

POLYMERIZABLE POLYOL(ALLYL CARBONATE) COMPOSITIONS

DESCRIPTION OF THE INVENTION

This application is a Continuation-In-Part (CIP) of
5 United States Patent Application having Serial Number
09/459,796 which was filed on December 13, 1999 and is pending
in the United States Patent and Trademark Office.

The present invention relates to a polymerizable
composition. More particularly, the present invention relates
10 to a polymerizable composition comprising polyol(allyl
carbonate) monomer and a urethane having at least two allyl or
substituted allyl groups. The present invention relates also
to polymerizates, e.g., lenses, obtained from the
polymerizable compositions.

15 Polymerizable organic compositions based on polyol(allyl
carbonate), particularly diethylene glycol bis(allyl
carbonate), and polymerizates obtained therefrom are well
known in the art. Polymerizates of polymerizable organic
compositions based on homopolymers of diethylene glycol
20 bis(allyl carbonate) possess excellent clarity, good
flexibility and abrasion resistance. Examples of applications
for which such polymerizates may be used include, ophthalmic
lenses, sunglasses, and automotive and aircraft
transparencies. It has been observed that tinting of
25 polymerizates prepared from such compositions by surface
impregnation of dyes can, in certain instances, result in an
uneven tinting of the surface. Such uneven tinting is
referred to as tinting failure.

When tinting failure occurs, it is often manifested as
30 visually observable defects on the tinted surface(s) of the
polymerizate, which are commonly referred to as "ferns" or
"moons." In the case of tinted ophthalmic lenses, such as
tinted ophthalmic lenses having a positive diopter, i.e., plus
lenses, and non-corrective lenses, e.g., sunglasses, such
35 tinting failure often results in rejection and scrapping of
the tinted lens. A solution to tinting failure is desirable

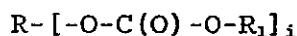
in order to avoid the economic loss that results from the scrapping of lenses having tinting defects.

United States Patent No.'s 4,994,208, 5,084,529, 5,110,881, 5,221,721, 5,236,978 and 5,246,630 describe
5 polymerizable compositions composed of polyol(allyl carbonate) monomer and at least 10 weight percent of aliphatic polyurethanes, the terminal portions of which contain allyl functional groups. United States Patent No. 5,200,483 describes organic resin compositions containing polyol(allyl
10 carbonate) monomer and a mixture of aliphatic urethanes, the terminal portions of which contain allyl or acrylyl functional groups.

It has now been discovered that cured polymerizates prepared from the polymerizable compositions of the present
15 invention are substantially free of tinting defects, for example, tinting defects referred to in the art as ferns or moons. In accordance with the present invention there is provided a polymerizable composition comprising:

(a) a major amount of a radically polymerizable
20 first monomer represented by the following general formula I,

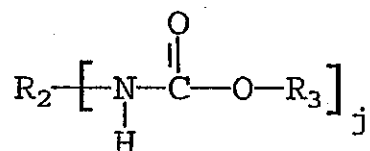
I



wherein R is a polyvalent residue of a polyol having at least two hydroxy groups, R₁ is an allyl or substituted allyl group,
25 and i is a whole number from 2 to 4; and

(b) a minor amount of a radically polymerizable second monomer represented by the following general formula II,

II



30

wherein R₂ is a polyvalent linking group that is free of urethane linkages; R₃ is a residue of a material having a single hydroxy group and at least one allyl group, R₃ being

free of urethane linkages, acryloyl groups and methacryloyl groups; and j is a number from 2 to 4, e.g., 2, 3 or 4.

In an embodiment of the present invention, said second monomer (b) is present in said composition in an amount at
5 least sufficient such that a polymerizate of said composition is substantially free of tinting defects.

The features that characterize the present invention are pointed out with particularity in the claims, which are annexed to and form a part of this disclosure. These and
10 other features of the invention, its operating advantages and the specific objects obtained by its use will be more fully understood from the following detailed description and the accompanying illustrative drawing.

Other than in the operating examples, or where otherwise
15 indicated, all numbers expressing quantities of ingredients, reaction conditions, etc. used in the specification and claims are to be understood as modified in all instances by the term "about."

20 BRIEF DESCRIPTION OF THE DRAWING

Figure 1 is a representation of a negative image of a tinted lens having tinting defects.

DETAILED DESCRIPTION OF THE INVENTION

25 In an embodiment of the present invention, the second monomer described with reference to general formula II is present in the polymerizable compositions in an amount at least sufficient such that polymerizates prepared from such compositions are substantially free of tinting defects. As
30 used herein and in the claims, the term "tinting defects" and similar terms refer generally to a visually observable uneven distribution of dye over the surface of a tinted polymerizate, such as a tinted lens. More particularly, tinting defects are often visually observable as lighter colored or untinted
35 surface patterns, sometimes in the form of ferns or moons.

Tinting defects in the form of ferns can be further described with reference to Figure 1. The tinted polymerizate 4 of Figure 1 is a tinted plus lens 11, prepared from diethylene glycol bis(allyl carbonate) monomer, and having tinting defects 15 thereon. For purposes of illustration, the tinting defects 15 of Figure 1 are shown as a negative image. As used herein, by "plus lens" is meant a lens having a positive (+) diopter, i.e., a lens having a positive focal length or real focal point. The tinting defects shown in the lens depicted in Figure 1 were observed in a lens having a plus five (+5) diopter.

Tinting defects in the form of moons (not shown in Figure 1) are typically observed as a series of concentric circles of varying tint strength on the surface of the tinted lens. In some instances a tinted lens will exhibit a combination of both moon and fern type tinting defects.

