

**INTERPENETRATING POLYMER NETWORKS**  
**FOR CONTACT LENS PRODUCTION**

**BACKGROUND OF THE INVENTION**

**1. FIELD OF THE INVENTION**

The present invention relates to interpenetrating polymeric network (IPN) compositions, and the use thereof in contact lenses. More particularly, the present invention relates to an IPN comprised of a polyurea network and polyacrylic network; the former network is prepared from amines and isocyanates while the latter network is prepared from acrylic esters polymerized with a free radical initiator. The polyurea/polyacrylic network may be cross-linked with triamines.

The IPN is used to prepare a lens. The resulting finished contact or intraocular lens produced from the IPNs of the present invention has the clarity, dimensional stability, oxygen permeability, wettability, and durability desired for either daily or extended wear contact lenses or intraocular lenses.

**2. DISCUSSION OF THE PRIOR ART**

The use of contact lenses as corrective ophthalmic devices as well as for cosmetic purposes is well known. Various materials have been utilized in making contact lenses, but these materials have been found less than ideal.

To be effective as a material for a contact lens, the material must possess certain key properties:

- 1 (a) a high oxygen permeability, (b) good wettability,  
(c) durability, (d) good mechanical strength, (e)  
optical clarity, (f) flexibility, (g) ability to  
transmit light in the visible range, and (h) homogeneity
- 5 and (i) control known changes in the lens parameters in  
the ocular environment.

Various materials possess one or more of these properties but lack one or more of the other required properties. For example, contact lenses derived from

10 hydrophobic polymers possess good mechanical strength and durability. Such hydrophobic polymers used in the prior art to make contact lens include urethanes, polyesters, polyamides, siloxanes, epoxides and the like. However, such contact lenses lack wettability and

15 oxygen permeability.

On the other hand, hydrophilic material permits wettability and oxygen permeability. Examples of hydrophilic monomers used in the prior art include hydroxyalkyl methacrylate, vinyl alcohol and vinyl

20 pyrrolidone. But, these materials lack such properties as good mechanical strength and durability.

Thus, the ideal contact lens material is one that is a composite of a hydrophilic and hydrophobic material that maximizes the advantages of both materials

25 and minimizes their weaknesses.

The standard contact lens used almost exclusively for many years was made from poly(methylmethacrylate) (PMMA). PMMA can be readily injection molded, compression molded, or cast molded to

30 give inexpensive, highly transparent, stable, hard, wettable contact lenses. However, as a result of the

- 1 very low oxygen permeability of PMMA, lenses made  
therefrom have to be removed from the eye at least once  
daily.

In order to overcome the deficiency of the  
5 PMMA lenses, numerous other organic polymers have been  
proposed for use as contact lenses. Cellulose acetate  
butyrate lenses, for example, have a somewhat higher  
oxygen permeability than PMMA and are readily fabricated  
by injection molding but have a lower dimensional  
10 stability than PMMA.

Soft contact lenses based upon crosslinked  
polymers from hydrophilic monomers, such as 2-  
hydroxyethyl methacrylate or N-vinyl-2-pyrrolidone, are  
found to be generally more comfortable to wear than PMMA  
15 lenses but are more fragile and have a tendency to  
become cloudy because of the ease by which proteinaceous  
material and other contaminants are deposited thereon.  
Soft lenses prepared from silicone rubber have a very  
high oxygen permeability but poor mechanical properties  
20 are resistant to wetting and adhere to the cornea.

Improvements in contact lens materials have  
been approached by utilizing copolymers. For example,  
U.S. Patent No. 3,503,942 to Seiderman describes a  
contact lens comprised of a mixture of hydrophilic  
25 monomers. The use of various combinations of monomers  
to produce copolymers is limited by the ability of these  
monomers to copolymerize. If monomers which do not  
copolymerize well are chosen (e.g., methyl methacrylate  
and vinyl pyrrolidinone), soluble polymer fragments are  
30 formed. These soluble fragments must be extracted from  
the lens.

1 Lenses prepared from copolymers of a silicone  
methacrylate with methyl methacrylate (Gaylord, U.S.  
Patent No. 4,120,570) or with methyl itaconate (Ellis,  
U.S. Patent No. 4,424,328) have greater but still  
5 limited oxygen permeability.

Wichterle in U.S. Patent No. 3,408,429  
describes a complex centrifugal casting technique for  
converting a mixture of hydroxyethyl methacrylate and  
ethylene glycol dimethacrylate into a cross-linked  
10 polymer lens which, upon being subjected to normal  
saline, is converted into a soft contact lens. This  
complex procedure inherently yields products having  
optics that are inferior to those of hard contact  
lenses.

15 Considerable attention has been given to the  
modification of polymer properties through the use of  
procedures involving the formation of an  
interpenetrating polymer network (IPN). An IPN can be  
defined broadly as an intimate network of two or more  
20 polymers at least one of which is either synthesized  
and/or cross-linked in the presence of the other.

Liu, for example, in U.S. Patent No.  
4,618,644, describes the polymerization of methyl  
methacrylate in the presence of a silicone polymer to  
25 obtain a product of improved toughness. The  
polymerization of ethylene glycol dimethacrylate and a  
crosslinkable poly- (dimethylsiloxane) to yield a  
product stated to be useful for the fabrication of  
contact lenses is described by Falcetta (Ger. Offen. DE  
30 2,518,904). Contact lenses have also been fabricated  
from the interpenetrating network polymer resulting from

1 the polymerization of 2-hydroxyethyl methacrylate in the  
presence of poly-N-vinylpyrrolidone (Ewell, U.S. Patent  
No. 3,647,736).

Neefe (U.S. Patent No. 4,632,773) shows the  
5 polymerization of methyl methacrylate in the presence of  
a syrup containing polymerized methacryloxypropyl-  
trimethoxysilane and a fluorescent colored pigment to  
obtain a solid contact lens blank material which can be  
readily identified. Tighe and Gee (U.S. Patent No.  
10 4,430,458) disclose the formation of soft contact lens  
material by the cross-linking of a polymeric hydrogel of  
a copolymer of N-vinyl-2-pyrrolidone during the final  
compression or injection molding process. Lim, et al.  
(U.S. Patent No. 4,536,554) describes the preparation of  
15 soft contact lenses made from the interpenetrating  
network polymer obtained by the polymerization of a  
mixture containing a hydrophilic and a hydrophobic  
monomer and at least two cross-linking agents.

However, until the present invention, no one  
20 had recognized that an IPN comprising a network of  
polyurea interpenetrated with polyacrylate would be the  
material of choice for contact lenses. This IPN  
combines a weak hydrophilic polymer with a hydrophobic  
polymer.

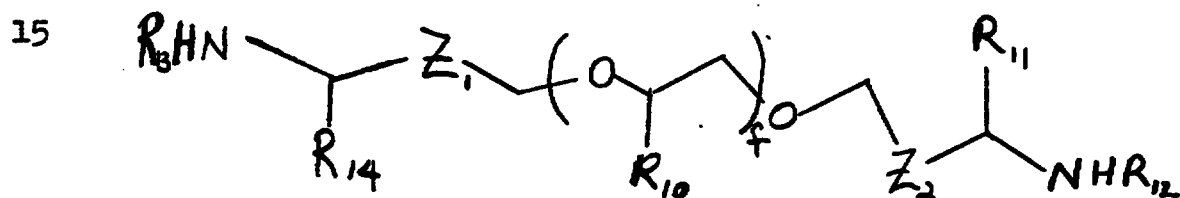
25 Moreover, the present inventors have  
discovered that both the ratio of polyurea to acrylate  
and the polyamine composition are critical for this  
material to be used in a contact lens; however, if the  
ratio is within certain specified limits and the  
30 polyamine is of certain composition, the resulting IPN  
material possesses all of the key properties described

1 hereinabove and is most suitable for making contact lenses.

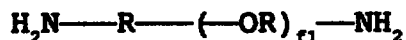
# SUMMARY OF THE INVENTION

5 Accordingly, the present invention is directed to a homogeneous interpenetrating polymer network exhibiting a single glass transition temperature prepared from polymerization of a reactive mixture of polymerizable components, said reactive mixture  
10 comprising

(a) an amine mixture comprising polyamines A and B, said amines being present in about 20-60% by weight of said reactive mixture, wherein A is



20 and B is



wherein

$f_1$  is an integer from 1-75;

R is an alkylene containing 3 carbon atoms and

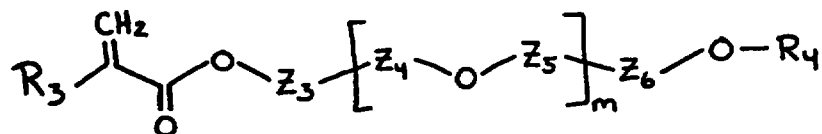
25 each R is the same;

f is an integer between 1 and 150, inclusive;

$R_{10}$ ,  $R_{11}$ ,  $R_{12}$ ,  $R_{13}$  and  $R_{14}$  are independently hydrogen or lower alkyl;

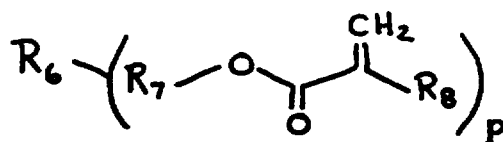
$Z_1$  and  $Z_2$  are independently a chemical bond or  
30 lower alkylene with A and B being present in relative weight ratios ranging from about 60/40 to about 100% A,

