, v, w, x, y, and z add up to total 100 weight percent relative to the total weight of the terpolymer;

y is from about 0 to about 40% by weight of the terpolymer;

v is from about 5% to about 75% by weight of the terpolymer;

u is from about 5% to about 80% by weight of the terpolymer;

z is from about 0% to about 60% by weight of the terpolymer;

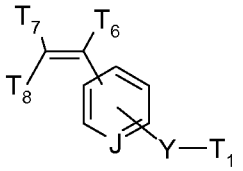
x is from about 1% to about 50% by weight of the terpolymer;

w is from about 0% to about 50% by weight of the terpolymer;

* is a terminal group, for example, a catalyst residue;

M, T, D, E, G, and H are covalently bonded to each other;

M is derived from at least one monomer of formula

(II)  , wherein

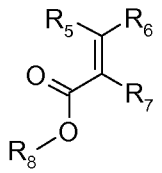
T_6, T_7, and T_8 are C_1-C_4alkyl or hydrogen;

Y is a direct bond, –O-, -S-, -N(H)- or –N(T_1)-;

T_1 is hydrogen or C_1-C_4alkyl; and

J is a nitrogen or carbon atom;

T, D, and E are independently derived from at least one monomer of formula

(III)  , wherein

R_5, R_6 and R_7 may be the same or different and represent hydrogen or C_1-C_{22}alkyl;

R_8 is C_1-C_{30}alkyl, C_6-C_{15}cycloalkyl, or C_6-C_{15}aryl; said substituted alkyl, said cycloalkyl or said aryl may also be substituted by one or more –OH and/or NH_2-groups; or said alkyl or said cycloalkyl may be interrupted by one or more –O- groups and/or –N(H)- groups;

G is derived from at least one monomer comprising a heterocyclic group having at least one basic ring nitrogen atom or to which such a heterocyclic group is attached following polymerization;

H is derived from at least one monomer selected from the group consisting of toluene diisocyanate (all isomers), 4,4'-diphenylmethane diisocyanate, tolidine diisocyanate, di-anisidine diisocyanate, m-xylylene diisocyanate, p-phenylene diisocyanate, m-phenylene diisocyanate, 1-chloro-2,4-phenylene diisocyanate, 3,3'-dimethyl-4,4'-bisphenylene diisocyanate, 4,4'-bis(2-methylisocyanatophenyl)methane, 4,4'-bisphenylene diisocyanate, 4,4'-bis(2-methoxyisocyanatophenyl)methane, 1-nitrophenyl-3,5-diisocyanate, 4,4'-diisocyanatodiphenyl ether, 3,3'-dichloro-4,4'-diisocyanatodiphenyl ether, 3,3'-dichloro-4,4'-diisocyanatodiphenyl methane, 4,4'-diisocyanatodibenzyl, 3,3'-dimethoxy-4,4'-diisocyanatodiphenyl, 2,2'-dimethyl-4,4'-diisocyanatodiphenyl, 2,2'-dichloro-5,5'-dimethoxy-4,4'-diisocyanatodiphenyl, 3,3'-dichloro-4,4'-diisocyanatodiphenyl, 1,2-naphthalene diisocyanate, 4-chloro-1,2-naphthalene diisocyanate, 4-methyl-1,2-naphthalene diisocyanate, 1,5-naphthalene diisocyanate, 1,6-naphthalene diisocyanate, 1,7-naphthalene diisocyanate, 1,8-naphthalene diisocyanate, 4-chloro-1,8-naphthalene diisocyanate, 2,3-

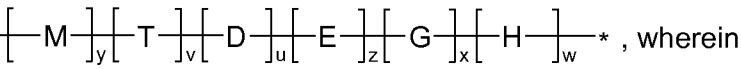
naphthalene diisocyanate, 2,7-naphthalene diisocyanate, 1,8-dinitro-2,7-naphthalene diisocyanate, 1-methyl-2,4-naphthalene diisocyanate, 1-methyl-5,7-naphthalene diisocyanate, 6-methyl-1,3-naphthalene diisocyanate, 7-methyl-1,3-naphthalene diisocyanate, 1,2-ethane diisocyanate, 1,3-propane diisocyanate, 1,4-butane diisocyanate, 2-chloropropane-1,3-diisocyanate, pentamethylene diisocyanate, propylene-1,2-diisocyanate, 1,8-octane diisocyanate, 1,10-decane diisocyanate, 1,12-dodecane diisocyanate, 1,16-hexadecane diisocyanate 1,3- and 1,4-cyclohexane diisocyanate, 1,6-hexamethylene diisocyanate, 2,2,4- and 2,4,4-trimethylhexamethylene diisocyanate, diisocyanates or a mixture thereof dimer acid derived diisocyanate obtained from dimerized linoleic acid, 4,4'-dicyclohexylmethane diisocyanate, isophorone diisocyanate, 3-isocyanatomethyl-3,5,5-trimethylcyclohexyl diisocyanate, lysine methyl ester diisocyanate, bis(2-isocyanatoethyl) fumarate bis(2-isocyanatoethyl) carbonate, m-tetramethylxylylene diisocyanate, and acrylonitrile;

with the proviso that T, D, and E are derived from different monomers.

The present invention is directed to a method of improved UV protection of mammalian hair and/or skin from the damaging effects of UV radiation wherein said method comprises applying to said skin and/or said hair an effective amount of a sunscreen composition comprising

(a) at least one UV screening agent;

(b) at least one random terpolymer of formula

(I)  , wherein

u, v, w, x, y, and z represent the percentage by weight that each repeating unit or derived monomer is contained within the terpolymer;

u, v, w, x, y, and z add up to total 100 weight percent relative to the total weight of the terpolymer;

y is from about 0 to about 40% by weight of the terpolymer;

v is from about 5% to about 75% by weight of the terpolymer;

u is from about 5% to about 80% by weight of the terpolymer;

z is from about 0% to about 60% by weight of the terpolymer;

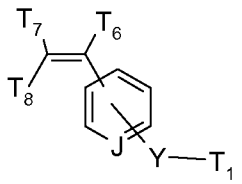
x is from about 1% to about 50% by weight of the terpolymer;

w is from about 0% to about 50% by weight of the terpolymer;

* is a terminal group, for example, a catalyst residue;

M, T, D, E, G, and H are covalently bonded to each other;

M is derived from at least one monomer of formula

(II)  , wherein

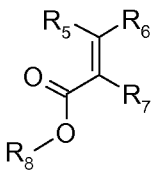
T_6, T_7, and T_8 are C_1-C_4alkyl or hydrogen;

Y is a direct bond, –O-, -S-, -N(H)- or –N(T_1)-;

T_1 is hydrogen or C_1-C_4 alkyl; and

J is a nitrogen or carbon atom;

T, D, and E are independently derived from at least one monomer of formula

(III)  ,wherein

R_5, R_6 and R_7 may be the same or different and represent hydrogen or C_1-C_{22}alkyl;

R_8 is C_1-C_{30}alkyl, C_6-C_{15}cycloalkyl, or C_6-C_{15}aryl; said substituted alkyl, said cycloalkyl or said aryl may also be substituted by one or more –OH and/or NH_2groups; or said alkyl or said cycloalkyl may be interrupted by one or more –O- groups and/or –N(H)- groups;

G is derived from at least one monomer comprising a heterocyclic group having at least one basic ring nitrogen atom or to which such a heterocyclic group is attached following polymerization;