The occurrence of tinting defects with polymerizates prepared from polyol(allyl carbonate) monomers is a largely statistical phenomenon. Accordingly, in order to determine if a polymerizable composition can be used to prepare polymerizates that are "substantially free of tinting defects," more than one polymerizate, e.g., several lenses, should be prepared. Optionally, a set of comparative polymerizates may also be prepared under similar conditions, e.g., using the same cure cycle, from a composition that is known to result in tinting defects. The specific number of polymerizates that must be prepared is often determined by trial and error. In the case of ophthalmic lenses, typically between 10 and 100 lenses are prepared to determine if they are substantially free of tinting defects. Such a determination is described in further detail in the Examples herein. Typically, a set of polymerizates, e.g., 100 ophthalmic plus lenses, prepared from a polymerizable composition according to the present invention, is considered to be substantially free of tinting defects if 10 percent or less, preferably 5 percent or less, and more preferably 0

percent of the tinted polymerizates have tinting defects, such as ferns.

Second monomer (b) is present in the polymerizable composition of the present invention in a minor amount (e.g.,
5 from 0.1 percent by weight to 49 percent by weight, based on the total weight of the composition). Typically, second monomer (b) is present in the composition of the instant invention in an amount of at least 0.1 percent by weight, preferably at least 0.2 percent by weight, and more preferably
10 at least 0.3 percent by weight, based on the total weight of the composition. Second monomer (b) is also typically present in the composition of the present invention in an amount of less than 10 percent by weight, preferably less than 5 percent by weight and more preferably less than 3 percent by weight,
15 based on the total weight of the composition. The amount of second monomer (b) present in the composition of the present invention may range between any combination of these values, inclusive of the recited values, e.g., from 0.1 percent by weight to 10 percent by weight or from 0.3 percent by weight
20 to 3 percent by weight, based on the total weight of the composition.

With reference to general formula II, second monomer (b) is distinguishable from polyurethanes having terminal allyl functional groups as described in, for example, United States
25 Patent No.'s 4,994,208, 5,084,529, 5,110,881, 5,221,721, 5,236,978 and 5,246,630. In general formula II, R_2 and R_3 are each free of urethane linkages, more particularly, R_2 and R_3 are each free of internal urethane linkages. As used herein and in the claims, the term "urethane linkage" is meant to
30 refer to the following structural linkage, $-N(H)-C(O)-O-$. In the case when R_2 is a residue of a polyisocyanate, second monomer (b) can be described as a polyisocyanate that is capped with the mono-hydroxy functional material of which R_3 is a residue.

35 Depending on the method by which second monomer (b) is prepared, R_2 may be a residue of, for example, a

polyisocyanate, i.e., a material having at least two isocyanate groups, or a polyamine, i.e., a material having at least two primary amine groups. When the second monomer is prepared by capping a polyisocyanate with the mono-hydroxy functional material of which R_3 is a residue, R_2 is a residue of a polyisocyanate. The second monomer may also be prepared by first reacting the mono-hydroxy functional material of which R_3 is a residue with phosgene to form the corresponding chloroformate, which is then reacted with a polyamine, in which case R_2 is a residue of a polyamine.

In an embodiment of the present invention, R_2 is a residue of a polyisocyanate having at least two isocyanate groups, and the polyisocyanate may be selected from aromatic polyisocyanates, aliphatic polyisocyanates, cycloaliphatic polyisocyanates and mixtures thereof. As used herein and in the claims, the term "polyisocyanate" is meant to be inclusive of dimers and trimers of polyisocyanates, for example, trimers of diisocyanates containing a core isocyanurate ring.

Classes of aromatic polyisocyanates of which R_2 may be a residue include, for example, aromatic polyisocyanates wherein the isocyanate groups are not bonded directly to the aromatic ring, e.g., α, α' -xylene diisocyanate; and aromatic polyisocyanates wherein the isocyanate groups are bonded directly to the aromatic ring, e.g., benzene diisocyanate.

Examples of aromatic polyisocyanates having isocyanate groups bonded directly to the aromatic ring, of which R_2 may be a residue include, but are not limited to, phenylene diisocyanate, ethylphenylene diisocyanate, isopropylphenylene diisocyanate, dimethylphenylene diisocyanate, diethylphenylene diisocyanate, diisopropylphenylene diisocyanate, trimethylbenzene triisocyanate, benzene triisocyanate, naphthalene diisocyanate, methylnaphthalene diisocyanate, biphenyl diisocyanate, ortho-tolidine diisocyanate, 4,4'-diphenylmethane diisocyanate, bis(3-methyl-4-isocyanatophenyl)methane, bis(isocyanatophenyl)ethylene, 3,3'-dimethoxy-biphenyl-4,4'-diisocyanate, triphenylmethane

triisocyanate, polymeric 4,4'-diphenylmethane diisocyanate,
naphthalene triisocyanate, diphenylmethane-2,4,4'-
triisocyanate, 4-methyldiphenylmethane-3,5,2',4',6'-
pentaisocyanate, diphenylether diisocyanate,
5 bis(isocyanatophenylether)ethyleneglycol,
bis(isocyanatophenylether)-1,3-propyleneglycol, benzophenone
diisocyanate, carbazole diisocyanate, ethylcarbazole
diisocyanate and dichlorocarbazole diisocyanate. Examples of
aromatic polyisocyanates wherein the isocyanate groups are not
10 bonded directly to the aromatic ring, of which R₂ may be a
residue include, but are not limited to,
bis(isocyanatoethyl)benzene, $\alpha,\alpha,\alpha',\alpha'$ -tetramethylxylene
diisocyanate, 1,3-bis(1-isocyanato-1-methylethyl)benzene,
bis(isocyanatobutyl)benzene, bis(isocyanatomethyl)naphthalene,
15 bis(isocyanatomethyl)diphenyl ether,
bis(isocyanatoethyl)phthalate, mesitylene triisocyanate and
2,5-di(isocyanatomethyl)furan.

