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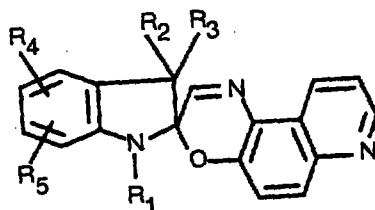
Description

The present invention relates to novel photochromic compounds, and to compositions and articles containing such photochromic compounds. Photochromism is a reversible phenomenon illustrated by a compound which, when exposed to the radiation of light involving ultraviolet rays such as sunlight or the light of a mercury lamp, changes color and then returns to its original color if the radiation is discontinued or the compound is stored in the dark. A compound illustrating this property is called a "photochromic compound".

Various types of photochromic compounds have been synthesized and suggested for use in applications in which a color change or darkening is induced by sunlight. In particular, spiro(indoline)naphthoxazine compounds, as described in U.S. Patents 3,562,172, 3,578,602, 4,215,010, and 4,342,668, show particular advantages for sunglasses and ophthalmic lenses.

Such photochromic compounds either in crystalline form or in a solution or dispersion in a transparent medium change rapidly from a colorless state to blue when exposed to sunlight or ultraviolet radiation and return to the original colorless state by being allowed to stand in the dark or in the absence of strong ultraviolet radiation.

In accordance with the present invention, there are provided novel photochromic compounds represented by the following formula



In the above formula I, R_1 is selected from the group consisting of C_1-C_8 alkyl, phenyl, phen(C_1-C_4)-alkyl, allyl and mono- and disubstituted phenyl, said phenyl substituents being selected from C_1-C_4 alkyl and C_1-C_5 alkoxy. Preferably, R_1 is a C_1-C_4 alkyl, phenyl or benzyl radical.

R_2 and R_3 of formula I are each selected from the group consisting of C_1-C_8 alkyl, phenyl, mono- and disubstituted phenyl, benzyl or combine to form a cyclic ring selected from the group consisting of an alicyclic ring containing from 6 to 8 carbon atoms (including the spiro carbon atom), norbornyl and adamantyl. The phenyl substituents may be selected from C_1-C_4 alkyl and C_1-C_5 alkoxy radicals. Preferably, R_2 and R_3 are each selected from C_1-C_5 alkyl. When one of R_2 or R_3 is a tertiary alkyl radical, such as tertiary butyl or tertiary amyl, the other is preferably an alkyl radical other than a tertiary alkyl radical.

R_4 and R_5 in formula I are each selected from the group consisting of hydrogen, C_1-C_8 alkyl, halogen, C_1-C_5 alkoxy, nitro, cyano and C_1-C_8 alkoxy carbonyl. R_4 and R_5 can be presented on any two of the available carbon atoms of the indolino portion of the compound, i.e., on the 4, 5, 6, or 7 positions. Preferably, when the substituents are other than hydrogen, they are present at the 4 and 5, 5 and 6, 4 and 7 or 6 and 7 carbon atoms of the indolino moiety. While any halogen, e.g., chlorine, bromine, iodine and fluorine can be used, chlorine and bromine, especially chlorine is preferred. Preferably, R_4 and R_5 are selected from the group consisting of hydrogen, C_1-C_2 alkyl, chlorine, bromine, and C_1-C_5 alkoxy.

Of particular interest, are photochromic compounds represented by graphic formula I wherein R_1 is a C_1-C_4 alkyl, such as methyl, ethyl, n-propyl, isopropyl, n-butyl, secondary butyl, isobutyl and tertiary butyl; R_2 and R_3 are each methyl, ethyl or phenyl; and R_4 and R_5 are each hydrogen, methyl, methoxy, or chloro.

The photochromic compounds of the present invention can be dissolved in common organic solvents such as benzene, toluene, chloroform, ethylacetate, methyl ethyl ketone, acetone, ethyl alcohol, methyl alcohol, acetonitrile, tetrahydrofuran, dioxane, methyl ether of ethylene glycol, dimethylformamide, dimethylsulfoxide, methyl Cellosolve, morpholine, and ethylene glycol. The compounds can also be dispersed in liquids containing water, alcohols and other solvents.

The amount of solvent used to dissolve the photochromic compound should be sufficient to provide a photochromic composition, which, when applied to a host material, will provide a photochromic amount of the compound in the host material.

The photochromic compounds of the present invention can also be dissolved in colorless or transparent solutions prepared from transparent polymers, copolymers or blends of such transparent polymers and a suitable organic solvent, e.g., polymers of transparent host materials described hereinafter dissolved in one or more of the aforesaid described organic solvents. Examples of such solutions include a polyvinylacetate-acetone solution, a nitrocellulose-acetonitrile solution, a polyvinylchloride-methyl ethyl ketone solution, a polymethylmethacrylate-acetone solution, a cellulose acetate-dimethylformamide solution, a polyvinylpyrrolidone-acetonitrile solution, a polystyrene-benzene solution, and an ethyl cellulose-methylene chloride solution.

