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(57)	Claim					
	1. A highly oxygen-permeable continuous-wear lens formed of a					

1. A highly oxygen-permeable continuous-wear lens formed of a polymer comprising an interpolymerized amount of the following monomers:

 (a) at least one hexafluoroisopropyl ester of an unsaturated carboxylic acid containing from 2 to 6 carbon atoms and 1 or 2 carboxyl groups;

(b) at least one organosilicon monomer copolymerizable with a hexafluoroisopropyl ester of an unsaturated carboxyric acid present in an amount of from 10 to 40 percent by weight based on the total weight of the monomers;

(c) at least one hydrophilic monomer capable of inducing wettability present in an amount sufficient to provide in the resultant polymer a receding contact angle of less than 45°; and

(d) at least one cross-linking monomer, the total of cross-linking monomer being present in an amount up to 5 percent by weight based on the total weight of the monomers,

(e) from 0 to 20% (by weight based on total weight of the monomers) of a UV-absorbing agent; and

(f) from 0 to 5% (by weight based on total weight of the monomers) of other monomers.

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16 May 1985 (33) Priority Country: (71) Applicant (for all designated States ex. BAUSCH AND LOMB INCORPORATED 42 East Avenue, Post Office Box 743, Rock 14603 (US).	<i>cept U</i> D jUS/U	US Published With international search report. Before the expiration of the time limit for amending the S): claims and to be republished in the event of the receipt of amendments.
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(54) Title: CONTINUOUS-WEAR LENSES	- · · · .	·
(57) Abstract		

Continuous-wear lenses formed by polymerizing a hexafluoroisopropyl ester of an unsaturated carboxylic acid which can have an oxygen permeability in excess of at least 150 x 10^{-11} (cm²/sec) (ml O₂/ml x inm Hg). A UV-absorbing agent is optionally present.

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<u>Abstract</u>

A highly oxygen-permeable continuous-wear lens formed of a polymer comprising an interpolymerized amount of the following monomers:

 (a) at least one hexafluoroisopropyl ester of an unsaturated carboxylic acid containing from 2 to 6 carbon atoms and 1 or 2 carboxyl groups;

(b) at least one organosilicon monomer copolymerizable with a hexafluoroisopropyl ester of an unsaturated carboxylic acid present in an amount of from 10 to 40 percent by weight based on the total weight of the monomers;

(c) at least one hydrophilic monomer capable of inducing wettability present in an amount sufficient to provide in the resultant polymer a receding contact angle of less than 45°; and

(d) at least one cross-linking monomer, the total of cross-linking monomer being present in an amount up to 5 percent by weight based on the total weight of the monomers,

(e) from 0 to 20% (by weight based on total weight of the monomers) of a UV-absorbing agent; and

(f) from 0 to 5% (by weight based on total weight of the monomers) of other monomers.

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CONTINUOUS-WEAR LENSES

Background of the Invention

The present invention is directed to eye-compatible lenses, particularly hard contact lenses having excellent oxygen permeability and wettability.

Contact lenses presently on the market are classified into two large groups: soft contact lenses and hard contact lenses. Hard contact lenses are better able than soft contact lenses to retain visual characteristics, but are less comfortable. The art has sought to increase oxygen permeability of hard contact lenses, to extend the length of time they can be worn without causing corneal damage or discomfort.

One proposed solution has been the formation of a copolymer of methyl methacryla'e and a siloxane methacrylate compound. This solution has been less than satisfactory, since the lenses offered are not as hard, rigid, nor wettable as lenses formed from polymethyl methacrylate. In addition, such lenses are fragile and have poor mechanical processability.

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The object of the present invention is to overcome the deficiencies in the state of the art by offering lenses having a high degree of oxygen permeability, excellent wettability, and, if desired, ultraviolet absorption. The primary benefit of UV absorptivity is the resistance to user development of cataracts.

According to this invention there is provided a highly oxygen-permeable contributes-wear lens formed of a polymer comprising an interpolymerized amount of the following monomers:

 (a) at least one hexafluoroisopropyl ester of an unsaturated carboxylic acid containing from 2 to 6 carbon atoms and 1 or 2 carboxyl groups;

(b) at least one organosilicon monomer copolymerizable with a hexafluoroisopropyl ester of an unsaturated carboxylic acid present in an amount of from 10 to 40 percent by weight based on the total weight of the monomers;

(c) at least one hydrophilic monomer capable of inducing wettability present in an amount sufficient to provide in the resultant polymer a receding contact angle of less than 45°; and

(d) at least one cross-linking monomer, the total of cross-linking monomer being present in an amount up to 5 percent by weight based on the total weight of the monomers,

(e) from 0 to 20% (by weight based on total weight of the monomers) of a UV-absorbing agent; and

(f) from 0 to 5% (by weight based on total weight of the monomers) of other monomers.