Aliphatic polyisocyanates of which R₂ may be a residue
may be selected from, for example, ethylene diisocyanate,
20 trimethylene diisocyanate, tetramethylene diisocyanate,
hexamethylene diisocyanate, octamethylene diisocyanate,
nonamethylene diisocyanate, 2,2'-dimethylpentane diisocyanate,
2,2,4-trimethylhexane diisocyanate, decamethylene
diisocyanate, 2,4,4,-trimethylhexamethylene diisocyanate,
25 1,6,11-undecanetriisocyanate, 1,3,6-hexamethylene
triisocyanate, 1,8-diisocyanato-4-(isocyanatomethyl)octane,
2,5,7-trimethyl-1,8-diisocyanato-5-(isocyanatomethyl)octane,
bis(isocyanatoethyl)-carbonate, bis(isocyanatoethyl)ether, 2-
isocyanatopropyl-2,6-diisocyanatohexanoate, lysinediisocyanate
30 methyl ester and lysinetriisocyanate methyl ester.

In an embodiment of the present invention, R₂ of general
formula II is a residue of a cycloaliphatic polyisocyanate.
Examples of cycloaliphatic polyisocyanates of which R₂ may be a
residue include, but are not limited to, isophorone
35 diisocyanate, cyclohexane diisocyanate, methylcyclohexane
diisocyanate, bis(isocyanatomethyl)cyclohexane,

bis(isocyanatocyclohexyl)methane, bis(isocyanatocyclohexyl)-
2,2-propane, bis(isocyanatocyclohexyl)-1,2-ethane, 2-
isocyanatomethyl-3-(3-isocyanatopropyl)-5-isocyanatomethyl-
bicyclo[2.2.1]-heptane, 2-isocyanatomethyl-3-(3-
5 isocyanatopropyl)-6-isocyanatomethyl-bicyclo[2.2.1]-heptane,
2-isocyanatomethyl-2-(3-isocyanatopropyl)-5-isocyanatomethyl-
bicyclo[2.2.1]-heptane, 2-isocyanatomethyl-2-(3-
isocyanatopropyl)-6-isocyanatomethyl-bicyclo[2.2.1]-heptane,
2-isocyanatomethyl-3-(3-isocyanatopropyl)-6-(2-
10 isocyanatoethyl)-bicyclo[2.2.1]-heptane, 2-isocyanatomethyl-2-
(3-isocyanatopropyl)-5-(2-isocyanatoethyl)-bicyclo[2.2.1]-
heptane and 2-isocyanatomethyl-2-(3-isocyanatopropyl)-6-(2-
isocyanatoethyl)-bicyclo[2.2.1]-heptane. In a preferred
embodiment of the present invention, R_2 is a residue of a
15 cycloaliphatic diisocyanate selected from, for example,
isophorone diisocyanate, cyclohexane diisocyanate,
methylcyclohexane diisocyanate,
bis(isocyanatomethyl)cyclohexane,
bis(isocyanatocyclohexyl)methane, bis(isocyanatocyclohexyl)-
20 2,2-propane, bis(isocyanatocyclohexyl)-1,2-ethane, and
mixtures thereof. When R_2 is a residue of a diisocyanate, such
as a cycloaliphatic diisocyanate, j of general formula II is
2.

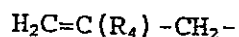
Classes of polyamines of which R_2 may be a residue,
25 include, aromatic polyamines, aliphatic polyamines,
cycloaliphatic polyamines, each having at least two primary
amines, and mixtures thereof. As is known to the skilled
artisan, polyisocyanates are typically prepared from the
corresponding polyamine precursors having two or more primary
30 amine groups. Accordingly, specific examples of polyamines
within these recited classes include, but are not limited to,
polyamine precursors corresponding to those polyisocyanates as
recited previously herein.

With further reference to general formula II, R_3 is a
35 residue of a material having a single hydroxy group and one or
more allyl groups. The mono-hydroxy functional material of

which R_3 is a residue is free of acryloyl groups and methacryloyl groups. The allyl group may be an unsubstituted allyl group or a substituted allyl group, as represented by the following general formula III,

5

III



wherein R_4 is hydrogen, halogen or a C_1 to C_4 alkyl group.

More typically, R_4 is hydrogen and consequently general formula III represents the unsubstituted allyl group, $H_2C=CH-CH_2-$.

10 More specifically, the allyl group of the material having a single hydroxy group, of which R_3 is a residue, may be an allyl ether, an allyl carbonate or an allyl ester group. The material of which R_3 is a residue typically has at least one allyl ether group.

15 The mono-hydroxy functional material of which R_3 is a residue may be selected from aromatic alcohols, aliphatic alcohols, cycloaliphatic alcohols, poly(alkylene glycols), each having at least one allyl group, and combinations thereof. Examples of aromatic alcohols having at least one
20 allyl group include, but are not limited to, allyloxy phenol, e.g., 4-allyloxy phenol, allyloxybenzyl alcohol, e.g., 4-allyloxybenzyl alcohol, and 4-allyl-2,6-dimethoxyphenol. Cycloaliphatic alcohols having at least one allyl group of which R_3 may be a residue include, for example, allyloxymethyl
25 cyclohexylmethanols, e.g., 4-allyloxymethyl cyclohexylmethanol.

Examples of aliphatic alcohols having at least one allyl group, of which R_3 may be a residue include, but are not limited to, allyl alcohol, substituted allyl alcohols, e.g.,
30 methallyl alcohol, allyl ethers of alkylene glycols, e.g., C_2 - C_4 alkylene glycols, such as, ethylene glycol allyl ether and 1,2- or 1,3-propylene glycol allyl ether. A preferred class of aliphatic alcohols, of which R_3 may be a residue, are poly(allyl ethers) of aliphatic polyols, e.g., trimethylol
35 propane di(allyl ether), trimethylol ethane di(allyl ether),

pentaerythritol tri(allyl ether), and di-trimethylolpropane tri(allyl ether).

