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NOTICE OF ENTITLEMENT

I(We) FREDERICK LYLE SCHILLING
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the applicant and nominated person in respect of an application for a patent for an invention entitled Lenses with high impact resistance and high scratch resistance
filed under Australian Application No. 42846/93, state the following:

PART 1 - *Must be completed for all applications.*
The person(s) nominated for the grant of the patent
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The basic application(s) listed in the declaration made under Article 8 of the PCT ~~is~~ (are) the first application(s) made in a Convention country in respect of the invention.

Dated this 15th day of July 1998

Signed [signature] Status Patent Attorney

Signatory's Name FREDERICK LYLE SCHILLING

F.B. RICE & CO PATENT ATTORNEYS

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The invention disclosed herein addresses two problems in the area of the production of ophthalmic lenses. The first problem is the need to provide a lens structure that has both high impact resistance and high scratch resistance. The second problem is the desire on the part of retail eyewear outlets to be able to produce plastic lenses on-site for customers, instead of merely grinding plastic lens blanks to a desired prescription. The art in these areas are considered below in order.

Claim

1. A free radical polymizerable composition, comprising

a) between 20 and 90 weight percent of an oligomer that is end terminated with acrylate methacrylate or both, wherein said oligomer is selected from the group consisting of (i) one or more epoxy oligomers, (ii) mixtures of one or more epoxy oligomers and one or more polyester oligomers, (iii) mixtures of one or more epoxy oligomers and one or more urethane oligomers, and (iv) mixtures of one or more epoxy oligomers, one or more polyester oligomers, and one or more urethane oligomers; and

b) between 5 and 80 weight percent of a diluent comprising one or

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more crosslinkable ethoxylated or propoxylated tri-, tetra-, penta- or hexa-acrylated or methacrylated aliphatic or aromatic monomers, or mixtures thereof.

20. A lens prepared from a free radical polymerizable composition comprising:

a) between 20 and 90 weight percent of an oligomer that is end terminated with acrylate, methacrylate, or both, wherein said oligomer is selected from the group consisting of (i) one or more polyester oligomers, (ii) mixtures of one or more polyester oligomers and one or more epoxy oligomers, (iii) mixtures of one or more polyester oligomers and one or more urethane oligomers, and (iv) mixtures of one or more polyester oligomers, one or more epoxy oligomers, and one or more urethane oligomers; and

b) between 5 and 80 weight percent of a diluent comprising one or more crosslinkable ethoxylated or propoxylated tri-, tetra-, penta-, or hexa-acrylated or methacrylated aliphatic or aromatic monomers, or mixtures thereof.

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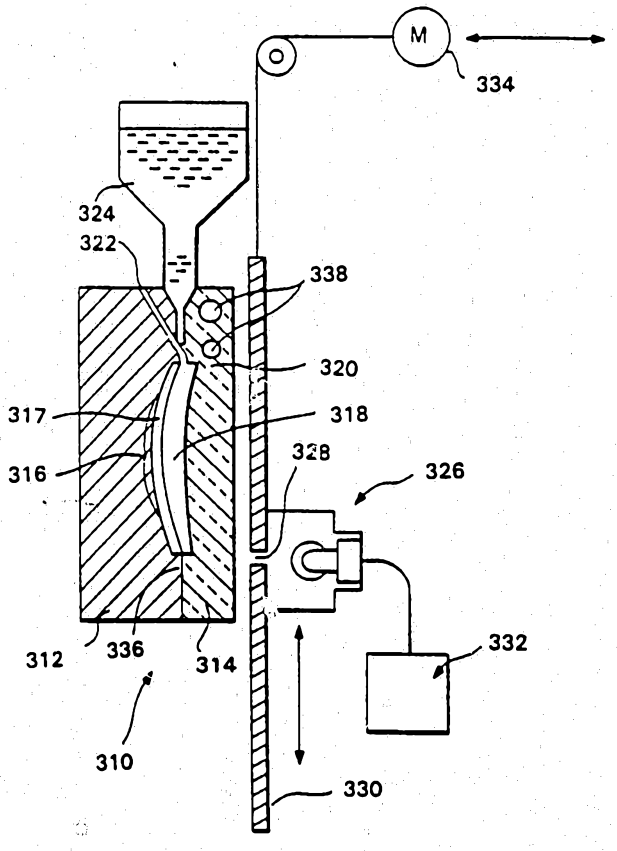
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(54) Title: LENSES WITH HIGH IMPACT RESISTANCE AND HIGH SCRATCH RESISTANCE

(57) Abstract

The invention is a composite lens that includes a front scratch-resistant polymeric wafer (317) and a back impact-resistant polymeric layer (318). The unique structure allows maximal design flexibility, and is easily and relatively quickly manufactured. The design allows simultaneous optimization of impact and scratch resistance. A polymerizable composition for the rapid preparation of high quality lenses is also provided that includes: a) between 20 and 90 weight percent, and preferably, at least 50 weight percent, of urethane, epoxy, or polyester oligomers end terminated with acrylate or mathacrylate (or mixtures of acrylate and methacrylate); b) between 5 and 50 to 80 percent, preferably between 10 and 40 percent, by weight of an optional diluent, such as a hydrocarbon diol end terminated with acrylate or methacrylate, or mixtures thereof, or a crosslinkable tri-, tetra-, or poly-acrylate or methacrylate, or mixtures thereof; and c) conventional optional additives.



Lenses With High Impact Resistance and High Scratch Resistance

This invention is in the area of composite lens structures, and in particular is a polymer-polymer composite lens structure exhibiting high impact resistance and high scratch resistance. This invention also includes fast curing polymeric compositions that are suitable for casting into ophthalmic lenses, lenses prepared from these compositions, and apparatus for the production of lenses.

Background of the Invention

The invention disclosed herein addresses two problems in the area of the production of ophthalmic lenses. The first problem is the need to provide a lens structure that has both high impact resistance and high scratch resistance. The second problem is the desire on the part of retail eyewear outlets to be able to produce plastic lenses on-site for customers, instead of merely grinding plastic lens blanks to a desired prescription. The art in these areas are considered below in order.

High Scratch Resistant, High Impact Resistant Ophthalmic Lenses

Ophthalmic (prescription) glasses and both prescription and nonprescription sun glasses have traditionally been prepared using inorganic glass as the lens material. Recently, organic polymers have been introduced as an alternative lens material. Currently, both inorganic glass and organic polymers play a major role in the prescription and nonprescription lens market.

Glass is considered a pristine optical-quality material and is extremely scratch resistant. However, glass is heavy and is easily shattered. Tempering (either by thermal or chemical processes) improves the impact resistance, but at the expense of lengthening process time and escalating production cost. Plastics perform better in impact resistance, and are light weight. However, the

scratch resistance of plastics is inferior to glass. A marriage of the two in the form of a front plano glass wafer with a back polymer layer has been used as a means to obtain the desired qualities of both materials. The outer glass layer is convex outward, where the majority of the scratch "incidences" would normally occur. Hence the structure offers protection against scratch. The inner plastic layer enhances the overall shatter resistance of the composite. The glass-plastic interface has to be chemically coupled to ensure strong adhesion over the complete service temperature range (from sub-zero to above standard room temperature). A significant disadvantage of the glass/plastic composite is that firm attachment of the two, especially in a stress-free and defect-free manner, is exceptionally difficult. Further, the inherently divergent thermal expansion properties of glass and most plastic materials make such composites prone to thermoelastic stresses and potential failures during thermal cycling and shocks.

In general, scratch resistance and impact resistance is difficult to attain in the same polymeric material. The former attribute requires a hard material with great internal cohesive energies, while the latter requires an elastomeric behavior (i.e., elasticity under sharp impulse stress loading conditions). It is extremely difficult, if not impossible, to optimize both scratch resistance and impact resistance in one material.

U.S. Patent No. 4,544,572 to Sandvig, et al., discloses a polymeric ophthalmic lens that has a thin (50 microns or less) abrasion-resistant polymeric coating. The lens is prepared by applying a layer of a composition comprising a material that contains ethylenically unsaturated groups to the first face of a lens mold, reacting the composition to a dry film, filing the mold with an organic material capable of solidification, and then hardening the organic material. This process is time consuming in that the first layer must be partially cured before injection of the back layer hardenable material. As stated in the patent, it

can take up to 16 hours to prepare one lens. Further, this method does not provide a means to impart contour shaping to the front layer.

There remains a need for a lens material that has high impact resistance and high scratch resistance, and that does not exhibit thermoelastic stress and failure during thermal cycling and shock. There is also a need for a process for the preparation of a lens composite with high impact resistance and high scratch resistance that does not impart significant stress and/or defects into the material during adhesion of the layers. Further, there is a strong need to provide a method to prepare high impact resistant, high scratch resistant lenses that can be accomplished in a relatively short timeframe, and that provides a means to impart contour shaping to the front wafer of the lens.

Rapid Preparation of High Quality Plastic Ophthalmic Lenses

Many of the plastic ophthalmic lenses sold today by optical dispensers such as retail eyewear outlets are made by machining the desired prescription into the back face of a semi-finished lens blank made from diethylene glycol bis(allyl carbonate) resin, also known as CR-39. These blanks are manufactured off-site by casting the starting monomer for CR-39 between a set of glass molds held together by a flexible gasket and restraints. The mold assembly is initially heated in an oven using a precise cure schedule. During the subsequent polymerization step, the liquid resin is converted into a glassy solid. Shrinkage of up to 16 percent of the material occurs during polymerization and crosslinking. The molds must be designed to account for the shrinkage, so that the lens blank has the desired front curvature. The complexity of design is increased if, instead of a semi-finished lens blank, a finished lens is desired in which both the front and back surfaces have defined curvatures. Another disadvantage in preparing CR-39 lenses is that they require cure schedules of as long as sixteen hours.

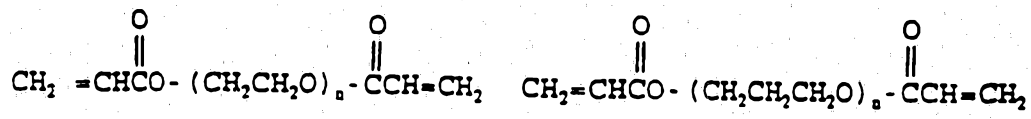
Casting lenses from polymerizable compositions on-site would be preferable to a retail eyewear outlet over machining lens blanks if problems associated with shrinkage of the polymerizable material during casting and the long cure time could be solved. One advantage of casting on-site is that the equipment needed for casting is less expensive than the lens generators and polishing instruments used in lens machining. Second, the casting process is cleaner and generates less waste than the machining process. In addition, the cost of the finished lens to the eyewear outlet using a casting process may be less than that when the lens is prepared by machining a lens blank, particularly for aspheric, multifocal, and progressive lenses.

CR-39 is unsuitable as a material for casting into lenses in one hour processing laboratories because of its slow reaction rate. It would be of great benefit to have a material that maintains most of the desirable properties of CR-39, such as good abrasion resistance, chemical resistance, impact resistance, clarity and generally superior optical properties, yet polymerizes in a short amount of time. It would also be of benefit to have an apparatus that can be used to produce lenses on-site in a short amount of time.

Urethanes have been used in coatings for ophthalmic lenses. U.S. Patent No. 4,800,123 to Boekeler discloses a scratch resistant coating prepared from a polymerizable composition that includes at least one polyfunctional monomer having three or more acryloloxy groups per molecule, and at least one N-vinyl imido group containing monomer. U.S. Patent No. 4,435,450 to Coleman discloses a method for applying abrasion resistant thin polyurethane coatings that includes forming a hydroxy-terminated prepolymer which is subsequently crosslinked using a relatively non-volatile triisocyanate, and applying the material by flow coating onto a glass or lens.

U.S. Patent No. 4,912,185 to Toh discloses a cross-linkable casting composition for ophthalmic lenses that includes (A) a polyoxyalkylene glycol dimethacrylate or

diacrylate, (B) at least one polyfunctional cross-linking agent, and (C) up to 40% by weight of a urethane monomer having from two to six terminal acrylic or methacrylic groups. The polymerizable composition disclosed in the '185 patent was designed to be used in conjunction with traditional methods for the preparation of ophthalmic lenses, wherein the polymerizable solution is poured into numerous molds, cast with blanket radiation, heated and then removed. The method of casting requires the use of a low viscosity polymerizable solution to minimize the problems that result from air entrapment. The '185 patent states that the viscosity of the polymerizable solution should not exceed approximately 200 cps at 25°C. The polyoxyalkylene glycol diacrylate or dimethacrylate, present in the polymerizable composition in a range of 40 to 60% by weight functions as a viscosity reducing agent for the composition. The polyoxyalkene moieties are based on ethylene oxide or propylene oxide repeating units, with 6 to 11 alkylene oxide repeating units preferred, as shown below.



ethylene oxide based system propylene oxide based system

Methacrylate terminated polyoxyalkylene glycols are preferred over acrylate terminated polyoxyalkylene glycols in the '185 patent because they have lower reactivities than the acrylate counterparts, which, using the traditional casting process, reduces surface aberration and internal stress. The patent indicates that this composition can be fully cured by two to four passes under a UV lamp followed by one hour of heat treatment at 100 degrees C.

Japanese Patent No. 61064716 (Chem. Abstract 105:192198b) discloses an impact resistant optical resin prepared by polymerizing acrylate or methacrylate, adducts of monoepoxide and brominated bis-phenol, poly-isocyanate and

other unsaturated compounds such as styrene or divinylbenzene.

An advance in the art of polymerizing shrinkable materials is disclosed in U.S. Patent Nos. 5,114,632 and 5,110,514 to David S. Soane. Briefly, polymerizable material is introduced between two mold halves, one of which is, or both are, constructed of a material that transmits energy, either thermal or UV. Stress related voids in the polymeric material are eliminated by causing the partially polymerized material to polymerize in a differential fashion along a moving front, so that the material ahead of the moving polymer zone remains liquid, and the material that the front has passed is solidified. In a typical method, the moving front is a slit through which UV or thermal energy is transmitted. The still-liquid material ahead of the moving polymer zone can then flow freely, at a rate that equals the rate of shrinkage, and a void-free, reduced stress polymeric network is produced. Using this process, lenses can be cast in a way to prevent cavitation, or voids caused by the shrinkage of material during polymerization. This method is referred to below as "sequential polymerization."

Accordingly, it an the object of the present invention to provide a polymerizable composition that can be polymerized into a lens that maintains or exceeds the mechanical and optical properties associated with CR-39, yet has a faster cure rate than CR-39.

It is still another object of this invention to provide a polymeric material that can be sequentially polymerized into a finished product in less than one hour, preferably less than thirty minutes.

It is another object of the present invention to provide a polymerizable composition for the production of high quality ophthalmic lenses that is suitable for use in combination with the apparatus and method for sequential polymerization disclosed in U.S. Patent Nos. 5,110,514 and 5,114,632.

Summary of the Invention

The invention relates to a polymerizable composition, and the polymer formed thereby, that is useful as the impact resistant or scratch resistant material in the polymer-polymer composite lens, or alternatively, can be used alone as a fast-curing material for the preparation of plastic lenses on-site by a commercial retail eyewear outlet.

Thus, in a first aspect, the present invention provides a free radical polymizerable composition, comprising

a) between 20 and 90 weight percent of an oligomer that is end terminated with acrylate methacrylate or both, wherein said oligomer is selected from the group consisting of (i) one or more epoxy oligomers, (ii) mixtures of one or more epoxy oligomers and one or more polyester oligomers, (iii) mixtures of one or more epoxy oligomers and one or more urethane oligomers, and (iv) mixtures of one or more epoxy oligomers, one or more polyester oligomers, and one or more urethane oligomers; and

b) between 5 and 80 weight percent of a diluent comprising one or more crosslinkable ethoxylated or propoxylated tri-, tetra-, penta- or hexa-acrylated or methacrylated aliphatic or aromatic monomers, or mixtures thereof.