The aforesaid photochromic solutions or compositions can be applied to a transparent support, such as cellulose triacetate, polyethylene terephthalate or baryta paper and dried to obtain a photochromic

material, which may be color formed by ultraviolet radiation to blue, and returned to colorless by removing the source of ultraviolet radiation.

The photochromic compounds of the present invention or compositions containing same can be applied to or incorporated within a solid transparent polymerized organic material, i.e., a synthetic plastic host material. Preferably, the host material is an optically clear material, e.g., materials suitable for ophthalmic elements, such as ophthalmic lenses or materials useful for applications such as windows or windshields. A host material containing the photochromic compounds of the present invention can be used in the preparation of photochromic plastic films, sheets and lenses, such as lenses for sunglasses, ski goggles, visors, camera lenses and filters. As used herein, the term "optical element" is meant to include lenses and transparencies.

Examples of transparent host materials which can be used with the photochromic compounds of the present invention include: polymers of polyol(allyl carbonate)-monomers, polyacrylates, poly(alkyl-acrylates) such as polymethylmethacrylates; cellulose acetate, cellulose triacetate, cellulose acetate propionate, cellulose acetate butyrate, poly(vinyl acetate), poly(vinyl alcohol), polyurethanes, polycarbonates, polyethyleneterephthalate, polystyrene, poly(styrene-methylmethacrylate) copolymers, polystyrene-acrylonitrile copolymer, and polyvinylbutyral. Transparent copolymers and blends of the transparent polymers are also suitable as host materials. Preferably, the host material is an optically clear polymerized organic material prepared from a polycarbonate, such as poly(4,4'-dioxydiphenol-2,2-propane), which is sold under the trademark, LEXAN; a polymethylmethacrylate, such as the material sold under the trademark, PLEXIGLAS; a polyol(allyl carbonate), especially diethylene glycol bis(allyl carbonate), which is sold under the trademark, CR-39, and its copolymers with for example vinyl acetate, e.g., copolymers of from 80-90 percent diethylene glycol bis(allyl carbonate) and 10-20 percent vinyl acetate; particularly 80-85 percent of the bis(allyl carbonate) and 15-20 percent vinyl acetate, cellulose acetate, cellulose propionate, cellulose butyrate, polystyrene and its copolymers with methyl methacrylate, vinyl acetate and acrylonitrile, and cellulose acetate butyrate.

Polyol(allyl carbonate) monomers which can be polymerized to form a transparent host material are the allyl carbonates of linear or branched aliphatic or aromatic liquid polyols, e.g., aliphatic glycol bis(allyl carbonate) compounds, or alkylidene bisphenol bis(allyl carbonate) compounds. These monomers can be described as unsaturated polycarbonates of polyols, e.g., glycols. The monomers can be prepared by procedures well known in the art, e.g., U.S. Patents 2,370,567 and 2,403,113.

The polyol (allyl carbonate) monomers can be represented by the formula:



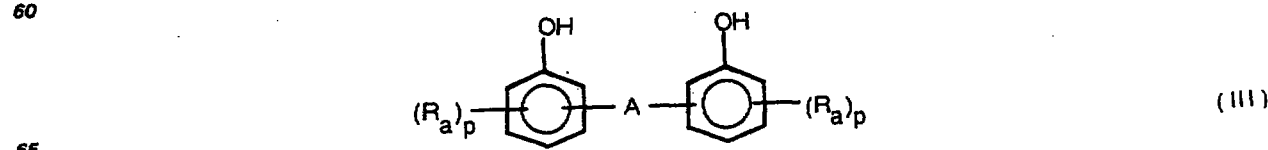
wherein R is the radical derived from an unsaturated alcohol and is commonly an allyl or substituted allyl group, R' is the radical derived from the polyol, and n is a whole number from 2-5, preferably 2. The allyl group (R) can be substituted at the 2 position with a halogen, most notably chlorine or bromine, or an alkyl group containing from 1 to 4 carbon atoms, generally a methyl or ethyl group. The R group can be represented by the formula:



wherein R₀ is hydrogen, halogen, or a C₁-C₄ alkyl group. Specific examples of R include the groups: allyl, 2-chloroallyl, 2-bromoallyl, 2-fluoroallyl, 2-methallyl, 2-ethylallyl, 2-isopropylallyl, 2-n-propylallyl, and 2-n-butylallyl. Most commonly, R is the allyl group, H₂C=CH-CH₂-.

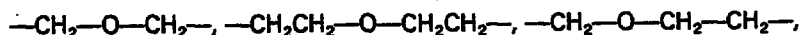
R' is a polyvalent radical derived from the polyol, which can be an aliphatic or aromatic polyol that contains 2, 3, 4 or 5 hydroxy groups. Typically, the polyol contains 2 hydroxy groups, e.g., a glycol or bisphenol. The aliphatic polyol can be linear or branched and contain from 2 to 10 carbon atoms. Commonly, the aliphatic polyol is an alkylene glycol having from 2 to 4 carbon atoms or a poly(C₂-C₄) alkylene glycol, i.e., ethylene glycol, propylene glycol, trimethylene glycol, tetramethylene glycol, or diethylene glycol, triethylene glycol, etc.