Poly(alkylene glycols) of which R_3 may be a residue include, for example, homopolymeric, block copolymeric, e.g.,
5 diblock and triblock copolymeric, and random copolymeric poly(alkylene glycols), such as poly(C_2 - C_4 alkylene glycols), having a single allyl ether group and a single hydroxy group. Examples of poly(alkylene glycol) allyl ethers of which R_3 may be a residue include, for example, poly(ethylene glycol) allyl
10 ether, poly(1,2-propylene glycol) allyl ether, poly(1,2-butylene glycol) allyl ether, poly(ethylene glycol)-b-poly(1,2-propylene glycol) allyl ether, poly(1,2-propylene glycol)-b-poly(ethylene glycol) allyl ether, poly(1,2-butylene glycol)-b-poly(ethylene glycol) allyl ether, poly(ethylene
15 glycol)-b-poly(1,2-butylene glycol) allyl ether and poly(ethylene glycol)-b-poly(1,2-propylene glycol)-b-poly(1,2-butylene) allyl ether.

The poly(alkylene glycol) allyl ethers of which R_3 may be a residue have at least 2 alkylene ether units. For example,
20 diethylene glycol allyl ether has two (2) ethylene ether units, i.e., $H_2C=CHCH_2O-(-CH_2CH_2-O-)_2-H$. Typically, the poly(alkylene glycol) allyl ether has less than 100 alkylene ether units, e.g., less than 50, less than 20 or less than 15 alkylene ether units. The poly(alkylene glycol) allyl ether
25 may have a number of alkylene ether units ranging between any combination of these values, inclusive of the recited values, e.g., from 2 to 100, 2 to 50, 2 to 20 or 2 to 15 alkylene ether units.

In an embodiment of the present invention, the material
30 of which R_3 is a residue is selected from a C_2 - C_4 alkylene glycol allyl ether, a poly(C_2 - C_4 alkylene glycol) allyl ether, trimethylol propane di(allyl ether), trimethylol ethane di(allyl ether), pentaerythritol tri(allyl ether), di-trimethylolpropane tri(allyl ether) and mixtures thereof. In
35 a preferred embodiment of the present invention, the material of which R_3 is a residue is selected from poly(ethylene glycol)

allyl ether, poly(1,2-propylene glycol) allyl ether and mixtures thereof.

The polymerizable organic composition of the present invention includes also a radically polymerizable first monomer as described above with reference to general formula I, which may be further described as a polyol(allyl carbonate) monomer. Polyol(allyl carbonate) monomers that may be used in the aforescribed polymerizable organic composition are allyl carbonates of, for example, linear or branched aliphatic polyols, e.g., aliphatic glycol bis(allyl carbonate) compounds, and cycloaliphatic polyols. The scope of the present invention also includes allyl carbonates of aromatic polyols, e.g., 4,4'-isopropylidenediphenol bis(allyl carbonate). These monomers may further be described as unsaturated polycarbonates of polyols, e.g., glycols. The polyol(allyl carbonate) monomer may be prepared by procedures well known in the art, e.g., as described in U.S. Patents 2,370,567 and 2,403,113.

In reference to general formula I, R_1 is an allyl group, which may be described with reference to general formula III. The allyl group R_1 of general formula I may be substituted at the 2-position with a halogen, most notably chlorine or bromine, or an alkyl group containing from 1 or 4, e.g., 1 to 2, carbon atoms, in which case R_1 is a substituted allyl group. More commonly, and with reference to general formula III, R_4 is hydrogen and consequently R_1 of general formula I is the unsubstituted allyl group, $H_2C=CH-CH_2-$.

With reference to general formula I, R is a polyvalent residue of a polyol, which can, for example, be an aliphatic or cycloaliphatic polyol, containing 2, 3 or 4 hydroxy groups. Typically, the polyol contains 2 hydroxy groups, i.e., a glycol. When the polyol is an aliphatic polyol, it may be linear or branched and contain from 2 to 10 carbon atoms. Commonly, the aliphatic polyol is an alkylene glycol having from 2 to 4 carbons atoms, e.g., ethylene glycol, propylene glycol, trimethylene glycol, tetramethylene glycol, or a

poly(C₂-C₄ alkylene glycol), e.g., diethylene glycol, triethylene glycol, etc.

Specific examples of polyol(allyl carbonate) monomers that may be used in the present invention include, but are not
5 limited to, ethylene glycol bis(2-chloroallyl carbonate), ethylene glycol bis(allyl carbonate), diethylene glycol bis(2-methylallyl carbonate), diethylene glycol bis(allyl carbonate), triethylene glycol bis(allyl carbonate), propylene glycol bis(2-ethylallyl carbonate), 1,3-propanediol bis(allyl
10 carbonate), 1,3-butanediol bis(allyl carbonate), 1,4-butanediol bis(2-bromoallyl carbonate), dipropylene glycol bis(allyl carbonate), trimethylene glycol bis(2-ethylallyl carbonate), pentamethylene glycol bis(allyl carbonate), 1,4-cyclohexanediol bis(allyl carbonate) and 4,4'-
15 isopropylidenebiscyclohexanol bis(allyl carbonate).

A preferred polyol(allyl carbonate) monomer in the composition of the present invention is diethylene glycol bis(allyl carbonate). Commercially available examples of diethylene glycol bis(allyl carbonate) monomers include CR-39®
20 monomer and HIGH ADC CR-39® monomer, Chemical Abstracts (CAS) No. 142-22-3, available from PPG Industries, Inc.

A detailed description of polyol(allyl carbonate) monomers that may be used in the polymerizable organic compositions of the present invention may be found in U.S.
25 Patent No. 4,637,698 at column 3, line 33 through column 5, line 61. That disclosure is hereby incorporated by reference, and is summarized above.

As used in the present description with reference to the radically polymerizable monomer represented by general formula
30 I, the term "polyol(allyl carbonate) monomer" and like names, e.g., diethylene glycol bis(allyl carbonate), is intended to mean and include the named monomers or prepolymers thereof and any related monomer or oligomer species contained therein.