- 1 (b) an organic di- or poly-isocyanate present  
in sufficient quantity to react with the amine mixture  
of (a), forming therefrom a polyurea network;  
5 (c) an acrylic ester of the formula



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or

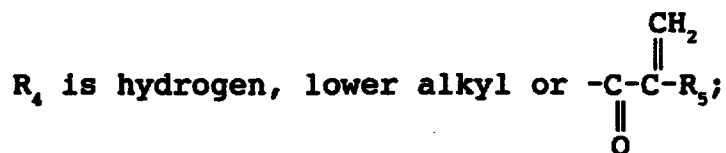


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wherein

- $R_3$  is hydrogen or lower alkyl;  
 $m$  is an integer from 0 to 150;  
20  $Z_3$  and  $Z_5$  are independently lower alkylene;  
 $Z_4$  and  $Z_6$  are independently a chemical bond or  
lower alkylene;

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- $R_5$  is hydrogen or lower alkyl;  
 $R_6$  and  $R_8$  are independently lower alkyl;  
 $p$  is an integer of 1 to 3;  
and  $R_7$  is lower alkylene or a chemical bond or  
 $\text{CH}_2(\text{OCH}_2\text{CH}_2)_q$ ;

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- 1           q is an integer between 0 and 200, inclusive,  
said acrylic ester being present in about 10-50% by  
weight in said reactive mixture; and  
          (d) a free radical initiator being present in  
5 sufficient quantity in said reactive mixture to  
polymerize the acrylic ester of (c), forming therefrom a  
polyacrylic network, wherein the ratio of polyurea to  
polyacrylic ranges from about 90:10 to about 50:50, and  
          (e) a triamine present in sufficient  
10 quantities to crosslink said amine mixture of (a).

#### DETAILED DESCRIPTION OF THE INVENTION

          As used herein, the term "lower alkyl", when  
used alone or in combination with other groups, refers  
15 to an alkyl chain containing 1-6 carbon atoms. The  
alkyl groups may be straight chained or branched.  
Examples include methyl, ethyl, propyl, isopropyl,  
butyl, sec-butyl, t-butyl, isobutyl, pentyl, isopentyl,  
neopentyl, hexyl, and the like. It is preferred that  
20 the alkyl group contains 1-3 carbon atoms.

          As used herein, the term "alkylene" refers to  
a hydrocarbyl group derived from an alkyl group by  
dropping a hydrogen from the formula. The alkylene is  
bonded to two other groups in the main chain. Examples  
25 include  $-\text{CH}_2-$ ,  $-\text{CH}_2-\text{CH}_2-$ ,  $-\text{CH}_2-\text{CH}_2-\text{CH}_2-$ ,  $-\text{CH}-\text{CH}_2-$ , and

$\begin{array}{c} | \\ \text{CH}_3 \end{array}$

the like. It is preferred that the alkylene groups  
contain 1-3 carbon atoms.

          The present invention is directed to  
30 interpenetrating network polymers suitable as materials  
in the manufacture of contact lens and particularly to

1 such polymers that have been prepared with modifiers and  
cross-linking agents and the optical contact lens  
prepared from such materials.

More specifically, the present invention is  
5 directed to a polyurea network interpenetrated with a  
polyacrylic network in such a manner as to form an  
interpenetrating network which is completely homo-  
geneous and exhibits a single glass transition  
temperature.

10 The polyurea network described hereinabove is  
a network comprised of amines, i.e., amine terminated  
chain extender, with organic di- or polyisocyanates. In  
addition, an amine cross-linking agent is required,  
which is described hereinbelow.

15 The amines suitable for the present invention  
are polymers having two or more terminal amino  
functionalities. The most preferred amines are amino  
terminated polyethers. Examples of the most preferred  
polyamines include poly (oxyethylene) diamine, poly  
20 (oxypropylene) diamine, triethylene glycol diamine, and  
the like.

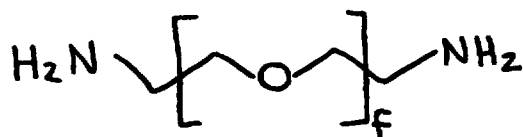
In a preferred embodiment, the amine component  
is comprised of a mixture of diamines, i.e., a  
polyoxyethylene diamine and a polyoxypropylene diamine.

25 It has been found by the present inventors that the  
balance between polyoxyethylene diamine and  
polyoxypropylene diamine is very important to the  
transparency and water absorption properties of the IPN  
elastomers. The presence of poly (oxyethylene) diamines  
30 in the formulation is necessary to permit the hydrogel  
to absorb water. As the content and molecular weight of

- 1 the polyoxyethylene diamine increases, the resulting hydrogels absorb more water. Unfortunately, the transparency suffers as the poly (oxyethylene) diamines tend to crystallize. The presence of poly  
5 (oxypropylene) diamines in the formulation is necessary to obtain transparent hydrogels.

The preferred poly (oxyethylene) diamine used in the present invention has the formula

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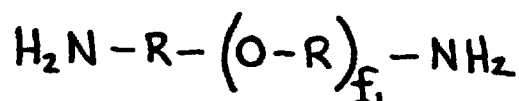


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wherein  $f$  is an integer from 30-70.

The poly (oxypropylene) diamine used herein is preferably of the formula

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wherein  $\text{R}$  is an alkylene chain containing 3 carbon  
25 atoms, and

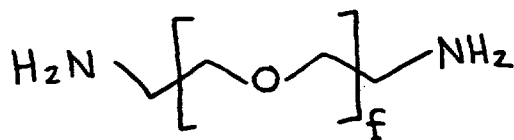
$f_1$  is an integer of 1-50.

It is preferred that  $f_1$  is 30 and  $f$  is 30-70.

In the preferred embodiment of the present invention, a mixture of amines preferably comprises poly  
30 (oxyethylene) diamine having the formula

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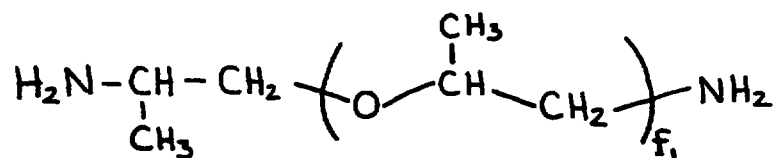
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wherein  $f$  is an integer of 1-50 and a poly (oxypropylene) diamine of formula IB

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15 wherein  $f_1$  is an integer of 1-50.

It is preferred that the amine be present in about 20-60% by weight in the starting monomeric mixture. The preferred relative weight of IA and IB ranges from about 60/40 to about 100% A, respectively.

20 It is to be noted that unless indicated to the contrary, the percentages and ratios are by weight.

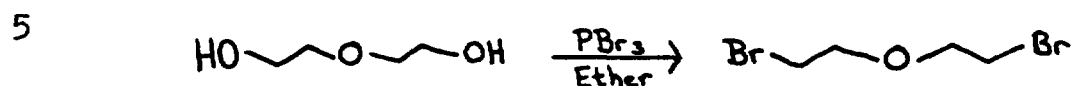
The diamines utilized in the present invention are either commercially available or are prepared by conventional techniques known to one skilled in the art.

25 The following examples are illustrative to show the techniques readily utilized by the skilled artisan to make the diamines used herein.

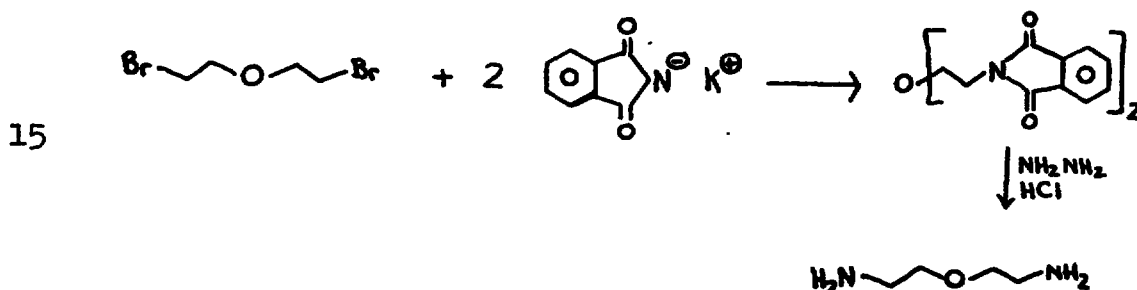
Exemplary procedures are shown below. In the first exemplification, the two terminal hydroxy groups  
30 in the glycol are functionalized into facile leaving

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1 groups, e.g., bromide, using phosphorus tribromide in ether.



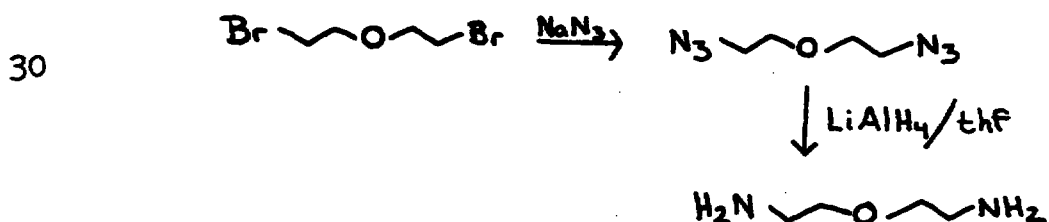
The dibromide can be converted into the  
10 diamine using the Gabriel Phthalimide synthesis, wherein potassium phthalimide is used to displace the bromide.



