

SPECIFICATION

Method of preparing tungsten hexacarbonyl containing polymers and polymers prepared thereby

5 This invention relates to light absorbing compositions including liquids and polymerizates thereof having a good near infrared absorption and to methods for making them. By "near infrared" is
10 meant that portion of the electromagnetic spectrum having a wave length of from about 700 to about 2,000 nanometers.

High quality optical lenses are widely made by polymerizing diglycol allyl carbonate, e.g., diethylene glycol bis(allyl carbonate), or mixtures thereof
15 with minor proportions of other monomers such as methyl methacrylate and vinyl acetate in molds. Tinted lenses are generally made by dip-dyeing in heated solutions of a variety of organic dyes. However,
20 most such lenses, whether tinted or colorless, transmit near infrared freely.

U.S. Patent 3,692,688 discloses essentially haze-free optical filters of polymethylmethacrylate containing an *in situ* reaction product of tungsten hexachloride and stannous chloride which is said to filter
25 near infrared radiation efficiently while retaining considerable transmittance of light in the visible region. It is there stated at the magnitude of the mole ratio of stannous chloride to tungsten hexachloride
30 is as important a factor as the concentration of the tungsten hexachloride in affecting the filtering efficiency.

It has been reported by El-Sayer in the *Journal of Physical Chemistry*, Vol. 68, pp. 433-434, (1964), that
35 tungsten hexacarbonyl is photochromic when dissolved in certain solvents. However, the compound reportedly displayed a color shift to yellow, which is not a desirable color for sunglasses.

U.K. Patent No. 1 544 348 describes a method of
40 preparing photochromic articles by polymerizing a diglycol bis(allyl carbonate) in the presence of tungsten hexacarbonyl. As there disclosed, the monomer may contain up to about 1.0 weight percent tungsten hexacarbonyl, although when more than about 0.1
45 weight percent tungsten hexacarbonyl is present in the monomer, a polymer containing bubbles is obtained. However, as there disclosed, the tendency to bubble formation may be reduced by exposing the mixture of glycol bis(allyl carbonate) and tungsten hexacarbonyl to ultraviolet radiation and thereafter degassing the mixture.
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It has now been found that the steps of exposing the mixture of glycol bis(allyl carbonate) and tungsten hexacarbonyl to ultraviolet radiation and thereafter degassing the mixture may be dispensed with if
55 the tungsten hexacarbonyl is first added to an olefinically unsaturated carboxylic acid and if the resulting composition is thereafter added to the glycol bis(allyl carbonate).

60 It has further been found that higher concentrations of tungsten hexacarbonyl may be provided in the glycol bis(allyl carbonate), e.g., high enough to provide a permanent coloration to the polymerizate rather than a photochromic tint, by first incorporating
65 the tungsten hexacarbonyl in an olefinically

unsaturated carboxylic acid and thereafter adding the resulting composition to the glycol bis(allyl carbonate). The composition of the olefinically unsaturated carboxylic acid and tungsten hexacarbonyl
70 may be either a liquid or a solid.

It has now been found that tungsten hexacarbonyl, $W(CO)_6$, may be incorporated in liquid allyl glycol carbonates and solid poly(allyl glycol carbonate) in high concentrations whereby to produce light
75 absorbing liquids and lenses, sheets, or other shapes which are optically clear and substantially haze-free, are permanently light absorbing, have substantial near infrared absorbance, and have a reasonable service life. By "permanently light
80 absorbing" is meant the substantial absence of a return to a water-white condition when shielded from ultraviolet radiation. By "substantial infrared absorbance" is meant absorbance in the near infrared region at least as great as the average absorbance in the visible region.
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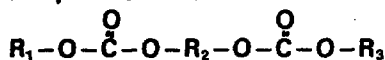
In accordance with the practice of this invention, tungsten hexacarbonyl may be dissolved or dispersed uniformly in an olefinically unsaturated carboxylic acid, e.g., a monocarboxylic acid as acrylic acid or a dicarboxylic acid as maleic acid or maleic acid anhydride, to provide a composition which may then be polymerized with a bis(allyl carbonate), e.g., diethylene glycol bis(allyl carbonate), in known ways to produce light absorbing, colored polymerizates
90 having substantial near infrared absorbance.

Solutions of tungsten hexacarbonyl in olefinically unsaturated carboxylic acid monomers are colorless to blue in color and, when protected from prolonged exposure to high temperatures, are sufficiently
100 stable to be shipped and stored. Such compositions may be made up and shipped to a lens maker who may add them to bis(allyl carbonate) monomer in a lens fabricating process. According to an alternative exemplification, a solution of tungsten hexacarbonyl
105 in an olefinically unsaturated carboxylic acid monomer may be made up as described hereinbelow and added to bis(allyl carbonate) and thereafter shipped to a lens maker for use in a lens making process. According to a still further exemplification of the method of this invention, a solution of tungsten hexacarbonyl in an olefinically unsaturated carboxylic acid monomer may be made up as described hereinbelow and added to bis(allyl carbonate). A suitable dye, for example, CIBA-Geigy IRGASET yellow, may be added to the liquid composition in order to obtain a green polymerizate. Thereafter, the resulting liquid composition of tungsten hexacarbonyl, the olefinically unsaturated carboxylic acid monomer, the bis(allyl carbonate) monomer, and the dye, may be shipped to a lens maker for use in a lens making process.
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115
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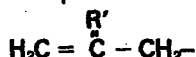
Tungsten hexacarbonyl is a known compound. Methods of preparation appear in the literature. See, for example, U.S. Patents 1,894,239 and 1,921,536.