The aromatic polyol can be represented by the formula:

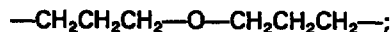


wherein A is a bivalent radical derived from an acyclic aliphatic hydrocarbon, e.g., an alkylene or alkylidene radical, having from 1 to 4 carbon atoms, e.g., methylene, ethylene, dimethylmethylene (isopropylidene), R_a represents lower alkyl substituents of from 1 to 3 carbon atoms, and p is 0, 1, 2, or 3. Preferably, the hydroxyl group is in the ortho or para position.

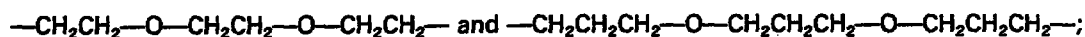
Specific examples of the radical R' include: alkylene groups containing from 2 to 10 carbon atoms such as ethylene, (—CH₂—CH₂—) trimethylene, methylethylene, tetramethylene, ethylethylene, pentamethylene, hexamethylene, 2-methylhexamethylene, octamethylene, and decamethylene; alkylene ether groups such as



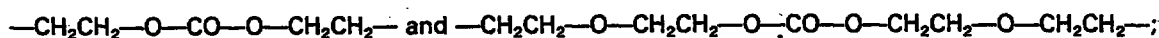
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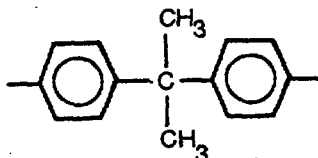
alkylene polyether groups, such as



alkylene carbonate and alkylene ether carbonate groups such as

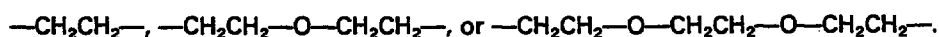


and isopropylidene bis(para-phenyl), i.e.,



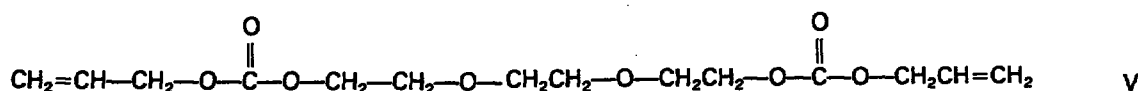
IV

Most commonly, R' is

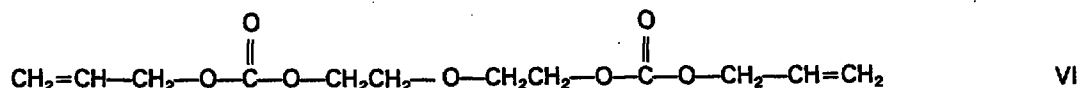


Specific examples of polyol (allyl carbonate) monomers include ethylene glycol bis(2-chloroallyl carbonate), ethylene glycol bis(allyl carbonate), diethylene glycol bis(2-methallyl carbonate), diethylene glycol bis(allyl carbonate), triethylene glycol bis(allyl carbonate), propylene glycol bis(2-ethylallyl 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), pentamethylene glycol bis(allyl carbonate), and isopropylidene bisphenol bis(allyl carbonate).

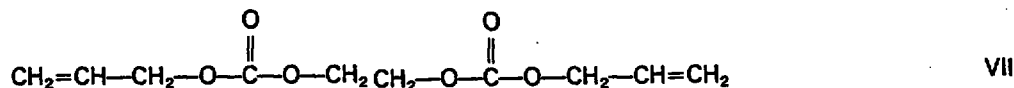
Industrially important polyol bis(allyl carbonate) monomers which can be utilized in the invention herein contemplated are:



Triethylene Glycol bis(Allyl Carbonate)



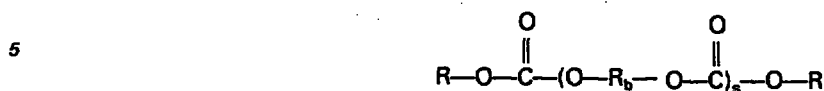
Diethylene Glycol bis(Allyl Carbonate) and



Diethylene glycol bis(allyl carbonate) is preferred.

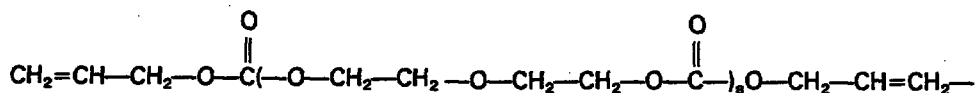
Because of the process by which the polyol(allyl carbonate) monomer is prepared, i.e., by phosgenation of the polyol (or allyl alcohol) and subsequent esterification by the allyl alcohol (or polyol), the monomer product can contain related monomer species in which the moiety connecting the allyl

carbonate groups contains one or more carbonate groups. These related monomer species can be represented by the formula:



VIII

wherein R is as defined above, R_b is a bivalent radical, e.g., alkylene or phenylene, derived from a diol, and s is a whole number from 2 to 5. The related monomer species of diethylene glycol bis(allyl carbonate) can be represented by the formula,



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wherein s is a whole number from 2 to 5. The polyol (allyl carbonate) monomer can typically contain from 2 to 20 weight percent of the related monomer species and such related monomer species can be present as mixtures, i.e., mixtures of the species represented by s being equal to 2, 3, 4 etc.

