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METHOD FOR PREPARING ULTRAVIOLET RADIATION
ABSORBING CONTACT LENSES

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BACKGROUND OF THE INVENTION

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The present invention relates to a process for producing ultraviolet radiation absorbing contact lenses. More particularly, the invention relates to a process for producing hydrophilic contact lenses having a UV radiation absorbing agent covalently bonded to polymeric material.

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Exposure to ultraviolet radiation, 200-400nm, is known to be damaging to the cornea and to be the cause of several ocular pathologies. For this reason it is important to provide adequate ocular protection against ultraviolet radiation. Such protection is particularly recommended for people who are prone to UV exposure, patients who have had cataract surgery and patients on photosensitizing drugs.

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Recently, contact lenses have been developed which serve to absorb UV radiation. For example, U.S. Patent No. 4,390,676 discloses a UV absorbing contact lens formed by copolymerizing a monomer suitable for making lenses and an ultraviolet absorber. The copolymerization efficiency of the compounds has proved to be inadequate, requiring the extraction of the UV absorbing compound prior to using the lens. The extraction process may take from 3 to 20 days.

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U.S. Patent No. 5,098,445 discloses a UV absorbing contact lens which has a reactive UV absorbing agent covalently bound to the polymeric material. The UV

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1 absorbing agent is applied to the lens by dipping the lens
into an aqueous medium having dissolved therein a
halotriazine which is substituted with a UV-absorbing
moiety. However, the triazinyl molecule that is thereby
5 incorporated into the lens polymer can be expected to
deleteriously affect the desirable physical and/or
refractive properties of the lens. Also, relying on the
halotriazine to react with the lens polymer introduces
uncertainty as to the degree of reaction that occurs, and
10 limits the scope of lens materials into which UV absorbers
can be incorporated by the disclosed techniques. Indeed,
this patent teaches that crosslinking a lens polymer
generally renders this technique ineffective, yet as is
well known many contact lenses, especially hydrophilic
lenses, must be made of crosslinked polymeric material.

15 There exists, therefore, a need for an improved
method for producing a UV absorbing contact lens.

There also exists a need for a method to produce a UV
absorbing contact lens which can be prepared in a
20 relatively short amount of time.

There further exists a need for a method to produce
a contact lens from which the absorbing agent has a
reduced tendency to leach out after preparation.

25 There exists a more particular need for a method to
produce a lens via in situ polymerization in which the
absorbing agent does not interfere with the polymerization
reaction.

SUMMARY OF THE INVENTION

30 The present invention relates to a process for
producing an ultraviolet radiation absorbing contact lens

1 which has a UV absorbing agent covalently bonded to the
polymeric material. In the present invention, a lens
shaped polymer having hydroxyl groups pendant therefrom
and having dispersed therein a UV absorbing agent
5 substituted with at least one anhydride group is exposed
to basic conditions such that the hydroxyl groups react
with the anhydride groups on the UV absorbing agent. As
a result the UV absorbing agent becomes fixed to the
polymer through the formation of a covalent ester bond.
10 Because of the covalent bonding, the absorbing agent does
not leach out after preparation of the lens. It is
critical in the present invention that the UV absorbing
agent at the level of inclusion does not interfere with
the UV initiated polymerization of the monomers used in
15 preparing the lens.

BRIEF DESCRIPTION OF THE DRAWING

FIG 1. is a plot of absorbance versus wavelength for
a contact lens prepared in accordance with the present
invention compared with a conventional contact lens.
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DETAILED DESCRIPTION OF THE INVENTION

While the present invention is applicable to
intraocular lenses and lenses used in spectacles, it will
be described in connection with contact lenses, both
25 corrective and noncorrective. The present invention
relates to a process for producing ultraviolet radiation
absorbing lenses comprising a UV absorbing agent
covalently bonded to polymeric lens material.

30 The UV absorbing agent is a UV absorbing compound
substituted with at least one anhydride group. It is

1 through the anhydride group that the UV absorbing agent is
capable of covalently bonding to the pendant hydroxyl
groups of the polymer. The UV absorbing compound is
5 chosen from the group of compounds that absorb radiation
having wavelengths within all or part of the range of 200-
450 nm and have functionality allowing bonding to an
anhydride group.

Possible UV absorbing compounds include oxalic acid
diamides, hydroxyphenyltriazines, benzotriazoles,
10 benzophenones, benzoic acid esters and cyano and
carbomethoxy acrylates.