125 Bis(allyl carbonate) monomers which may be used in the practice of this invention are normally liquid allyl carbonates, i.e., glycol bis(allyl carbonate) compounds, in which the allyl groups may be substituted at the 2 position with a halogen, notably
130 chlorine or bromine, of a 1 to 4 carbon alkyl group,

generally a methyl or ethyl group, and the glycol group may be an alkylene, alkylene ether, or alkylene polyether group having from 2 to 10 carbons and oxygens. These bis(allyl carbonate) monomers are represented by the formula:



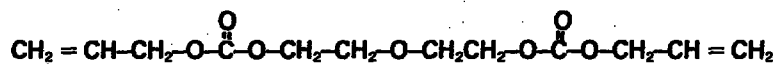
where R_1 and R_3 are allyl groups and R_2 is a glycol group. R_1 and R_3 are represented by the formula:



where R' may be hydrogen, halogen, or a 1 to 4 carbon alkyl group. Specific examples of R_1 and R_3 include allyl, 2-chloroallyl, 2-bromoallyl, 2-iodoallyl,

2-fluoroallyl, 2-methallyl, 2-ethylallyl, 2-isopropylallyl, 2-n-propylallyl, and 2-n-butylallyl groups. Most commonly, R_1 and R_3 are allyl groups, $H_2C = CH - CH_2-$. Such compounds and methods for making them are disclosed in U.S. Patents 2,370,567 and 2,403,113.

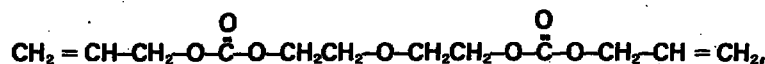
Specific examples of R_2 are alkylene groups such as ethylene, trimethylene, methylethylene, tet-



or

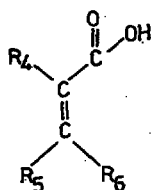


It is believed that all of the above-described bis(allyl carbonates) are useful in the practice of this

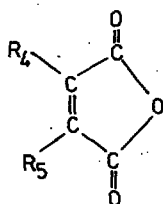


which has been tested and found useful. Diethylene glycol bis(allyl carbonate) is the preferred monomer for use in the practice of this invention.

Olefinically unsaturated carboxylic acid monomers which may be used in the practice of this invention are normally liquids with either α - β unsaturation or β - γ unsaturation. The acids with α - β unsaturation may be monocarboxylic or dicarboxylic and are represented by the formula:



where R_4 , R_5 , and R_6 may be hydrogen, a halogen, or an alkyl group of 1 to 4 carbon atoms, and either R_5 or R_6 , but not both of them, may be a carboxylic acid group. When R_6 is a carboxylic acid group, i.e., when the olefinically unsaturated carboxylic acid is a cis-decarboxylic acid, the acid may be utilized either as the acid or as the acid anhydride represented by the formula:



ramethylene, ethylethylene, pentamethylene, hexamethylene, 2-methylhexamethylene, octamethylene, and decamethylene groups, alkylene ether groups such as $-CH_2-O-CH_2-$, $-CH_2CH_2-O-CH_2CH_2-$, $-CH_2-O-CH_2CH_2-$, and $-CH_2CH_2CH_2-O-CH_2CH_2CH_2-$, and alkylene polyether groups such as $-CH_2CH_2-O-CH_2CH_2-O-CH_2CH_2-$ and $-CH_2-O-CH_2CH_2-O-CH_2-$ groups. Most commonly, R_2 is $-CH_2CH_2-$ or $-CH_2CH_2-O-CH_2CH_2-$.

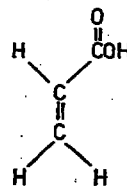
Specific examples of bis(allyl carbonate) monomers include ethylene glycol bis(2-chloroallyl carbonate), diethylene glycol bis(2-methallyl carbonate), triethylene glycol bis(allyl carbonate), proylene glycol bis(2-ethylallyl carbonate), 1,3-propanediol bis(allyl carbonate), 1,3-butanediol bis(allyl carbonate), 1,4-butanediol bis(2-bromoallyl carbonate), dipropylene glycol bis(allyl carbonate), trimethylene glycol bis(2-ethylallyl carbonate), and pentamethylene glycol bis(allyl carbonate).

Most commonly the bis(allyl carbonate) monomer moiety is:

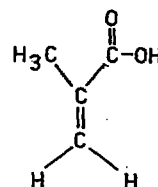
invention because of their similarity to diethylene glycol bis(allyl carbonate),

where R_4 and R_5 are as defined above.