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Workup typically involves cleavage using hydrazine and protonation to liberate the free diamine.

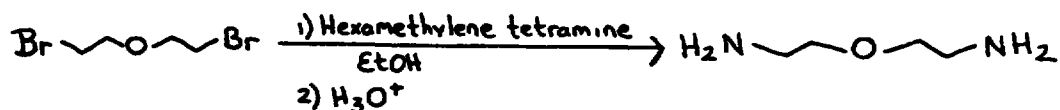
Another exemplary procedure for the synthesis of the diamine involves the displacement of the bromide  
25 using azide anion as the nucleophile. Subsequent reduction using lithium aluminum hydride yields the diamine.



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1 Yet another method of synthesizing the diamine  
uses hexamethylene tetraamine in ethanol to give a di-  
ammonium salt of the dibromide. Subsequent hydrolysis  
of the salt yields the diamine.

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Other leaving groups that can be used in place  
of the bromide are the other halides such as chloride,  
and iodide, tosylate, brosylate, triflates, benzoate and  
other anions whose  $\text{pK}_a$  value is low enough for  
15 displacement by nitrogen nucleophiles such as those  
described hereinabove.

The organic di- or polyisocyanates used to  
form the polyurea network of the present invention is  
represented by the formula  $\text{Q}(\text{NCO})_t$  wherein  $t$  is  
20 preferably 1-4 and  $\text{Q}$  is an hydrocarbyl group, i.e., an  
organic radical consisting solely of carbon atoms and  
hydrogen atoms.  $\text{Q}$  may be aliphatic, alicyclic,  
aromatic, or combination of any of these groups, such as  
aliphatic-aromatic group, aliphatic-alicyclic group, and  
25 the like. The  $\text{Q}$  group may be unsubstituted or  
substituted with lower alkyl, hydroxy or lower alkoxy.  
It is preferred that the isocyanate is aliphatic. In a  
preferred embodiment, it is preferred that  $\text{Q}$  contains

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1 from 3-26 carbon and more preferably from 4-20 carbon  
atoms and most preferably from 6-14 carbon atoms. In  
the above formula, t is an integer greater than 1 and  
preferably 2-4. These isocyanates are readily prepared  
5 using art recognized techniques or are commercially  
available. Representative examples of the above  
isocyanates include tetramethylene diisocyanate;  
hexamethylene diisocyanate; trimethylhexamethylene  
diisocyanate; dimer acid diisocyanate; isophorone  
10 diisocyanate; dimethylbenzene diisocyanate;  
diethylbenzene diisocyanate; decamethylene 1, 10-  
diisocyanate; cyclohexylene 1, 2-diisocyanate;  
cyclohexylene 1, 4-diisocyanate; 2, 4-and 2-6-tolylene  
diisocyanates; 4, 4-diphenylmethane diisocyanate; 1, 5-  
15 naphthalene diisocyanate; dianisidine diisocyanate;  
toluidine diisocyanate; 4,4-methylene bis(cyclohexyl-  
isocyanate); neopentyl tetraisocyanate; m-xylylene  
diisocyanate; tetrahydronaphthalene -1, 5-diisocyanate  
and bis-(4-isocyanatophenyl) methane, and the like.

20 The most preferred isocyanate is 4,4'-  
methylene bis (cyclohexylisocyanate). Other preferred  
isocyanates are trimethyl hexamethylene diisocyanate and  
isophorone diisocyanate.

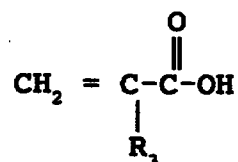
The isocyanates utilized in the present  
25 invention react with the amines to form the polyurea  
network. The isocyanates are present in such amounts as  
to react with the amines present. In essence, the  
amount of isocyanate is chosen to substantially equal  
the number of equivalents of amine. In the preferred  
30 embodiment, the isocyanate is present in 15-50% by

1 weight of the starting monomeric mixture, and preferably  
in the amount of 25-40% by weight.

The reaction of the isocyanate with the amines  
is spontaneous, and thus no catalyst is needed for the  
5 polyurea formation. Moreover, the reaction is  
exothermic. The heat generated from the amine-  
isocyanate reaction can accelerate the free radical  
initiated polymerization of the acrylate, the other  
network of the interpenetrating network polymer.

10 The other network is made from acrylic esters.  
The acrylic esters suitable for the present invention  
are polymerizable polyacrylate derivatives of polyhydric  
alcohols.

The acrylic esters are the ester derivatives  
15 of acrylic acid of the following formula:



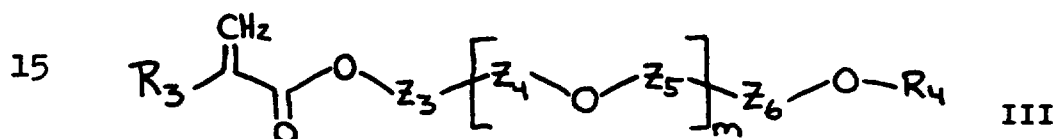
20 wherein  $\text{R}_3$  is hydrogen or lower alkyl. It is to be  
noted that when  $\text{R}_3$  is methyl, the acid is methacrylic  
acid.

Monohydric alcohols and polyhydric alcohols  
25 having a molecular weight of less than 7,000 daltons are  
suitable for esterification to the acrylic acids  
described hereinabove for use in the present invention.  
Preferred alcohols include monomethoxypolyethylene  
glycol and ethoxyethylene glycol, ethylene glycol,  
30 diethylene glycol, triethylene glycol, poly  
(oxyethylene) glycol, poly (oxypropylene) glycol, poly

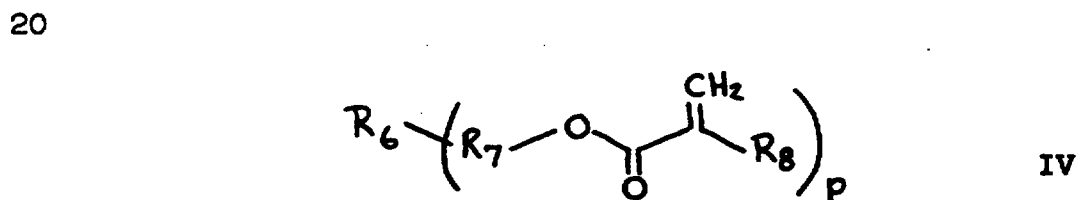
1 (oxypropylene) triol, glycerol, trimethylol ethane,  
trimethylol propane, 1, 4-cyclohexane diol,  
pentaerythritol, and the like.

Since the polyhydric alcohols contain more  
5 than one hydroxy group, when utilized, more than one  
acrylate unit can esterify to the polyhydric alcohols.  
Thus, acrylic esters of the present invention include  
mono-, di-, and poly acrylate derivatives of the  
alcohols described hereinabove, especially methacrylate  
10 derivatives thereof.

The acrylic esters useful in the present  
invention have the formulae:



or



25 wherein  $R_3$  is as defined hereinabove;  
m is an integer from 0 to 150; and  
 $Z_3$  and  $Z_5$  are independently lower alkylene;  
 $Z_4$  and  $Z_6$  are independently a chemical bond or  
30 lower alkylene;

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$R_4$  is hydrogen, lower alkyl or  $-\overset{\overset{\text{CH}_2}{\parallel}}{\underset{\underset{\text{O}}{\parallel}}{\text{C}}}-\text{C}-R_5$ ;

5

$R_5$  is hydrogen or lower alkyl;

$R_6$  and  $R_8$  are lower alkyl;

$p$  is an integer of 1 to 3; and

$R_7$  is a lower alkylene, a chemical bond or  $\text{CH}_2(\text{OCH}_2\text{CH}_2)_q$ , and

10

$q$  is an integer of 0 to 200 inclusive.

It is most preferred that  $R_3$ ,  $R_5$  and  $R_8$  are alkyl having 1-3 carbon atoms, especially methyl.

15

Preferred values of  $R_6$  and  $R_8$  are lower alkyl having 1-3 carbon atoms. Preferred  $R_6$  is ethyl and preferred  $R_8$  is methyl. It is preferred that  $R_7$  is methylene. Preferred values of  $R_4$  are hydrogen, lower

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alkyl having 1-3 carbon atoms and  $-\overset{\overset{\text{CH}_2}{\parallel}}{\underset{\underset{\text{O}}{\parallel}}{\text{C}}}-\text{C}-R_5$ , especially methacrylate.

It is preferred that  $m$  is 0 to 30, and more especially 0 to 20.

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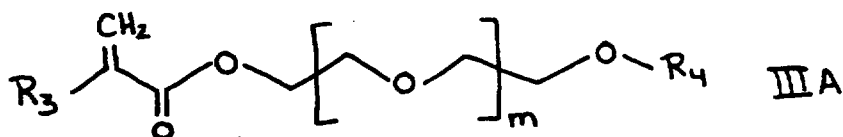
Preferred values of  $Z_4$  and  $Z_6$  are independently chemical bonds or alkylene group having 1-3 carbon atoms, while preferred values of  $Z_3$  and  $Z_5$  are alkylene having 1-3 carbon atoms. It is also preferred that  $Z_3$  is the same as  $Z_6$  and that  $Z_4$  is the same as  $Z_5$ .

