

DECLARATION IN SUPPORT OF A CONVENTION APPLICATION FOR A PATENT

In support of the Convention Application made for a patent for an invention entitled:

Title of Invention "CONTINUOUS-WEAR LENSES"

Full name(s) and address(es) of Declarant(s) I/We Stephen A. Hellrung, Esq. Vice President and General Counsel Bausch & Lomb Incorporated (P. O. Box 54) of One Lincoln First Square Rochester, NY 14601-0054

do solemnly and sincerely declare as follows:-

Full name(s) of Applicant(s) 1. I am/We are the applicant(s) for the patent (or, in the case of an application by a body corporate)

1. I am/We are authorised by BAUSCH AND LOMB INCORPORATED the applicant(s) for the patent to make this declaration on its/their behalf.

2. The basic application(s) as defined by Section 141 of the Act was/were made

Basic Country(ies) in United States of America

Priority Date(s) on 29 January, 1985; 10 April, 1985 and 16 May, 1985

Basic Applicant(s) all by NICK STOYAN

Full name(s) and address(es) of inventor(s) 3. I am/We are the actual inventor(s) of the invention referred to in the basic application(s) (or where a person other than the inventor is the applicant)

3. NICK STOYAN of 3841 Diamonte Place, Encino, California 91416, United States of America

(respectively)

is/are the actual inventor(s) of the invention and the facts upon which the applicant(s) is/are entitled to make the application are as follows:

Set out how Applicant(s) derive title from actual inventor(s) e.g. The Applicant(s) is/are the assignee(s) of the invention from the inventor(s) The said applicant is the assignee of the actual inventor.

4. The basic application(s) referred to in paragraph 2 of this Declaration was/were the first application(s) made in a Convention country in respect of the invention(s) the subject of the application.

Declared at Rochester, New York this 12th day of January 1987

Signature of Stephen A. Hellrung

Signature of Declarant(s) Stephen A. Hellrung

(12) PATENT ABRIDGMENT (11) Document No. AU-B-54548/86
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 593543

(54) Title
CONTINUOUS-WEAR LENSES

International Patent Classification(s)
(51)^a G02B 001/04 C08F 220/22 C08F 220/28 C08F 230/08
C08F 299/08 G02C 007/04

(21) Application No. : 54548/86 (22) Application Date : 28.01.86

(87) WIPO Number : WO86/04341

(30) Priority Data

(31) Number	(32) Date	(33) Country
696014	29.01.85	US UNITED STATES OF AMERICA
722121	10.04.85	US UNITED STATES OF AMERICA
734898	16.05.85	US UNITED STATES OF AMERICA

(43) Publication Date : 13.08.86

(44) Publication Date of Accepted Application : 15.02.90

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SPRUSON & FERGUSON

(56) Prior Art Documents
AU 543235 17794/83 G02C 7/04 G02B 1/04

(57) Claim

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.

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PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification⁴ : C08F 230/08, G02B 1/04 C08F 299/08</p>	<p>A1</p>	<p>(11) International Publication Number: WO 86/ 04341 (43) International Publication Date: 31 July 1986 (31.07.86)</p>
<p>(21) International Application Number: PCT/US86/00198 (22) International Filing Date: 28 January 1986 (28.01.86) (31) Priority Application Numbers: 696,014 722,121 734,898 (32) Priority Dates: 29 January 1985 (29.01.85) 10 April 1985 (10.04.85) 16 May 1985 (16.05.85) (33) Priority Country: US (71) Applicant (for all designated States except US): BAUSCH AND LOMB INCORPORATED [US/US]; 42 East Avenue, Post Office Box 743, Rochester, NY 14603 (US). (72) Inventor; and (75) Inventor/Applicant (for US only) : STOYAN, Nick [US/ US]; 3841 Diamonte Place, Encino, CA 91416 (US).</p>	<p>(74) Agent: GRINNELL, John, P.; Christie, Parker & Hale, Post Office Box 7068, Pasadena, CA 91109-7068 (US). (81) Designated States: AT (European patent), AU, BE (Eu- ropean patent), BR, CH (European patent), DE (Eu- ropean patent), DK, FR (European patent), GB (Eu- ropean patent), IT (European patent), JP, LU (Euro- pean patent), NL (European patent), NO, SE (Euro- pean patent), US. Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i> A. O. J. P. 11 SEP 1986 AUSTRALIAN 13 AUG 1986 PATENT OFFICE</p>	

(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 $150 \times 10^{-11} (\text{cm}^2/\text{sec})$ ($\text{ml O}_2/\text{ml} \times \text{mm Hg}$). A UV-absorbing agent is optionally present.