H is derived from at least one monomer selected from the group consisting of toluene diisocyanate (all isomers), 4,4'-diphenylmethane diisocyanate, tolidine diisocyanate, dianisidine diisocyanate, m-xylylene diisocyanate, p-phenylene diisocyanate, m-phenylene diisocyanate, 1-chloro-2,4-phenylene diisocyanate, 3,3'-dimethyl-4,4'-bisphenylene diisocyanate, 4,4'-bis(2-methylisocyanatophenyl)methane, 4,4'-bisphenylene diisocyanate, 4,4'-bis(2-methoxyisocyanatophenyl)methane, 1-nitrophenyl-3,5-diisocyanate, 4,4'-diisocyanatodiphenyl ether, 3,3'-dichloro-4,4'-diisocyanatodiphenyl ether, 3,3'-dichloro-4,4'-diisocyanatodiphenyl methane, 4,4'-diisocyanatodibenzyl, 3,3'-dimethoxy-4,4'-diisocyanatodiphenyl, 2,2'-dimethyl-4,4'-diisocyanatodiphenyl, 2,2'-dichloro-5,5'-dimethoxy-4,4'-diisocyanatodiphenyl, 3,3'-dichloro-4,4'-diisocyanatodiphenyl, 1,2-naphthalene diisocyanate, 4-chloro-1,2-naphthalene diisocyanate, 4-methyl-1,2-

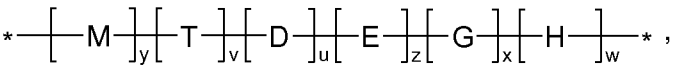
naphthalene diisocyanate, 1,5-naphthalene diisocyanate, 1,6-naphthalene diisocyanate, 1,7-naphthalene diisocyanate, 1,8-naphthalene diisocyanate, 4-chloro-1,8-naphthalene diisocyanate, 2,3-naphthalene diisocyanate, 2,7-naphthalene diisocyanate, 1,8-dinitro-2,7-naphthalene diisocyanate, 1-methyl-2,4-naphthalene diisocyanate, 1-methyl-5,7-naphthalene diisocyanate, 6-methyl-1,3-naphthalene diisocyanate, 7-methyl-1,3-naphthalene diisocyanate, 1,2-ethane diisocyanate, 1,3-propane diisocyanate, 1,4-butane diisocyanate, 2-chloropropane-1,3-diisocyanate, pentamethylene diisocyanate, propylene-1,2-diisocyanate, 1,8-octane diisocyanate, 1,10-decane diisocyanate, 1,12-dodecane diisocyanate, 1,16-hexadecane diisocyanate 1,3- and 1,4-cyclohexane diisocyanate, 1,6-hexamethylene diisocyanate, 2,2,4- and 2,4,4-trimethylhexamethylene diisocyanate, diisocyanates or a mixture thereof dimer acid derived diisocyanate obtained from dimerized linoleic acid, 4,4'-dicyclohexylmethane diisocyanate, isophorone diisocyanate, 3-isocyanatomethyl-3,5,5-trimethylcyclohexyl diisocyanate, lysine methyl ester diisocyanate, bis(2-isocyanatoethyl) fumarate bis(2-isocyanatoethyl) carbonate, m-tetramethylxylylene diisocyanate, and acrylonitrile; and

(c) optionally, other cosmetically acceptable ingredients,

with the proviso that T, D, and E are derived from different monomers.

The present invention is directed to a cosmetic or dermatological composition comprising a random terpolymer of formula (I)

(b) at least one random terpolymer of formula

(I)  , wherein

u, v, w, x, y, and z represent the percentage by weight that each repeating unit or derived monomer is contained within the terpolymer;

u, v, w, x, y, and z add up to total 100 weight percent relative to the total weight of the terpolymer;

y is from about 0 to about 40% by weight of the terpolymer;

v is from about 5% to about 75% by weight of the terpolymer;

u is from about 5% to about 80% by weight of the terpolymer;

z is from about 0% to about 60% by weight of the terpolymer;

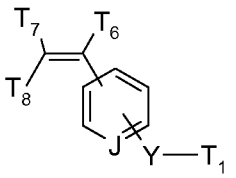
x is from about 1% to about 50% by weight of the terpolymer;

w is from about 0% to about 50% by weight of the terpolymer;

* is a terminal group, for example, a catalyst residue;

M, T, D, E, G, and H are covalently bonded to each other;

M is derived from at least one monomer of formula

(II)  , wherein

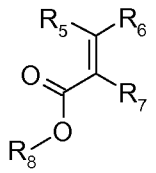
T_6, T_7, and T_8 are C_1-C_4alkyl or hydrogen;

Y is a direct bond, –O-, -S-, -N(H)- or –N(T_1)-;

T_1 is hydrogen or C_1-C_4alkyl; and

J is a nitrogen or carbon atom;

T, D, and E are independently derived from at least one monomer of formula

(III)  , wherein

R_5, R_6 and R_7 may be the same or different and represent hydrogen or C_1-C_{22}alkyl;

R_8 is C_1-C_{30} lkyl, C_6-C_{15}cycloalkyl, or C_6-C_{15}aryl; said substituted alkyl, said cycloalkyl or said aryl may also be substituted by one or more –OH and/or NH_2-groups; or said alkyl or said cycloalkyl may be interrupted by one or more –O- groups and/or –N(H)- groups;

G is derived from at least one monomer comprising a heterocyclic group having at least one basic ring nitrogen atom or to which such a heterocyclic group is attached following polymerization;

H is derived from at least one monomer selected from the group consisting of toluene diisocyanate (all isomers), 4,4'-diphenylmethane diisocyanate, tolidine diisocyanate, dianisidine diisocyanate, m-xylylene diisocyanate, p-phenylene diisocyanate, m-phenylene diisocyanate, 1-chloro-2,4-phenylene diisocyanate, 3,3'-dimethyl-4,4'-bisphenylene diisocyanate, 4,4'-bis(2-methylisocyanatophenyl)methane, 4,4'-bisphenylene diisocyanate, 4,4'-bis(2-methoxyisocyanatophenyl)methane, 1-nitrophenyl-3,5-diisocyanate, 4,4'-diisocyanatodiphenyl ether, 3,3'-dichloro-4,4'-diisocyanatodiphenyl ether, 3,3'-dichloro-4,4'-diisocyanatodiphenyl methane, 4,4'-diisocyanatodibenzyl, 3,3'-dimethoxy-4,4'-diisocyanatodiphenyl, 2,2'-dimethyl-4,4'-diisocyanatodiphenyl, 2,2'-dichloro-5,5'-dimethoxy-4,4'-diisocyanatodiphenyl, 3,3'-dichloro-4,4'-diisocyanatodiphenyl, 1,2-naphtha-

lene diisocyanate, 4-chloro-1,2-naphthalene diisocyanate, 4-methyl-1,2-naphthalene diisocyanate, 1,5-naphthalene diisocyanate, 1,6-naphthalene diisocyanate, 1,7-naphthalene diisocyanate, 1,8-naphthalene diisocyanate, 4-chloro-1,8-naphthalene diisocyanate, 2,3-naphthalene diisocyanate, 2,7-naphthalene diisocyanate, 1,8-dinitro-2,7-naphthalene diisocyanate, 1-methyl-2,4-naphthalene diisocyanate, 1-methyl-5,7-naphthalene diisocyanate, 6-methyl-1,3-naphthalene diisocyanate, 7-methyl-1,3-naphthalene diisocyanate, 1,2-ethane diisocyanate, 1,3-propane diisocyanate, 1,4-butane diisocyanate, 2-chloropropane-1,3-diisocyanate, pentamethylene diisocyanate, propylene-1,2-diisocyanate, 1,8-octane diisocyanate, 1,10-decane diisocyanate, 1,12-dodecane diisocyanate, 1,16-hexadecane diisocyanate 1,3- and 1,4-cyclohexane diisocyanate, 1,6-hexamethylene diisocyanate, 2,2,4- and 2,4,4-trimethylhexamethylene diisocyanate, diisocyanates or a mixture thereof dimer acid derived diisocyanate obtained from dimerized linoleic acid, 4,4'-dicyclohexylmethane diisocyanate, isophorone diisocyanate, 3-isocyanatomethyl-3,5,5-trimethylcyclohexyl diisocyanate, lysine methyl ester diisocyanate, bis(2-isocyanatoethyl) fumarate bis(2-isocyanatoethyl) carbonate, m-tetramethylxylylene diisocyanate, and acrylonitrile; and

(c) other cosmetically acceptable ingredients,

with the proviso that T, D, and E are derived from different monomers.