Summary of the Invention

The present invention is directed to eye-compatible, continuouslywearable, oxygen-permeable optical lenses of excellent wettability, formed of copolymers of at least one organosilicon monomer with at least one hexafluoroisopropyl ester of an unsaturated carboxylic acid containing from 2 to about 10 carbon atoms and 1 or 2 carboxyl groups, at least one hydrophilic monomer, and at least one crosslinking monomer. The preferred hexafluoroisopropyl ester of an unsaturated carboxylic acid is hexafluoroisopropylmethacrylate. The organosilicon monomer is preferably a monomer system comprising an organosilane or an organosiloxane of the general

formula:

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$$CH_{2} = C - R_{1} OH_{1} COO-(CH_{2}-CH-CH_{2}O)_{a}-(CH_{2})_{b}-X$$
(1)

wherein R_1 is hydrogen or methyl, a is 0 or 1, b is from 1 to about 4, and X is an organosilicon moiety containing up to about 16 silicon atoms. It is preferred that at least a portion, and as much as 100 percent, of the organosilicon monomer system is a hydroxyorganosilicon monomer which is a monomer having at least one hydroxyl group bonded to silicon. Preferably from 0.1 to about 10 percent by weight of the monomers is a hydroxyorganosilicon monomer. The presently preferred monomers are tris(trimethylsiloxy)- γ -methacryloxypropylsilane,

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hydroxy-di(trimethylsiloxy)silylpropylmethacrylate, and 1,3,-bis(-methacryloxypropyl)-1,1,3,3-tetra(-trimethylsiloxy)disiloxane, particularly mixtures thereof.

A second component is a fluoroorgano monomer system comprising at least one hexafluoroisopropyl ester of an unsaturated carboxylic acid containing from 1 to about 10 carbon atoms and 1 or 2 carboxyl groups. These monomers, as against monomers of close structure, such as hexafluorobutylmethacrylate, have been surprisingly and unexpectedly found to enable the formation of lenses of extremely high oxygen permeability. The use of hexafluoroisopropylmethacrylate, for instance, enables achievement of an oxygen permeability in excess of Dk 150, and even in excess of 300. Lenses formed can be worn continuously.

A final component is a crosslinking monomer which is a crosslinking agent, preferably an organosilicon monomer, present in an amount up to about 5, preferably up to about 2, percent by weight based on the total weight of the monomers.

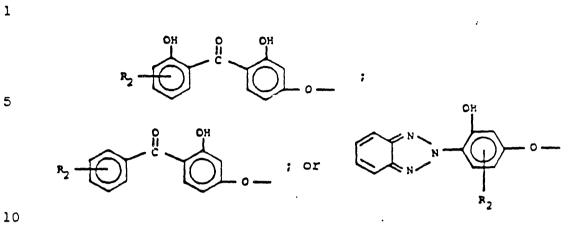
At least one hydrophilic monomer is included, preferably an unsaturated carboxylic acid capable of inducing wettability, and is present in an amount sufficient to provide in the resultant polymer a receding contact angle of about 45° or less. Methacrylic acid is preferred.

A UV-absorbing agent, if desired, may be included. In this instance, the agent may be a copolymerizable UV-absorbing monomer, preferably a hydroxybenzophenone or a benzotriazole compound of the formula:

 $CH_2 = C-R_1$ $COO-(CH_2-CHOH-CH_2O)_a - (CH_2)_b$ d (2)

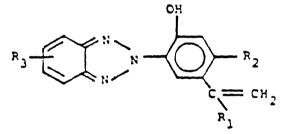
35 wherein R₁, a and b are as defined above, d is l or 2, and Z is:

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wherein R_2 is hydrogen, alkyl or hydroxy. Alternately or in addition, the UV-absorbing monomer may be a benzotriazole of the formula:



20 wherein R₁ and R₂ are as defined above, and R₃ is H or alkyl, preferably a C₁-C₁₀ alkyl. Alternately, UVabsorbing agents may be non-reactive homopolymers and copolymers comprising a UV-absorbing monomer which may be added to the monomer system and physically entrained in 25 the polymerized mass to achieve UV protection.