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A preferred embodiment of Formula III is

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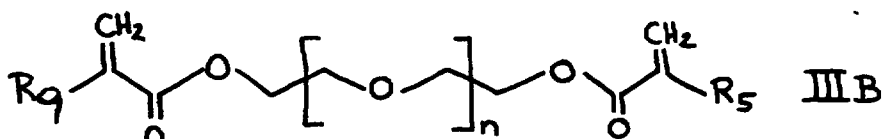
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wherein  $m$ ,  $\text{R}_3$  and  $\text{R}_4$  are as defined hereinabove. It is preferred that  $\text{R}_4$  is hydrogen or lower alkyl,  $\text{R}_3$  is lower alkyl, especially methyl, and  $m$  is 0-50, more preferably 0-30 and most preferably 0-20.

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Another preferred acrylic monomer of Formula III is the diacrylate of the formula:

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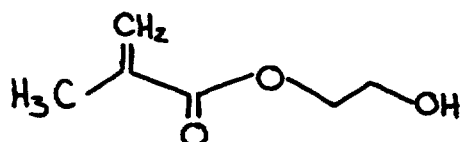


wherein  $\text{R}_5$  is as defined hereinabove, preferably methyl,  $\text{R}_9$  is hydrogen or lower alkyl and  $n$  is 0 to 50, more preferably 0 to 30, and most preferably 0-20.

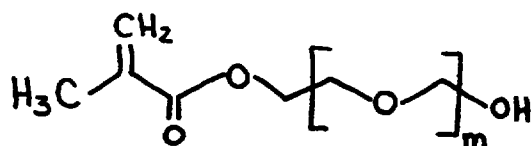
The acrylic esters are present in about 10-50% by weight in the starting monomer mixture, and more preferably from about 15 to about 35% by weight.

It is preferred that the acrylic ester component consists of a mixture of monomer acrylates. The first acrylic monomer is comprised of the acrylate of Formula IIIA, while the second acrylic monomer comprises the compound of IIIB, IV, or mixture thereof. The first and second acrylic monomers are present in relative weight ratios ranging from about 80/20 to about 95/5, respectively.

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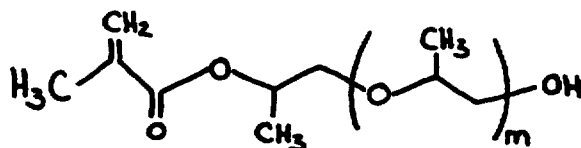


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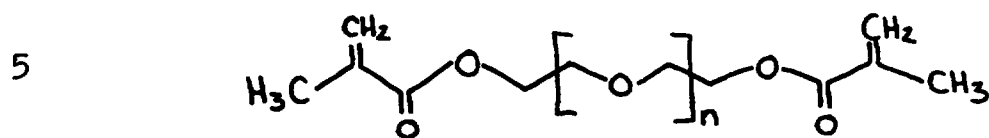
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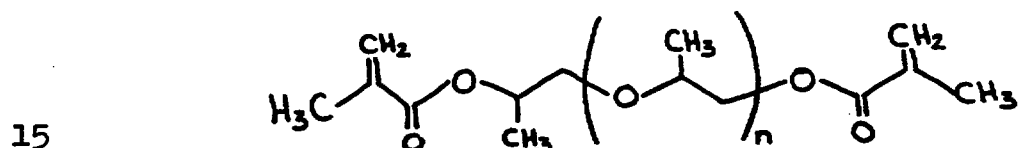
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1 A preferred dimethacrylate is poly (ethylene glycol) dimethacrylate, having the formula



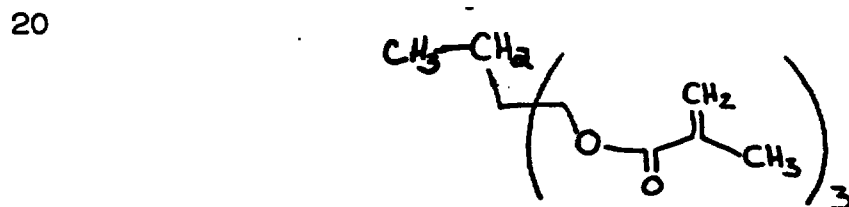
wherein n is an integer from 0 to 20.

10 Another preferred dimethacrylate is poly (propylene glycol) dimethacrylate having the formula



wherein n is integer from 0 to 20.

A preferred trimethacrylate is trimethylol propane trimethacrylate having the formula

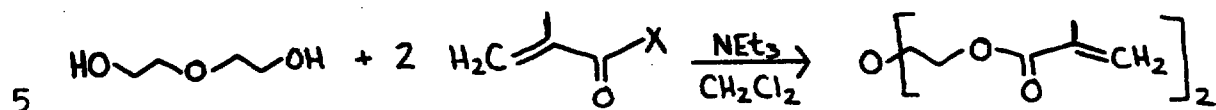


25 The acrylic esters used in the present invention are prepared by art recognized techniques of esterification known to one skilled in the art. The following descriptions are exemplary.

30 The acrylic esters can be synthesized by the condensation of alcohol with an acrylic acid derivative in the presence of a suitable weak base such as

35

1 triethylamine. This is illustrated below in the  
synthesis of a diacrylate from a diethylene glycol.



In the above synthesis, X is a good leaving group such as Cl, Br, NH<sub>2</sub>, OH, lower alkylamino or diloweralkylamino.

10 The corresponding monoacrylate can be synthesized using a stoichiometric amount of the acrylic acid derivative. The reaction can be conducted in polar aprotic solvents like dichloromethane and chloroform.

The use of alkyl substituted acrylic acid  
15 derivatives for the above condensation is equally feasible. The most preferred acrylic acid derivatives for the above condensation are methacrylate derivatives having the formula



25 wherein X is a good leaving group, e.g., halide, such as Cl or Br, OH, lower alkylamino or diloweralkylamino.

Another procedure is the reaction of the methacrylic acid and the alcohol in the presence of acid such as hydrochloric acid or p-toluene-sulfonic acid  
30 under Fischer esterification conditions.

1           To form the acrylate network, the acrylates  
described hereinabove are reacted with a free radical  
initiator under polymerization conditions. Free radical  
polymerization initiators of the type commonly used in  
5 polymerizing ethylenic compounds are suitable for use in  
the present invention. They include such representative  
initiators as benzoyl peroxide; t-butyl hydroperoxide;  
t-butyl peroxide; azo-bis (isobutyronitrile); 2, 5-  
dimethyl-2, 5-di (2-ethyl hexanoylperoxy) hexane; 1, 1-  
10 di (t-butylperoxy)-3, 3, 5-trimethylcyclohexane; di-t-  
butyl-diperoxyphthalate; organic peroxides;  
hydroperoxides; mixtures of peroxide and hydroperoxide  
(Lupersol DDM-9); 1, 1'-azobis-(1-  
cyclohexanecarbonitrile); 2, 2'-azobis [2- (2-  
15 imidazolin-2-yl) propane] dihydrochloride; 2, 2'-azobis  
(2,4-dimethylvaleronitrile); 2, 2'-azobis (4-methoxy-2,  
4-dimethyl valeronitrile); and the like.

The free radical initiators are present in  
amounts ranging from amounts greater than 0% to about 2%  
20 by weight of the reaction mixture, and preferably from  
0.01% to about 1%, and more preferably from 0.02% to  
about 0.5%, and most preferably from 0.03% to about 0.1%  
of the mixture.

In addition, a triamine is additionally  
25 present in the monomeric mix. The triamines are useful  
as crosslinker agents in the polyurea-acrylic IPNs.  
They also are used as compatibilizers in the polyamine  
mixture, especially when the reaction is conducted in  
the absence of a mixing device. In order to ensure  
30 homogeneity between the polyoxyethylene diamine and the  
polyoxypropylene diamine, the amine mixture is

1 preferably constantly stirred. The triamines are  
present in amounts ranging from about 30% to about 50%  
of the total equivalents of amines. They are preferably  
present in amounts ranging from about 1% to about 20% by  
5 weight and most preferably 3% - 5% by weight. Examples  
of the triamines include diethyltriamine, poly  
(oxypropylene) triamine, and the like.

Thus, the interpenetrating polymers of the  
present invention are prepared from the two  
10 interpenetrating networks, one network generated from  
the reaction of the amine and the isocyanate (to form  
polyurea), the other network from the free radical  
polymerization of the acrylates (to form the  
polyacrylate). In the resulting IPN, the ratio of  
15 polyurea to polyacrylate ranges from about 90:10 to  
about 50:50, although it is most preferred that the  
ratio ranges from 80:20 to 70:30 and most preferably  
75/25.

The polymerization reaction, i.e., reaction  
20 between the amino, acrylic ester, isocyanate, and free  
radical initiator is conducted under conditions to form  
simultaneous interpenetrating networks. The networks  
are in the same volume and the networks are formed  
substantially simultaneously. Techniques for preparing  
25 SINS are known to one skilled in the art and are  
applicable here. The monomeric precursors, i.e., the  
amines and the isocyanate and the acrylic ester and the  
initiator are mixed together, and the resultant  
polymerization reaction is simultaneous or substantially  
30 simultaneous, in accordance therewith. For a general  
procedure, see U.S. Patent No. 4,536,554 to Lim, et al.,

U.S. Patent No. 4,983,702 to Mueller, et al., 5,087,392 to Burke, et al., the contents of which are all incorporated by reference. The polymerization is  
5 generally carried out at temperatures ranging from about room temperature to about 145°C. It is generally preferred to initiate the polymerization at relatively low temperatures, such as from about 45°C to about 120°C, and then increase the temperature to about 110°C  
10 to 130°C as the reaction proceeds. Generally, post-curing is done at about 140°-145°C.