The following examples describe certain embodiments of this invention, but the invention is not limited thereto. It should be understood that numerous changes to the disclosed embodiments could be made in accordance with the disclosure herein without departing from the spirit or scope of the invention. These examples are therefore not meant to limit the scope of the invention. Rather, the scope of the invention is to be determined only by the appended claims and their equivalents. In these examples all parts given are by weight unless otherwise indicated.

Some of the solvents used for the synthesis of the instant copolymers may not be suitable for human physiological conditions. Once the synthesis is completed, the solvents can be removed and/or replaced with solvents that are more cosmetically acceptable.

EXAMPLE 1 – Random Terpolymer

In a reaction flask with reflux condenser suitable for polymerization are dissolved in 9.86 g xylene and 4.93 g methoxypropyl acetate 2.84 g vinyl toluene, 4.55 g isobutyl methacrylate,

7.36 g 2-ethylhexyl acrylate, 5.20 g 2-hydroxyethyl methacrylate, 1.80 g polyethylene glycol monomethacrylate having a molecular weight of approximately 400 and 0.44 g ditertiary butyl peroxide. Polymerization is effected at the boiling point of the mixture while stirring and introducing an inert gas. At the end of the polymerization, 9.79 g isophorone diisocyanate are dissolved in 16.58 g isobutyl acetate and 16.58 g methoxypropyl acetate, and the remaining free NCO groups are then converted with 3.60 g polyethylene glycol monomethacrylate having a molecular weight of approximately 400 and 4.51 g 1-(3-aminopropyl)imidazole.

The solid content is then adjusted to 40% by weight with butylacetate.

According to formula (I), component M is vinyl toluene and y is 7.2 weight percent relative to the total weight of the terpolymer; component T is a mixture of isobutyl methacrylate and 2-ethylhexyl acrylate and v is 30.1 weight percent relative to the total weight of the terpolymer; component D is polyethylene glycol monomethacrylate and u is 13.6 weight percent relative to the total weight of the terpolymer; component E is 2-hydroxyethyl methacrylate and z is 13.1 weight percent relative to the total weight of the terpolymer; component G is 1-(3-aminopropyl)imidazole and x is 11.4 weight percent relative to the total weight of the terpolymer; and component H is isophorone diisocyanate and w is 24.7 weight percent relative to the total weight of the terpolymer.

EXAMPLE 2 - Random Terpolymer

In the manner comparable with Example 1, 3.54 g vinyl toluene, 5.69 g isobornyl methacrylate, 9.20 g 2-ethylhexyl methacrylate, 7.15 g hydroxy ethyl methacrylate, and 1.28 g ditertiary butylperoxide dissolved in 11.94 g xylene and 5.97 g methoxypropyl acetate are polymerized.

Subsequently, 12.23 g isophorone diisocyanate dissolved in 20.36 g butylacetate and 20.36 g methoxypropyl acetate are added. The remaining free NCO groups are then converted with 4.50 g polyethylene glycol monomethacrylate having a molecular weight of approximate 400 and 3.78 g 3-amino-1,2,4-triazole in 11.34 g N-methylpyrrolidone.

The solid content is then adjusted to 40% by weight with butylacetate.

According to formula (I), component M is vinyl toluene and y is 7.7 weight percent relative to the total weight of the terpolymer; component T is a mixture of isobornyl methacrylate and 2-ethylhexyl methacrylate and v is 32.3 weight percent relative to the total weight of the terpolymer; component D is polyethylene glycol monomethacrylate and u is 9.8 weight percent relative to the total weight of the terpolymer; component E is 2-ethylhexylmethacrylate and z is 15.5 weight percent relative to the total weight of the terpolymer; component G is 3-amino-1,2,4-triazole and x is 8.2 weight percent relative to the total weight of the terpolymer; and component H is isophorone diisocyanate and w is 26.5 weight percent relative to the total weight of the terpolymer.

EXAMPLE 3 - Random Terpolymer

In the manner described in Example 1, 6.66 g isobornyl methacrylate, 5.46 g cyclohexyl methacrylate, 6.40 g n-butylacrylate, and 7.85 g 2-hydroxyethyl methacrylate are polymerized with 1.28 g ditertiary butyl peroxide dissolved in 11.98 g xylene and 5.99 g methoxypropyl acetate. To this polymer containing hydroxyl groups, 12.23 g isophorone diisocyanate dissolved in 20.4 g butylacetate and 20.40 g methoxypropyl acetate are added. The free NCO groups are then converted with 4.50 g polyethylene glycol monomethacrylate and 5.54 g 2-(2-pyridyl)-ethanol.

The solid content is then adjusted to 40% by weight with xylene.

According to formula (I), component T is a mixture of isobornyl methacrylate and cyclohexyl methacrylate and v is 24.9 weight percent relative to the total weight of the terpolymer; component D is polyethylene glycol monomethacrylate and u is 9.3 weight percent relative to the total weight of the terpolymer; component E is a mixture of 2-hydroxyethyl methacrylate and butylacrylate and z is 29.3 weight percent relative to the total weight of the terpolymer; component G is 2-(2-pyridyl)-ethanol and x is 11.4 weight percent relative to the total weight of the terpolymer; and component H is isophorone diisocyanate and w is 25.1 weight percent relative to the total weight of the terpolymer.

EXAMPLE 4 - Random Terpolymer

In the manner described in Example 1, the polymerization of 3.78 g vinyl toluene, 5.69 g isobutyl methacrylate, 7.38 g 2-ethyl hexyl methacrylate, 7.97 g stearyl methacrylate, 4.55 g

glycidyl methacrylate and 0.59 g ditertiary butylperoxide is effected in 14.98 g xylene and 4.99 g methoxypropyl acetate.

At the end of the polymerization, 24.97 g butylacetate and 4.01 g 1-(3-aminopropyl)imidazole are added to the polymer.

According to formula (I), component M is vinyl toluene and y is 11.3 weight percent relative to the total weight of the terpolymer; component T is a mixture of isobutyl methacrylate and 2-ethylhexyl methacrylate and v is 39.1 weight percent relative to the total weight of the terpolymer; component D is stearyl methacrylate and u is 23.9 weight percent relative to the total weight of the terpolymer; component E is glycidyl methacrylate and z is 13.6 weight percent relative to the total weight of the terpolymer; and component G is 1-(3-aminopropyl)imidazole and x is 12.0 weight percent relative to the total weight of the terpolymer.

EXAMPLE 5 - Random Terpolymer

In the manner described in Example 1, the polymerization of 6.66 g isobornyl methacrylate, 5.46 g cyclohexyl methacrylate, 9.96 g stearyl methacrylate, 9.22 g 2-ethyl hexyl methacrylate, 5.69 g glycidyl methacrylate and 0.74 g ditertiary butylperoxide is effected in 18.86 g xylene and 6.29 g methoxypropyl acetate.

At the end of the polymerization, 18.94 g butyl acetate and 4.05 g 3-mercapto-1,2,4-triazole dissolved in 16.20 g N-methyl pyrrolidone are added to the polymer.

According to formula (I), component T is a mixture of isobornyl methacrylate and cyclohexyl methacrylate and v is 29.5 weight percent relative to the total weight of the terpolymer; component D is a mixture of 2-ethylhexyl methacrylate and stearyl methacrylate and u is 46.8 weight percent relative to the total weight of the terpolymer; component E is glycidyl methacrylate and z is 13.9 weight percent relative to the total weight of the terpolymer; and component G is 3-mercapto-1,2,4-triazole and x is 9.9 weight percent relative to the total weight of the terpolymer.

EXAMPLE 6 - Random Terpolymer

In the manner described in Example 1, the polymerization of 12.0 g methyl methacrylate, 32.76 g cyclohexyl methacrylate, 35.84 g butylacrylate, 18.82 g vinyl imidazole and 2.0 g tertiary butyl perbenzoate is effected in 50.71 g xylene and 16.91 g n-butanol.