Examples of oxalic acid diamides include,
4,4'-dioctyloxyoxanilide, 2,2'-dioctyloxy-5,5'-di-tert-
butyloxanilide, 2,2'-didodecyloxy-5,5'-di-tert-
15 butyloxanilide, 2-ethoxy-2'-ethyloxanilide, N,N'-bis(3-
dimethylaminopropyl)oxalamide, 2-ethoxy-5-tert-butyl-2'-
ethyloxanilide and its mixture with 2-ethoxy-2'-ethyl-
5,4'-di-tert-butyloxanilide and mixtures of ortho- and
para-methoxy-disubstituted oxanilides and mixtures of o-
and p-ethoxy-disubstituted oxanilides.

20 Examples of hydroxyphenyltriazines include the 2-(2-
hydroxyphenyl)-1,3,5-triazines such as 2,4,6-tris(2-
hydroxy-4-octyloxyphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-
octyloxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-
25 triazine, 2-(2,4-dihydroxyphenyl)-4,6-bis(2,4-
dimethylphenyl)-1,3,5-triazine, 2,4-bis(2-hydroxy-4-
propyloxyphenyl)-6-(2,4-dimethylphenyl)-1,3,5-triazine, 2-
(2-hydroxy-4-octyloxyphenyl)-4,6-bis(4-methylphenyl)-1,3,5-
triazine, 2-(2-hydroxy-4-dodecyloxyphenyl)-4,6-bis(2,4-
30 dimethylphenyl)-1,3,5-triazine.

Examples of benzotriazoles include the 5'-methyl,

1 3',5'-di-tert-butyl, 5'-tert-butyl, 5'-(1,1,3,3-
tetramethylbutyl), 5-chloro-3',5'-di-tert-butyl, 5-chloro-
3'-tert-butyl-5'-methyl, 3'-sec-butyl-5'-tert-butyl, 4'-
octoxy, 3',5'-di-tert-amyl and 3',5'-bis(α,α -
5 dimethylbenzyl) derivatives of 2-(2'-hydroxyphenyl)-
benzotriazole.

Examples of benzophenones include the 4-hydroxy, 4-
methoxy, 4-octoxy, 4-decyloxy, 4-dodecyloxy, 4-benzyloxy,
4,2',4'-trihydroxy and 2'-hydroxy-4,4'-dimethoxy
10 derivatives of 2-hydroxybenzophenone.

Examples of esters of substituted and unsubstituted
benzoic acids include 4-tert-butylphenyl salicylate,
phenyl salicylate, octylphenyl salicylate,
dibenzoylrescorinol, bis(4-tert-butylbenzoyl)-rescorinol,
benzoylrescorinol, 2,4-di-tert-butylphenyl 3,5-di-tert-
15 butyl-4-hydroxybenzoate and hexadecyl 3,5-di-tert-butyl-4-
hydroxybenzoate.

Examples of acrylates include ethyl α -cyano- β - β -
diphenylacrylate, isooctyl α -cyano- β - β -diphenylacrylate,
methyl α -carbomethoxycinnamate, methyl α -cyano- β -methyl-p-
20 methoxy-cinnamate, butyl α -cyano- β -methyl-p-methoxy-
cinnamate, methyl α -carbomethoxy-p-methoxycinnamate and N-
(β -carbomethoxy- β -cyanovinyl)-2-methylindoline.

These UV absorbing compounds are commercially
25 available or can be synthesized by conventional techniques
familiar to one of ordinary skill in the art.

The UV absorbing agent used in the process of the
present invention is a UV absorbing compound substituted
with at least one anhydride group. The preferred UV
absorbing agent is benzophenonetetracarboxylic
30 dianhydride.

The UV absorbing agent is prepared by derivatizing the UV absorbing compounds described herein so as to add the anhydride group(s). This synthesis can be carried out using techniques familiar in the art. Common synthesis techniques include using thionyl chloride to activate a carboxylic acid by forming the corresponding acryloyl chloride which further reacts with free carboxylic acid; activation of carboxylic acid with phosphorous acid halides, e.g. $(\text{PhO})_2\text{POCl}$; use of carbodiimides to effect dehydration of carboxylic acid to anhydrides; and the use of dehydrating agents such as trimethylsilylethoxy acetylene ($\text{Me}_3\text{Si-C}\equiv\text{C-OEt}$). A well known method to provide unsymmetrical anhydrides involves reacting metal salts of carboxylic acids with acid halides.