It has been found that the total organosiliconmonomer content of the polymer may range from about 10 to about 40 percent by weight, preferably from about 15 to about 35 percent by weight, preferably from about 15 to about 25 percent by weight, based on the total weight of the monomers. The hydrophilic monomer may be present in an amount of from about 1 to about 15 percent by weight, preferably from about 2 to about 10 percent by weight based on the total weight of the monomers. The crosslinking monomer may be present in an amount up to about

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2 percent by weight based on the total weight of the The balance of the monomer system may be monomers. solely the fluoroorgano monomers. Monomers which may be advantageously added in adjusting physical properties of the lens include monomers such as acrylates, methacrylates, itaconic esters, styrenes, fluorinated styrenes, alkyl styrenes, fluorinated alkyl styrenes, and the like, generally provided in an amount up to about 50 percent by weight of the total organofluoro content of the polymer, typically 10 up to about 5 percent by weight of the monomers. The UVabsorbing agent, if present, may be present in an amount of from about 0.1 to about 20 percent, preferably from about 2 to about 10 percent by weight based on the total weight of the agent and monomers. For a hard lens, it is 15 desired that the lens have a Shore D hardness greater than about 78, preferably from about 80 to about 85. This may require inclusion of modifying monomers in a concentration of up to about 50 percent by weight of the concentration of the fluoroorgano monomer, typically up to about 5 per-

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It is desired to provide an oxygen permeability (Dk) measured at 35°C greater than about 150 x 10^{-11} (cm²/sec) $(ml O_2/ml x mm Hg)$. This is achieved by inclusion of a sufficient amount of the hexafluoroisopropyl ester of an unsaturated carboxylic acid.

cent by weight based on the total weight of the monomers.

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Detailed Description

The present invention is directed to eye-compatible, e.g., corneal-compatible, continuous-wear lenses, in particular, hard contact lenses formed of an interpolymerized amount of an organosilicon monomer system, preferably one containing at least one hydroxyorganosilicon monomer, at least one hexafluoroisopropyl ester of an unsaturated carboxylic acid containing from about 2 to about 10 carbon

- 10 atoms and 1 or 2 carboxyl groups, at least one monomeric unsaturated carboxylic acid hydrophilic monomer, and at least one crosslinking monomer. If desired, a UV-absorbing agent which is preferably a benzotriazole and/or a benzophenone monomer or non-leachable polymer comprising
- 15 one or more such monomers, may be incorporated in the system. Other reactive monomers such as acrylates, methacrylates, itaconic esters, styrenes, alkyl styrenes, and the like, may be included as part of the polymerizable composition, to achieve a lens of desired properties, such 20 as hardness for machinability, wettability, and oxygenpermeability.

The hexafluoroisopropyl esters of an unsaturated carboxylic acid containing from 2 to about 10 carbon atoms and 1 or 2 carboxyl groups, include reactive monomers of the structure:

$$CH_2 = C - M_1$$

$$i$$

$$COOM$$
(2)

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wherein M is hydrogen, alkyl or fluoroalkyl, and M₁ is hydrogen, alkyl, fluoroalkyl, alkyl carboxy, carboxyester, alkyl carboxyester, fluorinated carboxyester, fluorinated alkyl carboxyester, cyano, or phenyl, with the proviso that the structure contain at least one hexafluoroisopropyl ester group. Hexafluoroisopropylmethacrylate is presently preferred.

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By the term "organosilicon monomer" as used herein, there is meant unsaturated silicon monomers which are copolymerizable with hexafluoroisopropyl esters of an unsaturated carboxylic acid, to yield lenses of high oxygen permeability, and which, in the amounts employed, are non-deleterious to the lens user.

The presently preferred organosilicon monomers which may be used in accordance with the instant invention include organosilicon monomers which are organosilanes and/or organosiloxanes of the general formula:

$$CH_{2} = C-R_{1}$$

$$COO-(CH_{2}-CHOH-CH_{2}O)_{a}-(CH_{2})_{b}-X$$
(3)

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wherein R₁ is hydrogen or methyl, a is 0 cr 1, b is from 1 to about 4, and X is an organosilicon moiety containing up to about 26 silicon atoms. Desirably, at least a portion, or all, of the organosilicon monomer system is a hydroxyorganosilicon monomer, namely, a monomer having

at least one hydroxyl group bonded to silicon. Preferred organosilicon compounds are acrylates and

methacrylates of the general formula:

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 $CH_2 = C-R_1$ $COO(-CH_2-CHOH-CH_2-O-)_a-(CH_2)_b-X'$ (4)