The solid content is adjusted to 40% by weight with butyl acetate.

According to formula (I), component T is methyl methacrylate and v is 12.1 weight percent relative to the total weight of the terpolymer; component D is cyclohexyl methacrylate and u is 33.0 weight percent relative to the total weight of the terpolymer; component E is butyl acrylate and z is 36.0 weight percent relative to the total weight of the terpolymer; and component G is vinyl imidazole and x is 18.9 weight percent relative to the total weight of the terpolymer.

EXAMPLE 7 - Random Terpolymer

In 15.67 g secondary butanol and 47.0 g butyl acetate are polymerized, in the manner described in Example 1: 29.97 g isobornyl methacrylate, 9.36 g styrene, 38.71 g 2-ethyl hexyl acrylate, 14.12 g vinyl imidazole, 0.62 g tertiary butyl-per-2-ethyl hexoate and 1.23 g tertiary butyl perbenzoate.

At the end of the polymerization, the solid content is adjusted to 50% by weight with butyl acetate.

According to formula (I), component M is styrene and y is 10.2 weight percent relative to the total weight of the terpolymer; component T is isobornyl methacrylate and v is 32.5 weight percent relative to the total weight of the terpolymer; component D is 2-ethylhexyl acrylate and u is 42.0 weight percent relative to the total weight of the terpolymer; and component G is vinyl imidazole and x is 15.3 weight percent relative to the total weight of the terpolymer.

EXAMPLE 8 - Random Terpolymer

In 45.08 g xylene and 22.54 g n-butanol, 12.00 g methyl methacrylate, 32.76 g cyclohexyl methacrylate, 35.84 g butyl acrylate, 18.82 g vinyl imidazole and 2.0 g tertiary butyl perbenzoate are polymerized in the manner described in Example 1.

At the end of the polymerization, the solid content is adjusted to 50% by weight by adding 33.80 g xylene.

According to formula (I), component T is methyl methacrylate and v is 12.1 weight percent relative to the total weight of the terpolymer; component D is cyclohexyl methacrylate and u is 33.0 weight percent relative to the total weight of the terpolymer; component E is butyl methacrylate and z is 36.0 weight percent relative to the total weight of the terpolymer; and component G is vinyl imidazole and x is 18.9 weight percent relative to the total weight of the terpolymer.

EXAMPLE 9 - Random Terpolymer

In 47.00 g toluene and 15.67 g n-butanol, 29.97 g isobornyl methacrylate, 9.36 g styrene, 38.71 g 2-ethyl hexyl acrylate, 14.12 g vinyl imidazole and 11.85 g tertiary butyl perbenzoate are polymerized in the manner described in Example 1.

At the end of the polymerization, a polymer solution is obtained having a solid content of 60% by weight.

According to formula (I), component M is styrene and y is 10.2 weight percent relative to the total weight of the terpolymer; component T is isobornyl methacrylate and v is 32.5 weight percent relative to the total weight of the terpolymer; component D is 2-ethylhexyl acrylate and u is 42.0 weight percent relative to the total weight of the terpolymer; and component G is vinyl imidazole and x is 15.3 weight percent relative to the total weight of the terpolymer.

EXAMPLE 10 - Random Terpolymer

In 43.75 g xylene and 14.59 g n-butanol, 23.31 g isobornyl methacrylate, 31.35 g butyl acrylate, 10.92 g styrene, 3.71 g acrylonitrile, 16.47 g vinyl imidazole and 1.72 g tertiary butyl perbenzoate are polymerized.

At the end of the polymerization, the solid content of the polymer solution is adjusted to 50% by weight by adding xylene.

According to formula (I), component M is styrene and y is 12.7 weight percent relative to the total weight of the terpolymer; component T is isobornyl methacrylate and v is 27.2 weight

percent relative to the total weight of the terpolymer; component D is butylacrylate and u is 36.6 weight percent relative to the total weight of the terpolymer; component G is vinyl imidazole and x is 19.2 weight percent relative to the total weight of the terpolymer; and H is acrylonitrile and w is 4.3 weight percent relative to the total weight of the terpolymer.

EXAMPLE 11 - Random Terpolymer

In the manner described in Example 1, 19.98 g isobornyl methacrylate, 10.62 g vinyl toluene, 30.42 g 2-ethylhexyl acrylate, 6.75 g polyethylene glycol monomethacrylate, 16.38 g cyclohexyl methacrylate, 15.53 g vinyl imidazole, 0.67 g tertiary butyl peroctoate and 1.34 g tertiary butyl perbenzoate are polymerized in 50.85 g butyl acetate and 16.95 g secondary butanol.

At the end of the polymerization, the solid content of the polymer solution is adjusted to 50% by weight with butyl acetate.

According to formula (I), component M is vinyl toluene and y is 10.7 weight percent relative to the total weight of the terpolymer; component T is a mixture of isobornyl methacrylate and 2-ethylhexyl acrylate and v is 50.5 weight percent relative to the total weight of the terpolymer; component D is polyethylene glycol monomethacrylate and u is 6.8 weight percent relative to the total weight of the terpolymer; component E is cyclohexyl methacrylate and z is 16.4 weight percent relative to the total weight of the terpolymer; and component G is vinyl imidazole and x is 15.6 weight percent relative to the total weight of the terpolymer.

EXAMPLE 12 - Random Terpolymer

In 98.67 g butyl acetate and 19.74 g n-butanol, the following substances are polymerized, in the manner described in Example 1: 19.98 g isobornyl methacrylate, 10.92 g cyclohexyl methacrylate, 10.62 g vinyl toluene, 15.0 g methyl methacrylate, 6.75 g polyethylene glycol monomethacrylate, 14.12 g vinyl imidazole and 1.56 g tertiary butyl perbenzoate.

At the end of the polymerization, the solid content of the solution is adjusted to 40% by weight by adding butyl acetate.

According to formula (I), component M is vinyl toluene and y is 13.7 weight percent relative to the total weight of the terpolymer; component T is a mixture of isobornyl methacrylate and

cyclohexyl methacrylate and v is 39.9 weight percent relative to the total weight of the terpolymer; component D is polyethylene glycol monomethacrylate and u is 8.7 weight percent relative to the total weight of the terpolymer; component E is methyl methacrylate and z is 19.4 weight percent relative to the total weight of the terpolymer; and component G is vinyl imidazole and x is 18.2 weight percent relative to the total weight of the terpolymer.

EXAMPLE 13 - Random Terpolymer

The following substances are polymerized randomly, similar to the manner described in Example 11 except sec-butanol is used as the solvent: 9.0 g vinyltoluene, 6.6 g 2-hydroxyethyl methacrylate, 13.2 g vinyl imidazole, 14.1 g 2-ethylhexylacrylate, and 66.9 g monomethoxypolyethylene glycol monomethacrylate. After completion of the polymerization reaction, all solvents and volatiles are removed by vacuum distillation. A polymeric melt is obtained with a molecular weight of about 15,000-20,000 Dalton as determined by Gel Permeation Chromotography (GPC).

According to formula (I), component M is vinyl toluene and y is 8.2 weight percent relative to the total weight of the terpolymer; component T is 2-ethylhexyl methacrylate and v is 12.8 weight percent relative to the total weight of the terpolymer; component D is polyethylene glycol monomethacrylate and u is 60.9 weight percent relative to the total weight of the terpolymer; component E is 2-hydroxyethyl methacrylate and z is 6.0 weight percent relative to the total weight of the terpolymer; and component G is vinyl imidazole and x is 12.0 weight percent relative to the total weight of the terpolymer.

A solution of the random terpolymer synthesized above is prepared by dissolving 109.8 g of the random terpolymer in a solution containing 150 g of water, 6 g of polyethoxylated alcohol, 18 g of polyethylene glycol 200, and 12 g of tall oil fatty acid.
A suitable preservative system may be added.