The amount of UV absorbing agent added is determined empirically since each agent absorbs differently and since each would have a different level at which it could be incorporated into the lens before it would interfere with the polymerization. Where the UV absorbing agent is incorporated into the mixture of monomers which are thereafter polymerized to form the lens, it is critical that the UV absorbing agent at the level of inclusion not interfere with the UV initiated polymerization of the monomers used to make the contact lens; in such embodiments of the invention, an amount sufficient to increase the UV absorbance capability without interfering with polymerization is chosen.

In general, satisfactory amounts of the UV absorbing agent-anhydride derivative to use when it is added to the mixture of monomers are on the order of 0.5 to 4.0% and satisfactory amounts when it is soaked into the lens after

the polymerization are on the order of 0.5 to 5.0%. These ranges will vary depending upon such things as the reactive efficiency of the UV absorbing agent-anhydride derivative, the final hydrated lens thickness and the dispersion of the UV absorbing agent into the lens.

The compounds which form the polymeric lens material may vary so long as there is present in the monomer mixture a component which upon polymerization will provide the polymer with the required pendant hydroxyl groups. Examples of such monomers include, but are not limited to, hydroxyalkyl esters, hydroxy alkoxyalkyl, hydroxy(polyalkoxy), and poly(alkoxy) esters of polymerizable unsaturated acids, such as acrylic acid, methacrylic acid, fumaric, maleic, etc. Other suitable monomers include unsaturated acids per se, such as acrylic, methacrylic, fumaric, maleic, etc.; heterocyclic N-vinyl lactams, such as N-vinyl pyrrolidone, etc.; noncyclic amides such as N-(1,1-dimethyl-3-oxobutyl)-acrylamide; amino alkyl esters of unsaturated acids such as 2-aminoethylacrylate, methacrylate, fumarate, or maleate; mercapto alkyl esters of unsaturated acids such as 2-mercapto ethyl acrylate, methacrylate, fumarate or maleate. Other suitable monomers, particularly wherein each alkyl group contains 1-3 carbon atoms will be apparent to one of ordinary skill in the art.

It is preferable to use hydrophilic monomers, that is monomers in appropriate amounts, so that the polymerized product is hydrophilic. A hydrophilic polymer is a polymer capable of forming a hydrogel when contacted with water. It is more preferable for this reason to use hydroxy-substituted hydrophilic monomers.

1 The most preferred hydrophilic monomers are esters of
acrylic or methacrylic acid with alkyl groups (especially
containing 1 to 6 carbon atoms) that are substituted with
1,2 or more hydroxyl groups. Examples of such hydroxy
5 esters include, but are not limited to,
hydroxyethylmethacrylate, (HEMA), hydroxyethylacrylate,
(HEA), 2,3-dihydroxypropyl methacrylate
(glycerylmethacrylate), hydroxypropylmethacrylate and
hydroxypropylacrylate. The most preferred hydroxy ester
10 is HEMA, which is the monomer most commonly used in the
preparation of "soft" hydrogel contact lenses. HEMA is
disclosed in U.S. Patent No, 2,976,576 and U.S. Patent No.
Re. 27,401. An acceptable "hard" lens material is
cellulose acetate butyrate. Other suitable monomers
15 containing reactive hydrogen, such as OH or NH groups,
will be apparent to those of ordinary skill in the art.

 The hydrophilic monomer is preferably copolymerized
in a reaction mixture with hydrophilic or hydrophobic
comonomers such as methacrylic acid (MAA). In addition,
polyfunctional monomers, used as crosslinking agents, such
20 as ethylene glycol dimethacrylate (EGDMA) and
trimethylolpropane trimethacrylate (TMPTMA) can be used to
improve the dimensional stability and other physical
properties of the lens. Additional comonomers and
crosslinking comonomers include acrylate and methacrylate
25 diesters of polyethyleneglycol (PEG) wherein the molecular
weight of the PEG segment is 100 to 8,000, acrylate and
methacrylate diesters of bisphenol A (BPA) diols
ethoxylated at one or at each of the diol ends with 1-20
ethoxy units, C₁-C₆ aliphatic alcohol acrylates and
30 methacrylates, perfluoro alcohol C₁-C₆ methacrylates and

1 perfluoro C₁-C₆ alcohol acrylates. By "acrylate and
methacrylate diesters" is meant diacrylates,
dimethacrylates, and diesters carrying one acrylate moiety
and one methacrylate moiety. Examples include PEG 4500,
5 BPA (ethoxylated with a total of 10 moles of ethylene
oxide (EO)), PEG 350 monomethylether or dodecanol, that
has been reacted with one or more molar equivalents of an
end-capping group such as isocyanatoethyl methacrylate
(IEM), methacrylic anhydride or methacrylyl chloride to
10 produce compounds with one or more terminal methacrylate
groups bonded through linking moieties such as carbamate
or ester groups. Other comonomers and crosslinking
comonomers are well known to one of ordinary skill.