Usually, the polymerization is conducted under an inert nitrogen atmosphere in order to exclude the oxygen of the atmosphere which has deteriorating effects  
15 on the formation of polymers of the invention.

Contact lenses can be made by shaping the interpenetrating network polymer using conventional and well known procedures and apparatus such as a mold in the shape of a contact lens and thereafter hydrating the  
20 dry lens to the final configuration.

In a preferred embodiment, the interpenetrating polymer network of the present invention is prepared using a Reaction Injection Molding (RIM) Machine. The use of the RIM Machine and the  
25 subsequent molding of the IPNs of the present invention are described in copending application assigned to the assignee of the present invention, having Serial No. 08/415,000, entitled, A NOVEL REACTION INJECTION MOLDING PROCESS FOR THE MANUFACTURE OF PRECISION CONTACT LENSES,  
30 the contents of which are incorporated herein by reference.

1                Reaction injection molding requires that the  
monomer streams mix at high shear rates which produce  
turbulent flow. The turbulent mixing assures material  
uniformity and complete reaction.

5                The RIM process is well described by L.T.  
Manziona in The Encyclopedia of Polymer Science and  
Engineering; 2nd Edition Vol 14, pg. 72. It is a  
molding process wherein two or more streams of monomers  
react in the mold to form a polymer.

10              In a typical polymerization using a two stream  
RIM machine, a blend comprising diamines and triamines  
are placed in a material reservoir and heated to about  
80°C. A second blend comprising the diisocyanate,  
acrylic esters and an organic catalyst are placed in the  
15 second material reservoir.

                The two blends are mixed by impingement at a  
pressure between 400-3000 psi and the resulting liquid  
which forms an IPN upon curing is injected into a mold  
in the shape of a contact lens. The injection time  
20 ranges less than one minute, generally from 0.02-0.3  
seconds. The polymer may be post-cured for one hour in  
an oven at 100°C.

                In a typical polymerization using a three  
stream RIM machine, a blend (Stream 1) of diamines and  
25 triamines is placed in the first reservoir. A second  
blend (Stream 2) of acrylic esters is placed in the  
second reservoir, while a third blend (Stream 3) of a  
diisocyanate and free radical initiators is placed in  
the third material reservoir. The three streams are  
30 mixed by impingement at a mixhead in the RIM machine and

1 the resulting liquid which forms an IPN upon curing is  
injected into a mold in the shape of a contact lens.

The free radical polymerization of the  
acrylates is typically very fast, as is the reaction  
5 between the polyamines and the isocyanates. Optionally  
an inert diluent is added and moderates the reaction,  
allowing it to be compatible with the RIM process. The  
preferred inert diluent in the present invention is  
water. Additionally, water also acts as a mold release  
10 agent (see below) for removing the cured polymer from  
the mold assembly.

The contact lenses of the present invention  
are prepared by casting the IPN generated in the RIM  
apparatus in a suitable mold assembly for contact lens.  
15 The mold can be made of glass, metal or plastic, but it  
is preferred to be made of aluminum or stainless steel.  
The mold assembly is preferably comprised of two mold  
halves which are positioned to define a cavity in the  
shape of a contact lens between the convex surface of  
20 one mold half and the concave surface of the other mold  
half. The cavity may have variable thickness, as  
required to provide the correct dioptric power. The  
variable thickness may be calculated using optical  
formulas familiar to those skilled in the art. The  
25 central thickness of the cavity ranges from about  
0.00039 inches to about 0.0118 inches. The two mold  
halves are held together by clamping means, such as a  
clamp, bolt or hinges and the like. It is preferred  
that the molds are two-piece aluminum plates. The mold  
30 has a central sprue or gate and is equipped with at  
least one vent. The central sprue or gate is the

- 1 opening that connects the RIM machine to the mold and  
through which the streams of components are injected  
after being mixed at the mixhead. The vent may be  
located at each of the four mold edges, at the end of  
5 the mold furthest from the sprue, but preferably it is  
located within 4-5 inches of the sprue. In a preferred  
embodiment, an annular gated mold is utilized. The mold  
is usually heated at a temperature of 50°C to 150°C and  
preferably from 75-125° and most preferably at 100°C.
- 10 When the mold is at that temperature, the liquid capable  
of forming an IPN upon polymerization or curing is  
injected into the mold wherein the polymerization is  
completed, the resultant product is gelled and hardened.  
The material may additionally be post-cured in the mold.
- 15 After this step, the mold is opened manually, and the  
elastomeric film is removed from the mold wherein it is  
post-cured again in a heated environment such as an  
oven. The film is converted to a hydrogel by immersion  
in a buffered saline solution.
- 20 The polymeric material obtained by the present  
invention can be utilized to make contact lenses, by  
altering the shape and dimensions of the injection mold  
according to ophthalmic specifications.
- The contact lenses, thus prepared, exhibit  
25 excellent optical and mechanical properties.
- Along with a high tensile and shear strength,  
the contact lenses additionally show excellent  
elongation and wettability. In addition, the lenses  
formed from the IPNs of the present invention have high  
30 oxygen permeability and are transparent to visible  
light. The homogeneous nature of the interpenetrating

1 networks present in the lens is confirmed by the single  
glass transition temperature exhibited by the contact  
lens of the present invention. The simultaneous nature  
of the two polymerization reactions, occurring in the  
5 immediate vicinity of each other, is essential in  
determining the homogeneity of the resulting polymer  
network. In a comparative example, the polyurea and  
polyacrylic networks were produced sequentially; i.e.,  
the polyamines were condensed with the diisocyanate to  
10 give a pure polyurea material. This was mixed with a  
mixture of acrylic esters, and polymerized using a free  
radical initiator. Such a sequentially produced  
polyurea/polyacrylic material exhibited three separate  
glass transition temperatures. The pure polyurea  
15 material by itself exhibits two glass transition  
temperatures. The homogeneity observed in the contact  
lenses of the present invention ensures excellent  
optical properties in the lens.

The optical clarity of the lens is influenced  
20 by the polyurea/polyacrylic ratio present in the lens  
material. However at the indicated ratios hereinabove,  
the hydrogels are transparent to visible light.

Also, the water uptake decreases as the  
polyacrylic content increases. However, the water  
25 uptake remains almost constant when the  
polyurea/polyacrylic ratio is greater than 70/30.

The following examples will serve to  
illustrate the principles and scope of the present  
invention.

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1            In the following examples, various  
abbreviations are utilized. The table below contains  
the abbreviations to which reference is made in the  
examples.

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|    |  |                   |                                                               |                |
|----|--|-------------------|---------------------------------------------------------------|----------------|
| 1  |  | <b>CODE</b>       | <b>CHEMICAL NAME</b>                                          | <b>MOL.WT.</b> |
|    |  | Jeffamine ED-900  | Poly(oxyethylene) diamine                                     | 1179           |
|    |  | Jeffamine ED-2000 | Poly(oxyethylene) diamine                                     | 2277           |
| 5  |  | Jeffamine D-2000  | Poly(oxypropylene) diamine                                    | 2000           |
|    |  | Jeffamine T-403   | Poly(oxypropylene) triamine                                   | 440            |
|    |  | Jeffamine EDR148  | Triethylene glycol triamine                                   | 148            |
|    |  | DETA              | Diethylene triamine                                           | 103            |
|    |  | Desmodur W        | 4,4'-Methylene-bis-cyclohexylisocyanate), H <sub>12</sub> MDI | 262            |
| 10 |  | HEMA              | Hydroxyethyl methacrylate                                     | 130            |
|    |  | PEGMA             | Polyethylene glycol monomethacrylate                          | 306            |
|    |  | TEGDMA            | Triethylene glycol dimethacrylate                             | 286            |
|    |  | PEG (600)DMA      | Poly(ethylene glycol-600)dimethacrylate                       | 770            |
| 15 |  | L-256             | Lupersol 256                                                  |                |
|    |  | BPO               | Benzoyl peroxide                                              | 242            |

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EXAMPLE I

A blend was made of 589.5 parts ED-900, 400 parts D-2000, 155.4 parts EDR-148 and 34.3 parts DETA. This blend was called Stream 1. A second blend was made of 589.5 parts H<sub>12</sub>MDI, 560.1 parts HEMA, 29.48 parts TEGDMA and 11.9 parts L-256. This blend was called Stream 2. The streams were placed in the material reservoirs of a two stream laboratory scale RIM machine. Stream 1 was heated to about 80°C to maintain fluidity of the materials. Stream 2 was maintained at room temperature to insure stability of the materials. The streams were mixed by impingement at a pressure of 2500 psi. and injected into a two piece aluminum mold. The mixing ratio was 1.010 parts Stream 1 for each part of Stream 2. The injection time is 0.20 seconds. These conditions produced about 20 gm. of polymer in which both networks were separate and simultaneously produced.

The mold consisted of two aluminum plates. One of the plates was machined such that it had two compartments. One compartment was designed to produce a film 100 microns thick. The other compartment was designed to produce a film 800 microns thick. The mold was held together by bolts. The mold was heated to 100°C. It is attached to the RIM machine. The material was post-cured in the mold for 10 minutes following the injection molding operation.

The mold was opened manually and the elastomeric film was removed from the mold. The demolded film was post cured for one hour in an oven at

1 100°C. The film was converted to a hydrogel by immersion in a buffered saline solution.