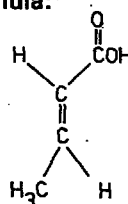
Specific examples of the α - β olefinically unsaturated carboxylic acids herein contemplated include monocarboxylic acids such as acrylic acid having the formula:



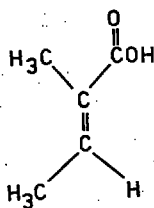
methacrylic acid having the formula:



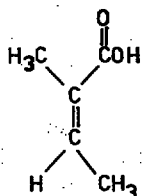
trans-2-butenic acid, also known as crotonic acid, and having the formula:



the two α -methyl crotonic acids, angelic acid,



and tiglic acid,

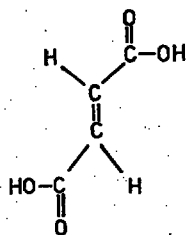


The preferred monocarboxylic acid is acrylic acid.

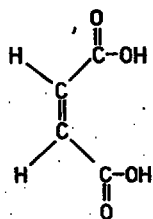
Specific examples of α - β olefinically unsaturated carboxylic acids herein contemplated also include

- 5 dicarboxylic acids and, in the case of *cis*-isomers, their acid anhydride forms. Such olefinically unsaturated dicarboxylic acids include the butenedioic acids such as butenedioic acid, methyl butenedioic acid, dimethyl butenedioic acid, itaconic acid; and aconitic acid, including both the *cis*-isomers and the *trans*-isomers.

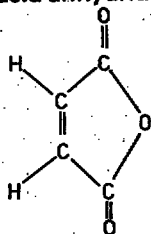
Thus, butenedioic acid may either be *trans*-butenedioic acid,



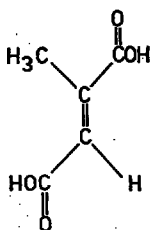
cis-butenedioic acid, i.e., maleic acid,



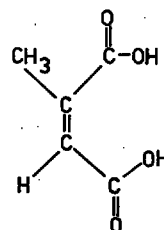
- 15 or *cis*-butenedioic acid anhydride, i.e., maleic anhydride,



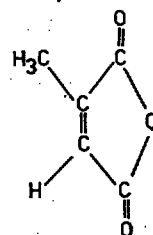
Methyl butenedioic acid may either be utilized in the method of this invention as *trans*-methyl butenedioic acid,



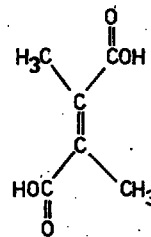
20 or *cis*-methyl butenedioic acid, i.e., citraconic acid,



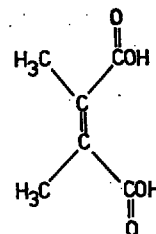
or *cis*-methyl butenedioic acid anhydride, i.e., citraconic acid anhydride,



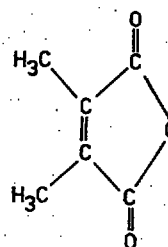
When the dicarboxylic acid is dimethyl butenedioic acid, the acid may be utilized in carrying out the 25 method of this invention as *trans*-dimethyl butenedioic acid,



cis-dimethyl butenedioic acid,



or *cis*-dimethyl butenedioic acid anhydride,



The preferred dicarboxylic acid having α - β unsaturation is maleic acid and its anhydride form, maleic acid anhydride.

The minimum amount of tungsten hexacarbonyl required to provide a permanent light absorbing coloration to the polymerizate where the tungsten hexacarbonyl has reacted with the acid prior to polymerization is generally above about 0.10 weight percent calculated as tungsten hexacarbonyl, basis total organics. Preferably, the amount of tungsten hexacarbonyl in the polymerizate is in excess of about 0.25 weight percent, calculated as described above, and up to the solubility limit of the tungsten hexacarbonyl in the acid, i.e., about 10 weight per-

cent of the acid, when the acid moiety is present in the polymerizate at up to about 25 weight percent of the total polymer. This is generally a tungsten content of about 2 to 3 weight percent tungsten hexacarbonyl, calculated as tungsten hexacarbonyl, basis total organics. Preferably, the concentration of tungsten hexacarbonyl in the polymerizate is from about 0.25 weight percent to about 1.0 weight percent, calculated as described above.

- 10 As herein contemplated, the tungsten hexacarbonyl is added to the acid in an amount up to the solubility limit of tungsten hexacarbonyl in the acid, i.e., up to about 10 weight percent tungsten hexacarbonyl, basis weight of the acid. In the case of maleic anhydride, amounts of tungsten hexacarbonyl greater than about 10 weight percent do not go into solution but remain as insoluble, solid particles. A 10 weight percent solution of tungsten hexacarbonyl in the unsaturated acid provides a polymerizate having less than about 2 to 3 weight percent tungsten hexacarbonyl.

The tungsten hexacarbonyl is added to the unsaturated acid, e.g., maleic acid, maleic acid anhydride, or acrylic acid. The composition of the unsaturated acid and the tungsten hexacarbonyl is then heated whereby to provide a color change. The composition is heated to above 95°C. and, if necessary, to between about 150°C and the boiling point of the liquid composition whereby to cause the liquid composition to become blue. The more severe the heating, that is, the longer that the composition is maintained at any given temperature and the higher the temperature for any given period of heating, the greater will be the degree of light absorbancy of the polymerizate produced thereby.