The polyol(allyl carbonate) monomer is present in the
35 polymerizable composition of the present invention in a major amount, e.g., from 51 percent by weight to 99.9 percent by

weight, based on the total weight of the polymerizable composition. Typically, the polyol(allyl carbonate) monomer is present in the polymerizable composition of the present invention in an amount of at least 90 percent by weight, 5 preferably at least 95 percent by weight, and more preferably at least 97 percent by weight, based on the total weight of the polymerizable composition. Also, the polyol(allyl carbonate) monomer is typically present in the composition in an amount of not greater than 99.9 percent by weight, 10 preferably not greater than 99.8 percent by weight, and more preferably not greater than 99.7 percent by weight, based on the total weight of the polymerizable composition. The polyol(allyl carbonate) monomer may be present in the composition of the present invention in an amount ranging 15 between any combination of these values, inclusive of the recited values.

Polymerization of the polymerizable composition of the present invention may be accomplished by adding to the composition an initiating amount of material capable of 20 generating free radicals, such as organic peroxy compounds, i.e., an initiator. Methods for polymerizing polyol(allyl carbonate) compositions are well known to the skilled artisan and any of those well known techniques may be used to polymerize the aforescribed polymerizable compositions.

25 Suitable examples of organic peroxy compounds, that may be used as initiators include: peroxy monocarbonate esters, such as tertiarybutylperoxy isopropyl carbonate; peroxydicarbonate esters, such as di(2-ethylhexyl) peroxydicarbonate, di(secondary butyl) peroxydicarbonate and 30 diisopropylperoxydicarbonate; diacylperoxides, such as 2,4-dichlorobenzoyl peroxide, isobutyryl peroxide, decanoyl peroxide, lauroyl peroxide, propionyl peroxide, acetyl peroxide, benzoyl peroxide, p-chlorobenzoyl peroxide; peroxyesters such as t-butylperoxy pivalate, t-butylperoxy 35 octylate, and t-butylperoxyisobutyrate; methylethylketone peroxide, acetylcyclohexane sulfonyl peroxide, and

azobisisobutyronitrile. Preferred initiators are those that do not discolor the resulting polymerizate. A preferred initiator is diisopropyl peroxydicarbonate.

The amount of initiator used to initiate and polymerize the polymerizable compositions of the present invention may vary and will depend on the particular initiator used. Only that amount that is required to initiate and sustain the polymerization reaction is required, i.e., an initiating amount. With respect to the preferred peroxy compound, diisopropyl peroxydicarbonate, typically between 2.0 and 5.0 parts of that initiator per 100 parts of the polymerizable organic composition (phm) may be used. More usually, between 2.5 and 4.0 phm is used to initiate the polymerization. The amount of initiator and the consequent cure cycle should be adequate to produce a polymerizate having a 15 second Barcol hardness of at least 1, preferably, at least 4, e.g., from 4 to 35. Typically, the cure cycle involves heating the polymerizable organic composition in the presence of the initiator from room temperature to 85°C over a period of from 15 hours to 30 hours.

Various conventional additives may be incorporated into the polymerizable composition of the present invention. Such conventional additives may include light stabilizers, heat stabilizers, ultraviolet light absorbers, mold release agents, pigments and flexibilizing additives that are not radically polymerizable, e.g., alkoxyated phenol benzoates and poly(alkylene glycol) dibenzoates. Conventional additives are typically present in the compositions of the present invention in amounts totaling less than 10 percent by weight, more typically less than 5 percent by weight, and commonly less than 3 percent by weight, based on the total weight of the polymerizable composition.

Polymerizates obtained from polymerization of polymerizable organic compositions of the present invention will be solid, transparent and substantially free of tinting defects. Solid articles that may be prepared from the

polymerizable compositions of the present invention include, but are not limited to, optical lenses, such as plano and ophthalmic lenses, sun lenses or sunglasses, windows, automotive transparencies, e.g., windshields, sidelights and backlights, and aircraft transparencies.

In a non-limiting embodiment, a polymerizate obtained from polymerization of a polymerizable organic composition of the present invention can be used to prepare a photochromic article, such as a lens. In this embodiment, the polymerizate should be transparent to that portion of the electromagnetic spectrum which activates the photochromic substance(s) incorporated in the matrix, i.e., the wavelength of ultraviolet (UV) light that produces the colored or open form of the photochromic substance and that portion of the visible spectrum that includes the absorption maximum wavelength of the photochromic substance in its UV activated form, i.e., the open form. Non-limiting examples of photochromic substances that may be utilized with the polymerizates of the present invention can include but are not limited to organic photochromic compounds or substances containing same that may be incorporated, e.g., dissolved, dispersed or diffused into such polymerizates.

In a non-limiting embodiment, suitable organic photochromic substances for use in the present invention can have an activated absorption maximum within the visible range of greater than 590 nanometers, or between greater than 590 to 700 nanometers. These materials can exhibit a blue, bluish-green, or bluish-purple color when exposed to ultraviolet light in an appropriate solvent or matrix. Non-limiting examples of such substances can include but are not limited to spiro(indoline)naphthoxazines and spiro(indoline)benzoxazines. Further non-limiting examples of these and other such photochromic substances are described in the open literature. See, for example, U.S. Patents: 3,562,172; 3,578,602; 4,215,010; 4,342,668; 5,405,958; 4,637,698; 4,931,219; 4,816,584; 4,880,667; 4,818,096.

In another non-limiting embodiment, suitable organic photochromic substances for use in the present invention can include at least one absorption maximum within the visible range of between 400 and less than 500 nanometers. In a further non-limiting embodiment, the organic photochromic substance can include two absorption maxima. These materials can exhibit a yellow-orange color when exposed to ultraviolet light in an appropriate solvent or matrix. Non-limiting examples can include chromenes, such as but not limited to benzopyrans and naphthopyrans. Further non-limiting examples of such chromenes are described in the open literature, see for example, U.S. Patents 3,567,605; 4,826,977; 5,066,818; 4,826,977; 5,066,818; 5,466,398; 5,384,077; 5,238,931; and 5,274,132.