The material produced was a clear IPN hydrogel of 75% (weight) urea component and 25% (weight)

5 methacrylic portion. Following hydration the material had the following properties:

|                        |         |
|------------------------|---------|
| Water content          | 34%     |
| Modulus                | 262 psi |
| Tensile strength       | 300 psi |
| 10 Elongation at break | 238%    |

This material was suitable for use as a contact lens.

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EXAMPLES II TO V

A series of IPN elastomers were prepared using the methods of Example 1. The formulations and properties are shown in Table II.

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| EXAMPLE                 | II    | III    | IV    | V      |
|-------------------------|-------|--------|-------|--------|
| Stream 1                |       |        |       |        |
| ED-900                  | 589.5 | 589.5  | 589.5 | 471.6  |
| ED-2000                 | -     | -      | -     | -      |
| D-2000                  | 200   | -      | 400   | 400    |
| EDR-148                 | 155.4 | 155.4  | 229.4 | -      |
| DETA                    | 34.3  | 34.3   | -     | 34.3   |
| Stream 2                |       |        |       |        |
| H <sub>12</sub> MDI     | 563.3 | 537.1  | 589.5 | 1133.8 |
| HEMA                    | 483.6 | 412.68 | 566.9 | -      |
| PEGMA                   | -     | -      | -     | 454.0  |
| TEGDMA                  | 25.4  | 21.7   | 29.8  | 23.9   |
| L-256                   | 10.2  | 8.7    | 11.9  | 9.6    |
| UREA/ACRYLIC RATIO      | 75/25 | 75/25  | 75/25 | 75/25  |
| STREAM 1/STREAM 2       | 0.90  | 0.76   | 1.02  | 1.37   |
| Water content (%)       | 37.5  | 47.1   | 33.1  | 60.8   |
| Modulus (psi)           | 218   | 87     | -     | 133    |
| Tensile strength (psi)  | 263   | 101    | 110   | 81     |
| Elongation at break (%) | 206   | 103    | 169   | 101    |
| Appearance              | clear | opaque | hazy  | clear  |

The materials of Example II and Example V were suitable for contact lens use.

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EXAMPLE VI

A blend was made of 471.6 parts ED-900, 228 parts ED-2000, 400 parts D-2000 and 34.3 parts DETA.

5 This blend was called Stream 1. A second blend was made of 314.4 parts H<sub>12</sub>MDI, 454.0 parts HEMA, 23.91 parts TEGDMA and 9.6 parts L-256. This blend was called Stream 2. The streams were placed in the material reservoirs of a two stream laboratory scale RIM machine.

10 Stream 1 was heated to about 80°C to maintain fluidity of the materials. The streams were mixed by impingement at a pressure of 900 psi. and injected into a two piece aluminum mold. The mixing ratio was 1.37 parts Stream 1 for each part of Stream 2. The injection time was 0.25  
15 seconds. These conditions produced about 25 gm. of polymer in which both networks are separate and simultaneously produced.

The mold used for this example was described in Example I.

20 The mold was opened manually within one minute of injection and the elastomeric film is removed from the mold. The demolded film was post-cured for about 40 minutes in an oven at 100°C. The film was converted to a hydrogel by immersion in a buffered saline solution.

25 The material produced was a clear IPN hydrogel of 75% (weight) urea component and 25%(weight) methacrylic portion. Following hydration the material has the following properties:

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|   |                     |        |
|---|---------------------|--------|
| 1 | Water content       | 50%    |
|   | Modulus             | 93 psi |
|   | Tensile strength    | 91 psi |
|   | Elongation at break | 239%   |

5 This material is suitable for use as a contact lens.

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EXAMPLES VII TO IX

A series of IPN elastomers were prepared using the methods of Example VI. The formulations and properties are shown in Table III.

TABLE III

| EXAMPLE             | VII   | VIII  | IX    |
|---------------------|-------|-------|-------|
| Stream 1            |       |       |       |
| ED-900              | 353.7 | 471.6 | 471.6 |
| ED-2000             | 227.9 | 455.8 | 455.8 |
| D-2000              | 400   | 200   | 200   |
| DETA                | 34.3  | 34.3  | 34.3  |
| Stream 2            |       |       |       |
| H <sub>12</sub> MDI | 288.2 | 314.4 | 314.5 |
| HEMA                | 408   | 463   | 463   |
| TEGDMA              | 21.5  | 24.3  | 24.3  |
| I-256               | 8.6   | 19.4  | 9.8   |
| UREA/ACRYLIC RATIO  | 75/25 | 75/25 | 75/25 |
| STREAM 1/STREAM 2   | 1.35  | 1.37  | 1.39  |
| Water content       | 40.1  | 43.1  | 42.2  |
| Modulus             | -     | 254   | 245   |
| Tensile Strength    | 141   | 292   | 221   |
| Elongation at break | 260   | 165   | 221   |
| Appearance          | clear | clear | clear |

The materials of Examples VII, VIII and IX were suitable for contact lens use.

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EXAMPLE X

A Hi-Tech three stream RIM machine was used for this example. The machine was fitted with an Edge-Sweets four component mixhead. The mixing was by impingement.

The chemical system consisted of eight separate chemicals. The materials were blended as follows:

10 Stream 1

|          |                   |                                    |
|----------|-------------------|------------------------------------|
| 870.9 gm | Jeffamine ED-900  | Poly(oxyethylene) diamine MW 1179  |
| 420.9 gm | Jeffamine ED-2000 | Poly(oxyethylene) diamine MW 2277  |
| 738.7 gm | Jeffamine D-2000  | Poly(oxypropylene) diamine MW 2000 |
| 63.5 gm  | DETA              | Diethylene Triamine                |

(Jeffamine is a trademark of the Texaco Chemical

15 Company)

Stream 2

|         |        |                                   |
|---------|--------|-----------------------------------|
| 3502 gm | HEMA   | Hydroxyethyl Methacrylate         |
| 72.4 gm | TMPTMA | Trimethylolpropanetrimethacrylate |

Stream 3

20 3140 gm H<sub>12</sub>MDI 4,4'-methylene bis (cyclohexyl isocyanate)

96.6 gm Benzoyl peroxide

The process conditions were:

|    | <u>Stream</u> | <u>Pressure</u> | <u>Orifice</u> | <u>Flow Rate</u> | <u>Viscosity</u> |
|----|---------------|-----------------|----------------|------------------|------------------|
| 25 | 1             | 2700psi         | 0.75mm         | 99.3gm/sec       | 52cps            |
|    | 2             | 1900psi         | 1.25mm         | 42.30gm/sec      | 6cps             |
|    | 3             | 1900psi         | 0.50mm         | 28.4gm/sec       | 24cps            |

Stream 1 was split and injected into two separate ports. The ports were chosen to be 90° apart. This gave direct impingement of one-half the amine and the isocyanate streams.

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1           The injection time was set at 0.03 sec. and a  
shot weight of 13.6gm obtained.

          The injection head of the RIM machine was  
affixed to a hardened steel mold. The mold had a  
5 channel 2mm wide and 4mm deep leading to a contact lens  
shaped cavity. The injection of the formulation into  
the mold produced a contact lens.

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EXAMPLES XI, XII, XIII

Examples XI, XII, XIII were duplicates of Example X except that the flow rate of Stream 2 was  
5 changed to change the ratio of urea to acrylic fractions of the IPN's. The flow rates of Stream 1 and Stream 3 were adjusted to obtain a constant shot size. The orifice size was controlled to maintain at the pressures of Example X.

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| Example            |                       | XI    | XII   | XIII  |
|--------------------|-----------------------|-------|-------|-------|
| Stream 1           | Flow rate<br>(gm/sec) | 104.0 | 78.3  | 92.8  |
| Stream 2           | Flow rate<br>(gm/sec) | 33.2  | 66.7  | 50.8  |
| 15 Stream 3        | Flow rate<br>(gm/sec) | 29.7  | 22.4  | 26.5  |
| UREA/ACRYLIC RATIO |                       | 80/20 | 60/40 | 70/30 |

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When these formulations were injected into a heated mold with a contact lens shaped cavity with an  
20 annular gate, a contact lens was formed.

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EXAMPLES XIV, XV, XVI

Examples XIV, XV, XVI were duplicates of  
Example XI, XII and XIII except that the flat plate mold  
5 of Example 1 was used.

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| Example            |                       | XIV   | XV    | XVI   |
|--------------------|-----------------------|-------|-------|-------|
| Stream 1           | Flow rate<br>(gm/sec) | 120.2 | 78.3  | 92.8  |
| Stream 2           | Flow rate<br>(gm/sec) | 38.4  | 66.7  | 50.8  |
| Stream 3           | Flow rate<br>(gm/sec) | 34.4  | 22.4  | 26.5  |
| UREA/ACRYLIC RATIO |                       | 80/20 | 60/40 | 70/30 |

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These materials were used for thermal property testing.

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1                    Comparative Example I

Polyurea films were prepared using the method of Example X except that Stream 2 was blocked to prepare a clear polyurea film.

5                    Comparative Example II

A solution of 47.5g HEMA, 2.5g polyethylene glycol (600) dimethacrylate and 1 g benzoyl peroxide was prepared. This is the acrylic portion of Example X.