			R4 	R6 		R6
	wherein X'	is	-Si-(C	$H_2)_b - \dot{S}i - R_7$	or	-Si-R7
)			R ₅	Ŕġ		Ŕ ₈

each of R₄ and R₅ is independently a C₁-C₅ alkyl, phenyl, hydroxyl, or $-O-Si(CH_3)_3$, and each of R₆, R₇ and R₈ is independently selected from C₁-C₅; $-CH_2=CH_2$; phenyl; hydroxyl; $-CH_2OH$;

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-8-CHA 1 CHA -0-\$i-OH -0-Śi-0-Si(CH3)3 ; | CH 3 ĊHa 5 $O-Si(CH_3)_3$ -O-SiCH3 ; $O-Si-[OSi(CH_3)_3]_3$; or $O-Si(CH_3)_3$ 10 $CH_2 = C-R_1$ COO-(CH2-CHO1-CH2-O-)a-(CH2)b- , wherein R_1 , a, and b are as defined above. The monomers included are: 15 tris(trimethylsiloxy)silylpropylmethacrylate, 1,3-bis(-1-methacryloxypropyl)-1,1,3,3-tetra(trimethylsiloxy)disiloxane. vinyl di(trimethylsiloxy)silylpropylmethacrylate, pentamethyldisiloxy)-/-methacryloxypropylsilane, 20 trimethylsilylpropylmethacrylate, methyl di(trimethylsiloxy)silylpropylmethacrylate, tris(trimethylsiloxy)silylpropylglycerolmethacrylate, and the like. Tris(trimethylsiloxy)-methacryloxypropylsilane is presently preferred. Another important monomer 25 is 1,3-bis-(1-methacryloxypropyl)-1,1,3,3-tetra(trimethylsiloxy)disiloxane, as it serves as a crosslinking agent without sacrificing oxygen permeability. When used for this purpose, concentration may vary from about 0.1 to about 2 percent by weight based on the total weight of 30 the reactants. Representative hydroxyorganosilicon monomers include hydroxy-di(trimethylsiloxy'silylpropylmethacrylate, hydroxy-di(trimethylsiloxy)-1-methacryloxypropylsilane, hydroxy-methyl(trimethylsiloxy)methacryloxymethylsilane, 35

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hydroxy-methyl(trimethylsiloxy)methacryloxyethylsilane, hydroxy-methyl(trimethylsiloxy)methacryloxypropylsilane, hydroxy-di(trimethylsiloxy)-f-methacryloxyethylsilane, hydroxy-di(trimethylsiloxy)-methacryloxy methylsilane, hydroxy-(trimethylsiloxy)-(pentamethyldisiloxy)-methacryloxy-methylsilane, hydroxy-(trimethylsiloxy)-(pentamethyldisiloxy)-f-methacryloxyethylsilane, and the like. Hyfroxy-di(trimethylsiloxy)silylpropylmethacrylate

is presently preferred.

Other useful organosilicon monomers are disclosed in U.S. Patents 4,152,508 to Ellis; 4,153,641 to Deichert et al; 4,189,546 to Deichert et al; and 4,463,149 to Ellis, each incorporated herein by reference.

While total concentrations of organosilicon monomers may range from about 10 to about 40 percent by weight based on the total weight of the monomers, the preferred range is from about 15 to about 35 percent by weight, more preferably from about 15 to about 25 percent by weight.

Oxygen permeability (all other factors being stant) will increase with an increase in organosilicon monomer content. At higher levels, the lens becomes more difficult to machine. Inclusion of monomers such as acrylates, methacrylates, itaconic esters, styrenes, alkyl styrenes and the like, may be employed as part of the monomer system to yield a lens having a desirable machinability, oxygen permeability, wettability, and the like. Lenses having a Shore D hardness greater than about 78, preferably from about 80 to about 85, are desired for hard, machinable lenses.

While hexafluoroiosopropylmethacrylate is essential to high oxygen permeability, oxygen permeability and wettability of the lens may be enhanced by the presence of a hydroxyorganosilicon monomer. Although the presently

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preferred concentration of the hydroxyorganosilicon monomer is from about 0.1 to about 10 percent by weight of the total monomers, it may be the exclusive organosilicon monomer, except for any multifunctional organosilicon 5 monomer used as a crosslinking monomer.

Critical to high oxygen permeability is the inclusion in the monomer system of hexafluoroisopropyl ester of an unsaturated carboxylic acid, which enables the achievement of an oxygen permeability (Dk) in excess of about 150. This renders the lens continuously wearable, i.e., wearable twenty-four hours a day for indefinite periods of time.