The monomer reaction mixture also includes an
15 initiator, usually from about 0.05 to 5.0 percent of a
free radical initiator which is thermally activated.
Typical examples include lauroyl peroxide, benzoyl
peroxide, isopropyl percarbonate, azobisisobutyronitrile
and known redox systems such as the ammonium persulfate
20 sodium metabisulfite combination and the like.
Irradiation by ultraviolet light, electron beam, or a
radioactive source may also be employed to initiate the
polymerization reaction, optionally with the addition of
a polymerization initiator, e.g. benzoin and its ethers.
25 It is preferred to use α -hydroxy- α , α -dimethylacetophenone
(Darocur 1173) which is a UV reactive initiator. Other
initiator compounds would be familiar to one of ordinary
skill.

The polymerization reaction is known to those of
30 ordinary skill in the art and is carried under conditions
that can be readily established for any particular set of

1 reactants. The polymerization can be carried out in the
presence or absence of an inert diluent. If the
polymerization is carried out in the absence of a diluent
the resulting polymeric composition can be formed, as for
5 example by lathe cutting, into the desired lens shape.
Alternatively, and more preferably, the polymerization is
carried out in the presence of a suitable inert diluent,
for example, the diluents described in U.S. Patent No.
4,680,336 which is incorporated by reference herein. The
10 polymerization may also be carried out in the presence of
a suitable water displaceable inert diluent, for example
the diluents such as methanol, ethanol, acetone, and
glycol, described in EPO Application No. 94305394.2 which
is incorporated herein by reference. The preferred inert
15 diluent is a water displaceable boric acid ester. The
characteristics of desired boric acid esters as well as
the preferred concentration of ester in the polymerization
reaction mixture is described in detail in U.S. Patent No.
4,495,313 which is incorporated by reference herein. For
20 instance, suitable boric acid esters include those
prepared by heating boric acid and one or more
polyhydroxyl compounds with three or more hydroxyl groups.
Suitable polyhydroxyl groups include glycerol,
trimethylolpropane, glucose, and mixtures of any of these
25 with compounds having two hydroxyl groups such as
propylene glycol, diethylene glycol, butane diol, and/or
sorbitol.

The preferred methods for forming the desired lens
when a diluent is used include centrifugal casting and
cast molding, for example using molds described in U.S.
30 Patent No. 4,565,348, as well as combinations of these

1 methods with the other methods described generally herein.

2 The UV absorbing agent (i.e. one or more UV absorbing
3 compounds substituted with at least one anhydride group)
4 must be dispersed throughout the polymer prior to
5 covalently bonding the agent to the polymer backbone.
6 This may occur one of two ways. One way is to add the UV
7 absorbing agent to the mixture of monomers and other
8 materials used to form the lens. The reaction mixture
9 undergoes polymerization under conditions such that the UV
10 absorbing agent does not react. The resulting polymer
11 contains the UV absorbing agent dispersed throughout.

12 The second way to disperse the agent throughout the
13 polymer is to soak the already formed polymer in a
14 solution, preferably an aqueous solution, containing the
15 UV absorbing agent. The solvent, if not water, should be
16 capable of carrying the UV absorber anhydride into and
17 throughout the lens polymer, without reacting with the
18 anhydride group or group(s), the UV absorbing compound,
19 nor with the polymer. Other solvents include methanol,
20 ethanol and isopropyl alcohol. By this method, a
21 preformed contact lens is placed in a solution containing
22 a UV absorbing agent.

23 The polymer, with the UV absorbing agent dispersed
24 throughout, is then treated to cause it to undergo base
25 hydration to covalently bond the agent to the polymer
26 through the hydroxyl groups pendant from the polymer.
27 This can be done using the conventional technique of
28 contacting the lens with an aqueous solution of a base
29 such as sodium hydroxide or potassium hydroxide prior to
30 hydration as disclosed, for example, in U.S. Patent No.
31 4,891,046 which is incorporated herein by reference. The

1 preferred base is an alkali or alkaline earth metal
carbonate, or phosphate, and the required contact time
will depend on the contact temperature and the components
of the hydrophilic polymer composition.