In a second aspect, the present invention provides a lens prepared from a free radical polymerizable composition comprising;

a) between 20 and 90 weight percent of an oligomer that is end terminated with acrylate, methacrylate, or both, wherein said oligomer is selected from the group consisting of (i) one or more epoxy oligomers, (ii) mixtures of one or more epoxy oligomers and one or more polyester oligomers, (iii) mixtures of one or more epoxy oligomers and one or more urethane oligomers, and (iv) mixtures of one or more epoxy oligomers, one or more polyester oligomers, and one or more urethane oligomers; and

b) between 5 and 80 weight percent of a diluent comprising one or more crosslinkable ethoxylated or propoxylated tri-, tetra-, penta- or hexa-acrylated or methacrylated aliphatic or aromatic monomers, or mixtures thereof.

In a third aspect, the present invention provides A free radical polymerizable composition, comprising:

a) between 20 and 90 weight percent of an oligomer that is end terminated with acrylate, methacrylate, or both, wherein said oligomer is



selected from the group consisting of (i) one or more polyester oligomers, (ii) mixtures of one or more polyester oligomers and one or more epoxy oligomers, (iii) mixtures of one or more polyester oligomers and one or more urethane oligomers, and (iv) mixtures of one or more polyester oligomers, one or more epoxy oligomers, and one or more urethane oligomers; and

b) between 5 and 80 weight percent of a diluent comprising one or more crosslinkable ethoxylated or propaxylated tri-, tetra-, penta-, or hexa-acrylated or methacrylated aliphatic or aromatic monomers, or mixtures thereof.

In a fourth aspect, the present invention provides a lens prepared from a free radical polymerizable composition comprising:

a) between 20 and 90 weight percent of an oligomer that is end terminated with acrylate, methacrylate, or both, wherein said oligomer is selected from the group consisting of (i) one or more polyester oligomers, (ii) mixtures of one or more polyester oligomers and one or more epoxy oligomers, (iii) mixtures of one or more polyester oligomers and one or more urethane oligomers, and (iv) mixtures of one or more polyester oligomers, one or more epoxy oligomers, and one or more urethane oligomers; and

b) between 5 and 80 weight percent of a diluent comprising one or more crosslinkable ethoxylated or propoxylated tri-, tetra-, penta-, or hexa-acrylated or methacrylated aliphatic or aromatic monomers, or mixtures thereof.

The composition may include, conventional optional additives, including but not limited to free radical initiators, UV absorbers, mold

release agents, stabilizers, dyes, antioxidants, and wetting agents.

This polymerizable composition can be cast using UV radiation to produce an optically transparent object with low haze that has impact and abrasion resistance approximately equal to or better than CR-39. In one embodiment, the polymerizable composition has a viscosity of greater than 200 cps.

In a preferred embodiment, this polymerizable composition is cast using the sequential polymerization method, as described in more detail below, in a time ranging from 10 minutes to 30 minutes depending on the polymerizable composition, initiator concentration, and UV intensity employed. Relatively high viscosity polymerizable solutions can be cast using the sequential polymerization method since the fluid can be introduced into the mold cavity without entrapping air using a procedure such as that illustrated in Figure 2. The ability to use high viscosity polymerizable solutions allows flexibility in choosing the kind and concentration of monomer and oligomer. Higher oligomer content can be used to impart superior impact resistance to the lens. Diluents that have high functionality (and thus viscosity) can be used to impart superior abrasion resistance.

In particular, urethane, epoxy, or polyester acrylate or methacrylate oligomers (or mixtures thereof) are selected that impart desired abrasion and impact resistance to the lens and reduce the amount of shrinkage that occurs during polymerization, because the ratio of non-reacting to reacting components is high. These oligomers have a relatively high viscosity, typically between one and one hundred megapoise at room temperature when undiluted. Therefore, these oligomers were not appropriate for use in the traditional manufacture of lenses using blanket radiation, in more than minor amounts. For example, U.S. Patent No. 4,912,185 to Toh indicates that tetraacrylic urethane monomers can be present in the polymerizable

composition for a lens using classical technology at up to 40 percent by weight of the composition. In the polymerizable composition disclosed herein, the urethane and/or epoxy acrylate or methacrylate oligomers is preferably at least 50% by weight of the polymerizable composition.

A diluent such as a hydrocarbon diol diacrylate or dimethacrylate is included as necessary for viscosity reduction, so that the solution can be cast between molds. The diluent can also impart desired mechanical properties to the final product, such as hydrophobicity and abrasion resistance. Since the diluent participates in the polymerization reaction, no solvent is evaporated. The diluent has a significantly lower molecular weight (typically less than 600) than the oligomers (400-9000 weight average molecular weight), and therefore shrinks more on a per-volume basis during polymerization. Typical concentrations of the diluent in the polymerizable composition are less than 50% by weight, preferably, between 10 and 40% by weight.

The polymerizable compositions can also be used in the preparation of materials other than ophthalmic lenses, such as plastic and glass laminates and specialty optics or lenses.

This invention also includes an apparatus that can be used for the preparation of ophthalmic lenses in retail eyewear outlets, using the sequential polymerization method.

Brief Description of the Figures

Figure 1 is a schematic side cross sectional view of a first embodiment of a carriage system for use in the sequential polymerization of a polymerizable composition into an ophthalmic lens.

Figure 2 is a schematic side cross sectional view of a portion of the carriage system embodiment of Fig. 1, illustrating the procedure for syringe filling of the lens mold.

Figure 3 is a schematic side cross sectional view of another portion of the carriage system embodiment of Fig. 1, with lens mold rotated 180 degrees, positioned in front of a movable UV source.

Figure 4 is a schematic side cross sectional view of an apparatus for the preparation of a polymer-polymer lens composite.

Detailed Description of the Invention

As used herein, the term "hard monomer" or "hard material" refers to a monomer or material that polymerizes to form a polymeric material that is below its glass transition temperature at the temperature of use (typically room temperature).

As used herein, the term "soft monomer" or "soft moiety" refers to a monomer or moiety that on polymerization forms a material that is above its glass transition temperature at the temperature of use (typically room temperature).

As used herein, the term "aryl" refers to phenyl, phenyl substituted with alkyl or halogen, naphthalene or naphthalene substituted with alkyl or halogen, or higher aromatics, either unsubstituted, or substituted with alkyl or halogen.

As used herein, the term "alkyl acrylate" refers to $H_2C{=}CHCO_2R$, wherein R is a straight, branched, or cyclic alkyl group, preferably C_1 to C_{20}, and specifically includes methyl, ethyl, propyl, isopropyl, butyl, isobutyl, t-butyl, pentyl, cyclopentyl, isopentyl, neopentyl, hexyl, isohexyl, cyclohexyl, 3-methylpentyl, 2,2-dimethylbutyl, and 2,3-dimethylbutyl, and other longer chain homologues.

As used herein, unless otherwise indicated, the term alkyl refers to a straight, branched, or cyclic alkyl group, preferably C_1 to C_{20}, and specifically includes methyl, ethyl, propyl, isopropyl, butyl, isobutyl, t-butyl, pentyl, cyclopentyl, isopentyl, neopentyl, hexyl, isohexyl,

cyclohexyl, 3-methylpentyl, 2,2-dimethylbutyl, and 2,3-dimethylbutyl and other long chain homologues.

As used herein, the terms diacrylate and dimethacrylate include mixtures of acrylate and methacrylate.

As used herein, the term (meth)acrylate refers to either acrylate, methacrylate, or a mixture of acrylate and methacrylate.

As used herein, the term "alkyl methacrylate" refers to $H_2C=C(CH_3)CO_2R$, wherein R is a straight, branched, or cyclic alkyl group, preferably C_1 to C_{20}, and specifically includes methyl, ethyl, propyl, isopropyl, butyl, isobutyl, t-butyl, pentyl, cyclopentyl, isopentyl, neopentyl, hexyl, isohexyl, cyclohexyl, 3-methylpentyl, 2,2-dimethylbutyl, and 2,3-dimethylbutyl, and other long chain homologues.

As used herein, the term "aryl" or "aromatic" refers to phenyl, phenyl substituted with alkyl, halogen, naphthalene or naphthalene substituted with alkyl or halogen, or higher aromatics, either unsubstituted, or substituted with alkyl or halogen.

The term aralkyl refers to an aryl group with an alkyl substituent.

The term alkaryl refers to an alkyl group that has an aryl substituent.

The term alkenyl, as referred to herein, and unless otherwise specified, refers to a straight, branched, or cyclic (in the case of C_{5-6}) hydrocarbon of C_2 to C_{20} with at least one double bond.

As used herein, the term oligomer refers to a compound with repeating units, of weight average molecular weight ranging from 400 to 9000, and preferably, between 800 and 2500.

As used herein, a diluent is a compound that is used to reduce the viscosity of a material, and typically has a viscosity of less than 600 CPS, and preferably, less than 150 cps at room temperature.

As used herein, the term aliphatic refers to an alkyl, alkenyl, or alkynyl group of C_1 to C_{20}.

As used herein, the term "chain polymerization" refers to a polymerization process in which there is a series of reactions each of which consumes a reactive particle and produces another, similar particle. The reactive particles are radicals, anions, or cations. The polymerization of reactive particles occurs without elimination of a small molecule (as in during a typical condensation reaction). Chain polymerization is typically carried out with ethylenically unsaturated monomers.

As used herein, the term "monomer" refers to the small reactive molecules that are subsequently joined together to form a polymer.

As used herein, the term "unsaturated hydrocarbon polymer" refers to a polymer that consists essentially of carbon and hydrogen atoms, and that includes alkene (vinyl) groups in the polymer.

As used herein, the term "oligomer" refers to a polymer with 20 or less repeating units.

As used herein, the term "high impact resistant material" refers to a material that will withstand sudden imposition of sudden force without fracture, and that passes the U.S. Food and Drug Administration's requirement for impact resistance for ophthalmic lenses (the standard drop-ball test).

As used herein, the term "high scratch resistant" material refers to a material that will withstand abrasion without substantial surface deterioration. A typical abrasion test consists of applying a known vertical pressure on the sample, while moving a steel-wool pad laterally against the surface. Visible scratches are then counted after a number of rubbing movements. A high scratch resistant material will exhibit only a few scratches after this process.

I. Polymer-Polymer Lens Composite

The invention as disclosed includes a polymer-polymer lens composite that exhibits superior impact and

scratch resistance. The front wafer is a very hard, scratch-resistant polymeric material, and the back wafer is a high impact resistant polymeric material. Since the thermal expansion properties of most plastics are similar, thermoelastic stress of the polymer-polymer composite lens is greatly reduced over a glass-polymer composite. Even if minor stresses are induced by extreme temperatures, polymers seldom fail catastrophically by virtue of their tendency to yield, i.e., elastically deform (or even plastically deform). In the case of the polymer composites disclosed herein, the strain field accompanying the thermoelastic stress field (both being time and temperature dependent) almost never exceeds the ultimate strain (failure limit) of either the front or the back material. This critical distinction between glass-polymer and polymer-polymer lenses is a key aspect of this invention.

By separating the refinements into front wafers and back layers, individual attributes including cost, transparency, hardness for the front wafer, impact resistance for the back layer, machinability, tint, grindability, and refractivity-dependent interface design can be optimized.

The front polymeric wafer can be mass manufactured with uniform thickness at low cost, by either resin transfer molding or casting (for thermosets) or injection molding (for thermoplastics), using known procedures.

The back layer of the lens composite must be rigid and machineable (for grind-polish). However, it must also exhibit significant elastomeric characteristics in order to endow the composite structure with adequate impact resistance. It has been discovered that a marshmallow-toothpick model super polymeric network, as disclosed in more detail below, is an ideal material for the back layer. Many other block copolymers, interpenetrating networks, graft copolymers, random copolymers, and even homopolymers that are elastomeric in nature yet sufficiently rigid, can be selected as well, as long as they are sufficiently optically transparent and dimensionally stable.

The use of a polymer-polymer lens composite provides a number of advantages other than individual optimization of properties of the front and back wafers and ease of fabrication.

The polymer-polymer composite structure can be made such that only the front layer or the back layer is colored, or alternatively, both layers are colored. Dye chemistry for polymers is well known to those skilled to the art.

As an example, the front wafers can be tinted as generally known to those skilled in the art after the wafers have been produced (but before incorporation into the composite) to provide either uniform or gradient tinting. Since the front wafer is typically uniform in thickness, the resulting lenses can appear uniformly colored when viewed from the front. These mass produced tinted front wafers are incorporated into the polymer-polymer composite by any of the methods described below. The back layer can be reserved for curvature formation, i.e., prescription. Alternatively, the back layer can be tinted differently from the front to give a host of colors and shades.

The polymer-polymer composites described herein can be dyed in a similar fashion to that of standard lenses (such as CR-39), for example, by immersion in one or more of a wide variety of dye-baths. The dye baths are typically maintained at elevated temperature, usually at or slightly below the boiling point of the bath. The finished lenses are dipped into the chosen baths for a fixed period, e.g., 2 minutes, to achieve the desired color. Longer times are employed for darker tints. If a gradient-color is desired, then the lenses are periodically withdrawn half-way from the bath so only half of the lens is richly tinted, whereas the other half is slightly tinted. Thermoset precursors (commonly liquid-like) can also be loaded with dyes, UV absorbers (e.g., melanin or synthetic dyes), antioxidants, mold release agents, etc., before resin transfer molding into the final wafer shape.

Another advantage of the composite structure is the "thickness" of the back layer. Since the front preformed wafer already possesses a degree of thickness greater than that of a mere coating, the back layer can be relatively thin and still effectuate prescription and shatter resistance, especially when a high-impact-resistant material is employed. Since the back polymeric layer can be thin, the dwell time of UV irradiation used to initiate polymerization of the layer can be relatively short. In addition, heat removal and temperature control accompanying exothermic polymerization/curing reactions are less troublesome with a thin layer. The speed of polymerization allows the on-site production of lenses in optometric outlets.

The front wafer (for example, an epoxy) and the back layer (for example, a polymer prepared as in Example 1) may be slightly mismatched in refractive index. The front wafer can be largely uniform in thickness, and therefore contribute little to prescription. Alternatively, curvature can be incorporated into its shape design as discussed in detail below.

In one embodiment, the front wafer has an anti-reflective coating on its convex surface. Reflectivity is measured in terms of percentage of light (intensity) reflected relative to the incident light (intensity). A number close to 0% reflectivity is ideal, while a number close to 100% would give a shining surface with much glare. Anti-reflective coatings are used to reduce the amount of light that is reflected off of a lens surface. This is achieved by depositing a dielectric film with a specific thickness and refractive index on the desired surface. The coating thickness determines the wavelength of light that is affected and is on the order of a quarter wavelength. Generally, for ophthalmic applications, the wavelength chosen is in the yellow-green portion of the visible spectrum where the eye is most sensitive. At wavelengths on either side of the yellow-green region, the amount of the reflected light increases. To improve efficiency usually more than one film

is deposited on the surface. For multi-layer systems, a combination of high and low refractive index coatings are used. Zirconium dioxide, titanium dioxide, and zinc sulfide are commonly used high refractive index layers while cerium fluoride and magnesium fluoride often serve as low refractive index layers. With a properly applied multi-layer coating, light transmission may be increased from 92% to 99.5%. The coatings are applied by a process known as vacuum deposition. Firms that apply antireflective coatings on ophthalmic lenses include VM Products and Silor, both of which are located in California.

The face of the front wafer that subsequently becomes the interface between the front and the back (the front wafer concave surface) can alternatively have carefully introduced diffraction patterns (mimicking the moth's eye). The patterns can be in the master mold and an imprint left on the sample after injection molding or resin transfer molding, similar to how compact disks are made. These patterns (after accounting for the refractive index discrepancy) can produce full-fledged anti-reflection effects, in a manner akin to the working principles of a moth's eye. The moth's eye has naturally engineered diffraction patterns, so light reflecting back from different locales interfere destructively. Hence, the net reflectivity is appreciably lower than that from the otherwise smooth interface.