Other fluoroorgano monomers may be used as diluent monomers, at some sacrifice of oxygen permeability. They ¹⁵ include compounds of the formula:

$$CH_2 = C - R_1$$

|
 $COO(M_2)_a - (CH_2)_c - Y$

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wherein R_1 and a are as defined above, M_2 is hydroxy alkyl, alkyl ether, or hydroxy alkyl ether, c is from 0 to 4, and Y is a fluorocarbon group. Preferably, Y has the general formula:

 C_nF_{2n+1} or $C_nF_{2n}H$.

Illustrative of fluoroorgano monomers are 2,2,2 -trifluoroethylmethacrylate, hexafluorobutylmethacrylate, pentafluoro-n-propylmethacrylate, and the like, with 2,2,2-trifluoroethylmethacrylate being preferred for

cost. Perfluoro or fluorinated styrenes may also be used. Hydrophilic monomers are included in the composition to induce wettability. They preferably comprise an unsaturated carboxylic acid, most preferably methacrylic acid, for compatability of monomers and wearer comfort.

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Acrylic acid is functional but less desirable. Other monomers such as 2-hydroxyethylmethacrylate, vinyl pyrrolidone, and the like may be used. Concentration may be from about 0.1 to about 15 or more percent by weight, preferably from about 2 to about 10 percent by weight based on the total weight of the monomers.

The amount of hydrophilic monomer present depends on whether a UV-absorbing agent, as described below, is employed, as the latter also has the capability of adding hydrophilic properties. If a UV-absorbing agent is employed, its concentration may range from about 0.1 to about 20 percent by weight, preferably from about 2 to about 10 percent by weight based on the total weight of the monomers and agent. The UV absorbing agents used herein cooperate with the hydrophilic monomer to induce wettability and antisepticability, i.e., self-steri-

lizable, in consequence of hydroxy-substituted benzene moieties. The UV absorbers absorb in the polymerized state in the range of from about 300nm to about 450nm,

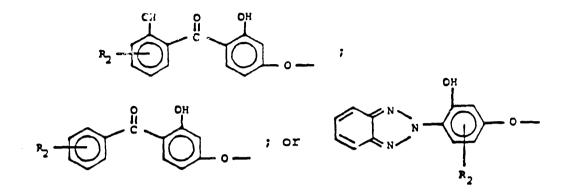
20 preferably with no less than about 70% UV radiation at 370nm. The UV-absorbing agent may be monomers that are interpolymerized with the monomers of the composition to become part of the formed copolymer, or they may be separately homopolymerized or copolymerized to non-25 reactive polymers of sufficient molecular weight so as to be physically entrained in the copolymer body formed by polymerizing the lens-forming monomers. The presently

preferred monomers are those of the formula:

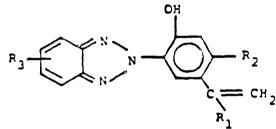
 $\begin{pmatrix} CH_2 = C - R_1 \\ I \\ COO - (CH_2 - CHOH - CH_2 - O -)_a - (CH_2 -)_b \\ - COO - (CH_2 - CHOH - CH_2 - O -)_a - (CH_2 -)_b \\ - COO - (CH_2 - CHOH - CH_2 - O -)_a - (CH_2 -)_b \\ - COO - (CH_2 - CHOH - CH_2 - O -)_a - (CH_2 -)_b \\ - COO - (CH_2 - CHOH - CH_2 - O -)_a - (CH_2 -)_b \\ - COO - (CH_2 - CHOH - CH_2 - O -)_a - (CH_2 -)_b \\ - COO - (CH_2 - CHOH - CH_2 - O -)_a - (CH_2 -)_b \\ - COO - (CH_2 - CHOH - CH_2 - O -)_a - (CH_2 -)_b \\ - COO - (CH_2 - CHOH - CH_2 - O -)_a - (CH_2 -)_b \\ - COO - (CH_2 - CHOH - CH_2 - O -)_a - (CH_2 -)_b \\ - COO - (CH_2 - CHOH - CH_2 - O -)_a - (CH_2 -)_b \\ - COO - (CH_2 - CHOH - CH_2 - O -)_a - (CH_2 -)_b \\ - COO - (CH_2 - CHOH - CH_2 - O -)_a \\ - COO - (CH_2 - CHOH - CH_2 - O -)_a \\ - COO - (CH_2 - CHOH - CH_2 - O -)_a \\ - CHOH - CH_2 - CHOH - CH_2 - O -)_a \\ - CHOH - CHOH - CH_2 - O -)_a \\ - CHOH - CHO$

wherein R_1 is hydrogen or methyl, a is 0 or 1, b is from about 1 to about 4, d is 1 or 2, and 2 is:

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wherein R_2 is hydrogen; an alkyl, preferably a C_1-C_5 alkyl or hydroxyl; and c is l or 2. In the alternative or in addition, there may be employed a phenyl benzotriazole of the formula:



Preferred UV-absorbing monomers for forming UVabsorbing agents include:

2-hydroxy-4-(2-methacryloyloxyethoxy)benzophenone,

2-hydroxy-4-(2-acryloyloxyethoxy)benzophenone,

2-hydroxy-4-(2-hydroxy-3-methacryloxypropyl)benzophenone, 2-(2-hydroxy-5-vinylphenyl)-2H-benzotriazole, and the like.

The lenses of the instant invention are formulated to a have high oxygen permeability (Dk) of at least about 150, preferably greater than about 200 [expressed in units of 10^{-11} (cm²/sec.)(ml O₂/ml x mm Hg), as determined at 35°C], as induced by the presence of a sufficient amount of a hexafluoroisopropyl ester of an unsaturated carboxylic acid. High oxygen permeability is surprisingly and unexpectedly attributed to the hexafluoroisopropyl moiety.

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With compositions of high organosilicon-monomer content there are displayed increased brittleness and a reduction in capability to undergo machining. At least one crosslinking agent, such as a multi-functional organosilicon monomer, a fluoroorgano monomer, an acrylate and/or a methacrylate, is employed in an amount sufficient to control hardness of the lens, which for hard lenses is in the range of Shore D hardness of greater than about 7ϵ , preferably from about 80 to about 85. A highly multi-10 functional organosilicon monomer is preferred, as it does not interfere with oxygen permeability. Other crosslinking agents which may be used include ethylene glycol dimethacrylate, ethylene glycol diacrylate, diethylene glycol dimethacrylate, diethylene glycol diacrylate, and 15 the like.

Lens formation may be by free radical polymerization such as azobisisobutyronitrile (AIBN) and peroxide catalysts under conditions set forth in U.S. Patent 3,808,179, incorporated herein by reference. Colorants and the like may be added prior to monomer polymerization. It is preferred to form the lens base in sheet form between layers of a non-adherent surface. The sheet is cut into smaller lense precursors from which the lens is ground to user specifications. Spin-casting, as described for instance in U.S. Patent 3,408,429, incorporated herein by reference, may also be used.

Without limiting, the following Example is illustrative of the instant invention. With reference to the Example, properties of the contact lenses were measured according to the following methods.

Oxygen permeability values were determined using a test method developed by Dr. Irving Fatt of Berkeley, California, and disclosed in the paper, entitled: "Oxygen Transmissibility and Permeability of Gas Permeable Hard Contact Lenses and Materials" by Irving Fatt, Ph.D., International Contact Lens Clinic, Vol. 11, No. 3, March 1984. The instrument was a polarographic cell with

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¹ a curved surface for finished lenses, polarographic amplifier, recorder and a constant temperature chamber equipped with a temperature control unit. The measurements were made at 35°C and the units of oxygen permeability are (cm²/sec)(ml 0₂/ml x mm Hg).

The water wettability of the contact lens material was determined by the sesile drop method using a Rame-Hart goniometer with an environmental chamber. Both the advancing and the receding contact angles were determined.

The hardness was measured as Shore D at 22°C using a hardness tester, and percent light transmission was measured using a recording spectrophotometer. The amount of materials extractable from the lenses were evaluated by first storing them in a saline solution for 10 days at

15 35°C. The lenses were then rinsed with distilled water, dried, weighed, and placed in stoppered, 25cc volumetric flasks, again containing saline as the extracting medium. The saline was analyzed daily for its extracted ultraviolet absorber by placing 4cc of the extract in a 20 spectrophotometer cell and determining the absorption The absorption values were compared against at 320 nm. the calibration curve made for the pure ultraviolet Extractables can also be determined by the absorber. Soxhlet extraction method, using water as the solvent. 25 The amount of extractables was determined only for a few of the materials in the Examples. Based on 0.04 gr average lens weight, extractables were found to be, on the average, less than 1 x 10^{-4} mc grams/lens/day, until a steady state was reached.

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The leachability-diffusibility was evaluated by cytotoxicity assay-agar overlay method.

The assay is based on the method described by Guess, W.L., Rosenbluth, S.A., Schmidt, B., and Autian, J., in "Agar Diffusion Method for Toxicity Screening of Plastics on Cultured Cell Monolayers", J. Pharm. Sci. 54:1545-1547, 1965, incorporated herein by reference, and is designed to detect the response of a mammalian monolayer cell 1 culture to readily diffusible components from materials or test solutions applied to the surface of an agar layer overlaying the monolayer.