In an alternate non-limiting embodiment, suitable organic photochromic substances for use in the present invention can include those having an absorption maximum within the visible range of between 400 to 500 nanometers and another absorption maximum within the visible range of between 500 to 700 nanometers. These materials can exhibit color(s) ranging from yellow/brown to purple/gray when exposed to ultraviolet light in an appropriate solvent or matrix. Non-limiting examples of these substances can include benzopyran compounds, having substituents at the 2-position of the pyran ring and a substituted or unsubstituted heterocyclic ring, such as but not limited to a benzothieno or benzofurano ring fused to the benzene portion of the benzopyran. Non-limiting examples of such materials are disclosed in U.S. Patent No. 5,429,774.

In a further non-limiting embodiment, the photochromic substance for use in the present invention can include photochromic organo-metal dithizonates, such as but not limited to (aryldazo)-thioformic arylhydrazidates, such as but not limited to mercury dithizonates which are described in, for example, U.S. Patent 3,361,706; and fulgides and fulgimides, such as but not limited to 3-furyl and 3-thienyl

fulgides and fulgimides which are described in U.S. Patent 4,931,220 at column 20, line 5 through column 21, line 38.

In a non-limiting embodiment, the photochromic substance for use in the present invention can include at least one naphthopyran. In a further non-limiting embodiment, the photochromic substance can include a mixture of at least two naphthopyrans.

The specific disclosures relating to such photochromic substances in the aforescribed patents are incorporated herein, *in toto*, by reference. The photochromic articles of the present invention can include one photochromic substance or a mixture of photochromic substances, as can be appreciated by one skilled in the art. In a non-limiting embodiment, a mixture of photochromic substances can be used to attain an activated color such as a near neutral gray or brown.

Each of the photochromic substances described herein can be used in an amount and in a ratio (i.e., when mixtures are used) such that a polymerizate to which the photochromic substance is applied or incorporated exhibits a desired resultant color. In a non-limiting embodiment, a photochromic substance can be applied on or incorporated into the polymerizate to produce a substantially neutral color such as a shade of gray or brown when activated with unfiltered sunlight. The relative amounts of the aforesaid photochromic substances used can vary and depend upon the relative intensities of the color of the activated species of such compounds, and the ultimate color desired.

The photochromic compounds or substances described herein can be applied to or incorporated into the polymerizate by various methods described in the art. In a non-limiting embodiment, the photochromic substance can be dissolved or dispersed within the polymerizate, such as imbibition of the photochromic substance into the polymerizate by immersion of the polymerizate in a hot solution of the photochromic substance or by thermal transfer. In an alternate embodiment, the photochromic substance can be a separate layer between

adjacent layers of the polymerizate, such as a part of a polymer film. In another alternate embodiment, the photochromic substance can be applied as a coating or as part of a coating placed on the surface of the polymerizate. As
5 used herein and the claims, the term "imbibition" or "imbibe" includes the permeation of the photochromic substance alone into the polymerizate, solvent assisted transfer absorption of the photochromic substance into a porous polymer, vapor phase transfer, and other such transfer mechanisms.

10 In a non-limiting embodiment, imbibition of the photochromic substance into the polymerizate can include coating the photochromic article with the photochromic substance; heating the surface of the photochromic article; and removing the residual coating from the surface of the
15 photochromic article.

The amount of photochromic substance or composition containing the same, applied to or incorporated into the polymerizate is not critical and can vary widely. In general, the amount should be sufficient to produce a photochromic
20 effect discernible to the naked eye upon activation. Such amount can be referred to as a photochromic amount. The particular amount used can depend upon the intensity of color desired upon irradiation thereof and upon the method used to incorporate or apply the photochromic substances. Typically,
25 the more photochromic substance applied or incorporated, the greater is the color intensity. In a non-limiting embodiment, the amount of total photochromic substance incorporated into or applied to a photochromic optical polymerizate may range from 0.15 to 0.35 milligrams per square centimeter of surface
30 to which the photochromic substance is incorporated or applied.

In a non-limiting embodiment, the photochromic substance can be added prior to polymerizing, e.g., cast curing, a polymerizable organic composition of the present invention.
35 In this embodiment, the photochromic substance can be chosen such that it is essentially resistant to potentially adverse

interactions with initiator(s) that may be present and/or the isocyanate, isothiocyanate and amine groups of the first and second components. These adverse interactions can result in deactivation of the photochromic substance, e.g., by trapping
5 them in either an open or closed form.

In a non-limiting embodiment, suitable photochromic substances for use in the present invention can include photochromic pigments and organic photochromic substances encapsulated in metal oxides, the latter of which are
10 described in U.S. Patents 4,166,043 and 4,367,170. In a further non-limiting embodiment, organic photochromic substances sufficiently encapsulated within a matrix of an organic polymerizate, as described in U.S. Patent 4,931,220, can be incorporated into the multi-component composition of
15 the present invention prior to curing. In another non-limiting embodiment, the photochromic substance can be incorporated into the second component prior to mixing the first and second components together.

The present invention is more particularly described in
20 the following examples, which are intended to be illustrative only, since numerous modifications and variations therein will be apparent to those skilled in the art. Unless otherwise specified, all parts and percentages are by weight.

25

Casting Composition Examples

The following summarizes polymerizable casting compositions that are comparative and compositions that are in accordance with the present invention. Casting composition A is a comparative composition, and Casting compositions B and C
30 represent compositions according to the present invention.

Casting Compositions			
Ingredients	Casting Composition A	Casting Composition B	Casting Composition C
CR-39® monomer (a)	100.0	99.0	99.0
diisopropyl peroxydicarbonate (b)	2.6	3.0	3.2
Second monomer (c)	0	1.0	0
Second monomer (d)	0	0	1.0

5 (a) CR-39® diethylene glycol bis(allyl carbonate) monomer available commercially from PPG Industries, Inc.