Abstract

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

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

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(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

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(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

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(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.

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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.

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One proposed solution has been the formation of a copolymer of methyl methacrylate 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 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,

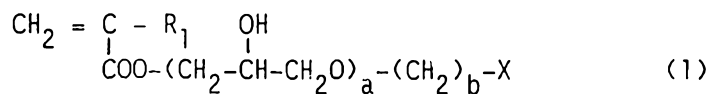
(e) from 0 to 20% (by weight based on total weight of the monomers) of a UV-absorbing agent; and

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

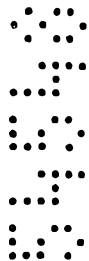
Summary of the Invention

The present invention is directed to eye-compatible, continuously-wearable, 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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wherein R₁ 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
10 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 hydroxyorgano-
silicon monomer. The presently preferred monomers are tris(trimethyl-
siloxy)-γ-methacryloxypropylsilane,



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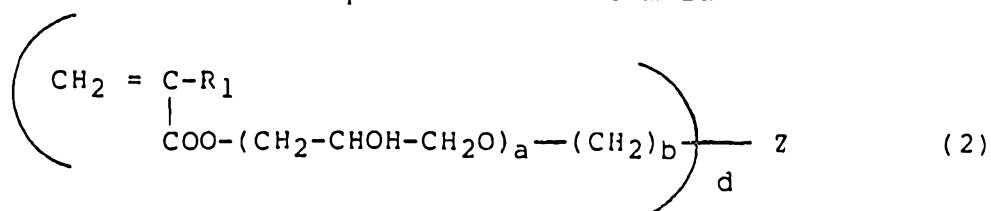
1 hydroxy-di(trimethylsiloxy)silylpropylmethacrylate, and
 1,3,-bis(-methacryloxypropyl)-1,1,3,3-tetra(-trimethyl-
 siloxy)disiloxane, particularly mixtures thereof.

5 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 hexa-
 fluorobutylmethacrylate, have been surprisingly and
 10 unexpectedly found to enable the formation of lenses of
 extremely high oxygen permeability. The use of hexa-
 fluoroisopropylmethacrylate, for instance, enables
 achievement of an oxygen permeability in excess of Dk
 150, and even in excess of 300. Lenses formed can be
 15 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
 20 weight of the monomers.

At least one hydrophilic monomer is included, prefer-
 ably 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
 25 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:



35 wherein R₁, a and b are as defined above, d is 1 or 2,
 and Z is:

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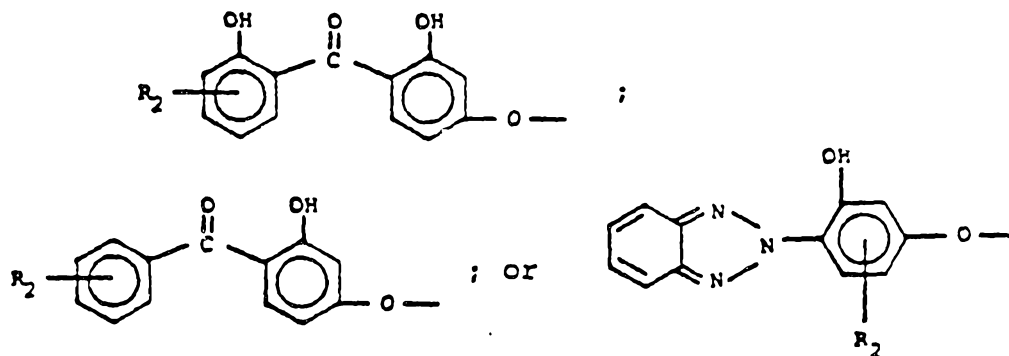
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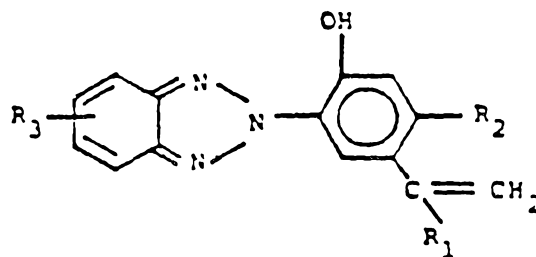
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wherein R₂ is hydrogen, alkyl or hydroxy. Alternately or in addition, the UV-absorbing monomer may be a benzotriazole of the formula:



wherein R₁ and R₂ are as defined above, and R₃ is H or alkyl, preferably a C₁-C₁₀ alkyl. Alternately, UV-absorbing 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 the polymerized mass to achieve UV protection.

It has been found that the total organosilicon-monomer 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 cross-linking monomer may be present in an amount up to about

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1 2 percent by weight based on the total weight of the
monomers. The balance of the monomer system may be
solely the fluoroorgano monomers. Monomers which may be
advantageously added in adjusting physical properties of
5 the lens include monomers such as acrylates, methacrylates,
itaconic esters, styrenes, fluorinated styrenes, alkyl sty-
renes, 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 UV-
absorbing 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-
20 cent by weight based on the total weight of the monomers.

It is desired to provide an oxygen permeability (Dk)
measured at 35°C greater than about $150 \times 10^{-11}(\text{cm}^2/\text{sec})$
(ml O₂/ml x mm Hg). This is achieved by inclusion of a
sufficient amount of the hexafluoroisopropyl ester of an
25 unsaturated carboxylic acid.

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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 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 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 as hardness for machinability, wettability, and oxygen-permeability.

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:



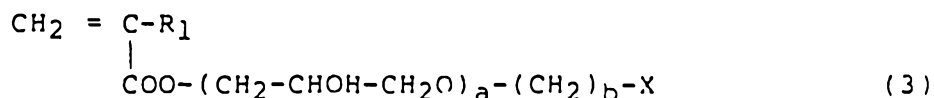
wherein M is hydrogen, alkyl or fluoroalkyl, and M₁ is hydrogen, alkyl, fluoroalkyl, alkyl carboxy, carboxyester, alkyl carboxyester, fluorinated carboxyester, fluorinated alkyl carboxyester, cyano, or phenyl, with the proviso that the structure contain at least one hexafluoroisopropyl ester group. Hexafluoroisopropylmethacrylate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

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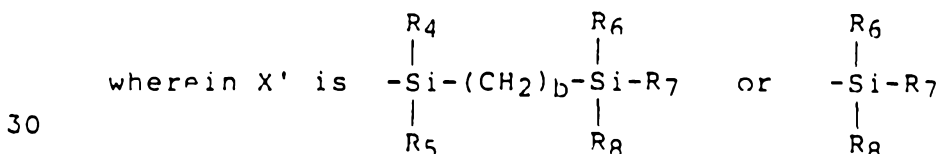
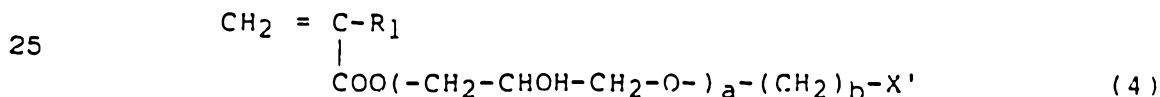
1 By the term "organosilicon monomer" as used herein,
 there is meant unsaturated silicon monomers which are
 copolymerizable with hexafluoroisopropyl esters of an
 5 unsaturated carboxylic acid, to yield lenses of high
 oxygen permeability, and which, in the amounts employed,
 are non-deleterious to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

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



15 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 26 silicon atoms. Desirably, at least a
 portion, or all, of the organosilicon monomer system is a
 hydroxyorganosilicon monomer, namely, a monomer having
 20 at least one hydroxyl group bonded to silicon.