Bifocal and multifocal polymer-polymer composite lenses can be easily produced by use of a Fresnel-like front wafer, stacked with a curvature forming back layer. The back layer can be polymerized and then ground/polished, or it can be produced with a known curvature by use of a specific mold half.

Bifocal, multifocal, progressive, and/or astigmatic lenses can also be prepared from the polymer-polymer composites by employing a high refractive index wafer in the front, with a low-refractive index material in the back layer, or vice versa. In this way, the outside surfaces of the front wafer (the convex surface) and back layer (the

concave surface) of the composite can be spherical. The progressive, bifocal, cylindrical, aspheric or other complex requirements can be incorporated through intricate shapes and contours at the interface between the front and back layers. Those skilled in the art of optical calculations can readily design the desired surface container with the aid of computer simulation programs. These refractive-index internally-complex designs can be used to achieve demanding vision-correction without the use of a thick lens, producing more comfortable eyewear.

The back and/or front layer can be polymerized in a way to prevent cavitation, or voids caused by the shrinkage of material during polymerization, using the sequential polymerization process and apparatus disclosed in U.S. Patent Nos. 5,114,632 and 5,110,514. Briefly, the partially polymerized material is inserted between two mold halves, one of which is, or both are, constructed of a material that transmits energy, either thermal or UV. Stress related voids in the polymeric material can be eliminated by causing the partially polymerized material to polymerize in a differential fashion along a moving front, so that the material ahead of the moving polymer zone remains liquid, and the material that the front has passed is solidified. In a typical method, the moving front is a slit through which UV or thermal energy is transmitted. The still-liquid material ahead of the moving polymer zone can then flow freely, at a rate that equals the rate of shrinkage, and a void-free, reduced stress polymeric network is produced.

The polymer-polymer lens composite described herein is distinct from lenses prepared by polymerization around an "insert". Insert technology involves covering both the front and back sites with photo or thermally cured material. Insert technology does not allow for the individual optimization of desirable attributes in the front and back layers, since both major exposed surfaces are of the same material. A stiff surface surrounding a soft core is not

impact resistant, as crack-initiation originates from the surface.

Hardenable materials useful for the front preformed polymeric wafer and back polymeric layer are described in detail below. Other suitable materials are disclosed in U.S. Patent No. 4,544,572, incorporated herein by reference.

1. Composition of the High Impact Resistant Polymeric Layer

The back polymeric layer should exhibit an impact resistance of at least that of CR-39, a well-known lens blank material. The material performance can be tested using the well known FDA "Drop-ball" test. The material should be able to withstand the impact of a standardized steel ball dropped from the same height as that endured by a CR-39 lens of similar size and thickness. It must be dimensionally stable at the service temperature, generally room temperature. Polymers that fulfill these requirements are known to those skilled in the art, and include block copolymers, interpenetrating networks, graft copolymers, random copolymers, and even homopolymers that are elastomeric in nature yet sufficiently rigid. The block or graft segments should be so small that they are on the order of molecular dimension so that they do not scatter light. A preferred high impact resistant macromolecular network is described in detail below. A preferred polymeric material for the impact resistant layer is the polymerizable composition described in detail in Section II. Another example of a polymeric material that is suitable material for this purpose is described below.

It has been discovered that an appropriate material for the back layer is a macromolecular network that includes stiff members interconnected by soft, elastomeric, multifunctional crosslinking sites. Polymerization is controlled so that the stiff monomers primarily self-polymerize to create members with controlled length that are attached to one another via chemical bonds on the soft crosslinking bridges. The crosslinking bridges (or cores)

are randomly dispersed in space, providing the shock-absorbing capacity for the overall rigid yet impact resistant, and optionally, transparent optical, material. Machinability (polish and grind) of the hard plastics is retained, while introducing resilience to the polymer networks.

The macromolecular network is prepared by mixing the soft joint material (the crosslinking substance) with the hard monomers or a hard material and a free radical initiating agent, or other suitable polymerization initiator. It is important that the hard monomers or hard material and the soft joint material are completely miscible, forming a homogeneous solution. The mixture is allowed to partially polymerize into a honey-like or molasses-like consistency (typical viscosity ranging from 100 centipoise to 1000 poise) with vigorous stirring, at which point the material is poured into a mold or cast onto sheets and polymerization completed without agitation.

A key aspect of this method is the pre-cast polymerization or "prepolymerization" step, which is employed to ensure true dispersion (molecular level dispersion) of the hard and soft reactants. Since the soft elements are multi-functional, the prepolymerization step effectively ties up the majority of the soft reactants so subsequent segregation of the hard and soft reactants not possible.

The polymeric rigid members (struts) are joined on both ends by soft, polymeric multifunctional crosslirking sites (soft joints). The invention as disclosed also includes macromolecular networks yielding hard plastics wherein the rigid framework is articulated, branched, or random coiling. Liquid crystal (rigid-rod) polymers can be used as the stiff segments. Liquid crystal struts with artificial molecular bends are articulated. High glass transition amorphous polymers are generally random coiling. In addition to these topographically linear rigid members, the rigid "struts" may themselves be further crosslinked by rigid crosslinkers.

In general, transparency of a clear material is affected when a heterogeneous material is introduced that has a size comparable to or greater than the wavelength of visible light. Since the crosslinking sites are molecular in dimension in the macromolecular network described herein, there is no appreciable light scattering and therefore no adverse effect on the transparency of the material. As long as the crosslinking molecules do not self aggregate to dimensions comparable to a wavelength of light, sample transparency is guaranteed.

The hard and soft segments can be random, alternating, block, or graft in their sequence distribution and spatial arrangement. Random, or alternating, copolymers are generally single-phased, and thus transparent in their pure form except for possible optical absorption bands. Block and graft copolymers are generally multi-phased, and the phase-separated domain size must be made small in order for the material to retain transparency. In all cases, the ultimate mechanical properties represent a compromise. The polymeric supernetwork described herein combines the best of mechanical and optical properties.

a). Description of Rigid Framework

Hard monomers or hard materials are chosen for the rigid framework portion of the macromolecular network that, once polymerized, give rigid transparent plastics with a glass transition temperature above the temperature of use (typically ambient temperatures) and with good optical properties. The monomer is in general one that polymerizes through a chain mechanism, such as an alkene derivative. A preferred monomer is methylmethacrylate. Other alkene derivatives include other alkyl methacrylates, alkylacrylates, allyl or aryl acrylates and methacrylates, cyanoacrylate, styrene, α-methyl styrene, vinyl esters, including vinyl acetate, vinyl chloride, methyl vinyl ketone, vinylidene chloride, acrylamide, methacrylamide, acrylonitrile, methacrylonitrile, acrylic acid and

methacrylic acids. Mixtures of monomers can also be used in the polymerization process.

Partially halogenated or perhalogenated hard monomers, including fluorine containing monomers, can also be used in the rigid framework, including but not limited to fluorine containing methacrylates and acrylates, such as C_1 to C_7 partially or fully fluorinated esters of methacrylic or acrylic acid, for example, 2,2,2-trifluoroethyl methacrylate, trifluoromethyl methacrylate, 2,2,2,3,4,4,4-heptafluorobutyl methacrylate, and 2,2,2,2',2',2'-hexafluoroisobutyl methacrylate.

Acrylate-terminated or otherwise unsaturated urethanes, carbonates, and epoxies can also be used in the rigid framework. An example of an unsaturated carbonate is allyl diglycol carbonate (CR-39). Unsaturated epoxies include, but are not limited to, glycidyl acrylate, glycidyl methacrylate, allyl glycidyl ether, and 1,2-epoxy-3-allyl propane.

Bisphenol-A-bis-2-hydroxypropylmethacrylate, and bisphenol-A-bis-2-hydroxypropylacrylate can also be used as hard monomers. In addition, allyl terephthalate, allyl isophthalate, aryl terephthalate or isophthalate, or acryl isophthalate or terephthalate can be used.

Preformed polymers that have ethylenically unsaturated groups can also be made more impact resistant by the methods described herein. Acrylate-terminated novolacs can be used as or in the rigid framework of the polymeric macromolecular network. Polyurethanes, polymeric epoxies, and polycarbonates that have been derivatized to include acrylate, methacrylate, or other unsaturated functional groups are well known and commercially available. Examples of commercially available photocurable materials are the line of Synocure products sold by Cray Valley Products (for example, Synocure 3101, a diacrylate derivative of bisphenol-A, and Synocure 3134, an aliphatic urethane diacrylate), and the Epon products sold by Shell Corporation (for example, Epon 1001 and Epon 828, which are both diacrylates of the

diglycidyl ether of bisphenol-A). Vinyl-terminated liquid crystalline polymers can also be used.

Poly(carbonyldioxy-1,4-phenyleneisopropylidene-1,4-phenylene) is sold under the trade names Lexan, Makrolon, and Merlon. This polycarbonate has good mechanical properties over a wide temperature range, good impact and creep resistance, high transparency, and good dimensional stability. Unsaturated derivatives of this polymer, such as the allyl or acrylate derivatives of poly(carbonyldioxy-1,4-phenyleneisopropylidene-1,4-phenylene) can be made more impact resistant by reacting the polymer with a soft moiety as described herein.

Optical grade epoxies with terminal unsaturation include those made from 1,2-propylene oxide, 1,2-butylene oxide, 1,2-epoxydecane, 1,2-epoxyoctane, 2,3-epoxynorbornane, 1,2-epoxy-3-ethoxypropane, 1,2-epoxy-3-phenoxypropane, oxetane, 1,2-epoxy-5-hexene-1,2-epoxyethylbenzene, 1,2-epoxy-1-methoxy-2-methylpropane, perfluorohexylethoxypropylene oxide, benzyloxypropylene oxide, and mixtures of these.

Mixtures of hard monomers can be used in the preparation of the macromolecular network. For example, methylmethacrylate can be polymerized in combination with alkylacrylate or arylacrylate, such as methylacrylate or ethylacrylate

The hard monomers can be mixed in any desired ratio, as long as the components remain compatible and miscible. Acrylates can be mixed with methacrylates over the entire composition range as long as the esters are compatible, typically of comparable length. Acrylates generally polymerize more rapidly than methacrylates using either photochemical or thermal initiation.

Additionally, preformed polymers with terminal or internal unsaturation can be copolymerized with hard monomers in the presence of a soft moiety with ethylenic unsaturation, to form a material with high impact resistance.

In an alternative embodiment, inert polymers can be added to the starting mixture, to thicken the mixture, for

ease of handling, to reduce the total reaction time, or for other reasons. The inert polymeric material can be any polymer, and can be used in any amount, that does not adversely affect the desired properties of the final material. Inert polymers in general are polymers that do not react with other components in the reaction solution. In one embodiment, an inert polymer of the hard monomer or hard material is added to the polymerization solution. For example, if methyl methacrylate is used as the hard monomer in the macromolecular network, polymethylmethacrylate can be added to the polymerization solution.

Additives such as UV absorbers, tinting agents, and anti-oxidants can also be added to the polymerization mixture to obtain the desired properties of the final product. See, e.g., R.B. Seymour Ed., "State of the Art; Additives for Plastics". Academic Press, New York, 1978.

b.) Description of Soft Joints

A polymer or oligomer should be chosen for use as the soft joints of the macromolecule that has a low glass transition temperature (ranging from below room temperature to as low as obtainable), that provides a soft, pliable material when homopolymerized, is stable to high and low temperatures, and is compatible with and soluble in the copolymerizing agent. The polymer or oligomer used for the soft joints must be of a size that does not scatter light, and therefore is less than approximately 100 nanometers, and optimally, no larger than approximately 10 nanometers in order of magnitude.

Examples of suitable polymers for the soft joints include vinyl substituted siloxanes, allyl substituted siloxanes, acrylate terminated or substituted siloxanes, and partially or perfluorinated derivatives of vinyl substituted siloxanes, allyl substituted siloxanes, or acrylate terminated or substituted siloxanes. For example, polydimethylsiloxane has a glass transition temperature of -123°C, which is the lowest known polymeric glass transition temperature. When one of the two methyl groups attached to

the silicon atom is replaced with a vinyl group, a reactive, multifunctional polymer, polyvinylmethylsiloxane (PVMS) is produced. This polymer is soft and can copolymerize with a variety of monomers through well-established free radical chemistry. The Si-O bonds are quite flexible and provide a cushion effect on impact. Polyvinylperfluoromethylsiloxane can also be used as the soft joint material.

Hydrocarbon polyunsaturated (multi-functional) compounds (both homo- and copolymers, and especially oligomers) can also be used as the soft joints in the macromolecular network. Hydrocarbon unsaturated compounds can be produced, among other ways, by the polymerization of conjugated dienes such as butadiene, isoprene, and chloroprene. Two different types of polymerization reactions occur with 1,3-dienes. One type involves the polymerization of one or the other of the double bonds in a typical chain polymerization. In a second pathway, the two double bonds act in concert to yield an allylic radical that can react with a successive monomer at either carbon 2 or carbon 4 (1,2-polymerization and 1,4-polymerization, respectively). The 1,2-polymer has pendant unsaturation, whereas the 1,4-polymer has unsaturation in the polymer backbone. All of these various types of polymerization products of conjugated dienes can be used to prepare the polymeric network described herein.

To ensure optical transparency while using a finite amount of soft segments, molecular compatibility is critical. Compatibility is usually optimized by using low molecular weight soft moieties.

c.) End Chain Tethers

The macromolecular network prepared as described above can be further crosslinked by including a small difunctional or multifunctional reactive molecule, or mixture of small di- or multifunctional molecules.

Crosslinking agents for hard monomers that are polymerized by a chain process are known to those skilled in the art, and include tri- or tetrafunctional acrylates or

methacrylates, divinylbenzene (DVB), alkylene glycol and polyalkylene glycol diacrylates and methacrylates, including ethylene glycol dimethacrylate and ethylene glycol diacrylate, vinyl or allyl acrylates or methacrylates, divinylbenzene, diallyldiglycol dicarbonate, diallyl maleate, diallyl fumarate, diallyl itaconate, vinyl esters such as divinyl oxalate, divinyl malonate, diallyl succinate, triallyl isocyanurate, the dimethacrylates or diacrylates of bis-phenol A or ethoxylated bis-phenol A, methylene or polymethylene bisacrylamide or bismethacrylamide, including hexamethylene bisacrylamide or hexamethylene bismethacrylamide, di(alkene) tertiary amines, trimethylol propane triacrylate, pentaerythritol tetraacrylate, divinyl ether, divinyl sulfone, diallyl phthalate, triallyl melamine, 2-isocyanatoethyl methacrylate, 2-isocyanatoethylacrylate, 3-isocyanatopropylacrylate, 1-methyl-2-isocyanatoethyl methacrylate, and 1,1-dimethyl-2-isocyanaotoethyl acrylate. Particularly useful are tetraethylene glycol diacrylate, tetraethylene glycol dimethacrylate, triethylene glycol diacrylate, triethylane glycol dimethacrylate, hexanediol dimethacrylate, hexanediol diacrylate, and other high alkane (including but not limited to C_4 to C_{10}) diol diacrylates or dimethacrylates. These bifunctional molecules are spaced by a relatively long bridge between the acrylates or methacrylates, providing flexibility.

The crosslinking agent is added to the hard monomers or polymers and soft joints prior to the initial prepolymerization step. The amount of crosslinking agent added will determine how tightly crosslinked the final network is. The crosslinking agent can be used in any amount that produces the desired results. It is typically added in an amount ranging from 0.1% to less than 30% by weight.