In addition, a partially polymerized form of the polyol (allyl carbonate) monomer can be used. In that embodiment, the monomer is thickened by heating or partially polymerized by using small, e.g., 0.5—1.5 parts of initiator per hundred parts of monomer (phm) to provide a non-gel containing, more viscous monomeric material.

As used in the present description and claims, the term polyol (allyl carbonate) monomer or like names, e.g., diethylene glycol bis(allyl carbonate), are intended to mean and include the named monomer or prepolymer and any related monomer species contained therein.

The amount of the photochromic compound or composition-containing same applied to or incorporated into the host material is not critical and depends generally upon the intensity of the color of the composition desired upon irradiation thereof and upon the method used to incorporate or apply the photochromic compound. Typically, the more compound added, the greater the color intensity. Generally such amount can be described as a photochromic amount. Usually, the amount of photochromic compound incorporated into the host material ranges from 0.01 to 20 percent by weight, more usually from 0.05 to 10 percent by weight, based on the weight of the host material. Stated another way, the amount of photochromic compound used to impart a photochromic effect will typically vary from 1 to 10 milligrams of the photochromic compound per 6.45 cm² of the surface of the host material independent of the thickness of the host material article. Hence, the photochromic compound is present in a higher concentration in thin samples, films, or coatings, and in a lower concentration in thick samples.

Solutions of the photochromic compounds of the present invention in ethanol are typically colorless or pale yellow, green or blue. These solutions undergo a rapid change in color to purple or blue upon exposure to ultraviolet radiation and return to their original color or colorless state upon removal of the source of ultraviolet radiation. Such color change may be repeated numerous times.

The photochromic compounds or compositions of the present invention can be applied to or incorporated into a host material by methods known in the art. Such methods include dissolving or dispersing the compound in the host material, i.e., imbibition of the photochromic compound in the host material, by immersion, thermal transfer, or coating, and incorporation of the photochromic compound as a separate layer between adjacent layers of the host material. The term "imbibition" or "imbibe" is intended to mean and include diffusion of the photochromic compound alone into the host material, solvent assisted diffusion, absorption of the photochromic compound into a porous polymer, vapor phase transfer, and other such transfer mechanisms. For example:

- (a) The photochromic compounds or compositions of the present invention can be mixed with a polymerizable composition that, upon curing, produces an optically clear polymeric host material and the polymerizable composition cast as a film, sheet or lens, or injection molded or otherwise formed into a sheet or lens;
- (b) The photochromic compounds of the present invention can be dissolved or dispersed in water, alcohol or other solvents or solvent mixtures and then imbibed into the solid host material by immersion for from several minutes to several hours, e.g., 2—3 minutes to 2—3 hours of the host material in a bath of such solution or dispersion. The bath is conventionally at an elevated temperature, usually in the range of 50—120°C. Thereafter, the host material is removed from the bath and dried;
- (c) The photochromic compounds and compositions may also be applied to the surface of the host material by any convenient manner, such as spraying, brushing, spin-coating or dip-coating from a solution or dispersion of the photochromic material in the presence of a polymeric binder. Thereafter, the photochromic compound is imbibed by the host material by heating it, e.g., in an oven, for from a minute to several hours at temperatures in the range from 80—180°C;
- (d) In a variation of the above imbibition procedure, the photochromic compound or composition can be deposited onto a temporary support, e.g., a sheet of craft paper, aluminum foil, polymer film or fabric, which is then placed in contact with the host material and heated, e.g., in an oven;

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- (e) The photochromic compounds can be dissolved or dispersed in a transparent polymeric material which can be applied to the surface of the host in the form of an adherent film by any suitable technique such as spraying, brushing, spin-coating or dip-coating; and
- (f) Finally, the photochromic compounds can be incorporated or applied to a transparent polymeric material by any of the above-mentioned methods, which can then be placed within the host material as a discrete layer intermediate to adjacent layers of the host material.

The photochromic compounds of the present invention can be synthesized by reaction of the corresponding nitroso-hydroxy quinoline compound with the corresponding indolines (Fischer's base) or indolium salt, e.g., the iodide salt, compound. The two precursor materials are refluxed in a suitable solvent, such as toluene or isopropanol, containing a base, such as triethylamine, until the reaction is completed. The photochromic compound is recovered from the reaction mixture, e.g., by filtration, and recrystallized, if necessary, to obtain a more purified product.

The present process is more particularly described in the following examples which are intended as illustrative only since numerous modifications and variations therein will be apparent to those skilled in the art.