Preferred organosilicon compounds are acrylates and
 methacrylates of the general formula:

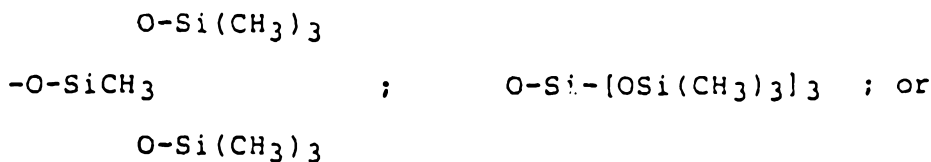


each of R_4 and R_5 is independently a C_1 - C_5 alkyl, phenyl,
 hydroxyl, or $-\text{O}-\text{Si}(\text{CH}_3)_3$, and each of R_6 , R_7 and R_8 is
 35 independently selected from C_1 - C_5 ; $-\text{CH}_2=\text{CH}_2$; phenyl;
 hydroxyl; $-\text{CH}_2\text{OH}$;

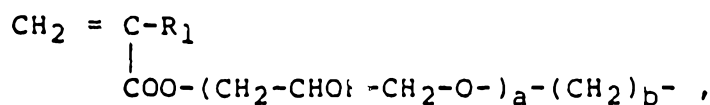
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wherein R₁, a, and b are as defined above.

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The monomers included are:

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tris(trimethylsiloxy)silylpropylmethacrylate,
 1,3-bis-(γ-methacryloxypropyl)-1,1,3,3-tetra(trimethylsiloxy)disiloxane,
 vinyl di(trimethylsiloxy)silylpropylmethacrylate,
 pentamethyldisiloxy-γ-methacryloxypropylsilane,
 trimethylsilylpropylmethacrylate,
 methyl di(trimethylsiloxy)silylpropylmethacrylate,
 tris(trimethylsiloxy)silylpropylglycerolmethacrylate,
 and the like. Tris(trimethylsiloxy)-methacryloxypropylsilane is presently preferred. Another important monomer is 1,3-bis-(γ-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 the reactants.

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Representative hydroxyorganosilicon monomers include hydroxy-di(trimethylsiloxy)silylpropylmethacrylate, hydroxy-di(trimethylsiloxy)-γ-methacryloxypropylsilane, hydroxy-methyl(trimethylsiloxy)methacryloxymethylsilane,

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1 hydroxy-methyl(trimethylsiloxy)methacryloxyethylsilane,
hydroxy-methyl(trimethylsiloxy)methacryloxypropylsilane,
hydroxy-di(trimethylsiloxy)- γ -methacryloxyethylsilane,
hydroxy-di(trimethylsiloxy)-methacryloxy methylsilane,
5 hydroxy-(trimethylsiloxy)-(pentamethyldisiloxy)-meth-
acryloxy-methylsilane, hydroxy-(trimethylsiloxy)-
(pentamethyldisiloxy)- γ -methacryloxyethylsilane, and the
like. Hydroxy-di(trimethylsiloxy)silylpropylmethacrylate
is presently preferred.

10 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.

15 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.

20 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,
25 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
30 hard, machinable lenses.

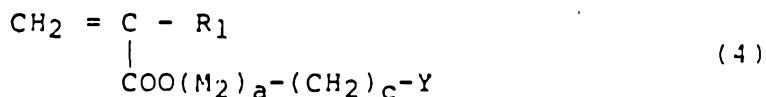
While hexafluoroisopropylmethacrylate is essential
to high oxygen permeability, oxygen permeability and
wettability of the lens may be enhanced by the presence
of a hydroxyorganosilicon monomer. Although the presently
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1 preferred concentration of the hydroxyorganosilicon mono-
 mer 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.
 10 This renders the lens continuously wearable, i.e., wear-
 able 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:



20 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:



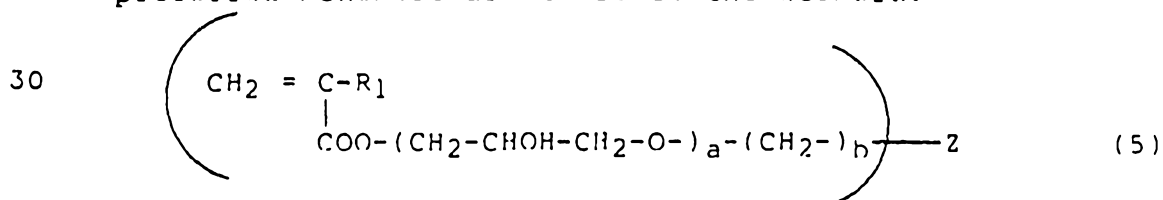
Illustrative of fluoroorgano monomers are 2,2,2
 -trifluoroethylmethacrylate, hexafluorobutylmethacrylate,
 pentafluoro-n-propylmethacrylate, and the like, with
 2,2,2-trifluoroethylmethacrylate being preferred for
 30 cost. Perfluoro or fluorinated styrenes may also be used.

Hydrophilic monomers are included in the composition
 to induce wettability. They preferably comprise an
 unsaturated carboxylic acid, most preferably methacrylic
 acid, for compatibility of monomers and wearer comfort.
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1 Acrylic acid is functional but less desirable. Other
 monomers such as 2-hydroxyethylmethacrylate, vinyl pyr-
 rolidone, and the like may be used. Concentration may
 be from about 0.1 to about 15 or more percent by weight,
 5 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
 10 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
 15 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:

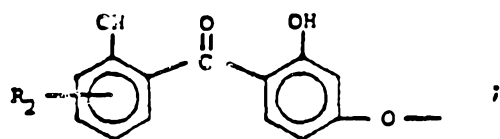


wherein R₁ is hydrogen or methyl, a is 0 or 1, b is from
 about 1 to about 4, d is 1 or 2, and 2 is:

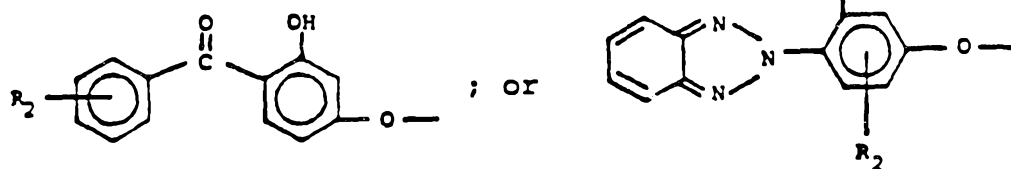
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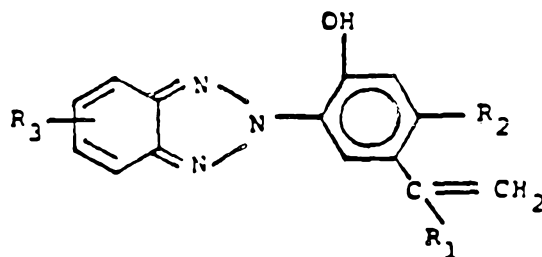
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wherein R_2 is hydrogen; an alkyl, preferably a C_1 - C_5 alkyl or hydroxyl; and c is 1 or 2. In the alternative or in addition, there may be employed a phenyl benzotriazole of the formula:

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Preferred UV-absorbing monomers for forming UV-absorbing agents include:

2-hydroxy-4-(2-methacryloyloxyethoxy)benzophenone,
 2-hydroxy-4-(2-acryloyloxyethoxy)benzophenone,
 25 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 have high oxygen permeability (Dk) of at least about 150, preferably greater than about 200 [expressed in units of 10^{-11} ($\text{cm}^2/\text{sec.})(\text{ml O}_2/\text{ml x mm Hg})$, 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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1 With compositions of high organosilicon-monomer content
there are displayed increased brittleness and a reduction
in capability to undergo machining. At least one cross-
linking agent, such as a multi-functional organosilicon
5 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 78,
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 cross-
linking 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 cata-
lysts under conditions set forth in U.S. Patent 3,808,179,
incorporated herein by reference. Colorants and the like
20 may be added prior to monomer polymerization. It is pre-
ferred 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
25 in U.S. Patent 3,408,429, incorporated herein by refer-
ence, may also be used.