In one embodiment, an acrylate-terminated polybutadiene (PB) is used as the soft joint material. The PB can be any molecular weight that provides the desired results, typically from 100 to 100,000. A mixture of the hard monomers methyl methacrylate and benzyl acrylate (or in

general aromatic esters of acrylates or methacrylates) is useful for polymerization with PB, because aromatic acrylates and methacrylates elevate the refractive index of the base polymeric material in such a way as to match, or approximate, that of PB. As a nonlimiting example, a high impact material can be prepared by mixing 38% benzylmethacrylate with 62% MMA. This mixture is then mixed with PB (13,000 MW) at a 73% to 27% by weight ratio, respectively. This solution is homogeneous. With a slight addition of photoinitiator, it can be prepolymerized in such a way that PB no longer phase separates in the subsequent casting step. Very thin (1 mm) disks of this material endure the FDA dropball test up to 8 times (i.e., 400 inches) the height required by FDA (50 inches) without cracking (even crazing). In contrast CR 39 sheets at comparable thickness fractured often before reaching the height (50 inches) required by the FDA. To this basic formulation can be added tetraethylene glycol diacrylate or dimethacrylate, triethyleneglycol acrylate or methacrylate, or hexanediol diacrylate to improve scratch resistance. The samples are transparent after 20% addition of the crosslinkers.

d). Preparation of the Network

To prepare a macromolecular network in which the soft joints are homogeneously dispersed throughout the polymer, it is important that the hard monomer and the soft component be continuously and efficiently stirred during the initial stages of polymerization. If the soft component and the rigid component are simply mixed and left to polymerize in a static, quiescent cavity, the two components will tend to phase separate during polymerization. Phase separation before polymerization causes hazy or opaque products. In addition, the two components typically have different densities. If left alone in a quiescent cavity for a long time, the heavier component will migrate to the bottom, and on polymerization, a product will be produced that has a composition gradient in the direction of the gravitational field. When polyvinylmethylsiloxane and methylmethacrylate

are combined, the PVMS collects near the bottom of the container. Polymerization of this stratified mixture produces a product that has a softer lower portion topped by a rigid upper portion.

In a preferred embodiment, in a first stage of polymerization, the two components in any desired ratio are continuously stirred while polymerization is initiated. Inert polymer can be included in the polymerization mixture as desired, to thicken the reaction mixture, to reduce the reaction time, or for other reasons. This prepolymerization step can be accomplished in an open vessel such as a beaker, exposed to the atmosphere, or preferably, under an inert gas such as N_2. Polymerization is allowed to proceed with continuous stirring until an incipient copolymer and partial network is formed. The viscosity of the partially-polymerized reaction solution increases to the point that phase separation and stratification does not occur when the solution is poured and then left undisturbed for a long time. The partial polymerization step that includes stirring during the early stages of polymerization before final mold filling and completion of polymerization, ensures that phase separation and sedimentation are totally suppressed, either by virtue of the slow kinetics, or for thermodynamic reasons since the incipient copolymer are structurally similar and uniform everywhere in the sample.

In the second stage of polymerization, the partially-polymerized material is poured into the final static and quiescent mold cavity, for example, a mold lens, to form the final object, that should be clear, transparent, and without composition gradient. The requirements of exact dimensions, shape, and curvature preclude injection, transfer, or compression molding. The resulting material may or may not be tightly attached to one or both sides of the mold, depending on whether a laminate or a pure plastic product is desired.

As an example, under intense UV irradiation, mixtures with from approximately 90% methylmethacrylate and

10% polyvinylmethylsiloxane (weight average molecular weight ranging from 300 to an upper limit that is low enough to ensure optical transparency), up to virtually all methylmethacrylate, with a trace of PVMS provide a transparent plastic with improved fracture resistance. The more PVMS used, the greater the improvement of fracture resistance. When a 90% methylmethacrylate and 10% polyvinylmethylsiloxane plastic network prepared as described in Example 1 is projected with great velocity against a hard concrete surface, the material recoils a large distance without shatter, chipping, or fracture. Even a 2 millimeter sheet prepared from 90% methylmethacrylate and 10% polyvinylmethylsiloxane passes the U.S. Food and Drug Administration's requirement for impact resistance for ophthalmic lenses (the standard drop-ball test).

The copolymerization of hard and soft monomers give final materials with intermediate properties, depending on their composition. A compromise is generally reached when the product polymer is neither extremely rigid nor unnecessarily soft.

Any ratio of components can be used in the macromolecular network that produces the desired results. The prepolymerization step and the final polymerization can be accomplished at any temperature that produces the desired product, and typically ranges from ambient temperature to the boiling point of the lowest boiling component. The prepolymerization step typically takes from approximately a few minutes to a few hours. Optical clarity can be maximized by insuring vigorous agitation, minimizing trapped air during agitation, and by allowing the prepolymerization step to proceed to the point that the soft joints are homogeneously and permanently distributed throughout the partially polymerized network.

The completion of polymerization is preferably carried out in an inert atmosphere if done in an open mold and free radical reactions are occurring. It is known that oxygen inhibits free radical polymerization, and gives rise

to extended polymerization times. If closed molds are used to form the article, the mold should be made from an inert material that has non sticking properties such as poly(tetrafluoroethylene), silicone rubber, polyethylene, polypropylene, and polyester. Glass and metallic molds can be used if a suitable mold-releasing agent is used. If it is desired to use the high impact plastic material as a laminate, the mold may actually be comprised of, or may include, the material to which the laminate is attached.

This final step of polymerization can be carried out in a method to prevent cavitation, or voids caused by the shrinkage of material during polymerization, using the sequential polymerization process and apparatus illustrated in Figure 4. Referring to Figure 4 a mold body 310 is shown in cross-section. The mold body is designed specifically for an ophthalmic lens that has convex and concave surfaces. The device 310 shown in Figure 4 is formed of at least two parts 312 and 314, brought together to form a cavity 316. Cavity 316 is formed having the shape of the precision lens that is desired to be molded. In the cavity is optionally inserted preformed lens 317, that has a convex surface that will become the convex surface of the finished lens, and a concave surface that interfaces with the convex surface of the back polymeric layer 318. It should be understood that the apparatus illustrated in Figure 4 can be adapted such that the preformed wafer ultimately forms the back layer of the lens and front layer is polymerized <u>in situ</u>. As is usual with a mold, a gate 320 provides access to the mold body 310 when the first and second part are engaged. Communicating with gate 320 is a reservoir 324 which is utilized to feed raw material to cavity 316 through gate 320. Reservoir 324 is represented in Figure 4 as a hopper-like device. A vent 322 may also be included to facilitate the filling of cavity 316. It should be understood that other means for providing raw material to cavity 316 through gate 318 may be advantageously used. For example, it may be appropriate to provide raw material to cavity 316 under pressure.

Mold body 310, as can be seen in Figure 4, necessarily has one part, in the case illustrated, part 314, that is transparent to a source of energy. A source of energy 326 is movable relative to mold body 310 and includes a focusing means such as gate 330. The source of energy 326 may be drawn across the second part 314 by means of a two-way motor 334. Source of energy 326 is selected according to the material to be molded. For example, if the monomers (the reaction mixture or polymer precursor) provided to the mold cavity 316 from reservoir 320 are to be polymerized by heat, then source of energy 326 is appropriately a heat source which is focused through an opening 328 in focusing gate 330. Opening 328 is preferably designed to focus a plane of energy on second part 314. The plane of energy is substantially normal to the movement of focusing gate 330. Alternatively if the monomers utilized in cavity 316 are polymerized by an ultra violet source or other light source, then source of energy 326 may be a light of the proper wave length. Again, second part 314 is of necessity transparent to the wave length of light utilized in source of energy 326 in the event polymerization takes place under the imposition of a light source. In the event that polymerization takes place as a result of the imposition of heat, second part 314 is appropriately thin and made of material that has little or no insulative qualities. It may also include passages 338 for cooling. These passages may be selectively used so that a time-dependent temperature gradient will be maintained.

Movement of focusing gate 330 relative to mold body 310 is controlled so that source of energy 326 scans across the mold body 310 starting at the closed end 336 of cavity 316 and moving toward gate 320.

The reaction mixture which is contained in reservoir 324 is constantly resupplied to cavity 316 through gate 320 thus as polymerization occurs at the lower end or closed end 336 of mold 310 the shrinkage that occurs and would eventually appear as a void is immediately replenished by the reaction mixture or mixture of polymers contained in

reservoir 324. It is of course understood that the reaction mixture is highly mobile and flows readily to fill the volume lost due to shrinkage of the part of the mixture that has already undergone reaction. The instantaneous replacement of the space formed by shrinkage by unreacted material ensures a final piece that is defect free and distortionless. The movement of the energy source 326 relative to the mold body 310 must, of necessity, start with opening 328 in focusing gate 330 moving from closed end 336 to gate 320 in a manner such that polymerization takes place at a steady rate from the closed end to the gate end.

In the event the source of energy 326 is by the nature of the monomer a heat source, movement of the focusing gate across the mold body 310 must be at a rate that does not permit heat transmission through second part 314 at a rate faster then polymerization is taking place. That is, as the heat source of energy 326 moves upwardly, second part 314 will absorb heat and conduct that heat inwardly to cavity 316 where polymerization takes place. The portion of second part 314 above opening 328 must be kept cool which may be accomplished by circulating a cooling fluid through passages 338 so that the upper portion of part 314 remains cool in relation to the lower portion of part 314 thereby providing differential heating of mold cavity 316.

Mold 310 is clamped together in a conventional manner with reservoir 324 in the position shown. Reservoir 324 is filled with the reacting mixture in this case a monomer, a mixture of monomers or a monomer/crosslinker mixture loaded with an initiator and/or other catalysts, such that the material will easily flow into cavity 316. It is important to ensure that cavity 316 is fully filled with the reacting mixture before polymerization is attempted. Accordingly, it may be appropriate to provide a vent 322 to the mold cavity 316. In the event a vent is employed, it should be closed and plugged before polymerization takes place. Closing the vent will assist in drawing additional

reaction mixture into cavity 316 during polymerization rather than permitting air to enter the mold.

Once mold cavity 316 is filled, the source of energy 322 may be activated and focusing gate 324 moved relative to mold body 310 thereby imposing either heat or light, as appropriate, to the mold body in a differential manner. Should heat be the source of energy, then it may be appropriate to activate cooling passages 338 at the upper end of the mold body to ensure that heat conduction through the mold body will not initiate polymerization in the upper portion of the mold before the focusing gate 324 traverses the entire face of the mold.

Once focusing gate 330 has completed its passage and polymerization is complete in the mold body 310, then the mold structure can be taken apart and the molded precision part removed.

Any UV or thermal free radical initiator known to those skilled in the art for free radical polymerization can be used to initiate this process. Examples of UV and thermal initiators include benzoyl peroxide, acetyl peroxide, lauryl peroxide, azobisisobutyronitrile, t-butyl peracetate, cumyl peroxide, t-butyl peroxide, t-butyl hydroperoxide, bis(isopropyl)peroxydicarbonate, benzoin methyl ether, 2,2'-azobis(2,4-dimethylvaleronitrile), tertiarybutyl peroctoate, phthalic peroxide, diethoxyacetophenone, and tertiarybutyl peroxypivalate, diethoxyacetophenone, 1-hydroxycyclohexyl phenyl ketone, 2,2-dimethyoxy-2-phenyl-acetophenone, and phenothiazine, diisopropylxanthogen disulfide. An example of a commercial product that provides non-yellowing products is Irgacure 184 (sold by Ciba Geigy Corporation, 1-hydroxycyclohexyl phenylketone).

Any amount of initiator can be used that produces the desired product. Typically, the amount of initiator varies from 0.1% to 5%, by weight of hard monomer, and is preferably in the range of 0.5% to 3%.

Example 1 Preparation of Macromolecular Network of Methylmethacrylate and Polyvinylmethylsiloxane.

Methylmethacrylate (94% by weight), polyvinylmethylsiloxane (5% by weight, M_w 300-500), and 1% UV photoinitiator (Irgacure) were mixed under UV light (300-400 nm) while stirring to provide strong agitation, until the mixture reached a consistency of that of honey or molasses. The solution was poured into a closed lens mold, and polymerization carried out sequentially as described above and illustrated in Figure 4 with UV light to provide a clear, transparent material that is highly shatter resistant.

The refractive index of the material prepared as in Example 1 is relatively high (approximately 1.51), and falls between common hydrocarbon polymers and inorganic glass.

Example 2 Preparation of Macromolecular Network from Methylmethacrylate, Styrene, Divinylbenzene, and Polyvinylmethylsiloxane

Methylmethacrylate (90% by weight), styrene (5% by weight), divinylbenzene (0.5%) and polyvinylmethylsiloxane (3% by weight), and 1.5% UV photoinitiator (cyclohexylbenzoin) are mixed under UV light (300-400 nm) with strong agitation, until the mixture reaches a consistency of that of honey or molasses. The solution is poured into a closed lens mold, and polymerization carried out sequentially as above and illustrated in Figure 4 with UV light to provide a clear, transparent material that is highly shatter resistant.

Alternatively, everything other than the divinylbenzene is first mixed and polymerized under UV until the desired consistency is reached. Then divinylbenzene is added to the mixture before pouring into the mold.

Example 3 Preparation of High Impact Polycarbonate

Allyldiglycol carbonate (CR-39) is stripped of its inhibitors by passing the liquid monomer through an absorption bed (basic alumina). It is then mixed with PVMS in a ratio of 98% carbonate to 2% PVMS by weight. The material is then polymerized as described in Example 1.

Example 4 Preparation of High Impact Optical Grade Epoxy

Synocure 3101 (95% by weight) is mixed with 4.5% by weight of polybutadiene, and 0.5% initiator, and polymerized as described in Example 1.

Example 5 Preparation of Macromolecular Network of Methylmethacrylate, Methylacrylate and Polyvinylmethylsiloxane.

Methylmethacrylate (42.5% by weight), and methylacrylate (42.5% by weight) were mixed, and polyvinylmethylsiloxane (4% by weight, M_w 300-500), and 1% UV photoinitiator (Irgacure) were mixed under UV light (300-400 nm) while stirring to provide strong agitation, until the mixture reached a consistency of that of honey or molasses. The solution was poured into a closed lens mold, and polymerization carried out sequentially as described above and in Example 4 with UV light to provide a clear, transparent material that is highly shatter resistant.

Example 6 Preparation of Macromolecular Network of Methylmethacrylate and Polyvinylmethylsiloxane With Ethyleneglycol Dimethacrylate as Crosslinking Agent

Methylmethacrylate (92% by weight), polyvinylmethylsiloxane (5% by weight), ethyleneglycol dimethacrylate (1% by weight) and (2%) UV photoinitiator (Irgacure) are mixed, and then reacted under UV light with strong agitation, until the mixture reached a consistency of that of honey or molasses. The solution is poured into a closed lens mold, and polymerization carried out sequentially as described above with UV light to provide a clear, transparent material that is highly shatter resistant.

Alternatively, ethyleneglycol dimethacrylate can be added after the prepolymerization step.

Example 7 Comparison of the Physical Properties of Traditional Polymers with a High Impact Resistant Polymer

The density, refractive index, Abbe number, flexural modulus, CTE (Coefficient of Thermal Expansion), glass transition temperature, and percent visible light transmission of a macromolecular network prepared as in Example 1 (referred to as S-5) were compared to a polycarbonate thermoplastic (Lexan), and a polycarbonate thermoset prepared from allyldiglycol carbonate (CR 39) obtained from PPG Industries. The results are provided in Table 1.

Table 1

Optical and Mechanical Properties of Selected Plastic

Type	Polycarbonate Thermoplastic	CR-39 Thermoset	S-5 Thermoset
Density (g/cc)	1.19	1.31	1.18
Refractive Index	1.59	1.49	~1.51
Abbe Number	26	59	~58
Flexural Modulus (dynes/cm2)	2.4×10^9	2×10^{10}	5×10^9
CTE (ppm/°C)	62	81 - 114	less than 90
Tg (°C)	150	85	~80
% Vis Transmission (400-800 nm)	90	93	91

2. Composition of the Front High Scratch-Resistant Wafer

The front wafer can be prepared from any polymer that exhibits a scratch resistance of at least that of bare (uncoated or untreated) CR-39. Any of the materials described above for use as the rigid component of the high impact resistant macromolecular network (without the soft moiety and with or without end tethers), that exhibit the desired scratch resistance can be used in the front plano wafer. Alternatively, the polymeric composition described in Section II. can be used.