After the liquid composition of tungsten hexacarbonyl in the unsaturated acid has been heated to provide a blue colored liquid composition, the liquid composition may be filtered. The filtration serves to remove any undissolved tungsten hexacarbonyl.

After filtration, if any, the tungsten hexacarbonyl-unsaturated acid composition is added to the bis(allyl carbonate) whereby to form a reaction medium of acid, bis(allyl carbonate), and the tungsten compound.

The acid, i.e., the light absorbing, colored, normally blue liquid obtained by heating the liquid olefinically unsaturated carboxylic acid in the presence of tungsten hexacarbonyl at a temperature and for a time sufficient to obtain the blue liquid, e.g., at a temperature above about 95°C. for more than about 15 minutes, is added to the bis(allyl carbonate) in an amount sufficient to provide an acid content of up to about 25 weight percent and a tungsten content, calculated as tungsten hexacarbonyl, of from about 0.10 weight to about 3 weight percent, basis total organics, and preferably from about 0.25 weight percent to about 2 weight percent.

Additionally, in order to obtain an aesthetically pleasing polymerizate, for example, a green polymerizate, a small amount of yellow dye as an internal colorant may be added to the reaction medium. For example, from about 0.001 to about 0.01 weight percent of yellow dye provides a pleasing green clear polymerizate. One yellow dye useful

in providing a green polymerizate is CIBA-Geigy IRGASET yellow.

- Mixtures of bis(allyl carbonate) monomers and olefinically unsaturated carboxylic acid monomers containing tungsten hexacarbonyl, including tungsten hexacarbonyl reaction products, may be polymerized in the presence of heat, radiation, or catalysts such as organic peroxides, for example, diisopropyl peroxydicarbonate, di-sec-butyl peroxydicarbonate, lauroyl peroxide, and benzoyl peroxide, to yield photochromic polymerizates having a wide range of physical properties such as hardness, abrasion resistance, and impact resistance. Other monomers, such as vinyl acetate and methyl methacrylate, may be included in minor proportions, up to a total of about 25 weight percent, in order to obtain terpolymers having desired physical properties. Such terpolymers having at least about 75 weight percent of the described allyl glycol carbonate units are also believed to be useful in the practice of this invention, but it is preferred to use only the bis(allyl carbonates), particularly diethylene glycol bis(allyl carbonate), in combination with the tungsten hexacarbonyl and the olefinically unsaturated carboxylic acids, particularly maleic acid anhydride or acrylic acid.

The addition of tungsten hexacarbonyl and an olefinically unsaturated carboxylic acid monomer to bis(allyl carbonate) monomer requires little, if any, modification in the methods ordinarily used to effect polymerization of such bis(allyl carbonate) monomers. High concentrations of tungsten hexacarbonyl, e.g., above about 0.3 weight percent, or more may retard cure; but an increase in the concentration of polymerization catalyst, higher temperature, or a longer cure time may be used to reduce this effect. At concentrations up to about 0.1 percent, there is little, if any, retardation of cure. Thus, any known method of polymerizing these monomers may be used to polymerize the monomers having tungsten hexacarbonyl dissolved therein. U.S. Patents 2,403,113 and 3,222,432 describe useful methods.

Additionally, there may be present mold release agents in the mixture of monomers. Typical mold release agents include silicones, silanes, and alkyl phosphates. Particularly preferred are alkyl phosphates such as DuPont ORTHOLEUM® 162 mold release agent.

Typically, the monomers are polymerized in full, air tight molds because air retards polymerization. A free radical catalyst such as an organic peroxide or peroxy carbonate is dissolved in the monomer in a concentration of between about 0.1 and 10 weight percent, typically between about 2 and 5 weight percent, and the catalyzed monomer is heated to effect the desired degree of polymerization. Temperatures between about 30°C. and 120°C. and times between about 1 and 24 hours are generally employed. Heating may be at a constant temperature, at gradually increasing temperatures, or at stepwise increasing temperatures. Useful heat cycles for the polymerization of allyl diglycol carbonate are disclosed in Dial et al, Polymerization Control in casting a Thermosetting Resin, *Industrial and Engineering Chemistry*, Vol. 49, page 2447 (Dec., 1955).

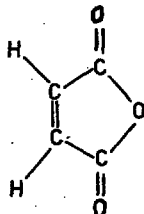
When in the green-colored state, the light absorbing polymerizates of this invention have low transmittance in the near infrared region from about 700 to about 2,000 nanometers and in the visible region from about 300 to about 700 nanometers.

The following examples illustrate how the present invention may be practiced. Although the examples describe polymerizates of diethylene glycol bis(allyl carbonate) and maleic acid anhydride, the methods described may be practiced with the use of the other allyl carbonate monomers and olefinically unsaturated carboxylic acid monomers, as well as mixtures thereof with third monomers.

Example I

Two diethylene glycol bis(allyl carbonate)-maleic acid anhydride copolymer sheets containing 0.50 and 0.25 weight percent tungsten hexacarbonyl were prepared and tested for light transmissivity.

A 5 weight percent composition of tungsten hexacarbonyl, $W(CO)_6$, in maleic acid anhydride,



was prepared. This composition was maintained at 95°C. for 16 hours, forming a clear, dark blue-green solution with a slight precipitate. The solution was then heated to about 150°C. for about 30 minutes until the precipitate disappeared.