Example 1

(Method A)

A suspension of 5-nitroso-6-quinolinol (1.74 grams, 0.01 mole) in 70 milliliters (ml) of toluene was heated to 100–108°C with stirring. To this heated suspension was slowly added over 15 minutes 3.43 grams of 1,2,3,5,6-pentamethyl-3-ethylindolium iodide (0.01 mole) suspended in 40 ml of toluene containing 2.01 grams of triethylamine (0.02 mole) and 0.5 ml of ethanol. The flask containing the indolium iodide was washed with 30 ml of toluene and the toluene wash liquor added to the reaction vessel. The mixture in the reaction vessel was refluxed for four hours and thereafter the reaction mixture was decanted and allowed to evaporate to almost dryness. A mixture of dark green gum and a small amount of crystalline material resulted. The almost dried mixture was soaked with 7–8 ml of fresh toluene, filtered and washed with 4 ml of toluene twice. The filtrate and washings were combined and allowed to evaporate. A crystalline material slowly formed in the gum over 5 days. The thick gum was soaked with 2–3 ml of ethanol, filtered, washed with ethanol and air dried. A yellowish-green powder (0.81 grams) was obtained. The filtrate and washings were combined and allowed to evaporate, thereby obtaining an additional 0.2 grams of the green crystalline material which was combined with the first crop of crystals.

The combined crude product was recrystallized from an acetone: n-hexanol mixture (2:3 V/V). A yellowish-green microcrystalline powder weighing about 0.76 grams was obtained. The material was identified as 1,3,5,6-tetramethyl-3-ethylspiro(indoline-2,3'-(3H) pyrido-(3,2-f (1,4)-benzoxazine) by Nuclear Magnetic Resonance (NMR) spectroscopy and elemental analysis. Elemental analysis of a sample of the product prepared from the same reactants but in another preparation was found to be 77.45 wt.% carbon, 6.88 wt.% hydrogen and 11.11 wt.% nitrogen. These values substantially agree with the theoretical values of 7.760 wt.% carbon, 6.78 wt.% hydrogen and 11.31 wt.% nitrogen.

(Method B)

A suspension of 5-nitroso-6-quinolino (0.73 grams, 0.0042 mole) in 30 ml of isopropanol was heated to reflux temperature. To this suspension was slowly added over 15 minutes 1.44 grams (0.0042 mole) of 1,2,3,5,6-pentamethyl-3-ethylindolium iodide dissolved in 35 ml of isopropanol containing 0.85 grams (0.0085 mole) of triethylamine. The resulting blue reaction mixture was refluxed for two hours and then allowed to cool to room temperature. The blue solution was allowed to evaporate overnight and crystals formed in the almost dry solution. The crystals were filtered, washed with about 2 ml of isopropanol and then air dried. A dark olive green powder (1.32 grams) was obtained. This powder was added to 120 ml of boiling n-hexane and insoluble powder removed by filtration. Active charcoal (1.5 grams) was added to the filtrate and the mixture stirred for a few minutes and then filtered. The charcoal-free filtrate was reduced in volume to about 40 ml and stored overnight in a refrigerator. Yellow crystals were found to have formed. After decantation, the yellow crystals were washed with fresh n-hexane and then air dried. The dried crystals (0.46 grams) were identified by NMR as 1,3,5,6-tetramethyl-3-ethylspiro(indoline-2,3'-(3H) pyrido-(3,2-f (1,4)-benzoxazine).

Examples 2–9

Other photochromic compounds within the scope of graphic formula I were prepared by reaction of 5-nitroso-6-quinolinol with other indoline or indolium iodide compounds having the substituents identified in Table I using toluene as the reaction solvent. When the indolium iodide was used, triethylamine was also used, as described in Example 1. The products of the reaction were purified by various conventional purification techniques as exemplified by Example 1 and other examples illustrating the preparation of the photochromic compounds of the present invention.

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TABLE I

Substituent

Example No.	R ₁	R ₂	R ₃	R ₄	R ₅	Description
2	CH ₃	CH ₃	CH ₃	H	H	Beige-Green Powder
3	CH ₃	CH ₃	CH ₃	5-CH ₃	6-CH ₃	Yellow-Green Powder
4	CH ₃	CH ₃	CH ₃	5-CH ₃ O	H	Yellow Powder
5	CH ₃	CH ₃	CH ₃	7-CH ₃	6-Cl	Yellow Powder
6	CH ₃	CH ₃	C ₂ H ₅	H	H	Dark Green Paste
7	CH ₃	CH ₃	phenyl	H	H	Dark Green Powder
8	CH ₃	phenyl	phenyl	H	H	Yellow-Green Powder
9	CH ₃	spiro(penta) methylene)		H	H	Pale Yellow Solid

Ethanol solutions of each of the compounds of Examples 1—9 change to blue when irradiated with ultraviolet light at room temperature. The solutions returned to their original hue or colorless condition after the UV light was removed.