5 When bonding of the UV absorbing agent to the polymer
is complete, the lens can be hydrated to its equilibrium
water content. Generally the water content of the lens
will vary from about 0 to about 85 weight percent,
preferably 30 to 60 weight percent.

10 The following examples are intended to illustrate the
claimed invention and are not in any way designed to limit
its scope. Numerous additional embodiments within the
scope and spirit of the claimed invention will become
apparent to those skilled in the art.

15 The components used in the preparation of the contact
lenses of the examples are abbreviated as follows: 2-
hydroxyethyl methacrylate (HEMA), methacrylic acid (MAA),
ethyleneglycol dimethacrylate (EGDMA), trimethylolpropane
trimethacrylate (TMPTMA), glycerine boric acid ester (BAE)
20 and α -hydroxy- α , α -dimethylacetophenone (Darocur 1173),
which is a UV reactive initiator. The monomers used in
all of the examples are highly purified monomers with less
than 0.1% impurities. Photonol 7025 is a polyether diol
used as an inert, water displaceable diluent and available
25 from the Henkel Corporation in Ambler, Pennsylvania.

EXAMPLE 1

Synthesis of Glycerin Boric Acid Ester (BAE).

30 A total of 61.83g (1.0 mols) of boric acid was placed
into a 3L rotary evaporator flask. To this flask was
added 322.32g glycerin (3.5 mols). The flask was then

1 placed on a rotary evaporator and the pressure was slowly
reduced to 0.5-1.0 mm Hg. After full vacuum was
established, the temperature of the bath was slowly raised
to 85°C at approximately 5°C per 20 minutes. Water was
5 recovered from the reaction as the boric acid ester was
formed. The clear viscous liquid BAE was used as is.

EXAMPLE 2

Preparation of the Monomer Reaction Mixture with BAE

10 A blend was prepared using 96.81% by weight of HEMA,
1.97% MAA, 0.78% EGDMA, 0.1% TMPTMA and 0.34% of DAROCUR
1173. To 48% by weight of this monomer mix was added 52%
of BAE as an inert, water displaceable diluent. After
thoroughly mixing the resulting formulation (hereinafter
15 the "reactive monomer mixture" or the "RMM") at ambient
conditions, the mixture was allowed to stir under reduced
pressure (40 mm Hg) for 30 min (at 25°C) and subsequently
transferred to contact lens molds. The filled molds were
exposed to UV light (wavelength = 300-380 nm, dose = 1.2-
1.6 Joules/cm²) for 20 minutes at approximately 50°C. The
20 molds were then separated, and placed in physiological
saline for 3.0 hrs at 70°C to remove the inert diluent and
any residual, unreacted monomers. The lenses were then
rinsed in fresh physiological saline at 40°C. After this
initial hydration period the lenses were allowed to
25 equilibrate in a fresh bath of physiological saline at
35°C for 3 hours.

EXAMPLES 3-8

Solubility of UV Absorbing Agent

30 To separate samples of the reactive monomer mix (RMM)

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1 prepared in accordance with Example 2, were added 0.05,
0.10, 0.25, 0.60, 0.80, and 1.0% of 3,3',4,4'-
benzophenonetetracarboxylic dianhydride. After thoroughly
mixing each sample at ambient conditions the mixtures were
5 allowed to stir under reduced pressure (40 mm Hg) for 30
min. at 25°C.

The samples were then used to determine the
solubility of the UV absorbing anhydride agent in the
polymer and the effect of the UV absorbing anhydride agent
on the polymerization reaction as monitored by DSC i.e.,
10 TTP and Enthaply.

EXAMPLE 9

Preparation of the Monomer Reaction Mixture with Photonol
7025 as an Inert, Water Displaceable Diluent

15 A blend was prepared using 96.81% by weight of HEMA,
1.97% MAA, 0.78% EGDMA, 0.1% TMPTMA and 0.34% of DAROCUR
1173. To 48% by weight of this monomer mix was added 52%
of Photonol 7025. After thoroughly mixing the resulting
formulation (hereinafter the "reactive monomer mixture" or
the "RMM") at ambient conditions the mixture was allowed
20 to stir under reduced pressure (40 mm Hg) for 30 min. at
25°C.