The liquid composition of maleic acid anhydride-tungsten hexacarbonyl was divided into two portions and added to diethylene glycol bis(allyl carbonate). One solution contained 10 weight percent maleic acid anhydride-tungsten hexacarbonyl and 90 weight percent diethylene glycol bis(allyl carbonate), thereby providing a liquid composition containing about 0.5 weight percent tungsten hexacarbonyl. The other solution contained 5 weight percent maleic acid anhydride-tungsten hexacarbonyl, thereby providing a liquid composition containing about 0.25 weight percent tungsten hexacarbonyl. Sufficient isopropyl peroxy dicarbonate initiator was added to both solutions to provide a total initiator content of 3.5 weight percent, basis total monomers, additives, and initiator.

The two solutions were then poured into 4 inch by 7 inch by 0.25 inch glass molds, formed of two sheets of glass separated by a 0.25 inch thick gasket. Upon heating of the molds, both liquids changed color from blue to green. The two molds were heated according to the following temperature sequence:

Cure Cycle

Elapsed time (hours)	Temperature °C.
0	42
2	44
4	45
6	46
8	47
10	48
12	50
14	52
16	54.5
18	57
20	61
22	69
23	79
24	98
24.1	100

During curing, both samples changed color from green to near water-white. After curing, both samples were removed from the molds.

The samples were then tested for percent transmission of 550 nanometer wave length green light by a sequence of exposure to a Fadeometer® carbon arc lamp followed by measurement of transmission during exposure and after dark storage. The following results were obtained:

Percent Transmission of 550 Nanometer Light

Preparation of sample

Weight percent maleic anhydride in original liquid composition	10%	5%
Weight percent tungsten hexacarbonyl in original liquid composition	0.5%	0.25%

Light transmission during exposure of Fadeometer®

0 minutes	72	84
30 minutes	32	57
60 minutes	26	51

Light transmission after exposure to Fadeometer® and storage in dark for the time shown

16 hours	28	54
4 days	30	57
8 days	31	58
12 days	34	60.5
14 days	34	62
27 days	39	65
40 days	41	67

Example II

A series of tests were conducted to determine the

effect of the method of incorporation of the tungsten hexacarbonyl into the diethylene glycol bis(allyl carbonate)-maleic anhydride copolymer.

- Two solutions of tungsten hexacarbonyl in monomer were prepared. One solution contained 0.04 grams of tungsten in 40 grams of diglycol bis(allyl carbonate). The second solution contained 1.25 grams of tungsten hexacarbonyl in 25 grams of maleic anhydride. Both solutions were heated at 95°C. for 16 hours. All of the tungsten hexacarbonyl in the first solution dissolved. The second solution was then heated to 155°C. for about 5 minutes and all of the tungsten hexacarbonyl dissolved.

- The solutions were then mixed, as shown in the table below, sufficient isopropyl peroxy dicarbonate initiator was added to each solution to provide a total initiator content of 3.5 weight percent, basis total monomer, additive, and initiator, and poured into 4 inch by 7 inch by 0.25 inch molds formed of two sheets of glass separated by a 0.125 inch thick gasket. The molds were then heated according to the following temperature sequence:

Cure Cycle	
Elapsed Time (hours)	Temperature °C.
0	42
2	44
4	45
6	46
8	47
10	48
12	50
14	52
16	54.5
18	57
20	61
22	69
23	79
24	98
24.1	100

The samples were then tested for percent transmission of 550 nanometer wave length green light after exposure to a Fadeometer® carbon arc lamp with measurement of transmission during exposure and after dark storage. The following results were obtained:

Percent Transmission of 550 Nanometer Light

Preparation of solutions

Grams of solution of 0.04 grams tungsten hexacarbonyl, 40 grams of diethylene glycol bis(allyl carbonate)	20	20	0
Grams of solution of 1.25 grams of tungsten hexacar- bonyl, 25 grams of maleic acid anhydride	—	2	2
Grams of diethylene glycol bis(allyl carbonate) with out additive	—	—	20

Composition of materials in molds

Diglycol bis(allyl carbonate), grams	20	20	20
Maleic anhydride, grams	—	2	2
Tungsten hexacarbonyl, grams	0.02	0.12	0.1

Light transmission during exposure to Fadeometer® carbon arc lamp

0 minutes	89	35	35
30 minutes	66	10	10
60 minutes	59	6	6

Light transimission after exposure to Fadeometer® carbon arc lamp and dark storage for indicated time

2 days	62	8	7
8 days	63	10	9
21 days	75	13	12
34 days	79	15	14

Example III

A series of tests were conducted to determine the effect of the preparation of the tungsten hexacarbonyl-maleic acid anhydride on the final maleic acid anhydride-diethylene glycol bis(allyl carbonate) copolymer.