Example 14 - Sunscreen Composition Preparation

Part	Trade name	INCI name	Function	% W/W*
A	Arlacel 165	Glyceryl Stearate (and) PEG-100 Stearate	Emulsifier, non-ionic	3.50
	Lanette 16	Cetyl Alcohol	Emulsion Stabilizer	1.00
	Cetiol B	Dibutyl Adipate	Emollient/solvent	5.00
	Cetiol CC	Dicaprylyl Carbonate	Emollient/solvent	5.00

Part	Trade name	INCI name	Function	% W/W*
	Tegosoft DEC	Diethylhexyl Carbonate	Emollient/solvent	2.00
	Neo Heliopan AV	Octinoxate	Sunscreen Active	7.50
	Neo Heliopan OS	Octisalate	Sunscreen Active	2.00
	Parsol 1789	Avobenzone	Sunscreen Active	3.00
	Tinosorb® S	Drug name (proposed): Bemotrizinol;INCI name: Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine	Sunscreen Active	1.50
	Orgasol 2002 EXD NAT COS	Nylon-12	Spherical Particulate to improve skin feel	1.50
B	Water	Water	Diluent/solvent	Qs to 100.00
	Keltrol CG RD	Xanthan Gum	Rheology Modifier	0.22
	Glycerin	Glycerin	Humectant	3.00
	Dissolvine NA2	Disodium EDTA	Chelating Agent	0.20
C	Dow Corning 345 Fluid	Cyclopentasiloxane	Emollient/Solvent	2.00
	Tinovis ADM	Sodium Acrylates Copolymer (and) Mineral Oil (and) PPG-1 Trideceth-6	Rheology Modifier	0.83
	Tinosorb® M	Drug name (proposed): Bisoctrizole; INCI name: Methylene Bis-Benzotriazolyl Tetramethylbutylphenol	Sunscreen Active	3.00 (as is) or 1.50 (active level)
	Phenonip	Phenoxyethanol (and) Methylparaben (and) Ethylparaben (and) Butylparaben (and) Propylparaben (and) Isobutylparaben	Preservative	1.00
	Sodium Hydroxide	Sodium Hydroxide (15% aqueous solution)	pH adjustor	Qs to pH ~5.3-6.1

*The components are added to the sunscreen composition on a % weight/weight of component (as active) based on the weight of the total composition.

Combine the ingredients of part A. Heat up part A to 80°C with mixing. Mix until uniform, and add Nylon-12 with moderate agitation.

Prepare part B: first, disperse Xanthan Gum into the water and heat up to 80°C. When uniform, add the rest of part B one by one, mix until uniform.

Add part A into part B under stirring, and then homogenize with an Ultra Turrax pos 2 for 40sec/100g.

Cool down under stirring, to 40°C and add the ingredients of part C one by one in the given order. Mix until uniform. If necessary, adjust pH with aqueous solution of sodium sydroxide to 5.3-6.1

Example 15 - Testing Protocol

The test protocol described below is used to mimic the application of the sunscreen composition to human skin and test the initial SPF and the SPF after eighty minutes of water exposure of the instant compositions.

The following laboratory equipment is used:

VITRO-SKIN® N-19, Foam block, Hydration Chamber, Powder Free Rubber Finger Cots and Glassless slide mounts are obtained from IMS, Inc. (70 Robinson Blvd, Orange, CT, USA);

Water bath (# 05-719-7F), Corning Hotplate Stirrer (#11-497-8A), Calfamo Compact Digital Stirrer (#14-500-7), Glycerol Aqueous Solution (#AC277366-0010) are obtained from Fisher Scientific Catalog; and

Optometrics SPF 290 is obtained from Optometrics LLC. (8 Nemco Way, Stony Brook Industrial Park, Ayer, MA, USA).

An aqueous solution of glycerin (300 g of 14.7% by weight) is prepared and poured on the bottom of the hydration chamber. The shelves are placed in the chamber that is covered with a lid. VITRO-SKIN substrate is cut into 4.1 cm x 4.1 cm pieces that are placed on the shelves in a hydration chamber and hydrated for 16-22 hours prior to the tests.

Optometrics SPF 290S is turned on followed by the manufacturer's directions for instrument calibration, blank and sample measurements.

A piece of substrate is placed in a slide mount and used as a reference for the *in vitro* SPF measurements. Another piece of substrate is placed on a plastic-covered foam block and

product application is made to the "topography" side of the substrate (the rough side). The test composition (0.033 g) is applied evenly across a 4 cm x 4 cm section of the substrate, which results in an application dose of 2 mg/sq. cm and rubbed into the substrate with a finger covered with finger cot. After this, the substrate is placed on a slide mount.

The *in vitro* SPF measurements are made both prior to and after sample immersion in water with stirring for 80 minutes at a water temperature of 37 +/-0.5C. All initial measurements are made after the 15 minute dry-down period. After water exposure, the samples are removed, air-dried for about 30 minutes, placed back in the controlled humidity chamber for 120 minutes followed by the 15 minute dry-down period. The reference slides are immersed in the water bath for the same amount of time.

An Optometrics SPF 290S is used to determine UV absorbance for each formulation in the 290 - 400 nm wavelength range. A minimum of three consecutive measurements on three separate areas of the slide are conducted. SPF, UVA/UVB and Critical Wavelength *in vitro* values for each sample - before and after water immersion are recorded. The %SPF remaining after eighty minute exposure to water is calculated by:

$$(a/b) \times 100 = \%SPF \text{ remaining}$$

(a) is SPF value after 80 minutes of water exposure and (b) is initial SPF value.

Example 16 - Sunscreen Composition Testing for Water Resistant Properties

The base sunscreen composition of Instant Example 14 is formulated with the terpolymer of Instant Example 13 and compared with other commercially available polymers and copolymers. The composition of Instant Example 14 is prepared individually with the specified amount of each test polymer or copolymer. Commercially available polymers were added to the oil phase or water phase of the formulation, or post-added according to the recommendations described in the manufacturer's literature.

Each sunscreen formulation is evaluated according to the protocol of Instant Example 15. The experimental results are given below.

Polymer Tested	wt/wt%*	%SPF remaining
None	0	3.1
Cosmedia DC	3	4.5
Polycrylene	3	5.7
DC FA 4001 CM	3	6.0
Silicone Acrylate Ganex V-220	3	6.8
DC FA 4002 ID	3	7.4
Silicone Acrylate Phospholipon 90H	3	35.0
Dermacryl AQF	3	40.5
Ganex WP-660	3	53.0
Stantiv OMA-2	3	53.3
Dermacryl-79	3	55.9
Allianz OPT	3	81.1
Avalure UR 450	3	83.5
Instant Example 13	1	87.4

*The commercially available polymers are added to the sunscreen composition at a 3 % weight/weight of component (as active) based on the weight of the total composition.

Instant Example 13 is added at a 1% weight/weight of component (as active) based on the weight of the total composition.

Cosmedia DC is a hydrogenated dimer Dilinoleyl/Dimethylcarbonate Copolymer and is obtained from Cognis.

Polycrylene is Polyester-8 which is a copolymer of adipic acid (q.v.) and neopentyl glycol (q.v.) end-capped with either octyldodecanol (q.v.) or a cyanodiphenylpropenoyl group and is obtained from RTD Hall Star.

DC FA 4001 CM Silicone Acrylate is a copolymer of polytrimethylsiloxymethacrylate and one or more monomers consisting of acrylic acid, methacrylic acid, or one of their simple esters dissolved in cyclopentasiloxane and is obtained from Dow Corning.

Ganex V-220 is a copolymer of vinylpyrrolidone and eicosene and is obtained from ISP.

DC FA 4002 ID Silicone Acrylate is a copolymer of polytrimethylsiloxymethacrylate and one or more monomers consisting of acrylic acid, methacrylic acid, or one of their simple esters dissolved in isododecane and is obtained from Dow Corning.