Example 10

A suspension of 5-nitroso-6-quinolinol (1.05 grams, 0.006 mole) in 30 milliliters (ml) of toluene was heated to reflux with stirring. To this heated suspension was slowly added over 20 minutes 1.37 grams of 1-butyl-3-methyl-3-ethyl-2-methylene indoline (0.006 mole) dissolved in 20 ml of toluene. The mixture in the reaction vessel was refluxed for three hours and thereafter the reaction mixture was transferred to an evaporating dish and allowed to evaporate to almost dryness. The almost dried mixture was soaked with 7 ml of fresh toluene, filtered and washed with 3 ml of toluene twice. The filtrate and washings were combined and allowed to evaporate. A viscous dark blue gum formed. The resulting gum-paste was redissolved in about 20 ml of diethyl ether, filtered and the filtrate allowed to evaporate in a hood. When one drop of the ether solution was diluted with ethanol and irradiated with ultraviolet light at room temperature for about 30 seconds, the solution turned a blue color. The blue color disappeared in about 5 minutes when the ultraviolet light was removed.

The gum paste obtained from evaporating the ether solution was dried in a vacuum desiccator for several days. The dried paste was dissolved in 10 ml of toluene and dehydrated with 5.6 grams of sodium sulfate, filtered, and washed with 3 ml of toluene. The filtrate and washing were combined and evaporated in a hood yielding a dark blue paste.

Example 11

One part of the photochromic compounds of Examples 1—10 were each incorporated into a sprayable lacquer solution of 10 parts of a commercial lacquer (3 M Company — lacquer No. 2253), 10 parts toluene and 10 parts methyl ethyl ketone. The lacquer solution was sprayed onto the surface of a 2.54 cm by 2.54 cm by 2 mm thick coupon of a polymer prepared from diethylene glycol bis(allyl carbonate). After drying, the coated coupon was heated in an air oven at 160°C for 20 minutes. After cooling, the residual lacquer was stripped off with adhesive tape and the surface cleaned with an acetone-wetted cloth. The photochromic response to activation by artificial sunlight. Results are tabulated in Table II.

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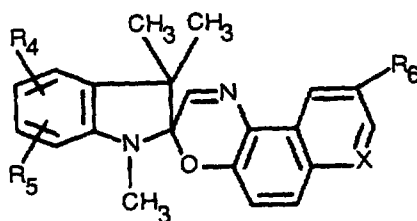
TABLE II

Example No.	ΔT_R , %	ΔOD , λ_{max}	$t_{1/2}$, s
1	76	1.33	57
2	48	0.41	14
3	72	1.13	41
4	66	0.98	45
5	—	0.16	8
6	—	0.49	18
7	—	0.61	21
8	37	0.29	21
9	46	0.40	26
10	59	0.67	21

1. ΔT_R — The percent reduction in visible light transmission (measured using a photopic filter) induced after 4 minutes irradiation with artificial sunlight.
2. ΔOD — The change in saturation optical density measured in the range of 580—620 nm induced by irradiation for 4 minutes with artificial sunlight.
3. $t_{1/2}$ — The half-life in seconds for the transmission of a sample to increase by 21% from 42% transmission (based on transmission in the clear state) after irradiation with artificial sunlight.

Example 12

Photochromic compounds of the prior art were applied to a coupon made from diethylene glycol bis(allyl carbonate) in the same manner as described in Example 11. The photochromic response to these articles is compared to that of Examples 2, 3 and 4 in Table III. These photochromic compounds can be depicted by the following graphic formula,



wherein R_4 , R_5 , R_6 and X are identified in Table III.

TABLE III

	Prior Art U.S. 3,562,172 $X=C$, $R_6=H$		Prior Art U.S. 4,215,010 $X=C$, $R_6=CH_3O$		Examples 2, 3, 4 $X=N$, $R_6=H$	
	R_4	R_5	ΔTR , %	ΔOD at max	ΔTR , %	ΔOD at max
	H	H	40	0.34	29	0.23
	H	CH_3O	34	0.31	53	0.46
	CH_3	CH_3	34	0.31	57	0.65

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Example 13

A suspension of 5-nitroso-6-quinolinol (0.52 grams, 0.003 mole) in 20 milliliters (ml) of toluene was heated to about 100°C with stirring. To this heated suspension was slowly added over about 20 minutes 1.75 grams of 1,2-dimethyl-3,3-bis(p-methoxyphenyl)-indolium iodide (0.003 mole) suspended in 20 ml of toluene containing 0.60 grams of triethylamine (0.006 mole). The mixture in the reaction vessel was maintained at about 100°C for 2.5 hours and the degree of reaction monitored by thin layer chromatography (TLC). The reaction was almost complete after 1 hour. After 2.5 hours at about 100°C, an additional 0.17 grams (0.001 mole) of 5-nitroso-6-quinolinol was added to the reaction vessel, but total reaction of the indolium iodide reactant was not obtained even after 2 hours at about 100°C. The solids in the reaction mixture were separated by decantation and the remaining liquid allowed to evaporate to almost dryness. Olive green crystals formed in the almost dried paste. The almost dried product was soaked with 7 ml of fresh toluene, filtered and slowly washed with 3 ml of toluene. A large amount of the crystalline powder product did not dissolve in the toluene. The crystalline insoluble powder was washed with ethanol and air dried. An olive green powder (0.79 grams) was obtained. A sample of the powder was dissolved in ethanol and irradiated with ultraviolet light (366 nm) for about 30 seconds. The solution turned from pale green to blue and returned to pale green when the ultraviolet light was removed.