In the typical case, the front wafer is a preformed wafer of at least 100 microns and more typically, from typically 0.5 mm to 1.5 mm.

Traditional scratch resistant polymers include CR-39, polymethylmethacrylate, and polycarbonate. CR-39 has long been the material of choice. It is offered by PPG Industries and is essentially the polymer of allyl diglycol carbonate (although it may also include mold release agents, dyestuffs, and/or antioxidants). It is currently the market leader for lens materials. Polymethylmethacrylate (PMMA) is less scratch resistant, but has been used extensively in precision optics.

Polycarbonates such as poly(carbonyldioxy-1,4-phenyleneisopropylidene-1,4-phenylene) have a higher refractive index and impact resistance than CR39, but typically exhibit less scratch resistance than CR39.

The scratch-resistant front plastics may also be selected from a number of other transparent, high-performance engineering thermoplastics, including, but not necessarily exhaustively, polyetherimides, polyimides, polyethersulfones, polysulfones, polyethyleneterephthalate, and other amorphous (random copolymer) polyamides, polyesters, and urethanes. Nonlimiting examples include the polymers illustrated below.

Alternatively, transparent, high-performance engineering thermosets, including but not limited to epoxies or bismaleimides, may be used. Thermosets require resin transfer molding to shape into plano (flat) wafers, in contrast to thermoplastics that are injection molded. Many hardeners (crosslinkers) for thermosets exist and are known, including aliphatic and aromatic amines and anhydrides. Homopolymerized epoxies can also be used. Rigid, transparent epoxy encapsulants that are useful as the front wafer material have long been formulated for integrated circuit protection and for covering LEDs.

III. Preparation of the Polymer-Polymer Composite

The polymer-polymer lens composites described herein can be prepared by a variety of methods that are ideal for a wide range of applications. The invention includes a method for the rapid, on site, preparation of a wide variety of high impact resistant, high scratch resistant lenses by eyewear manufacturers and retailers.

Lens molds typically include a front metal or glass mold and a back UV transparent or heat transmitting mold, as illustrated in Figure 4. These conventional molds can be used to produce the polymer-polymer composites. One of skill in the art, given the disclosure herein will be able to prepare the composite by using one of the methods set out below using traditional lens molds, or by other known methods. The composites can be prepared by polymerizing a back layer onto a preformed front wafer, polymerizing a front wafer onto a preformed back layer, or by attaching a preformed front wafer onto a preformed back wafer.

The surface of either layer of the composite can be modified by glow discharge to change the surface hydrophobicity or hydrophilicity, to obtain good antifogging properties, or other desired properties.

Attachment of a Prior Prepared Front Wafer to a Prior Prepared Back Wafer

In one embodiment, the polymer-polymer lens composite can be prepared by attaching a prior-prepared front scratch resistant polymeric wafer and a prior-prepared back impact resistant wafer with an adhesive. In a preferred embodiment, the front is a scratch resistant polymer and the back is an impact resistant polymer. The two layers can be adhered with any adhesive material that is known to those skilled in the art for adhering polymer-polymer or polymer-glass composites. In a preferred embodiment, the two layers are adhered with a partially polymerized impact resistant material as described in detail above, that is polymerized in situ by the sequential polymerization method described above.

The front and back layers can have different curvatures, so either positive or negative lenses can be made.

Example 8 Attachment of a Prior Prepared Front Lens with a Prior Prepared Back Lens

The front wafer is a CR-39 bifocal flat-top 1 mm wafer. The back layer (also CR-39) is glued to the front wafer by in-situ sequential polymerization of the partially polymerized material (honey-like consistency) of the material described in Example 1.

Polymerization of Back Layer onto Preformed Front Wafer

In an alternative embodiment, the polymer-polymer lens composite can be prepared by in situ polymerization of the back polymeric layer onto a prior-prepared front polymeric wafer. This procedure is illustrated in Examples 9-11.

Example 9 Preparation of Lens with CR-39 Front Wafer and PVMS/MMA Back Wafer

A CR-39 "flat top" (bifocal) thin front wafer (thickness approximately 1.2 mm, and diameter approximately 75 mm) is used as the front wafer. Behind the wafer is

formed a cavity with center spacing on the order of 1 mm. Into the cavity is inserted a partially polymerized mixture of 7% PVMS and 93% MMA. The material is then polymerized as described above and illustrated in Figure 4. The back mold is a clear, UV-transparent fused silica precisely curved piece, so that when the lens is finished, it has the correct prescription.

Example 10 Preparation of Lens with Epoxy Front Wafer and PVMS\MMA Back Layer.

An epoxy (novolac cured with dianhydride) thin front wafer (plano 6 curvature, 1 mm thick, 71 mm diameter) is used as the front wafer. On top of the wafer is formed a cavity with center spacing on the order of 1 mm. Into the cavity is inserted a partially polymerized mixture of 3% PVMS, 96% MMA, and 1% EGDMA (ethylene diglycol dimethacrylate). The material is then polymerized as described above, and illustrated in Figure 4. The back mold is a clear, UV-transparent fused silica precisely curved piece, so that when the lens is finished, it has the correct prescription.

Example 11. Preparation of Lens with PET (polyethylene terephthalate) Front Wafer and PVMS/MA Methylacrylate Back Layer

A PET thin front wafer (plano 6 curvature, 1 mm thick, 71 mm diameter) is used as the front wafer. On top of the wafer is formed a cavity with center spacing on the order of 1 mm. Into the cavity is inserted a partially polymerized mixture of 5% PVMS and 95% MMA. The material is then polymerized as described above, and illustrated in Figure 4. The back mold is a clear, UV-transparent fused silica precisely curved piece, so that when the lens is finished, it has the correct prescription.

III. Fast Curing Polymeric Compositions For Ophthalmic Lenses and Apparatus for Preparing Lenses

A polymerizable composition is disclosed for use in the preparation of ophthalmic lenses that can be cured into a high quality, impact and abrasion resistant material in thirty minutes or less using the sequential polymerization method. The polymerizable composition disclosed herein can also be polymerized using conventional methods and apparatus for polymerization known to those skilled in the art. The composition includes at least 50% by weight of urethane, epoxy, or polyester oligomers (or mixtures thereof) end terminated with acrylate or methacrylate (or mixtures of acrylate and methacrylate), and an optional diluent, such as hydrocarbon diol end terminated with acrylates or dimethacrylates, or a low molecular weight crosslinkable tri-, tetra-, or poly-acrylate or methacrylate.

1. Oligomers

Proper selection of the oligomer is important to obtaining the desired physical properties of the resulting lens as the oligomer is the predominant component by weight in the polymerizable composition. Polymers prepared from acrylate and methacrylate terminated oligomers are known for their outstanding optical and mechanical properties. Because they can be tailored to obtain desired mechanical properties by blending various materials, they are candidates for numerous applications including coatings, adhesives, medical plastics, lenses, fiber optics and glazing materials.

It has been discovered that three types of oligomers are preferred for the preparation of ophthalmic lenses using the sequential polymerization method: urethanes end terminated with acrylate or methacrylate (or mixtures thereof), and epoxies or polyesters that are end terminated with acrylate or methacrylate (or mixtures thereof). In general, urethane oligomers impart toughness and abrasion resistance to the final lens, while epoxy and polyester oligomers impart hardness and chemical resistance.

preferred embodiment, the oligomers used in the manufacture of lenses have molecular weights ranging from 400 to 9000, but preferably between 800 and 2500. High molecular weight oligomers can produce a lens with too much flexibility, while low molecular weight oligomers can produce a lens that is too rigid with low impact resistance. The functionality (acrylate or methacrylate) of the oligomers can range from two to six. The oligomers should comprise between 20% and 90% by weight of the final formulation, preferably greater than 50% of the composition, and more typically, between 50% and 75% by weight in the composition.

a) Urethane Acrylates

Polyurethanes are a general class of polymers that contain at least two -NHCOO- linkages in the backbone of the polymer, optionally along with other functional groups in the backbone such as esters, ethers, urea and amides. Polymers prepared from urethane oligomers exhibit good abrasion resistance, toughness, flexibility for impact resistance, clarity, and stain resistance. These properties, which have made urethanes useful in the coatings industry, are also important attributes of ophthalmic products.

There are a wide variety of ways known to those skilled in the art to prepare urethane polymers. Urethane prepolymers are typically reaction products of aliphatic or aromatic polyols, polyesters, or polyethers of diverse composition with a stoichiometric excess of diisocyanate. Typically, the number of terminal hydroxyl groups of the polyol, polyester, or polyether is two or greater. The terminal hydroxyl groups react with the diisocyanate to produce urethane linkages, and the resulting prepolymer becomes end capped with isocyanate groups. Depending on the stoichiometric ratio of NCO/OH groups, the urethane linkage can also be incorporated into the backbone of the isocyanate terminated oligomer. Different urethanes can be obtained by changing (1) the diisocyanate, (2) the polyol, polyester, or polyether, or (3) the NCO/OH stoichiometric ratio. For a

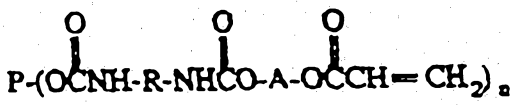
description of urethane oligomers and polymers, see Frisch, K.C., Applied Polymer Science (eds. J.K. Craver & R.W. Tess), Chapter 54, p. 828, ACS, ORPL, Washington, 1975.

Examples of suitable diisocyanates include 4,4'-diphenylmethane diisocyanate (MDI, available from ICI Polyurethanes Group, West Deptford, New Jersey; PBA 2259 (a more stable water dispersible version of MDI also available from ICI Polyurethanes Group); 3-isocyanatomethyl-3,5,5-trimethylcyclohexyl isocyanate (IPDI, or isophorone diisocyanate, available from Huls America, Inc.); 2,4- and 2,6-toluene diisocyanate (TDI); ethylene diisocyanate, trimethylene diisocyanate, tetramethylene diisocyanate, hexamethylene diisocyanate, octamethylene diisocyanate, decamethylene diisocyanate, cyclohexyl diisocyanate, methylenebis-(4-cyclohexylisocyanate), phenylene diisocyanate, diphenylether-4,4'-diisocyanate, 2,2,4-trimethylhexamethylene diisocyanate, xylene diisocyanate, tetramethyl xylene diisocyanate, polyether diisocyanate, polyester diisocyanate, polyamide diisocyanate, dianisidine diisocyanate, 4,4'-diphenylmethane diisocyanate, toluidine diisocyanate, and dimer acid diisocyanate (a diisocyanate prepared from the reaction product of two unsaturated carboxylic acids).

Urethane prepolymers are made radiation curable by adding acrylate or methacrylate groups to the prepolymer. This is typically accomplished by reacting the isocyanate terminated oligomer with hydroxy substituted acrylates or methacrylates. Examples include but are not limited to 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, dodecyloxyhydroxypropyl (meth)acrylate, and glycerin (meth)acrylate. Higher (meth)acrylate functionality can be obtained by reacting the isocyanate terminated oligomer with compounds such as pentaerythritol tri(meth)acrylate, which contains approximately one equivalent of hydroxyl and three (meth)acrylate groups per mole of compound. Alternatively, acrylate or methacrylate esters that include other functional groups that can react with an isocyanate can also be used,

such as epoxy containing compounds such as glycidyl acrylate or methacrylate, or amino containing esters such as aminoalkyl or aminoaryl acrylate or methacrylate.

A nonlimiting example of a difunctional or trifunctional urethane prepolymer is shown below:



wherein P is an aliphatic or aromatic polyether, polyester or polyol, R is the residue of the diisocyanate to which the isocyanate moieties are attached, n = 2 or 3 and A is the aliphatic (typically alkyl) or aromatic ester portion of the hydroxylated acrylate or methacrylate used to end-cap the oligomer. Urethane (meth)acrylates containing between two and six acrylate or methacrylate functional groups are readily available in industry.

The properties of the acrylate or methacrylate terminated oligomers depend on the backbone structure. Alkyl esters and ethers yellow less and are more stable to light than aromatic esters and ethers. However, aromatic esters and ethers impart hardness to the composition, and possess a higher refractive index than their alkyl counterparts, which is desirable to reduce lens thickness for a given prescription. Also, polyester based urethane acrylates or methacrylates are generally harder than polyether based systems because polyesters provide a more polar bond structure and a more basic oxygen with which stronger dipolar and hydrogen bonding interactions can occur with the urethane segments.

Hydroxy terminated polyester starting materials are often prepared from dicarboxylic acids or anhydrides, including but not limited to adipic acid, phthalic anhydride, and dimerized linoleic acid, with monomeric glycols and triols. Examples of glycols include ethylene glycol,

propylene glycol, 1,2-butylene glycol, 1,4-butylene glycol, 1,6-hexylene glycol, trimethylolpropane, glycerol, and 1,2,6-hexanetriol.

Widely used polyether diols and polyols used to produce urethane oligomers include poly(oxypropylene)glycol, poly (1,4-oxybutylene)glycol, random copolymers of alkylene oxides and copolymers of tetrahydrofuran and alkylene oxides. Depending on the diisocyanate monomer, polyol group and stoichiometric ratio, urethane oligomers with widely different mechanical and chemical properties result.

Branched oligmers based on branched polyols, polyesters, or polyethers are also useful in the polymerizable composition.

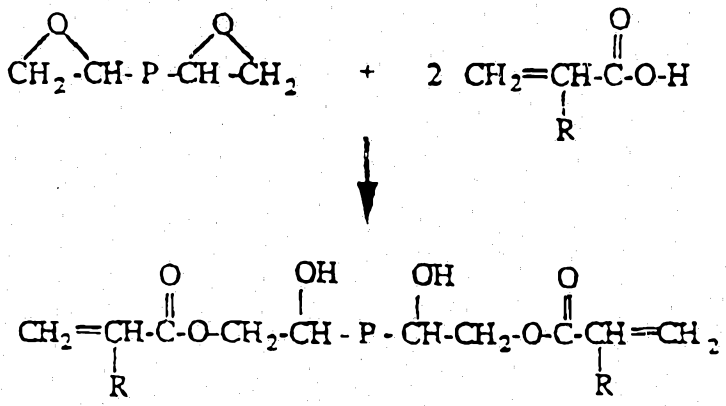
Since the urethane methacrylate or acrylate has a functionality greater than one, the resulting material after polymerization is a thermoset rather than a thermoplastic material. The material cannot be reprocessed once it is cast, but has the advantage of significant chemical resistance and thermo-mechanical stability. An important factor that affects the mechanical properties of thermosets is the crosslink density of the network. Increasing the density, which is achieved by either decreasing the molecular weight between acrylate groups or increasing the functionality of the oligomer, in general leads to a higher Tg and a more abrasion resistant system. However, loss of flexibility, which causes poor impact resistance and greater shrinkage during casting, is also a result of high crosslink density.

Examples of suitable commercial acrylate or methacrylate terminated urethanes that can be used in the polymerizable composition disclosed herein include but are not limited to urethane acrylates 2264, 284, 4881, 4866, 8301 and 8804 from UCB Radcure, urethane acrylates CN955, CN960, CN961, CN963 and CN970 from Sartomer Company, and urethane acrylate NR2075 from Imperial Chemical Ind.

b) Epoxy and Polyester Acrylates

Epoxy and polyester acrylates and methacrylates are also useful oligomers for inclusion in a fast curing polymerizable solution for ophthalmic lenses because polymers prepared from these materials exhibit desired properties such as hardness, chemical resistance, and high refractive index. Polymers prepared from these monomers can be less flexible, and thus less impact resistant, than the urethane systems. Aromatic epoxy and polyester acrylates and methacrylates have poorer light stability than alkyl urethane acrylates or methacrylates. In a preferred embodiment, epoxy and polyester acrylates do not replace, but are instead used in any suitable combination with urethane acrylate or methacrylate oligomers. In one embodiment, epoxy and or polyester acrylates or methacrylates comprise from 0% up to 50% by weight of the total oligomer content.