Phospholipon 90H is hydrogenated lecithin and is obtained from Phospholipid GmbH.

Dermacryl AQF is a copolymer of acrylates and is obtained from National Starch and Chemical Company.

Ganex WP-660 is a copolymer of vinyl pyrrolidone and 1-triacontane and is obtained from ISP.

Stantiv OMA-2 is a linear copolymer of maleic anhydride and octadecene and is dissolved a mixture of methyl acetyl ricinoleate and dimethylheptyl adipate.

Dermacryl-79 is a copolymer of octylacrylamide and one or more monomers consisting of acrylic acid, methacrylic acid or one of their simple esters and is obtained from National Starch and Chemical Company.

Allianz OPT is a copolymer of: methacrylic acid, methyl methacrylate, butyl acrylate, and cetyl-eicosinyl methacrylate and is obtained from ISP.

Avalure UR 450 is a copolymer of PPG-17, isophorone diisocyanate and dimethylol propionic acid monomers and is obtained from Noveon.

The data demonstrate the instant terpolymer provide excellent water proofing properties in sunscreen compositions at one-third of the concentration when compared to other polymers and copolymers of the prior art and commerce.

Example 17 - Sunscreen Composition Testing for Water Resistant Properties

A commercial sunscreen formulation (Cetaphil SPF 15, Galderma) is obtained and is thoroughly mixed individually with the specified amount of each test polymer or copolymer. Each sunscreen formulation is evaluated according to the protocol of Instant Example 15. The experimental results are given below.

Polymer Tested	wt/wt%*	%SPF remaining
None	0	10.1
Dermacryl AQF	2	9.1
Allianz OPT	1	49.1
Instant Example 13	1	62.9

*The polymers are added to the sunscreen composition on a % weight/weight of component (as active) based on the weight of the total composition.

Dermacryl AQF is a copolymer of acrylates and is obtained from National Starch and Chemical Company.

Allianz OPT is a copolymer of: methacrylic acid, methyl methacrylate, butyl acrylate, and cetyl-eicosinyl methacrylate and is obtained from ISP.

Cetaphil SPF 15 ia a commercial sinscreen formulation that contains sunscreen actives: Avobenzone 3%; Octocrylene 10%; and

Inactive Ingredients (Function):
Water (solvent),
Isopropyl adipate (emollient, solvent),
Cyclomethicone (emollient, solvent),
Glyceryl Stearate (and) PEG-100 Stearate (emulsifier, non-ionic),
Glycerin (humectant),
Polymethyl Metacrylate (spherical particulate to improve the skin feel,
Phenoxyethanol (preservative),
Benzyl Alcohol (preservative),
Acrylates/C10-30 Alkyl Acrylate Crosspolymer (polymeric emulsifier, rheology modifier),
Tocopheryl Acetate (antioxidant),
Carbomer (rheology modifier),
Disodium EDTA (chelating agent), and
Triethanolamine (pH adjustor).

The data demonstrate the instant terpolymer provide excellent water proofing properties in sunscreen compositions when compared to other polymers and copolymers of the prior art and commerce.

Example 18. Very Water Resistant Properties of the Sunscreen Formulations

The water resistant properties of the instant terpolymers are studied according to: the FDA Final Monograph "Evaluation of Sunscreen Efficacy – Sun Protection Factor (SPF) Assay and Very Water Resistant Assay" (*in vivo*). The instant terpolymers are studied at 1% w/w based on solids and the data obtained from the *in vivo* evaluation of the very water resistant properties of the sunscreen formulations containing the instant terpolymers is given below.

Sample	Initial SPF	Final SPF After Exposure	Per Cent SPF After Exposure
Control*	15.26	7.46	48
Instant 13	15.0	11.14	74

*A commercial daily moisturizing sunscreen formulation (Cetaphil SPF 15, Lot 049957, Galderma) is obtained and is thoroughly mixed with the specified amount of each instant terpolymer.

It is found that, at concentration 1% w/w based on solids, the instant terpolymers provide a significant improvement of very water-resistant properties of a sunscreen formulation.

Example 19. Residual Monomer Level

The Instant Terpolymer of Example 13 is analyzed for the residual monomer vinyl imidazole and is found to contain 240 ppm by quantitative gas chromatographic analysis. Instant Example 13 is subjected to boiling water stripping (distillation) three different times. The amount of vinyl imidazole is determined to be 180 ppm, 154 ppm, and 114 ppm, respectively.

Gel Permeation Chromoatographic (GPC) analysis is performed for all samples after steam distillation. The purified samples have identical GPC spectra as compared to the original unpurified terpolymer sample, therefore the polymer backbone remains unchanged after purification.

Example 20. Residual Monomer Level

The purification procedure of Instant Example 19 is repeated. A residual monomer level of 50 ppm is obtained.

Example 20. Residual Monomer Level

The purification procedure of Instant Example 19 is repeated. A residual monomer level of 5 ppm is obtained.

Example 21. Contact Angles of Water and Surface Properties

A test methodology that utilizes measurements of the contact angle of water to quantify the effects on the surface properties of a skin-substitute substrate is employed. This methodology is used as an effective tool for optimizing product development, differentiating among skin care products, competitive benchmarking, and screening of the polymers. It is described in the article entitled "Correlating Water Contact Angles and Moisturization/Sensory Claims" by Olga V. Dueva-Koganov, Scott Jaynes, Colleen Rocafort, Shaun Barker and Jianwen Mao - Cosmetics & Toiletries, January 2007, Vol. 122, No. 1, pp. 20-27. The data presented in the graph of this article shows that contact angle measurements can be used to quantify and compare the effects of skin care products on the surface properties of a skin-like substrate and is presented in tabular form below. Products that generate relatively low contact angles tend to make more sensory claims related to light and non-greasy feel, while products that produce relatively high contact angles tend to make more claims related to long-term moisturization.

Contact Angles	% Products in A*	% Products in B**	%Products in C***
40-50	100	50	0
50-60	100	40	20
60-70	60	30	60
70-80	70	15	70
80-90	50	0	100

*A = Products that are light and/or nongreasy.

**B = Products that provide 8-12 hours moisturization.

**C = Products that provide 24 hours moisturization.

Example 22. Measurement of Contact Angles after Application of the Instant Terpolymers

Contact angles are measured instrumentally according to the static or sessile drop method and using deionized water as a probe solution and VITRO SKIN that mimics the surface properties of human skin as a substrate. A piece of hydrated substrate is mounted in a glassless slide and air-dried in a flat position with application side up for 15 minutes. It is used as a reference for untreated substrate during the contact angle measurements. Exactly 0.032 g of aqueous solutions or dispersions of test polymers are applied evenly across a 4 cm x 4 cm

section of the substrate (on the "skin topography" side). Immediately after product application, the product is rubbed into the substrate with a finger covered with fingercot. After that the substrate is placed in a slide mount and air-dried for 15 minutes. Before measurements, substrate is removed from the slide mount and cut to several small pieces, which are used for the measurements. The use of small size piece is necessary to assure its flat position on the sample table. Extra care is taken to ensure that the rough side is up and the film is flat. Contact angle measurements are conducted expeditiously - within approximately 1 minute. Controlled humidity conditions are utilized.

Materials

DSA-10 Contact Angle Measuring System, Krüss Gmb.

VITRO SKIN (N-19), IMS Inc.,

Powder Free Rubber Finger Cots (# 11-392-9B) are available from the Fisher Scientific Catalog.

Instant terpolymers and competitive water-resistant polymers Allianz OPT (ISP) and Dermacryl AQF (National Starch) are evaluated according to the methodology described above.