EXAMPLE 10

25 To a sample, 99.0%, of the reactive monomer mix (RMM)
of Example 9 was added 1.0% of 3,3',4,4'-benzophenone-
tetracarboxylic dianhydride. After thoroughly mixing the
above sample at ambient conditions the mixture was allowed
to stir under reduced pressure (40 mm Hg) for 30 min. at
25°C.

30 This sample was then used to determine the solubility
of the UV absorbing anhydride agent in the polymer and the

1 effect of the UV absorbing anhydride agent on the
polymerization reaction as monitored by DSC i.e., TTP and
Enthaply.

EXAMPLE 11

5 Preparation of Contact Lenses with UV Absorbing Agent.

To a sample, 99.2%, of the reactive monomer mix (RMM)
of Example 9 was added 0.8 % of 3,3',4,4'-benzophenone-
tetracarboxylic dianhydride. After thoroughly mixing the
above sample at ambient conditions the mixture was allowed
10 to stir under reduced pressure (40 mm Hg) for 30 min (at
25°C) and subsequently transferred to contact lens molds.
The filled molds were exposed to UV light (wavelength =
300-380 nm, dose = 1.2-1.6 Joules/cm²) for 20 minutes at
approximately 50°C. The molds were then separated, and
15 placed in physiological saline for 3.0 hrs at 70°C to
remove the inert diluent and any residual, unreacted
monomers.

Then, the lenses were hydrated in a 2 wt.% aqueous
solution of potassium carbonate at 50°C for 60 minutes.
After this initial hydration period the lenses were rinsed
20 in fresh physiological saline at 50°C for 15 minutes. The
lenses were allowed to equilibrate in fresh physiological
saline at 35°C for 3 hours, whereupon they were ready for
packaging.

25 The test methods for determining the physical
properties set forth in Tables I, II and III are as
follows:

DIFFERENTIAL SCANNING PHOTOCALORIMETER

A sample size of 5.0 milligrams was used. Nitrogen
was purged at 40mL/min and temperature of 45°C isothermal.
30 Cure cycle began at 10 minutes at an intensity of

1 2.5mW/cm² and continued for 10 minutes. "Acuvue 14.0" polymer cured under the same conditions was used as the reference material.

TABLE I

5 I.D. %RMM %DIANHYDRIDE TIME TO ENTHALPY
PEAK

Control	100	0	1.16 min	163.0 J/g
Example 3	99.95	0.05	1.35	186.7
10 Example 4	99.90	0.10	1.47	181.7
Example 5	99.75	0.25	1.58	193.4
Example 6	99.40	0.60	1.77	192.0
Example 7	99.20	0.80	1.85	183.3
15 Example 8	99.00	1.00	1.88	165.3

TABLE II

I.D. %RMM %DIANHYDRIDE TIME TO ENTHALPY
PEAK

Control	100	0	1.63 min	217.1 J/g
20 Example 10	99.00	1.00	3.68	218.5

TABLE III

25 I.D. %RMM %DIANHYDRIDE TIME TO ENTHALPY
PEAK

Control	100	0	1.18 min	176.6 J/g
Example 11	99.20	0.80	2.65	175.7

30 The results shown in Table I (BAE as diluent) and Tables II and III (Photonol 7025 as diluent) indicate that

1 the polymerization was not adversely interfered with by
the inclusion of the UV absorbing species. It is critical
that the UV absorbing material at the level of inclusion
not interfere with the UV initiated polymerization of the
5 monomers used to prepare the hydrogel. The Time to Peak
(TTP) and Enthalpy (E) results were obtained using a
Differential Scanning Photocalorimeter. The TTP is the
point at which the maximum heat of reaction occurs and is
the point after which the reaction rate slows.

UV-VIS SPECTROSCOPY

10 Three separate samples prepared according to Example
11 were analyzed using a Cary Model 2300 UV-Vis
spectrometer with a 1 nm/sec scan speed, 1nm resolution
and scan range of 800-200nm. A lens clamped into a lens
holder with 6mm aperture was inserted into a 10mm quartz
15 cuvette filled with physiological saline. Background
correction was made with a quartz cuvette, lens holder and
physiological saline with no lens. The control was
"Acuvue" prepared in accordance with Example 2.

20 The results in Figure 1 show the increased UV
absorbing ability of the samples containing the UV
absorbing agent as compared to a lens without.