Epoxy acrylates are typically obtained by reacting epoxide functionalities with acrylic acid, methacrylic acid, or a mixture thereof, to form an esterified acrylate or methacrylate resin. The reaction is shown below for a difunctional epoxy terminated resin:



wherein P represents an aliphatic or aromatic chain that optionally includes heteroatoms such as oxygen, nitrogen, and sulfur and functional groups in the backbone such as amide, ester epoxy, ether, and amino; R is H (in the case of

acrylate) and CH_3 (in the case of methacrylate). The acrylate or methacrylate group then undergoes normal free radical polymerization. Typical epoxies used include aliphatic or aromatic glycidyl ethers, epoxy phenol novolac, epoxy cresol novolac, polyamine or polyamide modified epoxies, cycloaliphatic epoxy resins, and others. A portion of the epoxy moieties can remain unesterified. The final epoxy acrylate or methacrylate oligomeric composition can include (meth)acrylates, epoxies, esters, and acids.

Epoxy acrylates are disclosed in Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd 3d. Vol. 8, pages 294-312 by John Wily & Sons, Inc., New York (1965), incorporated herein by reference.

Polyester acrylates are prepared by esterification of polyesters having an excess of hydroxyl groups using acrylic or methacrylic acid. Preparation of the hydroxy terminated polyesters are usually obtained by reacting acids such as adipic acid, phthalic anhydride, isophthalic acid, azelaic acid, or dimerized linoleic acid, with monomeric glycols, triols and ε-caprolactone. Alkyl glycols and triols can be based on, as a nonlimiting example, ethylene, propylene, 1,2-butylene, 1,4-butylene, and 1,6 hexylene glycol. Triols used, for example, include trimethylolpropane, glycerol, and 1,2,6 hexanetriol. More highly branched systems can also be used to provide greater crosslinking density. Polyester acrylates can impart both elastic and rigid properties to the final product. As an example, polyesters that include aromatic acids such as phthalic anhydride or isophthalic acid impart rigidity and temperature resistance to the final product. Also, highly branched systems impart rigidity, increased chemical and heat resistance, hardness and low elongation.

2. Diluent

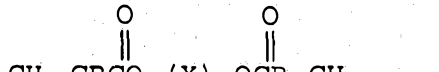
Low viscosity reactive diluents are included in the polymerizable composition to improve the processability of the final resin. Since the diluents are incorporated into

the lens, they should be selected appropriately to impart the desired characteristics such as hydrophobicity, abrasion resistance and impact resistance. The diluents can be monofunctional, difunctional, or multi-functional, wherein the term "functional" is used to refer to groups that are reactive on curing with radiation, such as acrylate and methacrylate.

In general, acrylates are preferred over methacrylates for use in both the oligomeric component and the diluent component of the polymerizable composition, because acrylates cure more quickly than methacrylates, reducing processing time.

The diluent should be chemically compatible with the urethane acrylate or methacrylate, or epoxy acrylate or methacrylate used in the polymerizable composition. The diluent is considered compatible if phase separation does not occur on polymerization of the composition.

In one embodiment, the polymerizable composition includes a diluent of the structure:



hydrocarbon diol series

wherein R is independently H or methyl, and X is a straight or branched alkane of C_2 to C_{14}. Hydrocarbon diol and branched hydrocarbon diol based diacrylates and dimethacrylates are preferred over polyoxyalkylene glycol diacrylates or dimethacrylates. The hydrocarbon diol acrylate series of diluents, which includes but is not limited to ethylene glycol diacrylate and dimethacrylate, 1,4-butane diol diacrylate and dimethacrylate, 1,6-hexane diol diacrylate and dimethacrylate, decamethylene diol diacrylate and dimethacrylate, and neopentyl glycol diacrylate and dimethacrylate, are more hydrophobic than the polyoxyalkylene glycol based systems. They are also superior in withstanding chemical attack from polar solvents such as alcohols, which are frequently used as cleaning solutions. In addition,

butanediol and hexanediol diacrylate and dimethacrylate in particular impart good hardness and abrasion resistance without sacrificing impact resistance. They also exhibit good light stability and are low in viscosity. Typical concentrations of the diacrylate or dimethacrylate diluent are between 0 and 50% by weight, and preferably between 2% and 20% by weight.

In another embodiment, multi-functional acrylates and methacrylates are included in the composition to provide a strong thermoset network. These higher functional systems impart good abrasion resistance to the final lens product. Examples include tri-, tetra-, penta- and hexa- acrylated and methacrylated aliphatic or aromatic monomers that can be ethoxylated, and include, but are not limited to, ethoxylated trimethylolpropane tri(meth)acrylate, propoxylated trimethylolpropane tri(meth)acrylate, ethoxylated pentaerythritol tetra(meth)acrylate, pentaerythritol tri(meth)acrylate, glyceryl propoxy tri(meth)acrylate, dipentaerythritol penta(meth)acrylate, dipentaerythritol hexa(meth)acrylate, trimethylolpropane tri(meth)acrylate, pentaerythritol tetra(meth)acrylate, di-trimethylolpropane. The ethoxylated and propoxylated monomers, that can include any desired amount, but typically from three to nine moles of ethoxylation, provide increased flexibility, reduced shrinkage, and lower toxicity at the expense of reduced Tg and higher viscosity.

3. Initiator

Any UV or thermal free radical initiator or mixture of initiators known to those skilled in the art of free radical polymerization can be used to initiate polymerization. Mixtures of the photoinitiators are sometimes preferred since they can in certain cases provide a more efficient production of radicals. The initiator should be non-yellowing, have a broad absorption spectrum if it is a UV initiator, and good curing efficiency. It should also be nontoxic and have low odor. Concentrations of the initiator

in the polymerizable composition typically range from 0.1 to 5% by weight, although any amount can be used that provides the desired product. A relatively low concentration of initiator, between 0.1 to 0.8% by weight, is preferred to reduce yellowing.

There are a number of non-yellowing commercially available UV initiators. Examples include but are not limited to Irgacure 184 (1-hydroxycyclohexyl phenyl ketone), and Darocur 2959 or 1173 sold by Ciba Geigy Corporation, and KIP 100F (2-hydroxyalkyl phenone) sold by Fratelli Lamberti Esacure. KIP 100F and Darocur 2959 and 1173 are liquids, that are readily miscible with the other components of the polymerizable composition. Irgacure 184 is a white powder with extremely good absorbance and non-yellowing properties.

Other UV and thermal initiators include benzophenone, trimethylbenzophenone, isopropylthioxanthone, and ethyl 4-(dimethylamino)benzoate, benzoyl peroxide, acetyl peroxide, lauryl peroxide, azobisisobutyronitrile, t-butyl peracetate, cumyl peroxide, t-butyl peroxide, t-butyl hydroperoxide, bis(isopropyl)peroxydicarbonate, benzoin methyl ether, 2,2'-azobis(2,4-dimethylvaleronitrile), tertiarybutyl peroctoate, phthalic peroxide, diethoxyacetophenone, and tertiarybutyl peroxypivalate, diethoxyacetophenone, 1-hydroxycyclohexyl phenyl ketone, 2,2-dimethoxy-2-phenyl-acetophenone, phenothiazine, and diisopropylxanthogen disulfide.

4. Inhibitors

Inhibitors are optionally added to the polymerizable composition to inhibit polymerization under normal storage conditions, by acting as radical scavengers. Any inhibitor known to those skilled in the art can be used in any effective concentration. The most common inhibitors are hydroquinone (HQ) and hydroquinone monomethylether (MEHQ). HQ has been found to increase yellowing at high concentrations while MEHQ does not. Inhibitor levels should be minimized since they retard the speed of the initiation

and propagation process during polymerization. Typical concentrations in the final formulations are optimally between 0.002 to 0.2 weight percent.

5. UV Stabilizers

Stabilizers can be used to prevent changes in lens properties with time. These include UV absorbers (UVA), hindered light amine stabilizers (HALS) and antioxidants (AO). UVAs preferentially absorb incident UV radiation, thereby preventing the radiation from reaching the casted polymer. Examples include Tinuvin 328, Tinuvin 900, and Tinuvin 1130 from Ciba Geigy. HALS do not function by absorbing UV radiation, but inhibit degradation of the casted polymer by binding with free radicals. Examples include Tinuvin 292, and Tinuvin 144 from Ciba Geigy. AOs also terminate free radicals, particularly those associated with peroxy radicals. They are not generally used as light stabilizers. Examples include Irganox 1010 and Irganox 1076 from Ciba Geigy.

The lens material can also be protected from UV radiation after casting, by applying an anti-UV coating or by dipping the lens in a suitable solution.

6. Other Additives

Internal mold releases can be added to the polymerizable composition to improve releasability from the molds, but are not required, and if possible, should be avoided as they can reduce clarity. Examples of release agents include butyl stearate, dioctylphthalate, Zelec UN and Zelec NE sold by E.I. DuPont NeMours and Company. Other additives, such as dyes and wetting agents, can also be included.

7. Process of Polymerization

The problems of shrinkage and lengthy cure time associated with the traditional casting process for ophthalmic lenses are solved by casting the polymerizable

composition disclosed herein using the sequential polymerization technique as described in detail above. Using sequential polymerization, mold design is straightforward. The costly experimentation required to engineer a mold that accounts for resin shrinkage is avoided. The sequential process is easily adapted to either radiation or thermal curing. Radiation curing is preferred because it is more convenient and in general requires a shorter cure time. Radiation curing can be performed at moderately elevated temperature to further reduce polymerization time.

The apparatus for the production of a lens from a polymerizable composition preferably includes a carriage frame; a concave (or convex) mold that allows the transmission of energy that is capable of initiating polymerization attached to the carriage frame; a moving stage that can be driven across the carriage frame; a means for moving the stage across the carriage frame; a convex (or concave) mold, wherein the convex (or concave) mold is attached to the moving stage, and wherein the convex (or concave) mold can be moved adjacent to the transparent concave (or convex) mold to define an internal cavity there between, the cavity corresponding to the precise dimensions of the lens; a means for introducing polymerizable composition into the internal cavity; a source of energy for transmission through the concave (convex) mold in a sequential manner; and a means for sequentially exposing the polymerizable material to the energy source beginning at a point opposite to that wherein the polymerizable composition is introduced, and proceeding to the point wherein the polymerizable composition is introduced.

One embodiment of a method and apparatus for the preparation of a lens by sequential polymerization is illustrated in Figures 1 to 3. Figure 1 illustrates a carriage system that holds a concave 10 mold that forms the convex surface of the finished lens and a convex mold 20 that forms the concave surface of the finished lens. In a preferred embodiment, the convex mold 20 is attached to a

moving stage 30 while the concave mold 10 is snapped into a holder that is part of the carriage frame 40. Experiments have shown that the abrasion resistance of the face closer to the lamp source (i.e., the front mold) can be greater than the face away from it. Since most ophthalmic retail outlets have the capability of coating the concave surface of the lens, this embodiment is preferred. The opposite arrangement (i.e., convex mold attached to the stage, with the concave mold attached to the holder) is also possible. The mold attached to the holder should be made of a material that is UV transparent, such as BK-7 glass. Note that the back mold 20 does not need to be UV transparent. Therefore, metal, non-UV transmitting glass, or even plastic molds may be utilized. While glass or metal molds provide a longer usage life if not mishandled, they are extremely expensive and can easily be damaged. Plastic molds, particularly those that may be injection molded, are inexpensive to produce. Materials such as polystyrene, polyester (PET or PBT), polyacetals, polyfluorinated alcohols, teflon, polyamides, polysulfones, polyimides, etc. that possess hardness, heat stability, and low surface energy to allow release of the finished part are possible mold candidates for this process. This mold 10, attached to the carriage frame, can be enclosed by an outer ring that serves as a goniometer indicating the degree of rotation about an axis. This feature is necessary for non-spherical molds. Rotation is required with respect to the mold attached to the stage 20 to dial in the desired cylinder orientation particularly when aspheric, multi-focal, or progressive lenses are being fabricated.

A lead screw 50 drives the stage 30 forward and backward along a guide rod 60. A distance indicator 70 informs the user of the location of the stage.

The carriage forms a cavity between the two molds 10,20 that is filled with the fluid polymerizable composition. Figure 2 is a schematic side cross sectional view of a portion of the carriage system embodiment of Fig. 1, illustrating the procedure for filling of the lens mold.

Before the molds are brought together, a flexible gasket 100 made of an inert material such as flexible PVC, silicone, or rubber, is fitted around mold 10. A rigid clamp 110 is then attached around the gasket to provide support. The stage 30 is then positioned such that the molds are separated by a desired distance. A brake or locking system is then employed so that even under high pressure (between 30 and 50 psi), the stage is fixed in its locked position. Any suitable locking system, such as a back stop or even a brake, can be used. In a preferred embodiment, the inside of the cavity other than the UV transparent mold 10 is black or lined with an anti-reflective coating to prevent light scattering.

The polymerizable resin is contained in a reservoir 80 and can be introduced into the mold cavity by a number of methods. Mechanical methods, such as a motorized piston, may be employed. However, an easier and preferred system is to use gas pressure to drive the fluid (see Figure 2). A piston may be added to separate the gas from the fluid. However, if the gas is in contact with the fluid, it is preferred that the gas be inert (for example nitrogen or helium), to minimize dissolved oxygen in the composition. The reservoir is connected to the mold cavity by a flexible plastic hose which ends with a valve 85 and a tapered tip 90. The tapered tip is pushed through a small hole in the bottom of the gasket and resins introduced. Fluid flows from the bottom of the cavity to allow bubble free filling. Air is allowed to escape through a tiny vent hole 120 at the top of the gasket. After the cavity is filled, a cap 130 is screwed on to plug the air vent sealing the cavity.

The carriage is transferred to a curing station for sequential polymerization. Figure 3 is a schematic side cross sectional view of another portion of the carriage system embodiment of Fig. 1, with lens mold rotated 180 degrees, positioned in front of a movable UV source. The curing station consists of a long wave UV light source (250 to 400 nm) 150, that preferably emits collimated light that is attached to a moving stage 160. A colored glass filter

165 that allows U.V. light to pass but retards the transmission of visible and IR radiation is added to minimize radioactive heating of the resin by the light source. The stage is driven by a lead screw 170 attached to a motor 180 and drive system 190. The motor is preferably connected to a control system, such as a computer, that sets and varies scan rates as desired. A slit 200 of adjustable vertical opening of between 0.25 and 2.0 inches, attached to a frame 210 provides a plane band of UV light. The frame is attached to the moving stage 160 to allow the light source and slit to move as a single unit. In the preferred embodiment, during sequential polymerization, movement of the light source/slit assembly relative to the carriage assembly is controlled such that the plane band of UV light scans across the carriage starting at the top of the cavity 230 and moving toward the bottom 220 where the resin line is located.

The opposite arrangement wherein the plane band of UV light scans across the carriage starting at the bottom of the cavity 220 and moves towards the top 230 is also feasible if the carriage 140 is rotated in such a manner that the resin feed source is repositioned to the top of the carriage. However, this method requires an additional rotation step over the preferred arrangement. Also, if air in the cavity is not completely removed during the filling stage, rotation of the cavity after filling may induce the trapped air bubbles to rise up the cavity during cure which would produce a defective lens. An alternate arrangement that does not involve rotation is to move the carriage and fix the light source and slit arrangement.