Contact Angles after Application of the Polymers

Polymer Tested	wt/wt%*	Contact Angle, Theta (M) deg.
Control (Vitro Skin)	None	103.6
Instant Example 13	5	60.8
Instant Example 13	2.5	62.8
Instant Example 13	1	62.7
Instant Example 13	0.5	60.3
Instant Example 13	0.25	71.3
Allianz OPT	5	109.8
Allianz OPT	2.5	108.6
Allianz OPT	1	111.9
Allianz OPT	0.5	99.7
Allianz OPT	0.25	104.8
Dermacryl AQF	5	116.1
Dermacryl AQF	2.5	117.3

*Indicates aqueous solutions of the test sample as per cent polymer solids based on the total weight of the solution.

The instant terpolymers and competitive water-resistant polymers demonstrate strong differences in their effects on the surface properties of VITRO SKIN. The results presented in

the table above indicate that the instant terpolymers can potentially contribute to light skin feel – a desirable characteristic for water resistant polymers. On the contrary – the competitive benchmarks (Allianz OPT and Dermacryl AQF) generate primarily a hydrophobic modification of the substrate and are less likely to produce light skin feel.

Example 23. Sensory Characteristics of Formulations Containing Instant Terpolymers

Formulations of Instant Example 14 are prepared and tested for sensory characteristics according to testing protocols published in: 1) ASTM, American Society for Testing and Materials; Annual Book of ASTM Standards, E 1490 -92 (reapproved 1997), or 2) Meilgaard M, Civille G, Carr B (2007), Sensory Evaluation Techniques, CRC Press, 4th ed.].

The results are given below.

Sensory Characteristics	Form. A	Form. B	Form. C
Spreadability	2	2	2
Playtime	3	3	3
Softness	4	4	4
Shiny	3	3	3
Greasy	2	2	2
Sticky	2	2	2

Form. A is Instant Example 14 with no instant terpolymers added.

Form. B is Instant Example 14 with 1 per cent by weight (solids) of Example 13.

Form. C is Instant Example 14 with 2 per cent by weight (solids) of Example 13.

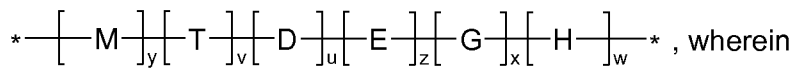
These data demonstrate that the terpolymers of the instant invention do not negatively impact the sensory parameters of the formulation.

WHAT IS CLAIMED:

1. A sunscreen composition comprising

(a) at least one UV screening agent;

(b) at least one random terpolymer of formula

(I)  , wherein

u, v, w, x, y, and z represent the percentage by weight that each repeating unit or derived monomer is contained within the terpolymer;

u, v, w, x, y, and z add up to total 100 weight percent relative to the total weight of the terpolymer;

y is from about 0 to about 40% by weight of the terpolymer;

v is from about 5% to about 75% by weight of the terpolymer;

u is from about 5% to about 80% by weight of the terpolymer;

z is from about 0% to about 60% by weight of the terpolymer;

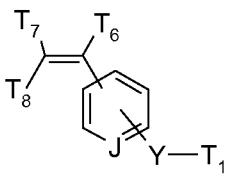
x is from about 1% to about 50% by weight of the terpolymer;

w is from about 0% to about 50% by weight of the terpolymer;

* is a terminal group, for example, a catalyst residue;

M, T, D, E, G, and H are covalently bonded to each other;

M is derived from at least one monomer of formula

(II)  , wherein

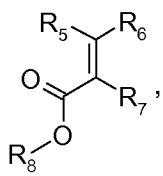
T_6, T_7, and T_8 are C_1-C_4alkyl or hydrogen;

Y is a direct bond, –O-, -S-, -N(H)- or –N(T_1)-;

T_1 is hydrogen or C_1-C_4alkyl; and

J is a nitrogen or carbon atom;

T, D, and E are independently derived from at least one monomer of formula

(III)  , wherein

R_5, R_6 and R_7 may be the same or different and represent hydrogen or C_1-C_{22}alkyl;

R_8 is C_1-C_{30} lkyl, C_6-C_{15}cycloalkyl, or C_6-C_{15}aryl; said substituted alkyl, said cycloalkyl or said aryl may also be substituted by one or more –OH and/or NH_2-groups; or said alkyl or said cycloalkyl may be interrupted by one or more –O- groups and/or –N(H)- groups;

G is derived from at least one monomer comprising a heterocyclic group having at least one basic ring nitrogen atom or to which such a heterocyclic group is attached following polymerization;

H is derived from at least one monomer selected from the group consisting of toluene diisocyanate (all isomers), 4,4'-diphenylmethane diisocyanate, tolidine diisocyanate, dianisidine diisocyanate, m-xylylene diisocyanate, p-phenylene diisocyanate, m-phenylene diisocyanate, 1-chloro-2,4-phenylene diisocyanate, 3,3'-dimethyl-4,4'-bisphenylene diisocyanate, 4,4'-bis(2-methylisocyanatophenyl)methane, 4,4'-bisphenylene diisocyanate, 4,4'-bis(2-methoxyisocyanatophenyl)methane, 1-nitrophenyl-3,5-diisocyanate, 4,4'-diisocyanatodiphenyl ether, 3,3'-dichloro-4,4'-diisocyanatodiphenyl ether, 3,3'-dichloro-4,4'-diisocyanatodiphenyl methane, 4,4'-diisocyanatodibenzyl, 3,3'-dimethoxy-4,4'-diisocyanatodiphenyl, 2,2'-dimethyl-4,4'-diisocyanatodiphenyl, 2,2'-dichloro-5,5'-dimethoxy-4,4'-diisocyanatodiphenyl, 3,3'-dichloro-4,4'-diisocyanatodiphenyl, 1,2-naphthalene diisocyanate, 4-chloro-1,2-naphthalene diisocyanate, 4-methyl-1,2-naphthalene diisocyanate, 1,5-naphthalene diisocyanate, 1,6-naphthalene diisocyanate, 1,7-naphthalene diisocyanate, 1,8-naphthalene diisocyanate, 4-chloro-1,8-naphthalene diisocyanate, 2,3-naphthalene diisocyanate, 2,7-naphthalene diisocyanate, 1,8-dinitro-2,7-naphthalene diisocyanate, 1-methyl-2,4-naphthalene diisocyanate, 1-methyl-5,7-naphthalene diisocyanate, 6-methyl-1,3-naphthalene diisocyanate, 7-methyl-1,3-naphthalene diisocyanate, 1,2-ethane diisocyanate, 1,3-propane diisocyanate, 1,4-butane diisocyanate, 2-chloropropane-1,3-diisocyanate, pentamethylene diisocyanate, propylene-1,2-diisocyanate, 1,8-octane diisocyanate, 1,10-decane diisocyanate, 1,12-dodecane diisocyanate, 1,16-hexadecane diisocyanate 1,3- and 1,4-cyclohexane diisocyanate, 1,6-hexamethylene diisocyanate, 2,2,4- and 2,4,4-trimethylhexamethylene diisocyanate, diisocyanates or a mixture thereof dimer acid derived diisocyanate obtained from dimerized linoleic acid, 4,4'-dicyclohexylmethane diisocyanate, isophorone diisocyanate, 3-isocyanatomethyl-3,5,5-trimethylcyclohexyl diisocyanate, lysine methyl ester diisocyanate, bis(2-isocyanatoethyl) fumarate bis(2-isocyanatoethyl) carbonate, m-tetramethylxylylene diisocyanate, and acrylonitrile; and

(c) other cosmetically acceptable ingredients,

with the proviso that T, D, and E are different from each other.

2. A composition according to claim **1** wherein for component b) formula (I) M is derived from at least one monomer selected from the group consisting of styrene, alpha-methylstyrene, 2-vinyltoluene, 3-vinyltoluene, 4-vinyltoluene, ethylvinylbenzene and mixtures thereof.