(b) In each of casting compositions B and C, the level of diisopropyl peroxydicarbonate initiator was adjusted such that
 10 tinted polymerizates obtained from these compositions had substantially the same percent transmission as tinted polymerizates obtained (under the same tinting conditions) from composition A, e.g., having about 35 percent
 'transmission. The percent transmittance was determined using
 15 a HunterLab Model ColorQuest II colorimeter employing the CIE Tristimulus XYZ scale, illuminant D65 and 10°C observer.

(c) Diallyl urethane monomer obtained from Sartomer Company, Inc. and having the designation NTX-4434.

20

(d) Tetraallyl urethane monomer obtained from Sartomer Company, Inc. and having the designation NTX-4439.

Cast Lens Examples

25 The casting compositions A - C were each mixed at room temperature and injected separately into glass lens molds used to prepare circular lenses having a +5 diopter and an outer rim diameter of 6.5 cm. Twenty (20) lens molds were filled at a time and their contents polymerized using the same cure

cycle. The cure cycle used involved heating the molds in an electric forced air oven in stages from 48°C to 85 °C over a period of 18 hours, followed by cooling to and holding at 60°C until demolding of the lenses.

5 The cast lenses were then tinted by imbibing them with a black dye. An aqueous tinting solution of 1 part BPI® Molecular Catalytic™ Black Dye, commercially available from Brain Power Incorporated, and 10 parts deionized water was heated to and held at a temperature of 94°C - 95°C. The
10 lenses cast from casting compositions A - C were fully immersed in the heated dye solution for a period of 5 minutes, after which they were thoroughly rinsed with deionized water. The tinted lenses were evaluated for tinting defects, the results of which are summarized in Table 1.

15

TABLE 1

Evaluation of Tinted Lenses

Casting Composition	Number of Tinted Lenses Evaluated	Number of Tinted Lenses Having Tinting Defects (e)	Percent of Tinted Lenses Having Tinting Defects (f)
A	228	57	25
B	529	30	5.7
C	436	23	5.3

20 (e) The lenses were evaluated for tinting defects by means of visual naked eye inspection. Tinting defects were observed as having a lighter colored vein or fern-like appearance relative to the rest of the tinted lens.

25 (f) $100 \times (\text{the number of tinted lenses observed to have tinting defects} / \text{the number of tinted lenses evaluated})$. For example, with casting composition A: $100 \times (57/228) = 25$ percent (%).

30 The results summarized in Table 1 show that articles, e.g., lenses, cast from polymerizable compositions according

to the present invention, such as Compositions B and C, have fewer tinting defects than lenses cast from comparative compositions, such as Composition A.

5 Photochromic Article Example

In 98.5 grams of diethylene glycol bis(allyl carbonate) monomer (mid ADC grade), commercially available from PPG Industries, Inc. under the designation CR-39® monomer, was blended 1.5 gm of tetraallyl urethane monomer (TAU) using a
10 magnetic bar. The TAU was obtained from Sartomer Company, Inc. under the designation NTX-4439. The mixture was blended for about 30 minutes. To this blend was added 2.8 gm of diisopropyl peroxydicarbonate (IPP) as a free radical
15 initiator. The mixture was then blended for an additional 10 minutes.

A control sample was prepared using the same procedure with the exception that the sample did not contain TAU monomer.

The resulting mixtures were poured between two flat glass
20 sheets and cured by heating the sheets in an electric forced air oven in stages from 48°C to 85°C over a period of 18 hours, followed by cooling to and holding at 60°C. The flat sheets were cut into 1.5" x 1.5" square samples which were used for photochromic dye imbibition. A photochromic dye was
25 prepared and imbibed at a temperature of 135°C, for a time period of 4 hours.

Imbibition Coating

The following photochromic mixture was used in the
30 imbibition coating. The total concentration of photochromic in the coating was 4 weight percent. The materials were added in the order and manner shown below, to a vessel equipped with an agitator and a means for heating.

Material	Weight percent of Imbibition coating
<u>SOLVENTS</u>	
Tetrahydrofurfuryl alcohol	24.6
5 Diethyleneglycol dimethylether	28.7
NMP	12.3
Dowanol® PNB	16.4
<u>SILICA</u>	
10 Hi Sil - T-700	1.8
<u>RESIN</u>	
Hydroxypropyl cellulose	9.818
15 <u>PHOTOCHROMIC DYE PACKAGE</u>	
Photochromic No. 3 ⁽⁶⁾	0.707
Photochromic No. 4 ⁽⁷⁾	0.353
Photochromic No. 5 ⁽⁸⁾	0.589
Photochromic No. 6 ⁽⁹⁾	1.257
20 Photochromic No. 7 ⁽¹²⁾	0.079
Photochromic No. 8 ⁽¹³⁾	0.628
Photochromic No. 9 ⁽¹⁴⁾	0.314
<u>STABILIZER PACKAGE</u>	
25 TINUVIN® 144 UV	
Stabilizer ⁽¹⁰⁾	1.718
IRGANOX® 3114	
Antioxidant	0.736
30	

⁽⁶⁾A Photochromic naphtho[1,2-b]pyran that exhibits a blue color when irradiated with ultraviolet light.

35 ⁽⁷⁾A Photochromic naphtho[1,2-b]pyran that exhibits a blue-green color when irradiated with ultraviolet light.

⁽⁸⁾A Photochromic naphtho[1,2-b]pyran that exhibits a yellow-orange color when irradiated with ultraviolet light.

40 ⁽⁹⁾A Photochromic naphtho[1,2-b]pyran that exhibits a yellow-orange color when irradiated with ultraviolet light.

(10) Hindered amine ultraviolet light stabilizer available from Ciba-Geigy Corporation.