Other similar schemes may be envisioned to produce the sequential effect. Instead of a slit, a curtain may be lowered (or raised) first exposing UV light to the area opposite the feed port. The curtain is moved until the entire lens is exposed. Note that for this arrangement, the UV exposure time is not constant throughout the sample, but depends on position. Another possible arrangement is to continually open a slit starting from the center of the lens.

Here, the central portion of the lens will have the longest exposure to the UV light. A major disadvantage of this scheme is that two feed ports will be required at opposite ends of the direction the slit opens. Only one port will be required if instead of an increasingly expanding slit, an expanding hole is employed. This may be accomplished using an iris diaphragm. With the diaphragm, the initial UV exposure area is a small circular hole at the center of the lens assembly. This exposure area is radially increased by opening the diaphragm. By continuously opening the diaphragm, the entire lens assembly can be fully exposed. Since the edge will be the final area exposed to UV light, only one port is necessary for this process. The expansion rate will require adjustment depending on the reactivity of the sample, the UV intensity, and the thickness of the part being irradiated. The lens assembly may be held vertically or even horizontally during the curing process.

The fluid polymerizable composition, that is contained in the reservoir 240, is constantly resupplied to the cavity. A known positive pressure or force, typically between 20 and 50 psi, is applied to the syringe during the polymerization step. The optimal pressure is dictated by the flow arrangement, system viscosity, and cure rate. Thus, as polymerization occurs in the region exposed to the light, the shrinkage that occurs is immediately replenished by additional polymerizable composition. The polymerizable composition is highly mobile and flows readily to fill the volume lost during shrinkage of the part of the mixture that has already polymerized. The nearly instantaneous replacement of the space formed by shrinkage with unreacted fluid ensures a final object that is virtually defect free and distortionless.

In an optional embodiment, after sequential polymerization is completed, a post cure step can be carried out wherein the entire mold cavity is exposed to blanket UV radiation. To ensure that defects do not appear post curing should be carried out only when the entire lens is at a

sufficiently advanced stage of cure that shrinkage is minimal. Post curing is preferably performed while the article is still in the mold to prevent oxygen inhibition of the curing process. At the completion of the curing process, the mold structure can be taken apart and the precision cast part removed.

The equipment described above can be used to produce spherical, progressive and aspheric lenses. The final lenses can optionally be tinted with dye or anti-UV agents after the polymerization process is complete.

Finished spherical lenses of 74 mm diameter with a -2.0 diopter power were prepared using a variety of embodiments of the polymerizable composition described herein, using the sequential polymerization method illustrated in Figures 1 to 3. The initiator and other additives were added to the diluent and stirred vigorously. This mixture was then added to the oligomers and the sample heated carefully to approximately 50 degrees C in a water bath, and stirred vigorously for between two and three hours (stirring can range from thirty minutes to three hours), taking care to ensure that the oligomer is completely incorporated in the solution. The resin was then degassed in a vacuum oven to remove dissolved gas. The resulting polymerizable fluid was poured into the reservoir and introduced between two glass molds that were separated with a center distance of 2 mm (see Figure 2). The glass molds were constructed of BK-7 glass that transmits long wave UV radiation. The molds were coated with an external release agent. The fluid was retained between the molds using a flexible PVC gasket and clamp assembly. Pressure of between 25 and 35 psi was maintained on the fluid during the entire curing process. The composition was sequentially polymerized using mercury vapor lamps of between 160 and 300 W and a horizontal slit assembly as described above and in U.S. Patent No. 5,114,632. The slit opening was varied from 0.5 to 1.0 inches. Sequential polymerization time varied from 8

to 27 minutes. Initiator concentration was varied from 0.2 to 0.5 weight percent.

Example 12 Preparation of Plastic Ophthalmic Lens

A mixture of 50 percent by weight Radcure 284 urethane diacrylate, 20 percent by weight Radcure 8301 urethane hexaacrylate, 29.6 percent by weight ethoxylated trimethyolpropane triacrylate, and 0.4 percent by weight KIP 100F initiator was prepared and cast as described above, using a 3/4 inch slit size. The sample was sequentially irradiated for 22 minutes.

Example 13 Preparation of Plastic Ophthalmic Lens

A mixture of 75 percent by weight Radcure 284 urethane diacrylate, 24.6 percent by weight hexane diol diacrylate, and 0.4 percent by weight Darocur 1173 initiator was prepared, as cast as described above. A 3/4 inch slit size was used with an irradiation time of 22 minutes.

Example 14 Preparation of Plastic Ophthalmic Lens

A mixture of 75 percent by weight Sartomer 963E75 urethane diacrylate, 24.6 percent by weight pentaerythritol triacrylate, and 0.3 percent by weight Irgacure 184 initiator was prepared, and cast as described above. A one inch slit size was used with an irradiation time of 18 minutes.

Example 15 Preparation of Plastic Ophthalmic Lens

A mixture of 37.5 percent by weight Radcure 264 urethane triacrylate, 37.5 percent by weight Sartomer 963E75 urethane diacrylate, 24.7 percent by weight hexane diol, and 0.3 percent by weight Darocure 1173 initiator was prepared, and cast as described above. A one inch slit size was used with a run time of 18 minutes.

Example 16 Preparation of Plastic Ophthalmic Lens

A mixture of 40 percent by weight Radcure 284 urethane diacrylate, 40 percent by weight Radcure 264

urethane triacrylate, 19.7 percent by weight trimethylol propane triacrylate, and 0.3 percent by weight Irgacure 184 initiator was prepared, and cast as described above. A one inch slit size was used with an irradiation time of 18 minutes.

Example 17 Preparation of Plastic Ophthalmic Lens

A mixture of 37.5 percent by weight Radcure 284 urethane diacrylate, 37.5 percent by weight Radcure 264 urethane triacrylate, 24.7 percent by weight ethoxylated trimethyolpropane triacrylate, and 0.3 percent by weight Darocure 1173 initiator was prepared, and cast as described above. A one inch slit was used with an irradiation time of 18 minutes.

Example 18 Preparation of Plastic Ophthalmic Lens

A mixture of 43 percent by weight Radcure 284 urethane diacrylate, 37 percent by weight Radcure 264 urethane triacrylate, 10 percent by weight ethoxylated trimethyolpropane triacrylate, 9.7 percent by weight trimethyolpropane triacrylate, and 0.3 percent by weight KIP 100F initiator was prepared, and cast as described. A one inch slit was used with an irradiation time of 18 minutes.

Example 19 Preparation of Plastic Ophthalmic Lens

A mixture of 40 percent by weight Radcure 284 urethane diacrylate, 40 percent by weight Radcure 264 urethane triacrylate, 19.8 percent by weight ethoxylated pentaerythritol tetraacrylate, and 0.2 percent by weight Irgacure 184 initiator was prepared, and cast as described above. A 0.75 inch slit size was used with an irradiation time of 15 minutes.

Example 20 Preparation of Plastic Ophthalmic Lens

A mixture of 37 percent by weight Radcure 284 urethane diacrylate, 33 percent by weight Radcure 264 urethane triacrylate, 29.8 percent by weight ethoxylated

pentaerythritol teraacrylate, and 0.2 percent by weight Irgacure 184 initiator was prepared, and cast as described above. A 0.75 inch slit size was used with an irradiation time of 15 minutes.

Example 21 Preparation of Plastic Ophthalmic Lens

A mixture of 60 percent by weight Radcure 284 urethane diacrylate, 10 percent by weight polyester acrylate, 29.6 percent by weight ethoxylated trimethylolpropane triacrylate, and 0.4 percent by weight Irgacure 184 initiator was prepared, and cast as described above. A 0.75 slit size was used with an irradiation time of 18 minutes.

Example 22 Evaluation of Lenses Prepared in Examples 12-21

The lenses prepared in Examples 12-21 were evaluated for impact and abrasion resistance. A Nikon lensometer was used to evaluate the optical power of the lenses. The optical powers of all of the lenses were within 1/8 diopta of the specified power (-2.0 diopta) and no cylinder was found throughout the lens.

The lenses were subjected to abrasion testing using the Bayer test (ASTM F-735), which is based on a haze reading of an abraded lens. The results of the abrasion test are presented in Table 2, which indicates the difference in abrasion resistance between the test lens and CR-39.

Impact resistance was evaluated using the FDA drop ball test. FDA regulations require that lenses not crack when impacted with a 5/8" stainless steel ball dropped from a height of 50 inches. All of the lenses prepared as described herein easily pass this test. The lenses were also tested by dropping progressively heavier balls from the 50 inch height until the lens cracked. Table 2 indicates the relative increase in ball weight over the 5/8" FDA ball required to crack the lens. The greatest weight used was 8 times heavier than the 5/8" ball. Some formulations did not crack even under this weight.

Table 2

	Oligomer		Diluent		Abrasion	Impact Test
Ex#	Name	wt%	Name	wt%	(x CR39)	(x FDA)
12	8301	20	ETMPTA	30	0.9	5.8
	284	50				
13	284	75	ETMPTA	25	1.3	>8
14	963E75	75	PETA	25	0.8	3.4
15	264	37	HD	25	1.2	4.1
	963E75	37				
16	284	40	TMPTA	20	1.4	5.8
	264	40				
17	284	37	ETMPTA	25	1.8	>8
	264	37				
18	284	43	TMPTA	10	1.5	6.9
	264	37	ETMPTA	10		
19	284	40	EPETA	20	1.9	>8
	264	40				
20	284	37	EPETA	30	1.6	>8
	264	33				
21	284	60	ETMPTA	30	-	>8
	770	10				

8301 - Radcure Urethane hexaacrylate
284 - Radcure Urethane diacrylate diluted with HD
264 - Radcure Urethane triacrylate diluted with HD
963-E75 - Sartomer Urethane diacrylate diluted with ETMPTA
770 - Radcure polyester acrylate oligomer diluted with hydroxyethylmethacrylate
TMPTA - trimethylol propane triacrylate
ETMPTA - ethoxylated trimethylol propane triacrylate
PETA - pentaerythritol triacrylate
EPETA - ethoxylated pentaerythritol tetraacrylate
HD - 1,6 hexane diol diacrylate

This invention has been described with reference to its preferred embodiments. Variations and modifications of the invention described herein will be obvious to those skilled in the art from the foregoing detailed description of the invention. It is intended that all of these variations and modifications be included within the scope of the appended claims.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:-

1. A free radical polymizerable composition, comprising

a) between 20 and 90 weight percent of an oligomer that is end terminated with acrylate methacrylate or both, wherein said oligomer is selected from the group consisting of (i) one or more epoxy oligomers, (ii) mixtures of one or more epoxy oligomers and one or more polyester oligomers, (iii) mixtures of one or more epoxy oligomers and one or more urethane oligomers, and (iv) mixtures of one or more epoxy oligomers, one or more polyester oligomers, and one or more urethane oligomers; and

b) between 5 and 80 weight percent of a diluent comprising one or more crosslinkable ethoxylated or propoxylated tri-, tetra-, penta- or hexa-acrylated or methacrylated aliphatic or aromatic monomers, or mixtures thereof.

2. The composition of claim 1, further comprising an additive selected from the group consisting of free radical initiators, UV absorbers, mold release agents, stabilizers, dyes, antioxidants, and wetting agents

3 The composition of claim 1, wherein the diluent is present in the composition in an amount between 10 and 40% by weight

4. The composition of claim 1, wherein the urethane, epoxy or polyester oligomer contains between 2 and 6 acrylate or methacrylate groups.

5. The composition of claim 1, wherein the oligomer has a molecular weight of between 400 and 7000.

6. The composition of claim 1, wherein the oligomer has a molecular weight of between 800 and 2500.

7. The composition of claim 1, wherein the oligomer comprises between 50% and 75% by weight of the composition.

8. The composition of claim 1, wherein the diluent is a mixture of 1,6-hexane diol diacrylate and ethoxylated pentaerythritol tri- or tetra-acrylate.

9. The composition of claim 1, wherein the diluent is a mixture of 1,6 hexane diol diacrylate and ethoxylated trimethylol propane triacrylate.

10. A lens prepared from a free radical polymerizable composition comprising;

a) between 20 and 90 weight percent of an oligomer that is end terminated with acrylate, methacrylate, or both, wherein said oligomer is selected from the group consisting of (i) one or more epoxy oligomers, (ii)

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mixtures of one or more epoxy oligomers and one or more polyester oligomers, (iii) mixtures of one or more epoxy oligomers and one or more urethane oligomers, and (iv) mixtures of one or more epoxy oligomers, one or more polyester oligomers, and one or more urethane oligomers; and

b) between 5 and 80 weight percent of a diluent comprising one or more crosslinkable ethoxylated or propoxylated tri-, tetra-, penta- or hexa-acrylated or methacrylated aliphatic or aromatic monomers, or mixtures thereof.

11. The lens of claim 10 wherein the composition further comprises an additive selected from the group consisting of free radical initiators, UV absorbers, mold release agents, stabilizers, dyes, antioxidants, and wetting agents.

12. The lens of claim 10, wherein the diluent is present in the composition in an amount between 10 to 40% by weight.

13. The lens of claim 10, wherein the urethane, epoxy or polyester oligomer contains between 2 and 6 acrylate or methacrylate groups.

14. The lens of claim 10, wherein the oligomer has a molecular weight of between 400 and 7000.

15. The lens of claim 10, wherein the oligomer has a molecular weight of between 800 and 2,500.

16. The lens of claim 10 wherein the oligomer comprises between 50 and 75% by weight of the composition.

17. The lens of claim 10, wherein the diluent is a mixture of 1,6 hexane diol diacrylate and ethoxylated pentsaerythritol tri- or tetra-acrylate.

18. The lens of claim 10, wherein the diluent is a mixture of 1,6 hexane diol diacrylate and ethoxylated trimethylol propane triacrylate.

19. A free radical polymerizable composition, comprising:

a) between 20 and 90 weight percent of an oligomer that is end terminated with acrylate, methacrylate, or both, wherein said oligomer is selected from the group consisting of (i) one or more polyester oligomers, (ii) mixtures of one or more polyester oligomers and one or more epoxy oligomers, (iii) mixtures of one or more polyester oligomers and one or more urethane oligomers, and (iv) mixtures of one or more polyester oligomers, one or more epoxy oligomers, and one or more urethane oligomers; and

b) between 5 and 80 weight percent of a diluent comprising one or more crosslinkable ethoxylated or propaxylated tri-, tetra-, penta-, or hexa-

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acrylated or methacrylated aliphatic or aromatic monomers, or mixtures thereof.

20. A lens prepared from a free radical polymerizable composition comprising:

a) between 20 and 90 weight percent of an oligomer that is end terminated with acrylate, methacrylate, or both, wherein said oligomer is selected from the group consisting of (i) one or more polyester oligomers, (ii) mixtures of one or more polyester oligomers and one or more epoxy oligomers, (iii) mixtures of one or more polyester oligomers and one or more urethane oligomers, and (iv) mixtures of one or more polyester oligomers, one or more epoxy oligomers, and one or more urethane oligomers; and

b) between 5 and 80 weight percent of a diluent comprising one or more crosslinkable ethoxylated or propoxylated tri-, tetra-, penta-, or hexa-acrylated or methacrylated aliphatic or aromatic monomers, or mixtures thereof.

21. A lens prepared from the polymerizable composition of any preceding claim and substantially as hereinbefore described with reference to the drawings.

DATED this fifteenth day of July 1996

SOANE TECHNOLOGIES INC
Patent Attorneys for the Applicant:

F.B. RICE & CO.