Example 14

A suspension of 5-nitroso-6-quinolinol (1.39 grams, 0.008 mole) in 35 ml of toluene was heated to about 100°C with stirring. To this heated suspension was slowly added over 20—30 minutes 2.95 grams of 1,2,5,6-tetramethyl-3,3-spiro (cyclohexyl)-3H)-indolium iodide suspended in 35 ml of toluene containing 1.6 grams of triethylamine (0.016 mole). The progress of the reaction was checked by TLC. The mixture in the reaction vessel was maintained at about 100°C for three hours. Thereafter, the reaction mixture (a dark brown solution) was allowed to evaporate to almost dryness. The resulting paste was soaked with 6 ml of fresh toluene for several minutes, filtered to remove insoluble material and the resulting solids washed with 2 ml of toluene. The filtrate and washing were combined and allowed to evaporate. A dark brown paste (2.07 grams) resulted. A small amount (about 1 milligram) of the paste was dissolved in about 2—3 ml of ethanol and the resulting solution exposed to ultraviolet light (366 nm) at room temperature. The solution turned pale blue and returned to its original hue in about 2 minutes after the ultraviolet light source was removed.

Example 15

In accordance with the procedure of Example 14, 1.22 grams (0.007 mole) of 5-nitroso-6-quinolinol was reacted with 1.70 grams (0.007 mole) of 1-allyl-3,5,6-trimethyl-3-ethyl-2-methylene indoline in 60 ml of toluene at about 100°C for about three hours. The reaction mixture was evaporated to almost dryness and the resulting paste soaked with 6 ml of toluene for several minutes and then filtered. The insoluble material was washed with 2 ml of toluene. The filtrate and washing were combined and allowed to evaporate. A dark (greenish) brown paste (2.49 grams) was obtained. A small amount of the paste was dissolved in 2—3 ml of ethanol and the resulting pale yellow solution exposed to ultraviolet light (366 nm). The solution turned green and returned to its original hue in about 1—2 minutes after the ultraviolet light source was removed.

Example 16

In accordance with the procedure of Example 14, a suspension of 1.74 grams (0.01 mole) of 5-nitroso-6-quinolinol in 40 ml of toluene was reacted with 3.57 grams (0.01 mole) of 1,3-diethyl-2,3,5,6-tetramethyl indolium iodide in 40 ml of toluene containing 2 grams (0.02 mole) of triethylamine. After three hours of reaction, a dark blue-green solution was obtained and this solution allowed to evaporate to almost dryness. The resulting paste was soaked with 6 ml of toluene for several minutes and filtered. The resulting solid was washed with 2 ml of toluene and combined with the filtrate. The resulting dark solution was allowed to evaporate to form 3.28 grams of a dark green paste. A small amount of the paste was tested for photochromicity in accordance with the procedure of Example 14. The ethanol solution of the paste was a pale green which became deep blue upon exposure to ultraviolet light. The solution returned to pale green in about 3—4 minutes after removal of the ultraviolet light.

Example 17

In accordance with the procedure of Example 14, 1.74 grams (0.01 mole) of 5-nitroso-6-quinolinol and 2.57 grams of 1-butyl-2-ethyl-3,5,6-trimethyl-2-methylene indoline were refluxed in 70 ml of toluene for 3 hours. The resultant product was a dark blue paste. An ethanol solution of a small amount of the paste was a pale to medium blue which became sky blue upon exposure to ultraviolet light. The solution returned to its original hue in about 5 minutes after removal of the ultraviolet light.

Example 18

In accordance with the procedure of Example 14, 1.22 grams of 5-nitroso-6-quinolinol was suspended in 50 ml of hot toluene. To this suspension was added slowly over about 10 minutes 1.70 grams of 1-butyl-3,3,5,6-tetramethyl-2-methylene indoline diluted in 20 ml of toluene. The resulting mixture was refluxed for

3 hours. An ethanol solution of the resultant product turned a dark blue upon exposure to ultraviolet light and returned to its original hue in about 4—5 minutes after the light was removed.

The above procedure was repeated using isopropanol as the solvent. The product was a very dark green paste.

Example 19

The procedure of Example 18 was followed except that 2.04 grams (0.007 mole) of the Fischer's base, 1-benzyl-2,5,6-trimethyl-3-ethyl-2-methylene indoline, was used. An ethanol solution of the resultant product was pale green. The solution turned medium blue upon exposure to ultraviolet light and returned to its original hue in about 3—4 minutes after the light was removed.