The test methods for determining the physical
properties set forth in Table IV are as follows:

TENSILE PROPERTIES (MODULUS, ELONGATION AND STRENGTH)

25 A sample prepared in accordance with Example 11 was
cut to the desired specimen size and shape, and the cross
sectional area measured. The sample was then attached to
the upper grip of a constant rate of crosshead movement
type of testing instrument equipped with a load cell. The
30 sample was elongated at a constant rate of strain and the

1 resulting stress-strain curve recorded. The results are
shown in Table IV; elongation is expressed in percent, and
tensile modulus and strength in psi (lbs/in²).

GRAVIMETRIC WATER CONTENT

5 The water content of a lens prepared in accordance
with Example 11 was determined by first weighing a lens
that had been equilibrated in saline, and subsequently
drying the lens for two hours at 65°C under reduced
pressure (<5 mm Hg). The dried lens was weighed and the
gravimetric water content calculated as follows:

10
$$\% \text{ water} = 100 \times (m_{\text{wet}} - m_{\text{dry}}) / m_{\text{wet}}$$

where m_{wet} represents the wet lens mass (mass of polymer
plus mass of saline) and m_{dry} represents the dry polymer
mass.

VISCOSITY

15 Viscosity was measured using a Brookfield Digital
Viscometer Model DV-II, Brookfield Engineering
Laboratories, Inc. A sample prepared according to Example
11 was equilibrated to $\pm 0.5^\circ\text{C}$ in the viscometer fluid
container using a Fisher Scientific refrigerating
20 circulator (Model 9100 series) and monitored with an Omega
microprocessor thermometer (Model HH23). The direct
reading obtained from the viscometer was multiplied by the
factor appropriate to the spindle and speed used and is
expressed in centipoise. Blends using mPEG 2000 had
25 spindle 18 and speed of 6 rpm; blends using PEG 4500 had
spindle 18 and speed of 3 rpm.

Water Content

30 Water content was measured using a Coulomatic K-F
Titrimeter Model 447, Fisher Scientific. A sample
prepared in accordance with Example 11 was injected into

1 the reaction vessel using a 1 cc syringe. Sample weight
was 0.4-0.6 grams, with an extraction time of 20 seconds.
The direct reading of water content was expressed in
weight percent.

5 Table IV

	<u>Water%</u>	<u>Viscosity</u>	<u>Modulus</u>	<u>Elongation</u>	<u>EWC</u>
Example 11	0.5603	72.5 cps	35.1 psi	116.7%	65.9

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We claim:

1. A process for producing a UV absorbing contact lens comprising the steps of:

(a) providing a lens-shaped polymer having hydroxyl groups pendant therefrom and having dispersed therein a UV-absorbing agent substituted with at least one anhydride group; and

(b) exposing said polymer to basic conditions effective to cause said hydroxyl groups to react with anhydride groups on said UV-absorbing agent, whereby said UV-absorbing agent becomes covalently bound with said polymer.

2. A process according to claim 1 wherein said step(a) comprises providing a homogeneous monomer solution comprising therein one or more polymerizable monomers including at least one polymerizable hydroxyl-substituted monomer, wherein said solution contains dispersed therein said UV-absorbing agent, under conditions effective to polymerize said one or more polymerizable monomers without causing said UV absorbing agent to react.

3. A process according to claim 1 wherein said step (a) comprises providing a lens-shaped polymer having hydroxyl groups pendant therefrom, and contacting said polymer with a solution of said UV-absorbing agent under conditions effective to cause said UV-absorbing agent to soak into said polymer.

4. A process according to claim 1 wherein said UV-absorbing agent is 3,3',4,4'- benzophenonetetracarboxylic dianhydride.

5. A process according to claim 1 wherein said UV-absorbing agent is an anhydride derivative of 4,4'-



1 dioctyloxyoxanilide, 2,4,6-tris(2-hydroxy-4-octyloxyphenyl)-1,3,5-triazine, 4-tert-butylphenylsalicylate, dibenzoyl resorcinol, or 3'-sec-butyl-5'-tert-butyl-2-(2'-hydroxyphenyl)benzotriazole.

5 6. A process according to claim 2 wherein said monomer solution comprises one or more hydroxyalkyl esters of acrylic or methacrylic acid.