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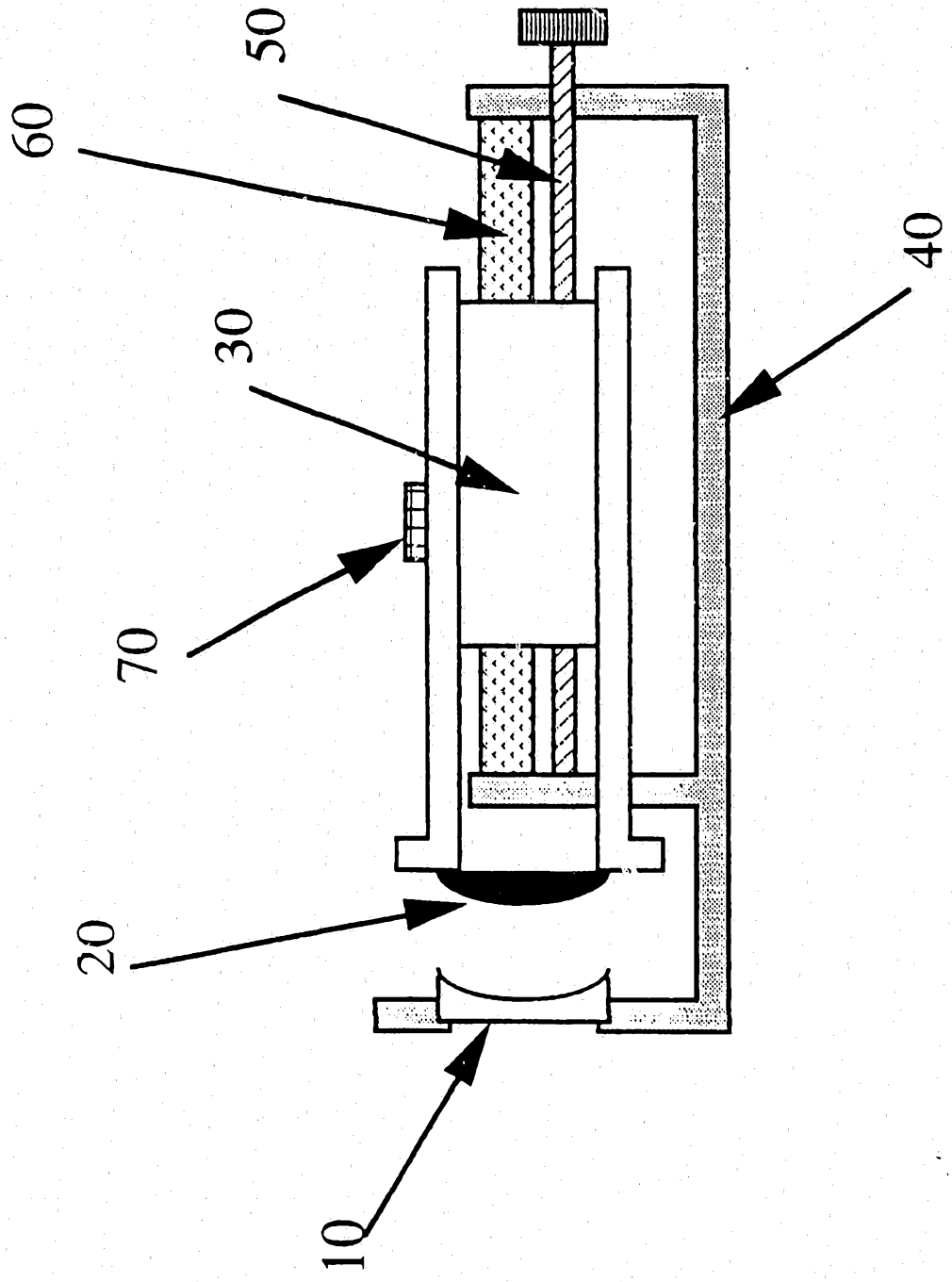


FIGURE 1

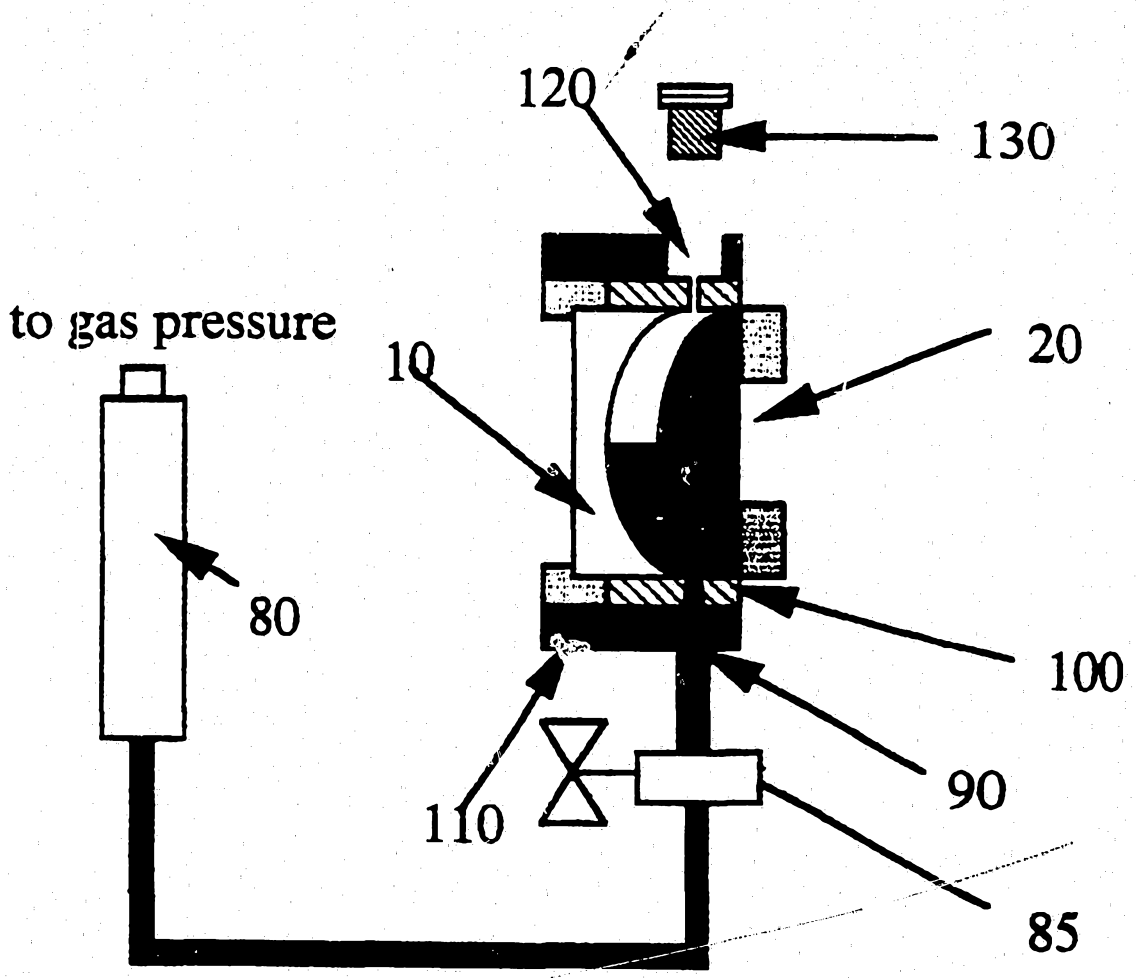


FIGURE 2

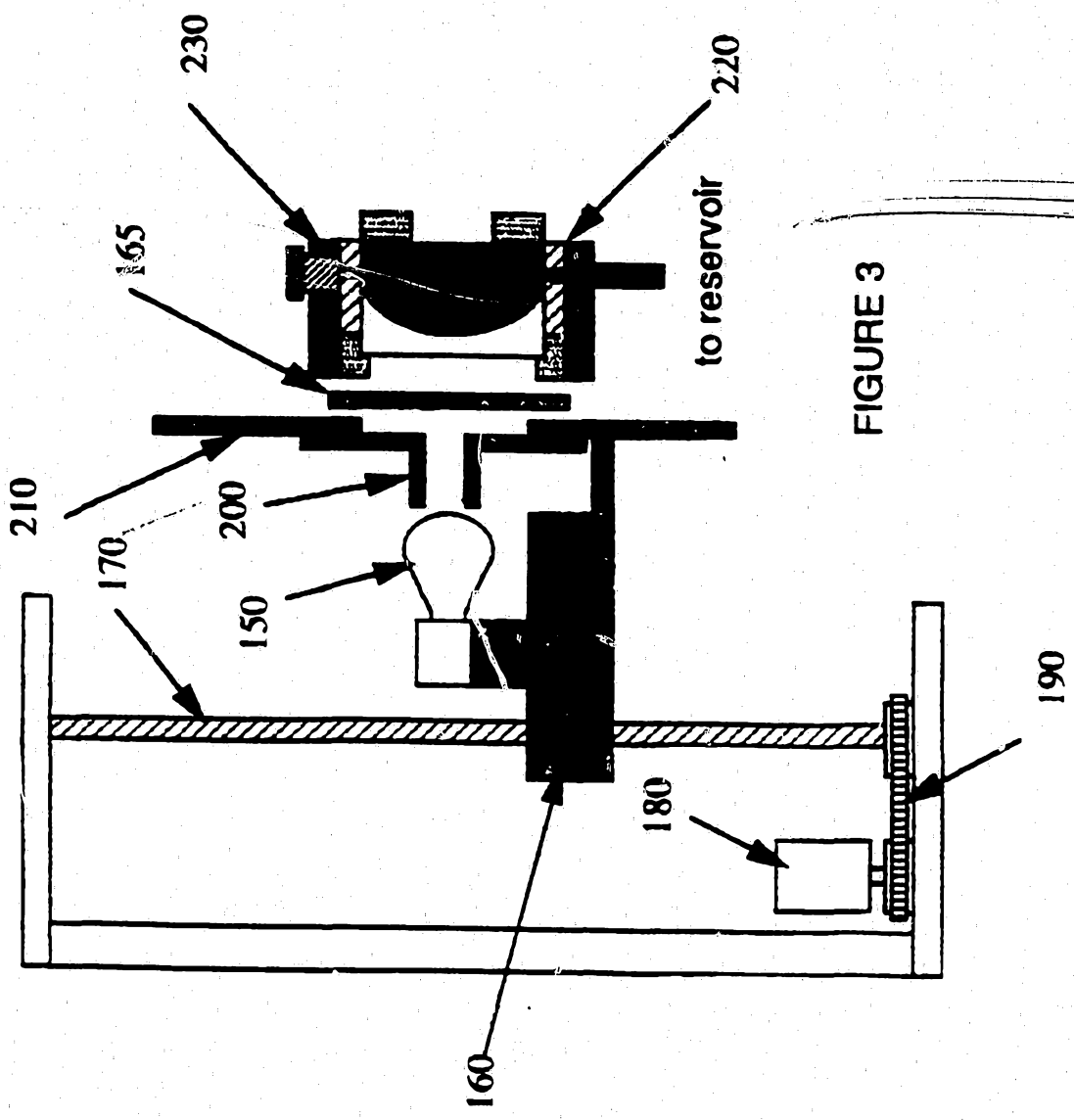


FIGURE 3

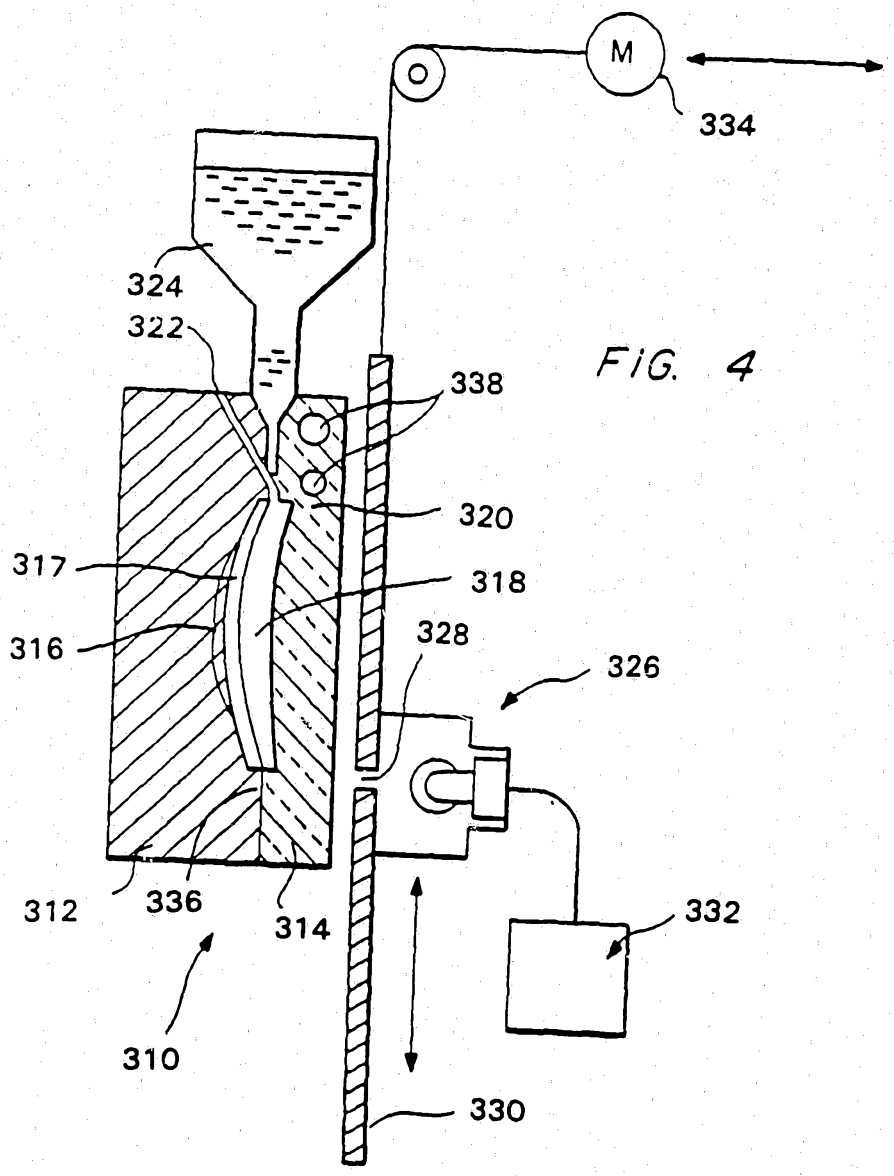


FIG. 4

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US93/03470

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) :B32B 3/00; B29D 11/00; G02B 3/00
US CL :Please See Extra Sheet.
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : Please See Extra Sheet.

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 5,063,112 (GROSS) 05 NOVEMBER 1991. See the entire document.	1-8,11-44
A	US, A, 5,023,305 (ONOZUKA) 11 JUNE 1991. See the entire document.	1-8,11-44
A	US, A, 4,977,229 (CULBERSON) 11 DECEMBER 1990. See the entire document.	1-8,11-44
A	US, A, 4,769,431 (RATKOWSKI) 06 SEPTEMBER 1988. See the entire document.	1-8,11-44
A	US, A, 4,544,572 (SANDVIG) 01 OCTOBER 1985. See the entire document.	1-8,11-44

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be part of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E"	earlier document published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search	Date of mailing of the international search report
17 JUNE 1993	19 JUL 1993
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. NOT APPLICABLE	Authorized officer DONALD J. LONEY Telephone No. (703) 308-2351

Form PCT/ISA/210 (second sheet)(July 1992)*

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US93/03470

A. CLASSIFICATION OF SUBJECT MATTER:
US CL :

156/245, 272.2; 264/1.4, 1.7, 1.8, 1.9, 241, 250, 328.8; 359/642, 738, 754; 428/172, 174, 412, 413, 414, 423.1, 423.3, 480, 483; 522/96, 103, 107; 525/48, 530; 526/301

B. FIELDS SEARCHED
Minimum documentation searched
Classification System: U.S.

156/245, 272.2; 264/1.4, 1.7, 1.8, 1.9, 241, 250, 328.8; 359/642, 738, 754; 428/172, 174, 412, 413, 414, 423.1, 423.3, 480, 483; 522/96, 103, 107; 525/48, 530; 526/301

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US93/03470

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☒ Claims Nos.: 9 & 10
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.