- 5 A 5 weight percent solution of tungsten hexacarbonyl in maleic anhydride was prepared. The solution was heated over one hour to 150°C. and maintained thereat with continuous stirring and total reflux in an Erlenmeyer Flask. Samples were then taken periodically, as shown in the table, added to diglycol bis(allyl carbonate), initiated with 3.5 weight percent isopropyl peroxydicarbonate initiator, and placed in a 4 inch by 7 inch by 0.25 inch glass mold. The mold was then heated according to the following temperature sequence:

Cure Cycle

Elapsed Time (hours)	Temperature °C.
0	42
2	44
4	45
6	46
8	47
10	48
12	50
14	52
16	54.5
18	57
20	61
22	69
23	79
24	98
24.1	100

The results shown below were obtained:

Appearance of Solution and Castings

Elapsed Time Since Heating Commenced	Time at 150°C.	Solution	Casting
2	1	blue	green-gray
3	2	dark blue	light blue-gray
4	3	dark blue	blue-gray
5	4	dark blue with precipitate	blue-gray (hazy)
6	5	dark blue with precipitate	blue-gray (hazy)

Example IV

- 20 A green casting was formed by copolymerizing ethylene diglycol bis(allyl carbonate) and maleic acid anhydride in the presence of tungsten hexacarbonyl and IRGASET yellow.

- 25 A 5 weight percent solution of tungsten hexacarbonyl in maleic anhydride was prepared. This solution was heated over a period of one hour to 150°C. and maintained at 150°C. for 5 hours in an Erlenmeyer Flask with continuous stirring and total reflux. One part of the above maleic anhydride-tungsten

- hexacarbonyl solution was mixed with four parts of ethylene diglycol bis(allyl carbonate). Sufficient CIBA-Geigy IRGASET yellow dye was added to provide 0.007 weight percent dye and sufficient dioctyl phthalate release agent was added to provide 100 parts per million release agent. The reaction mixture, containing sufficient isopropyl peroxydicarbonate to provide a 3.5 weight percent initiator was then placed in a mold and cured according to the following cycle:

Cure Cycle

Elapsed Time (hours)	Temperature, °C.
0	42
2	44
4	45
6	46
8	47
10	48
12	50
14	52
16	54.5
18	57
20	61
22	69
23	79
24	98
24.1	100

- 40 The resulting casting had a deep green color. After exposure to a Fadeometer® carbon arc for 55 minutes, it had 550 nanometer green light transmission of only 15 percent.

- 45 The casting was then analyzed on a Cary Spectrophotometer and exhibited the following transmission characteristics:

Wavelength (NM)	% Transmission
350	4
400	16
500	18
550	15
600	13
700	6
800	3
900	2
1000	2
1100	2
1200	6
1300	6
1400	10
1500	19
1600	24
1650	25
1700	13
1800	24
1875	31
1900	24
2000	40
2100	26

Example V

A series of tests were conducted to determine the effect of lubricants and release agents on copolymers of maleic acid anhydride-diethylene glycol bis(allyl carbonate).

A reaction mixture of 7.5 weight percent maleic acid anhydride, 0.42 weight percent tungsten hexacarbonyl, 4.2 weight percent isopropyl peroxydicarbonate and balance ethylene diglycol bis(allyl carbonate) was prepared. This was divided into eight samples. The mold release agents were added in the amount shown below. The samples were then cured according to the following time temperature sequence:

Cure Cycle

Elapsed Time (hours)	Temperature, °C.
0	42
2	44
4	45
6	46
8	47
10	48
12	50
14	52
16	54.5
18	57
20	61
22	69
23	79
24	98
24.1	100

Effect of Release Agent on Properties

Name	Release Agent Concentration	Barcol Hardness	Percent Transmission			Appearance	Release (qualitative)
			1 day	3 days	12 days		
DOP	100 ppm	31-26	12	14	17	Light blue-green	Difficult
	1000 ppm	29-24	11	14	17	Light blue-green	Medium
Ortholwum® 162	100 ppm	32-27	11	13	16	Light blue-green	Fair
	1000 ppm	31-26	7	7	8	Blue	Easy
Ortholeum® 535	100 ppm	32-27	11	13	16	Light blue-green	Easy
	1000 ppm	34-29	11	13	15	Light blue	Pre-released
Silane 174	100 ppm	30-26	13	16	20	Green-brown	Medium
	1000 ppm	30-24	20	22	26	Brown	Difficult

Example VI

A lens was prepared by copolymerizing ethylene diglycol bis(allyl carbonate) and maleic acid anhydride in the presence of tungsten hexacarbonyl and DuPont Ortholeum® 162 alkyl phosphate mold release agent.

A 5 weight percent solution of tungsten hexacarbonyl in maleic acid anhydride was prepared by adding 0.5 gram of tungsten hexacarbonyl to 10.0

Thereafter the castings were exposed to a Fadeometer® carbon arc lamp for one hour and the 550 nanometer transmissions shown in the table were obtained. The castings were also tested for initial and 15 second Barcol hardness reading and the values shown in the table were obtained.

30 grams of maleic acid anhydride. This solution was heated to 150°C. for three hours with total reflux. The resulting deep blue solution was then added to 90.0 grams of diethylene glycol bis(allyl carbonate). Thereafter, 0.75 gram of DuPont Ortholeum® 162 alkyl phosphate mold release agent was added to the composition. The composition was then cooled to room temperature, about 20 grams of silica gel was added to dry the composition. The composition

was stirred for 20 minutes and then filtered through No. 40 paper.