Without limiting, the following Example is illus-
trative of the instant invention. With reference to the
Example, properties of the contact lenses were measured
30 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
35 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 measure-
ments were made at 35°C and the units of oxygen permea-
5 bility are (cm²/sec)(ml O₂/ml x mm Hg).

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

10 The hardness was measured as Shore D at 22°C using a
hardness tester, and percent light transmission was meas-
ured 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
at 320 nm. The absorption values were compared against
the calibration curve made for the pure ultraviolet
absorber. Extractables can also be determined by the
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 1×10^{-4} mc grams/lens/day, until
a steady state was reached.

30 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,
35 1965, incorporated herein by reference, and is designed
to detect the response of a mammalian monolayer cell

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1 culture to readily diffusible components from materials
or test solutions applied to the surface of an agar layer
overlying the monolayer.

5 The response of the cell monolayer is evaluated,
with respect to the discoloration of the red-stained mono-
layer, 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 sig-
10 nificant reaction of the cells. The extent of discolora-
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
20 by weight 1,3-bis(γ -methacryloxypropyl)-1,1,3,3-tetra
(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 polymer-
ization 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
35 into squares, then formed to discs which were used to

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

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Table I

Oxygen permeability x 10 ⁻¹¹ (cm ² /sec)(ml O ₂ /ml x mm Hg)	234
Contact angle, receding	28
Shore D hardness	79
10 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(tri-
methylsiloxy)silylpropylmethacrylate, 0.2 parts by weight
1,3-bis(-methacryloxypropyl)-1,1,3,3-tetra(trimethyl-
20 siloxy)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 x 10⁻¹¹(cm²/sec)(ml O₂/ml x mm Hg).

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Control

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

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Table II

Oxygen permeability x 10 ⁻¹¹ (cm ² /sec.)(ml O ₂ /ml x mm Hg)	42
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;

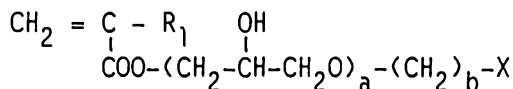
(c) at least one hydrophilic monomer capable of inducing wettability present in an amount sufficient to provide in the resultant polymer a receding contact angle of less than 45°; and

(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.

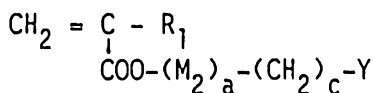
2. The lens as claimed in claim 1 in which the organosilicon monomer is an organosilicon monomer system comprised of at least one monomer of the formula:



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:



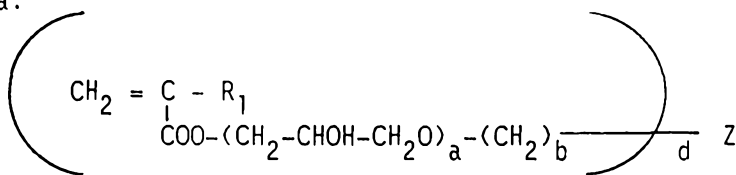
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wherein R_1 is hydrogen or methyl, M_2 is hydroxy alkyl, alkyl ether, or hydroxy alkyl ether, a is 0 or 1, c is from 0 to 4, and Y is a fluorocarbon group.