- The response of the cell monolayer is evaluated, 5 with respect to the discoloration of the red-stained monolayer, under and around the sample when the petri dish is viewed against a white background. Loss of color of the stained cells is considered to be a physiologically significant reaction of the cells. The extent of discolora-10 tion is confirmed by examination of the monolayer on an inverted microscope, and the extent of lysis of the cells within the discoloration zone is estimated. Typically, discoloration of cells precedes lysis, as manifested by a region and a region showing lysis. A sample is reported 15
 - as "cytotoxic" only if lysis is observed.

Example 1

There was formulated a mixture of 19 parts by weight tris(trimethylsiloxy)silylpropylmethacrylate, 0.1 parts by weight 1,3-bis(&-methacryloxypropyl)-1,1,3,3-tetra 20 (trimethylsiloxy)disiloxane, 0.9 parts by weight hydroxy -di(trimethylsiloxy)silylpropylmethacrylate, 75 parts by weight hexafluoroisopropylmethacrylate, 5 parts by weight methacrylic acid, and 0.2 parts by weight AIBN. The mix-25 ture was homogenized, degassed and placed in a polymerization cell made of two glass plates separated by a seal and held together by spring clamps. After filling, the cell was purged with nitrogen, sealed and placed in a circulating water bath at 60°C for 10 hours. After the

30 initial polymerization period, the cell was heated at 80°C for 3 hours, 100°C for one hour, and then allowed to cool to room temperature. The clamps were then removed and the transparent sheet heated for 2 hours at 100°C. The plastic sheet, about 1/4-inch in thickness, was cut into squares, then formed to discs which were used to 35

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prepare corneal cortact lenses using conventional hardcontact-lens-making equipment. The properties of this lens material are also shown in Table I.

Table I

Oxygen permeability	
$\times 10^{-11}$ (cm ² /sec) (ml O ₂ /ml x mm Hg)	234
Contact angle, receding	28
Shore D hardness	79
Cytotoxicity assay	negative

Lenses of another batch give an average permeability of 164 x 10^{-11} (cm²/sec.)(ml O₂/ml x mm Hg).

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Example 2

The procedure of Example 1 was repeated, except that the formulation contained 28.5 parts by weight tris(trimethylsiloxy)silylpropylmethacrylate, 0.2 parts by weight 1,3-bis(-methacryloxypropyl)-1,1,3,3-tetra(trimethylsiloxy)disiloxane, 1.3 parts by weight hydroxy-di(tri-

methylsiloxy)silylpropylmethacrylate, 65 parts by weight hexafluoroisopropylmethacrylate, and 5 parts by weight methacrylic acid. Average oxygen permeability was $398 \times 10^{-11} (\text{cm}^2/\text{sec.}) (\text{ml O}_2/\text{ml x mm Hg}).$

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The procedure of Example 1 was repeated, except that hexafluorobutylmethacrylate was used instead of hexafluoroisoprocylmethacrylate. The properties are shown in Table II.

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Table II

	Oxygen permeability x 10 ⁻¹¹ (cm ² /sec.)(ml O ₂ /ml x mm Hg)	42
5	Contact angle, receding	26
	Shore D hardness	78
	Cytotoxicity assay	negative

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The claims defining the invention are as follows:

1. A highly oxygen-permeable continuous-wear lens formed of a polymer comprising an interpolymerized amount of the following monomers:

 (a) at least one hexafluoroisopropyl ester of an unsaturated carboxylic acid containing from 2 to 6 carbon atoms and 1 or 2 carboxyl groups;

(b) at least one organosilicon monomer copolymerizable with a hexafluoroisopropyl ester of an unsaturated carboxylic acid present in an amount of from 10 to 40 percent by weight based on the total weight of the monomers;

(c) at least one hydrophilic monomer capable of inducing wettability present in an amount sufficient to provide in the resultant polymer a receding contact angle of less than 45°; and

(d) at least one cross-linking monomer, the total of cross-linking monomer being present in an amount up to 5 percent by weight based on the total weight of the monomers,

(e) from 0 to 20% (by weight based on total weight of the monomers) of a UV-absorbing agent; and

(f) from 0 to 5% (by weight based on total weight of the monomers) of other monomers.