(12) A Photochromic naphtho[1,2-b]pyran that exhibits a yellow-orange color when irradiated with ultraviolet light.

5 (13) A Photochromic naphtho[1,2-b]pyran that exhibits a yellow-green color when irradiated with ultraviolet light.

(14) A Photochromic naphtho[1,2-b]pyran that exhibits a purple color when irradiated with ultraviolet light.

10 The imbibition coating was imbibed into the sample sheets by applying a film of the imbibition coating onto the surface of the sample sheets. The film was applied by spin coating. The applied film was allowed to dry. The sample sheets were then heated in a hot-air oven at 135-140°C for 4 hours. After
15 cooling, the resin film was removed from the test samples by rinsing with water and wiping with an acetone soaked tissue.

 The samples were screened for ultraviolet absorbance and test samples having comparable UV absorbance at 390 nanometers were tested for photochromic response on an optical bench. The
20 ultraviolet absorbance value gives an indication of the amount of photochromic compounds in the sample. The optical bench was maintained at a temperature of 72°F (22°C). The sample sheets imbibed with the imbibition coating were activated for 15 minutes and the Percent Transmission (%Ta) was measured after
25 15 minutes.

 Prior to testing on the optical bench, the photochromic samples were exposed to 365 nanometer ultraviolet light for about 20 minutes to activate the photochromic compounds and then placed in a 75°C oven for about 20 minutes to bleach
30 (inactivate) the photochromic compounds. The samples were then cooled to room temperature, exposed to fluorescent room lighting for at least 3 hours and then kept covered for at least 1 hour prior to testing on an optical bench. The bench was fitted with a 300 watt Xenon arc lamp, a remote controlled
35 shutter, a Schott 3mm KG-2 band-pass filter, which removes short wavelength radiation, neutral density filter(s), a

quartz water cell/sample holder for maintaining sample temperature in which the sample to be tested was inserted. Measurements were made on the optical bench in the Photochromic Performance Test with the power output adjusted to 0.67 milliwatts per square centimeter (mW/cm^2).

The power output was measured using a GRASEBY Optronics Model S-371 portable photometer (Serial #21536) with a UV-A detector (Serial # 22411) or comparable equipment. The UV-A detector was placed into the sample holder and the light output was measured. Adjustments to the power output were made by increasing or decreasing the lamp wattage or by adding or removing neutral density filters in the light path. A monitoring, collimated beam of light from a tungsten lamp was passed through the sample at 30° normal to the surface of the lens. After passing through the sample sheet, the light from the tungsten lamp was directed through a photopic filter attached to a detector. The output signals from the detector were processed by a radiometer. The control of the test conditions and acquisition of data was handled by the Labtech Notebook Pro software and the recommended I/O board.

The results are shown in Table 2 below.

TABLE 2

Sample	IPP (wt%)	TAU (wt%)	Imbibition Time (hr)	Photochromic abs @ 390 nm	%Ta (activated)
Control	2.8	0	4	0.1889	62.4
Invention	2.8	1.5	4	1.09	18

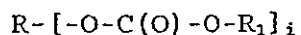
These results show that TAU has a significant effect on the photochromic imbibition when compared with a control sample.

The present invention has been described with reference to specific details of particular embodiments thereof. It is not intended that such details be regarded as limitations upon

the scope of the invention except insofar as and to the extent that they are included in the accompanying claims.

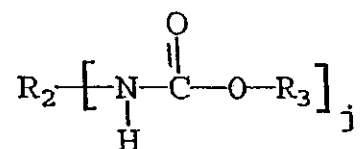
What is claimed :

1. A photochromic article adapted to be free of tinting defects comprising an at least partially cured substrate, at least a photochromic amount of a photochromic substance and a tinting defect inhibiting additive.
2. The photochromic article of claim 1 wherein said photochromic substance is at least partially imbibed into said substrate.
3. The photochromic article of claim 1 wherein said substrate is at least partially coated with a coating composition comprising at least a photochromic amount of a photochromic substance.
4. The photochromic article of claim 1 wherein said tinting defect inhibiting additive is present in an amount such that a polymerizate of said composition is substantially free of tinting defects.
5. A photochromic article adapted to be free of tinting defects comprising at least a photochromic amount of a photochromic substance, a tinting defect inhibiting additive, and an at least partially cured substrate comprising:
 - (a) a major amount of a radically polymerizable first monomer represented by the following general formula,



wherein R is a polyvalent residue of a polyol having at least two hydroxy groups, R₁ is an allyl group, and i is a whole number from 2 to 4; and

(b) a minor amount of a radically polymerizable second monomer represented by the following general formula,



wherein R₂ is a polyvalent linking group that is free of urethane linkages; R₃ is a residue of a material having a single hydroxy group and at least one allyl group, R₃ being free of urethane linkages; and j is a number from 2 to 4.

6. A photochromic article adapted to be free of tinting defects comprising an at least partially cured substrate comprising diethylene glycol bis(allyl carbonate) monomer, at least a photochromic amount of a photochromic substance and a tinting defect inhibiting additive.

7. The photochromic article of claim 6 wherein said photochromic substance is at least partially imbibed into said substrate.

8. The photochromic article of claim 6 wherein said photochromic substance comprises at least one naphthopyran.

9. The photochromic article of claim 6 wherein said photochromic substance is chosen from spiro(indoline)naphthoxazines, spiro(indoline)benzoxazines, benzopyrans, naphthopyrans, organo-metal dithizonates, fulgides and fulgimides, and mixtures thereof.

10. A photochromic article adapted to be free of tinting defects comprising at least a partially cured substrate, a photochromic amount of a photochromic material

wherein said photochromic material is at least partially imbibed into said substrate, and a tinting defect inhibiting additive.

11. A photochromic article adapted to be free of tinting defects comprising at least a partially cured substrate wherein said substrate is at least partially coated with a coating composition comprising at least a photochromic amount of a photochromic material, and a tinting defect inhibiting additive.