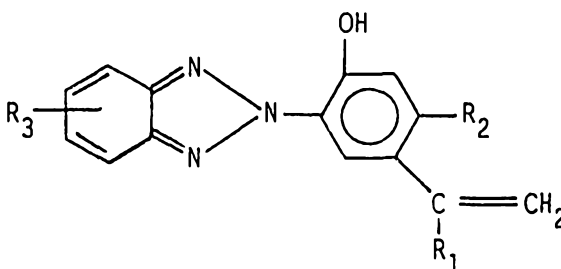
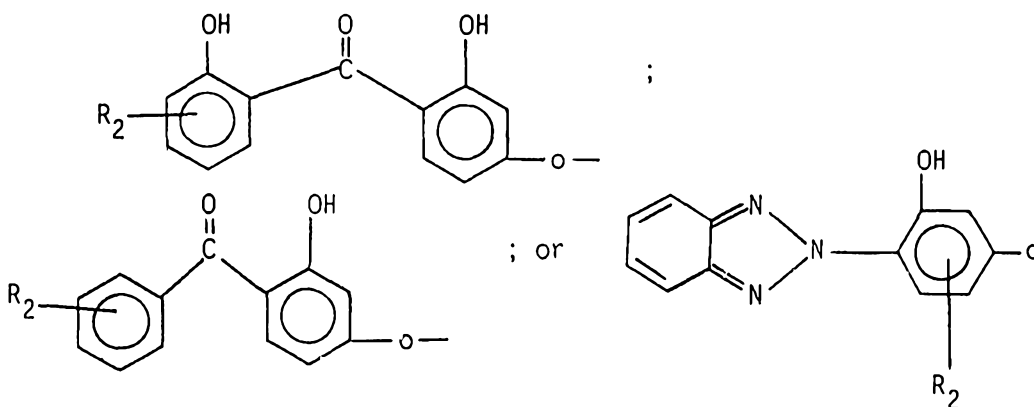
5. The lens as claimed in any one of claims 1 to 4 wherein the number of fluorine atoms is between 2 and 21.

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_1 and R_2 are as defined above, and R_3 is H; alkyl, preferably a 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 organosilicon monomer is selected from tris(trimethylsiloxy)- γ -methacryloxypropylsilane, 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 5 parts by weight methacrylic acid.

12. The lens as claimed in any one of claims 1 to 11 in which the lens has an oxygen permeability of at least about 150×10^{-11} ($\text{cm}^2/\text{sec.}$) ($\text{ml O}_2/\text{ml} \times \text{mm}^2/\text{g}$).

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

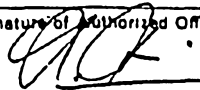
DATED this TWENTY-SECOND day of NOVEMBER 1989
Bausch and Lomb Incorporated

Patent Attorneys for the Applicant
SPRUSON & FERGUSON



INTERNATIONAL SEARCH REPORT

International Application No. PCT/US 86/00198

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC ⁴ : C 08 F 230/08; G 02 B 1/04; C 08 F 299/08		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
IPC ⁴	C 08 F ; 02 B 08 L	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
Y	US, A, 4419505 (D.J. RATKOWSKI) 6 December 1983, see claims 1-4; column 3, lines 23-69; column 5, lines 19-37 --	1
P, YUS	A, 4535138 (D.J. RATKOWSKI) 13 August 1985, see claims 1,2; column 3, lines 29-55; column 5, lines 59-68, column 6, lines 1-9, 10-31; column 7, lines 55-61 --	1
Y	GB, A, 2119951 (TOYO CONTACT LENS) 23 November 1983, see claim 1 --	1
X	EP, A, 0114894 (HOYA LENS) 8 August 1984, see claims 1,3,4,6; page 5, lines 8-27; page 9, lines 6-18 --	1,2,3
A	US, A, 4390676 (S. LOSHAEK) 28 June 1983, see claims 1,2,3 -----	10
<p>¹⁰ Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
14th May 1986	9 1 JUIN 1986	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	 L. ROSSI	

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON

INTERNATIONAL APPLICATION NO. PCT/US 86/00198 (SA 12202)

This Annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 04/06/86

The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A- 4419505	06/12/83	None	
US-A- 4535138	13/08/85	JP-A- 59081320	11/05/84
GB-A- 2119951	23/11/83	FR-A- 2526551	10/11/83
		DE-A- 3304089	10/11/83
		AU-A- 1062983	10/11/83
		JP-A- 59028127	14/02/84
		US-A- 4433125	21/02/84
		JP-A- 58194014	11/11/83
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		US-A- 4540761	10/09/85
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