A sequential IPN was prepared from 6.06g piece  
10 of film from Example X and 2.54g of the above described HEMA solution. The HEMA solution was mixed with 30ml of methyl alcohol. This step was performed to assure a uniform distribution of the HEMA mixture through the film. The urea film was immersed in the methanol HEMA  
15 mixture. The jar containing the components was placed on a roller mill (US Stoneware) and mixed 24 hours. The methanol was removed using a vacuum of 20 mmHg. The methanol free sample was placed in an 80°C oven for 4 hours. The recovered film has a mass of 6.61g. This  
20 indicates that the HEMA evaporated more quickly than it polymerized under these conditions.

Comparative Examples III and IV

The procedure of Comparative Example II was repeated using different urea/HEMA ratios. 30 ml of  
25 methanol was used in all cases.

| <u>Comparative<br/>Example</u> | <u>urea (g)</u> | <u>HEMA (g)</u> | <u>post<br/>polymerization<br/>weight (g)</u> |
|--------------------------------|-----------------|-----------------|-----------------------------------------------|
| III                            | 7.24            | 2.41            | 7.92                                          |
| IV                             | 5.36            | 1.34            | 5.31                                          |

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1            In both of these examples the final weight  
indicated that the HEMA was lost before polymerization  
could occur.

Comparative Example V

5            A 1.45g piece of polyurea film was immersed in  
0.48g of HEMA and 5 ml of methanol. The methanol was  
removed with a vacuum of 20mmHg. The HEMA containing  
polyurea film was tightly wrapped in aluminum foil. The  
foil packet was placed in an 80°C oven for 4 hours. The  
10 resulting film had a mass of 1.92g and a dry feel. The  
sequential IPN was evaluated by thermal analysis.

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1                                    Comparative Example VI

          The HEMA mix of Comparative Example I was  
polymerized by placing 1g in an aluminum weighing dish.  
The material was placed into an oven at 80°C for four  
5 hours. A clear glassy solid was formed.

Determination of the Glass Transition Temperature

          The glass transition is a second order  
transition where the motions of a polymer chain are  
abruptly increased or decreased. The temperature at  
10 which the transition occurs is the glass transition  
temperature. The change in chain motion results in a  
change of polymer properties. One property that changes  
is known as Tan  $\delta$ .

          The glass transition temperatures of the  
15 materials of Examples XIII, XIV and XV were determined  
using a Perkin Elmer dynamic mechanical analyzer (DMA  
7). Samples were rectangular samples in an extension  
geometry. The samples were heated at a rate of 2°C per  
minute. The samples were heated from -50°C to 150°C.

| 20 | <u>EXAMPLE</u> | <u>urea/acrylic</u> | <u>Glass Transitions</u> |          |          |
|----|----------------|---------------------|--------------------------|----------|----------|
|    |                |                     | <u>1</u>                 | <u>2</u> | <u>3</u> |
|    | XIII           | 75/25               | 2.3°C                    |          |          |
|    | XIV            | 80/20               | -28.3°C                  | 2.4°C    |          |
|    | XVI            | 70/30               | 7.0°C                    |          |          |
| 25 | Comparative I  | 100/1               | -41.7°C                  | -8.0°C   |          |
|    | Comparative VI | 75/25               | -29.2°C                  | 5.0°C    | 48.6°C   |

          These data show that the base urethane  
30 material has two glass transitions. The simultaneous  
IPN materials disclosed herein have a single glass

1 transition. This is characteristic of a homogeneous  
material. The sequential material exhibits three glass  
transitions. This is characteristic of a non-  
homogeneous material. Clearly, the simultaneous process  
5 produces a different material than the sequential  
material.

The above preferred embodiments and examples  
are given to illustrate the scope and spirit of the  
present invention. These embodiments and examples will  
10 make apparent to those skilled in the art other  
embodiments and examples. These other embodiments and  
examples are within the contemplation of the present  
invention. Therefore, the present invention should be  
limited only by the appended claims.

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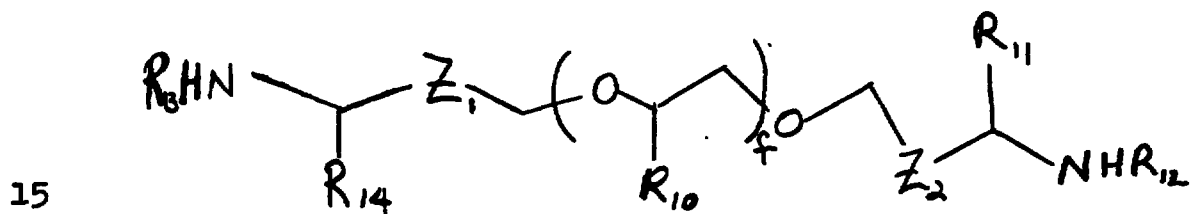
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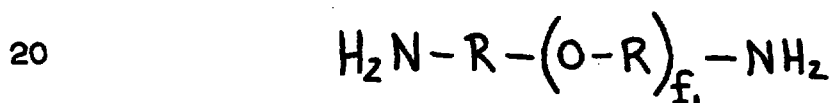
1 WHAT IS CLAIMED IS:

1. A homogenous interpenetrating polymer network exhibiting a single glass transition temperature  
 5 formed by polymerization of a reactive mixture of polymerizable components, said reactive mixture comprising

(a) an amine mixture consisting of diamines A and B, said amine mixture being present in about 20-60%  
 10 by weight in said reactive mixture wherein A is



and B is



$f_1$  is an integer from 1-75;  
 25 R is an alkylene containing 3 carbon atoms and each R is the same;  
 f is an integer between 1 and 150 inclusive;  
 $\text{R}_{10}$ ,  $\text{R}_{11}$ ,  $\text{R}_{12}$ ,  $\text{R}_{13}$  and  $\text{R}_{14}$  are independently  
 hydrogen or lower alkyl;

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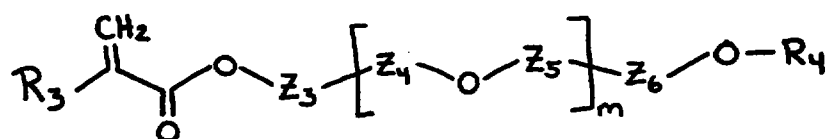
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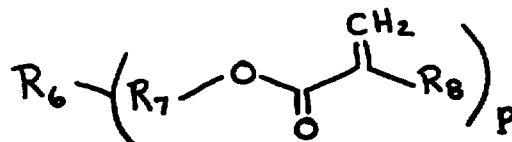
1             $Z_1$  and  $Z_2$  are independently a chemical bond or lower alkylene with A and B being present in relative weight ratios ranging from about 60/40 to about 100% A;

5            (b) an organic di- or poly-isocyanate present in sufficient quantity in said reactive mixture to react with the amine mixture of (a), forming therefrom a polyurea network;

          (c) an acrylic ester of the formula:



or



wherein

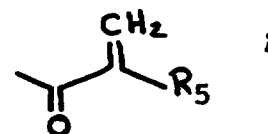
$R_3$  is hydrogen or lower alkyl;

$m$  is an integer from 0 to 150;

$Z_3$  and  $Z_5$  are independently lower alkylene.

$Z_4$  and  $Z_6$  are independently a chemical bond or lower alkylene;

$R_4$  is hydrogen, lower alkyl or





- 1  $R_5$  is hydrogen or lower alkyl;  
 $R_6$  and  $R_8$  are independently lower alkyl;  
 $p$  is an integer of 1 to 3; and  
 $R_7$  is lower alkylene or chemical bond or -

5  $\text{CH}_2(\text{OCH}_2\text{CH}_2)_q$ ;

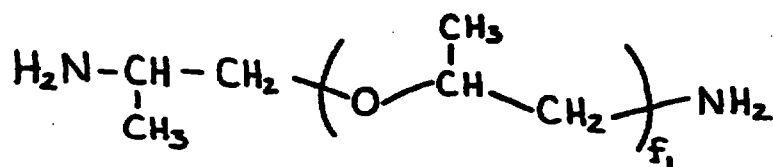
$q$  is an integer from 0 to 200 inclusive;  
said acrylic ester being present in about 10-50% by  
weight in the reactive mixture; and

(d) a free radical initiator being present in  
10 sufficient quantity in the reactive mixture to  
polymerize the acrylic esters of (c), forming a  
polyacrylic network;

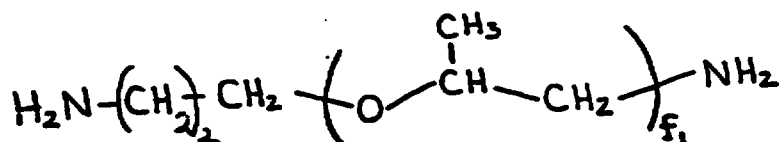
(e) a triamine being present in sufficient  
amount to crosslink the amine mixture of (a);

15 wherein the ratio of polyurea to polyacrylic  
ranges from about 50:50 to about 90:10, and wherein the  
weights of the components in the reactive mixture sum up  
to 100%.

2. The interpenetrating polymer network  
20 according to Claim 1 wherein B is a polyoxypropylene  
diamine of the formula:



or





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3. The interpenetrating polymer network according to Claim 1 wherein the triamine is present in the reactive mixture in an amount ranging from 30 to 50% total amine equivalents.

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4. The interpenetrating polymer network according to Claim 1 wherein the triamine is diethylene triamine or polyoxypropylene triamine.

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5. The interpenetrating polymer network according to Claim 1 wherein the isocyanate is methylene-bis (4,4'-cyclohexylisocyanate) or isophorone diisocyanate.