3. A composition according to claim **1** wherein for component b) formula (I) T, D, and E are independently derived from at least one monomer selected from the group consisting of methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, butyl (meth)acrylate, isobutyl (meth)acrylate, hexyl (meth)acrylate, cyclohexyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, octyl (meth)acrylate, decyl (meth)acrylate, dodecyl (meth)acrylate, 2-ethyl hexyl (meth)acrylate, dimethyl aminoethyl (meth)acrylate, isobornyl (meth)acrylate, stearyl (meth)acrylate, behenyl (meth)acrylate, polypropylene glycol mono(meth)acrylate, glycidyl (meth)acrylate, polyethylene glycol mono(meth)acrylate, EO-PO-mono(meth)acrylate and mixtures thereof.

4. A composition according to claim **1** wherein for component b formula (I) G is selected from the group consisting of vinylimidazole, 2-vinylpyridine, 4-vinylpyridine, 2-methyl-N-vinylimidazole, vinylpyrrolidone, vinylcarbazole and mixtures thereof.

5. A composition according to claim **1** wherein for component b formula (I) G is selected from the group consisting of 1-(2-hydroxyethyl)-pyrrolidine, 2-(1-pyrrolidyl)-ethylamine, 2-(1-piperidyl)-ethylamine, 1-(2-hydroxyethyl)-piperidine, 1-(2-aminopropyl)-piperidine, N-(2-hydroxyethyl)-hexamethylenimine, 4-(2-hydroxyethyl)-morpholine, 2-(4-morpholinyl)-ethylamine, 4-(3-aminopropyl)-morpholine, 1-(2-hydroxyethyl)-piperazine, 1-(2-aminoethyl)-piperazine, 1-(2-hydroxyethyl)-2-alkylimidazoline, 1-(3-aminopropyl)-imidazole, (2-aminoethyl)-pyridine, (2-hydroxyethyl)-pyridine, (3-hydroxypropyl)-pyridine, (hydroxymethyl)-pyridine, N-methyl-2-hydroxy-methyl-piperidine, 1-(2-hydroxyethyl)-imidazole, 2-amino-6-methoxybenzothiazole, 4-aminomethyl-pyridine, 4-amino-2-methoxypyrimidine, 2-mercaptopyrimidine, 2-mercapto-benzimidazole, 3-mercapto-1,2,4-triazole, 3-amino-1,2,4-triazole, 2-isopropyl-imidazole, 2-ethyl-imidazole, 4-methyl-imidazole, 2-methyl-imidazole, 2-ethyl-4-methyl-imidazole, 2-phenyl-imidazole, 4-nitro-imidazole and mixtures thereof.

6. A composition according to claim **1** wherein for component b) formula (I) H is derived from at least one monomer selected from the group consisting of toluene diisocyanate, 4,4'-diphenylmethane diisocyanate, tolidine diisocyanate, m-xylylene diisocyanate, p-phenylene diisocyanate, m-phenylene diisocyanate, 1-chloro-2,4-phenylene diisocyanate, 3,3'-dimethyl-4,4'-bisphenylene diisocyanate, 4,4'-bisphenylene diisocyanate, 4,4'-bis(2-methoxyisocyanatophenyl)methane, 4,4'-diisocyanatodiphenyl ether, 4,4'-diisocyanatodibenzyl, 3,3'-dimethoxy-4,4'-diisocyanatodiphenyl, 2,2'-dimethyl-4,4'-diisocyanatodiphenyl, 2,2'-dichloro-5,5'-dimethoxy-4,4'-diisocyanatodiphenyl, 3,3'-dichloro-4,4'-diisocyanatodiphenyl, 1,3-propane diisocyanate, 1,4-butane diisocyanate, 2-chloropropane-1,3-diisocyanate, pentamethylene diisocyanate, propylene-1,2-diisocyanate, 1,8-octane diisocyanate, 1,10-decane diisocyanate, 1,12-dodecane diisocyanate, 1,16-hexadecane diisocyanate 1,3- and 1,4-cyclohexane diisocyanate, 1,6-hexamethylene diisocyanate, 2,2,4- and 2,4,4-trimethylhexamethylene diisocyanate, 4,4'-dicyclohexylmethane diisocyanate, isophorone diisocyanate, 3-isocyanatomethyl-3,5,5-trimethylcyclohexyl diisocyanate, lysine methyl ester diisocyanate, m-tetramethylxylylene diisocyanate and mixtures thereof.

7. A composition according to claim **1** wherein

y is from about 0.1 to about 35% by weight of the terpolymer of formula (I);

v is from about 5% to about 70% by weight of the terpolymer of formula (I);

u is from about 5% to about 75% by weight of the terpolymer of formula (I);

z is from about 0.1% to about 50% by weight of the terpolymer of formula (I);

x is from about 1% to about 40% by weight of the terpolymer of formula (I); and

w is from about 0.1% to about 45% by weight of the terpolymer of formula (I).

8. A composition according to claim **7** wherein

y is from about 1 to about 30% by weight of the terpolymer of formula (I);

v is from about 5% to about 60% by weight of the terpolymer of formula (I);

u is from about 5% to about 65% by weight of the terpolymer of formula (I);

z is from about 1% to about 50% by weight of the terpolymer of formula (I);

x is from about 1% to about 30% by weight of the terpolymer of formula (I); and

w is from about 1% to about 40% by weight of the terpolymer of formula (I).

9. A composition according to claim **8** wherein

y is from about 5 to about 20% by weight of the terpolymer of formula (I);
v is from about 10% to about 60% by weight of the terpolymer of formula (I);
u is from about 5% to about 60% by weight of the terpolymer of formula (I);
z is from about 1% to about 40% by weight of the terpolymer of formula (I);
x is from about 5% to about 25% by weight of the terpolymer of formula (I); and
w is from about 5% to about 30% by weight of the terpolymer of formula (I).

10. A composition according to claim **1** wherein component b) formula (I) has a weight average molecular weight of from about 500 to about 1 million Daltons.

11. A composition according to claim **10** wherein component b) formula (I) has a weight average molecular weight of from about 500 to about 500,000 Daltons.

12. A composition according to claim **11** wherein component b) formula (I) has a weight average molecular weight of from about 500 to about 100,000 Daltons.

13. A composition according to claim **12** wherein component b) formula (I) has a weight average molecular weight of from about 1000 to about 75,000 Daltons.

14. A composition according to claim **1** wherein component b) formula (I) is present in an amount from about 0.01 weight per cent to about 50 weight per cent based on the weight of the total composition.

15. A composition according to claim **14** wherein component b) formula (I) is present in an amount from about 0.1 weight per cent to about 25 weight per cent based on the weight of the total composition.

16. A composition according to claim **15** wherein component b) formula (I) is present in an amount from about 0.1 weight per cent to about 10 weight per cent based on the weight of the total composition.

17. A composition according to claim **1** wherein component a) comprises at least one UV screening agent selected from the group consisting of organic sunscreens, inorganic sunscreens and mixtures thereof.

18. A composition according to claim **17** wherein said inorganic sunscreen is selected from the group consisting of titanium oxide, iron oxide, zinc oxide, zirconium oxide, cerium oxide and mixtures thereof.

19. A composition according to claim **17** wherein said organic sunscreen is selected from the group consisting of triazines, benzotriazoles, benzophenones, vinyl group-containing amides, cinnamic acid amides, sulfonated benzimidazoles and mixtures thereof.

20. A composition according to claim **17** wherein component a) is present in micronized or non-micronized form.

21. A composition according to claim **1** wherein component a) is present in an amount from about 0.1 weight per cent to about 30 weight per cent based on the weight of the total composition.

22. A composition according to claim **21** wherein component a) is present in an amount from about 1 weight per cent to about 20 weight per cent based on the weight of the total composition.

23. A composition according to claim **22** wherein component a) is present in an amount from about 1 weight per cent to about 5 weight per cent based on the weight of the total composition.

24. A method of increasing the sun protection factor of a sunscreen composition wherein said method comprises incorporating into said composition an effective amount of at least one random terpolymer according to formula (I) of claim **1**.

25. A method of improved UV protection of mammalian hair and/or skin from the damaging effects of UV radiation wherein said method comprises applying to said skin and/or said hair an effective amount of a sunscreen composition according to claim **1**.