7. A process according to claim 2 wherein said monomer solution comprises hydroxyethylmethacrylate.

10 8. A process according to claim 2 wherein said monomer solution comprises one or more compounds selected from the group consisting of hydroxyethylacrylate, 2,3-dihydroxypropyl methacrylate, hydroxypropylmethacrylate and hydroxypropylacrylate.

15 9. A process according to claim 2 wherein said monomer solution comprises hydroxyethylmethacrylate and methacrylic acid.

20 10. A process according to claim 2 wherein said monomer solution comprises hydroxyethylmethacrylate, methacrylic acid and ethylene glycol dimethacrylate.

11. A process according to claim 2 wherein said monomer solution comprises hydroxyethylmethacrylate, methacrylic acid, ethylene glycol dimethacrylate and trimethylolpropane trimethacrylate.

25 12. A process according to claim 2 wherein said monomer solution comprises α -hydroxy- α , α -dimethylacetophenone.

30 13. A process according to claim 3 wherein the polymer is formed by copolymerizing a monomer mixture comprising one or more hydroxyalkyl esters of acrylic or methacrylic acid.



1 14. A process according to claim 3 wherein the
polymer is formed by copolymerizing a monomer mixture
comprising hydroxyethylmethacrylate.

5 15. A process according to claim 3 wherein the
polymer is formed by copolymerizing a monomer mixture
comprising hydroxyethylacrylate, 2,3-dihydroxypropyl
methacrylate, hydroxypropylmethacrylate and
hydroxypropylacrylate.

10 16. A process according to claim 3 wherein the
polymer is formed by copolymerizing a monomer mixture
comprising hydroxyethylmethacrylate and methacrylic acid.

15 17. A process according to claim 3 wherein the
polymer is formed by copolymerizing a monomer mixture
comprising hydroxyethylmethacrylate, methacrylic acid and
ethylene glycol dimethacrylate.

18 18. A process according to claim 3 wherein the
polymer is formed by copolymerizing a monomer mixture
comprising hydroxyethylmethacrylate, methacrylic acid,
ethylene glycol dimethacrylate and trimethylolpropane
trimethacrylate.

20 19. A process according to claim 3 wherein the
polymer is formed by copolymerizing a monomer mixture
comprising α -hydroxy- α , α -dimethylacetophenone.

25 20. A process according to claim 2 wherein said
monomer solution includes a water displaceable inert
diluent.

21. A process according to claim 2 wherein said
monomer solution includes boric acid ester.

30 22. A process according to claim 2 wherein said
monomer solution comprises one or more compounds selected
from the group consisting of acrylate and methacrylate



1 diesters of polyethylene glycol wherein the molecular
weight of the polyethylene glycol is 100 to 8,000,
acrylate and methacrylate diesters of bisphenol A diols
ethoxylated at one or each of the diol ends with 1-20
5 ethoxy units, C₁-C₆ aliphatic alcohol acrylates and
methacrylates, perfluoro C₁-C₆ alcohol methacrylates and
perfluoro C₁-C₆ alcohol acrylates.

23. A process according to claim 2 wherein said
monomer solution comprises one or more compounds selected
10 from the group consisting of PEG 4500, bisphenol A diols
ethoxylated with a total of 10 moles of ethylene oxide,
PEG 350 monomethylether, and dodecanol, which compounds
have been end-capped with isocyanatoethyl methacrylate,
methacrylic anhydride or methacrylyl chloride.

24. A process according to claim 3 wherein said
15 monomer solution includes a water displaceable inert
diluent.

25. A process according to claim 3 wherein said
monomer solution includes a boric acid ester.

26. A process according to claim 3 wherein said
20 monomer solution comprises one or more compounds selected
from the group consisting of acrylate and methacrylate
diesters of polyethylene glycol wherein the molecular
weight of the polyethylene glycol is 100 to 8,000,
25 acrylate and methacrylate esters of bisphenol A diols
ethoxylated at one or each of the diol ends with 1-20
ethoxy units, C₁-C₆ aliphatic alcohol acrylates and
methacrylates, perfluoro C₁-C₆ alcohol methacrylates and
perfluoro C₁-C₆ alcohol acrylates.

27. A process according to claim 3 wherein said
30 monomer solution comprises one or more compounds selected



1 from the group consisting of PEG 4500, bisphenol A diols
ethoxylated with a total of 10 moles of ethylene oxide,
PEG 350 monomethylether, and dodecanol, which compounds
have been end-capped with isocyanatoethyl methacrylate,
5 methacrylic anhydride or methacrylyl chloride.

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