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6. The interpenetrating polymer network according to Claim 1 wherein the free radical initiator is 2,5-dimethyl-2,5-di-(2-ethylhexanoylperoxy) hexane, benzoyl peroxide, t-butyl hydroperoxide, t-butyl peroxide or lauryl peroxide.

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7. The interpenetrating polymer network according to Claim 1 wherein the polyurea/polyacrylic weight ratio ranges from about 80:20 to about 70:30.

8. The interpenetrating polymer network according to Claim 1 wherein the polyurea/polyacrylic weight ratio is about 75:25.

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9. The interpenetrating polymer network according to Claim 1 wherein the isocyanate is present in the reactive mixture in an amount ranging from about 15% to about 50% by weight.

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10. The interpenetrating polymer network according to Claim 9 wherein the isocyanate is present in an amount ranging from about 25% to about 40% by weight.

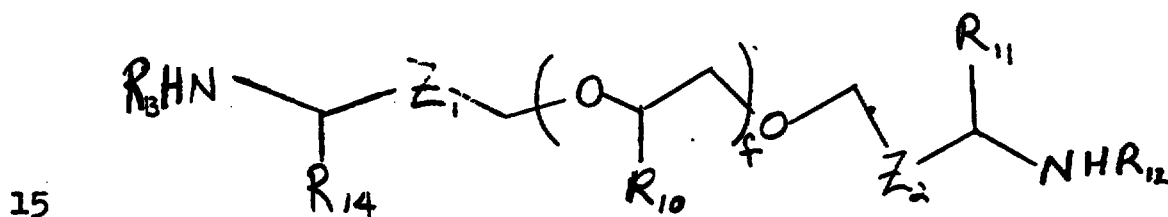
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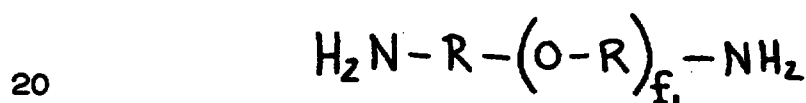
11. The interpenetrating polymer network according to Claim 1 wherein the free radical initiator is present in the reactive mixture an amount ranging from about 0.01% to about 1% by weight.

12. The interpenetrating polymer network according to Claim 1 formed by polymerization of a reactive mixture comprising

(a) an amine mixture consisting of polyamines A and B, said polyamines being present in said reactive mixture in about 20-60% by weight, wherein A is



and B is



$f_1$  is an integer from 1-75;

R is an alkylene containing 3 carbon atoms and each R is the same;

f is an integer between 1 and 150, inclusive,  $R_{10}$ ,  $R_{11}$ ,  $R_{12}$ ,  $R_{13}$  and  $R_{14}$  are independently hydrogen or lower alkyl;

$Z_1$  and  $Z_2$  are independently a chemical bond or lower alkylene with A and B being present in relative weight ratios ranging from about 60/40 to about 100% A;



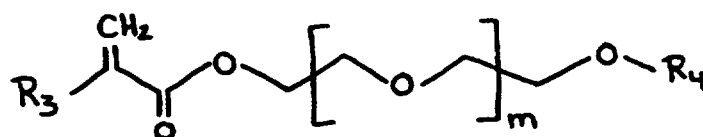
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(b) an organic di- or poly-isocyanate present in sufficient quantity in said reactive mixture to react with the amine mixture of (a), forming therefrom a polyurea network;

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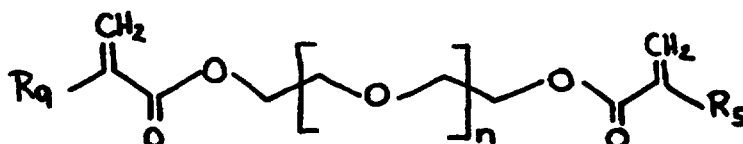
(c) 10-50% by weight in the reactive mixture of an acrylic ester component consisting of a mixture of a first acrylate of the formula

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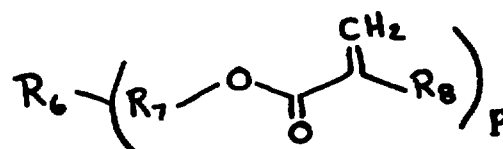
and a second acrylate being a diacrylate of the formula



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or a triacrylate of the formula

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or a mixture thereof, wherein

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$\text{R}_3$ ,  $\text{R}_4$ ,  $\text{R}_3$ ,  $\text{R}_5$  and  $\text{R}_6$  are independently hydrogen or lower alkyl;

$\text{R}_6$  is lower alkyl;

$\text{R}_7$  is a chemical bond or lower alkylene;

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m and n are independently integers of 0-30 and  
p is an integer of 1-3;

5

said ratio of the first acrylate to second acrylate  
ranges from about 80:20 to about 95:5,

(d) a free radical initiator being present in  
sufficient quantity in said reactive mixture to  
polymerize the acrylic ester of (c), forming therefrom a  
polyacrylic network, and

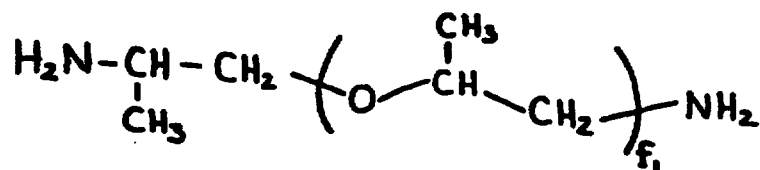
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(e) a triamine present in sufficient quantity  
to crosslink the amine mixture of (a), wherein the ratio  
of polyurea to polyacrylic ranges from about 90:10 to  
about 50:50.

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13. The interpenetrating polymer network  
according to Claim 12 wherein B is a polyoxypropylene  
diamine of the formula:

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14. The interpenetrating polymer network  
according to Claim 12 wherein the triamine is present in  
the reactive mixture in an amount ranging from about 30  
to 50% of the total amine equivalents.

15. The interpenetrating polymer network  
according to Claim 14 wherein the triamine is diethylene  
triamine or polyoxypropylene triamine.

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16. The interpenetrating polymer network  
according to Claim 12 wherein the isocyanate is

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1 methylene-bis (4,4'-cyclohexylisocyanate) or isophorone diisocyanate.

17. The interpenetrating polymer network according to Claim 12 wherein the free radical initiator  
5 is 2,5-dimethyl-2,5-di-(2-ethylhexanoylperoxy) hexane, benzoyl peroxide, t-butyl hydroperoxide, t-butyl peroxide or lauryl peroxide.

18. The interpenetrating polymer network according to Claim 12 wherein the polyurea/polyacrylic  
10 weight ratio ranges from about 70:30 to 80:20.

19. The interpenetrating polymer network according to Claim 12 wherein the polyurea/polyacrylic weight ratio is about 75:25.

20. The interpenetrating polymer network  
15 according to Claim 12 wherein the isocyanate is present in the reactive mixture in an amount ranging from about 15% to about 50% by weight.

21. The interpenetrating polymer network according to Claim 20 wherein the isocyanate is present  
20 in an amount ranging from about 25% to about 40% by weight.

22. The interpenetrating polymer network according to Claim 12 wherein the free radical initiator is present in the reactive mixture an amount ranging  
25 from about 0.01% to about 1% by weight.

23. The interpenetrating polymer network according to Claim 12 wherein  $R_3$ ,  $R_4$ ,  $R_5$  and  $R_6$  are  $\text{CH}_3$ .

24. The interpenetrating polymer network according to Claim 12 wherein  $R_3$ ,  $R_5$ , and  $R_6$  are  $\text{CH}_3$ ,  $m$   
30 is 0,  $R_4$  is hydrogen and  $n$  is 2.



1           25. The interpenetrating polymer network  
according to Claim 12 wherein  $R_3$ ,  $R_5$  and  $R_9$  are  $\text{CH}_3$ ,  $m$  is  
4,  $R_4$  is hydrogen and  $n$  is 2.

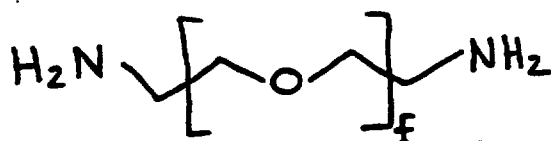
5           26. The interpenetrating polymer network of  
Claim 12 wherein  $m$  is 4,  $R_4$  is hydrogen,  $p$  is 3,  $R_6$  is  
ethyl,  $R_7$  is ethylene, and  $R_3$  and  $R_8$  are  $\text{CH}_3$ .

          27. An article of manufacture comprised of  
the interpenetrating polymer network of any one of  
Claims 1-26.

10           28. The article of manufacture according to  
Claim 27 which is a contact lens.

          29. The interpenetrating polymer network of  
Claim 1 in which A is

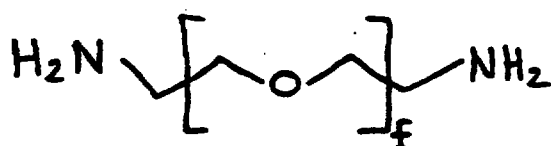
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          30. The interpenetrating polymer network of  
Claim 12 wherein A is

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INTERPENETRATING POLYMER NETWORKS  
FOR CONTACT LENS PRODUCTION

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ABSTRACT

5 The present invention is directed to an  
interpenetrating polymer network comprised of a polyurea  
network interpenetrated with a polyacrylic network and  
the article of manufacture, such as a contact lens, made  
therefrom.

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