2. The lens as claimed in claim 1 in which the organosilicon monomer is an organosilicon monomer system comprised of at least one monomer of the formula:

 $CH_{2} = C - R_{1} OH_{1} COO-(CH_{2}-CH-CH_{2}O)_{a}-(CH_{2})_{b}-X$

wherein R₁ is hydrogen or methyl, a is 0 or 1, b is from 1 to 4, and X is an organosilicon moiety containing up to 16 silicon atoms.

3. The lens as claimed in claim 1 or claim 2 wherein the hexafluoroisopropyl ester is hexafluoroisopropylmethacrylate.

4. The lens as claimed in claim 3 in which there is present, in addition to hexafluoroisopropylmethacrylate, at least one other fluoroorgano monomer of the formula:



$$CH_2 = C - R_1$$

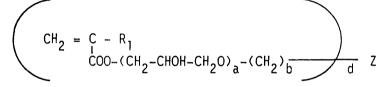
 $COO - (M_2)_a - (CH_2)_c - Y$

wherein R_1 is hydrogen or methyl, M_2 is hydroxy alkyl, alkyl ether, or hydroxy alkyl ether, a is 0 or 1, c is from 0 to 4, and Y is a fluorocarbon group.

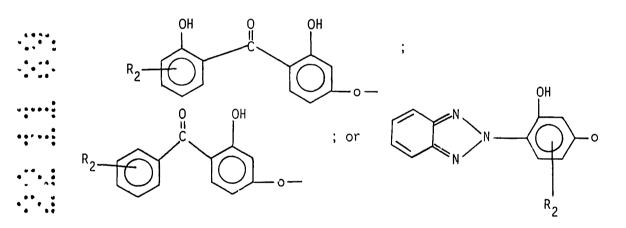
5. The lens as claimed in any one of claims 1 to 4 wherein the number of fluorine atoms is between 2 and 21.

6. The lens as claimed in any one of claims 3 to 5 wherein the fluorocarbon is 2,2,2-trifluoroethylmethacrylate, hexafluorobutylmethacrylate, pentafluoro- n-propylmethacrylate or perfluoro or fluorinated styrenes

7. The lens as claimed in any one of claims 1 to 6 in which the UV-absorbing agent comprises a polymerized amount of a monomer selected from the group consisting of a hydroxybenzophenone or benzotriazole of the formula:



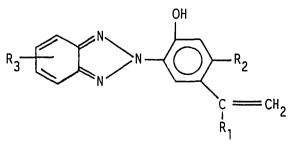
wherein R_1 is hydrogen or methyl, a is 0 or 1, b is from 1 to 4, d is 1 or 2, and Z is:



wherein R_2 is hydrogen, alkyl or hydroxy and a phenyl benzotriazole of the formula:



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wherein $\rm R_1$ and $\rm R_2$ are as defined above, and $\rm R_3$ is H; alkyl, preferably a $\rm C_1-C_{10}$ alkyl.

8. The lens as claimed in any one of claims 1 to 7 in which the concentration of organosilicon monomer is 15 to 35 percent.

9. The lens as claimed in any one of claims 1 to 7 in which the concentration of organosilicon monomer is 15 to 25 percent.

10. The lens as claimed in any one of claims 1 to 9 in which the organocilicon monomer is selected from tris(trimethylsiloxy)- γ -metha-cryloxypropylsilane, 1,3-bis-(γ -methacryloxypropyl-)1,1,3,3-tetra(trimethylsiloxy)disiloxane and mixtures thereof.

11. A highly oxygen-permeable continuous-wear lens comprising a polymer containing on an interpolymerized basis, from 19 to 30 parts by weight tris(trimethylsiloxy)silylpropylmethacrylate, from 0.1 to 0.2 parts by weight 1,3-bis-(γ -methacryloxypropyl)-1,1,3,3-tetra(trimethylsiloxy) disiloxane, from 65 to 75 parts by weight hexafluoroisopropylmethacrylate, and 3 parts by weight methacrylic acid.

12. The lens as claimed in any one of claims 1 to 11 in which the lers mas an oxygen permeability of at least about 150 x 10^{-11} (cm²/sec.) (ml O₂/ml x mm "g).

13. A highly-oxygen-permeable continuous-wear lens formed of a polymer substantially as hereinbefore described with reference to Example 1 or Example 2.

> DATED this TWENTY-SECOND day of NOVEMBER 1989 Bausch and Lomb Incorporated

> > Patent Attorneys for the Applicant SPRUSON & FERGUSON

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ANNEX TO THE INTERNATIONAL SEARCH	REPORT ON	
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This Annex lists the patent family mem patent documents cited in the above-me search report. The members are as cont Patent Office EDP file on 04/06/86	ntioned international	•
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