The filtrate was allowed to stand under vacuum for 15 minutes. Sufficient isopropyl peroxydicarbonate 5 was added to provide an initiator content of 4 weight percent. The composition was then divided into four portions and placed into four lens molds.

The four portions were heated to 37°C. for 1-1/2 hours and thereafter cured according to the following cycle:

Cure Cycle

Elapsed Time (hours)	Temperature, °C.
1-1/2	42
3-1/2	44
5-1/2	45
7-1/2	46
9-1/2	47
11-1/2	48
13-1/2	50
15-1/2	52
17-1/2	54.5
19-1/2	57
21-1/2	61
23-1/2	69
24-1/2	79
25-1/2	98
25.6	100

Four blue lenses were produced.

Example VII

A lens was prepared by copolymerizing ethylene diglycol bis(allyl carbonyl) and maleic acid anhydride in the presence of tungsten hexacarbonyl, 15 IRGASET yellow and DuPont Ortholeum® 162 alkyl phosphate mold release agent.

A 5 weight percent solution of tungsten hexacarbonyl in maleic acid anhydride was prepared by adding 1.0 grams of tungsten hexacarbonyl to 20.0 grams of maleic acid anhydride. This solution was heated to 150°C. for three hours with total reflux resulting in a deep blue solution.

CIBA-Geigy IRGASET yellow (0.007 gram) and 0.075 gram of DuPont Ortholeum® 162 alkyl phosphate mold release agent were added to 90.0 grams of diethylene glycol bis(allyl carbonate). Ten grams of the 5 weight tungsten hexacarbonyl-maleic acid anhydride was then added to the diglycol bis(allyl carbonate). The composition was then cooled to room temperature and about 20 grams of silica gel was added to dry the composition. The composition was stirred for 20 minutes and then filtered through No. 40 paper.

The filtrate was allowed to stand under vacuum for 15 minutes. Sufficient isopropyl peroxydicarbonate was added to provide an initiator content of 4 weight percent. The composition was then divided into four portions and placed into four lens molds.

The four portions were heated to 37°C. for two hours and thereafter cured according to the following cycle:

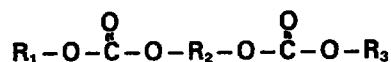
Cure Cycle

Elapsed Time (hours)	Temperature, °C.
2	42
4	44
6	45
8	46
10	47
12	48
14	50
16	52
18	54.5
20	57
22	61
24	69
25	79
26	98
26.1	100

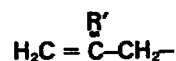
Four green lenses were produced.

CLAIMS

1. A light absorbing liquid composition provided by heating an olefinically unsaturated carboxylic acid in the presence of tungsten hexacarbonyl.
2. A liquid composition as claimed in claim 1 wherein the olefinically unsaturated acid is chosen from the group consisting of maleic acid, maleic acid anhydride, and acrylic acid.
3. A polymerizate of an olefinically unsaturated carboxylic acid and a bis(allyl carbonate) containing a light absorbing component provided by tungsten hexacarbonyl.
4. A polymerizate as claimed in claim 3 wherein the bis(allyl carbonate) is represented by the formula:

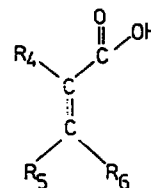


where R_1 and R_3 are allyl groups represented by the formula:



where R' is H, a halogen, or a 1 to 4 carbon alkyl group and R_2 is a group derived from a glycol.

5. A polymerizate as claimed in claim 4 wherein the bis(allyl carbonate) is diethylene glycol bis(allyl carbonate).
6. A polymerizate as claimed in claim 3, 4 or 5 wherein the olefinically unsaturated carboxylic acid is represented by the formula:



where R_4 , R_5 , and R_6 are hydrogen, halogen, or alkyl groups of 1 to 4 carbon atoms and where either R_5 or R_6 may be a carboxylic acid group.

7. A polymerizate as claimed in claim 6 wherein the olefinically unsaturated acid is acrylic acid, maleic acid, or maleic acid anhydride.
8. A polymerizate as claimed in any one of claims



was stirred for 20 minutes and then filtered through No. 40 paper.

The filtrate was allowed to stand under vacuum for 15 minutes. Sufficient isopropyl peroxydicarbonate 5 was added to provide an initiator content of 4 weight percent. The composition was then divided into four portions and placed into four lens molds.

The four portions were heated to 37°C. for 1-1/2 hours and thereafter cured according to the following cycle:

Cure Cycle

Elapsed Time (hours)	Temperature, °C.
1-1/2	42
3-1/2	44
5-1/2	45
7-1/2	46
9-1/2	47
11-1/2	48
13-1/2	50
15-1/2	52
17-1/2	54.5
19-1/2	57
21-1/2	61
23-1/2	69
24-1/2	79
25-1/2	98
25.6	100

Four blue lenses were produced.

Example VII

A lens was prepared by copolymerizing ethylene diglycol bis(allyl carbonyl) and maleic acid anhydride in the presence of tungsten hexacarbonyl, 15 IRGASET yellow and DuPont Ortholeum® 162 alkyl phosphate mold release agent.

A 5 weight percent solution of tungsten hexacarbonyl in maleic acid anhydride was prepared by adding 1.0 grams of tungsten hexacarbonyl to 20.0 20 grams of maleic acid anhydride. This solution was heated to 150°C. for three hours with total reflux resulting in a deep blue solution.

CIBA-Geigy IRGASET yellow (0.007 gram) and 0.075 gram of DuPont Ortholeum® 162 alkyl phosphate mold release agent were added to 90.0 grams of diethylene glycol bis(allyl carbonate). Ten grams of the 5 weight tungsten hexacarbonyl-maleic acid anhydride was then added to the diglycol bis(allyl carbonate). The composition was then cooled to 30 room temperature and about 20 grams of silica gel was added to dry the composition. The composition was stirred for 20 minutes and then filtered through No. 40 paper.

The filtrate was allowed to stand under vacuum for 35 15 minutes. Sufficient isopropyl peroxydicarbonate was added to provide an initiator content of 4 weight percent. The composition was then divided into four portions and placed into four lens molds.

The four portions were heated to 37°C. for two 40 hours and thereafter cured according to the following cycle:

Cure Cycle

Elapsed Time (hours)	Temperature, °C.
2	42
4	44
6	45
8	46
10	47
12	48
14	50
16	52
18	54.5
20	57
22	61
24	69
25	79
26	98
26.1	100

Four green lenses were produced.

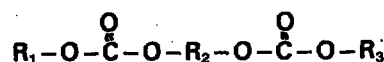
CLAIMS

1. A light absorbing liquid composition provided by heating an olefinically unsaturated carboxylic acid in the presence of tungsten hexacarbonyl. 45

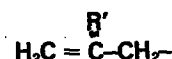
2. A liquid composition as claimed in claim 1 wherein the olefinically unsaturated acid is chosen from the group consisting of maleic acid, maleic acid anhydride, and acrylic acid.

3. A polymerizate of an olefinically unsaturated carboxylic acid and a bis(allyl carbonate) containing a light absorbing component provided by tungsten hexacarbonyl. 50

4. A polymerizate as claimed in claim 3 wherein the bis(allyl carbonate) is represented by the formula: 55



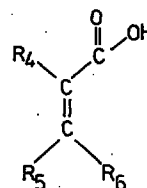
where R_1 and R_3 are allyl groups represented by the formula: 60



where R' is H, a halogen, or a 1 to 4 carbon alkyl group and R_2 is a group derived from a glycol.

5. A polymerizate as claimed in claim 4 wherein the bis(allyl carbonate) is diethylene glycol bis(allyl carbonate). 65

6. A polymerizate as claimed in claim 3, 4 or 5 wherein the olefinically unsaturated carboxylic acid 70 is represented by the formula:



where R_4 , R_5 , and R_6 are hydrogen, halogen, or alkyl groups of 1 to 4 carbon atoms and where either R_5 or R_6 may be a carboxylic acid group.

7. A polymerizate as claimed in claim 6 wherein the olefinically unsaturated acid is acrylic acid, maleic acid, or maleic acid anhydride. 75

8. A polymerizate as claimed in any one of claims

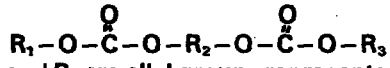
23



3 to 7 comprising from 0.10 to 3 weight percent tungsten, calculated as tungsten (hexacarbonyl), basis total organics, up to 25 weight percent acid, and balance bis(allyl carbonate).

- 5 9. A method of preparing a light absorbing polymerizate comprising:
heating a liquid, olefinically unsaturated carboxylic acid in the presence of tungsten hexacarbonyl to form a light absorbing liquid;
- 10 adding the light absorbing liquid to bis(allyl carbonate) and
polymerizing the light absorbing liquid and the bis(allyl carbonate).

10. A method as claimed in claim 9 wherein the
- 15 bis(allyl carbonate) is represented by the formula:



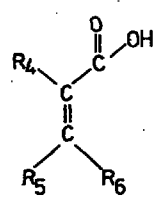
where R₁ and R₃ are allyl groups represented by the formula:

- 20
$$H_2C = \overset{\overset{R'}{\mid}}{C} - CH_2 -$$

where R' is H, a halogen, or a 1 to 4 carbon alkyl group.

11. A method as claimed in claim 10 wherein the
- 25 bis(allyl carbonate) is diethylene glycol bis(allyl carbonate).

12. A method as claimed in claim 9, 10 or 11 wherein the olefinically unsaturated carboxylic acid is represented by the formula:



- 30 where R₄, R₅, and R₆ are hydrogen, halogen, or alkyl groups of 1 to 4 carbon atoms and where wither R₅ or R₆ may be a carboxylic acid group.

13. A method as claimed in claim 12 wherein the olefinically unsaturated acid is chosen from the
- 35 group consisting of acrylic acid, maleic acid, and maleic acid anhydride.

14. A liquid composition as claimed in claim 1 and substantially as hereinbefore described with reference to any one of the Examples.

- 40 15. A polymerizate as claimed in claim 3 and substantially as hereinbefore described with reference to any one of the Examples.

16. A method as claimed in claim 9 and substantially as hereinbefore described with reference to
- 45 any one of the Examples.