Example 20

To a suspension of 0.89 grams of 5-nitroso-6-quinolinol (0.005 mole) in boiling isopropanol was slowly added 1.32 grams (0.005 mole) of 1,3,5,6-tetramethyl-3-phenyl-2-methylene indoline dissolved in 25 ml of isopropanol. The reaction mixture was refluxed for one hour. The resulting dark blue reaction solution was evaporated overnight and a dark blue (almost black) gum was formed. Further evaporation resulted in the formation of a hard cake with significant decomposition. Photochromicity of the product was confirmed in silica gel matrix after the gum had been chromatographed on a thin layer chromatograph plate.

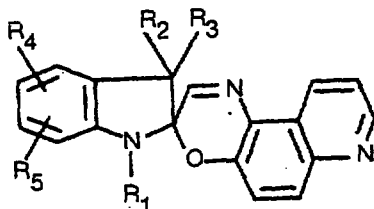
A summary of the compounds of Examples 17—20 is found in Table IV.

TABLE IV

Example No.	R ₁	R ₂	R ₃	R ₄	R ₅	Description
17	n-C ₄ H ₉	C ₂ H ₅	CH ₃	CH ₃	CH ₃	Dark Blue Paste
18	n-C ₄ H ₉	CH ₃	CH ₃	CH ₃	CH ₃	Dark Green Paste
19	benzyl	C ₂ H ₅	CH ₃	CH ₃	CH ₃	Dark Green Paste
20	CH ₃	phenyl	CH ₃	CH ₃	CH ₃	Dark Blue Gum

Claims

1. A photochromic compound represented by the following formula:



wherein

(a) R₁ is selected from the group consisting of C₁—C₈ alkyl, phenyl, phen(C₁—C₄)alkyl, allyl and mono- and disubstituted phenyl, said phenyl substituents being selected from C₁—C₄ alkyl and C₁—C₅ alkoxy;

(b) R₂ and R₃ are each selected from the group consisting of C₁—C₅ alkyl, phenyl, C₁—C₄ alkyl and C₁—C₅ alkoxy mono- and disubstituted phenyl, benzyl or combine to form a cyclic ring selected from the group consisting of an alicyclic ring containing from 6 to 8 carbon atoms (including the spiro carbon atoms), norbornyl and adamantyl, and

(c) R₄ and R₅ are each selected from the group consisting of hydrogen, C₁—C₅ alkyl, halogen, C₁—C₅ alkoxy, nitro, cyano and C₁—C₈ alkoxy carbonyl.

2. A photochromic compound of claim 1, characterized in that

(a) R₁ is selected from the group consisting of C₁—C₄ alkyl, phenyl and benzyl,

(b) R₂ and R₃ are each selected from C₁—C₅ alkyl,

(c) and R₄ and R₅ are each selected from the group consisting of hydrogen, C₁—C₂ alkyl, chlorine, bromine, and C₁—C₅ alkoxy.

3. A photochromic compound of claim 1, characterized in that R₁, R₂ and R₃ are methyl, and R₄ and R₅ are hydrogen.

4. A photochromic compound of claim 1, characterized in that R₁, R₂ and R₃ are methyl, R₄ is methoxy and R₅ is hydrogen.

5. A photochromic compound of claim 1, characterized in that R₁, R₂, R₃ and R₄ are methyl and R₅ is chloro.

3 hours. An ethanol solution of the resultant product turned a dark blue upon exposure to ultraviolet light and returned to its original hue in about 4—5 minutes after the light was removed.

The above procedure was repeated using isopropanol as the solvent. The product was a very dark green paste.

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Example 19

The procedure of Example 18 was followed except that 2.04 grams (0.007 mole) of the Fischer's base, 1-benzyl-2,5,6-trimethyl-3-ethyl-2-methylene indoline, was used. An ethanol solution of the resultant product was pale green. The solution turned medium blue upon exposure to ultraviolet light and returned to its original hue in about 3—4 minutes after the light was removed.

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Example 20

To a suspension of 0.89 grams of 5-nitroso-6-quinolinol (0.005 mole) in boiling isopropanol was slowly added 1.32 grams (0.005 mole) of 1,3,5,6-tetramethyl-3-phenyl-2-methylene indoline dissolved in 25 ml of isopropanol. The reaction mixture was refluxed for one hour. The resulting dark blue reaction solution was evaporated overnight and a dark blue (almost black) gum was formed. Further evaporation resulted in the formation of a hard cake with significant decomposition. Photochromicity of the product was confirmed in silica gel matrix after the gum had been chromatographed on a thin layer chromatograph plate.

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A summary of the compounds of Examples 17—20 is found in Table IV.

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TABLE IV

Example No.	R ₁	R ₂	R ₃	R ₄	R ₅	Description
17	n-C ₄ H ₉	C ₂ H ₅	CH ₃	CH ₃	CH ₃	Dark Blue Paste
18	n-C ₄ H ₉	CH ₃	CH ₃	CH ₃	CH ₃	Dark Green Paste
19	benzyl	C ₂ H ₅	CH ₃	CH ₃	CH ₃	Dark Green Paste
20	CH ₃	phenyl	CH ₃	CH ₃	CH ₃	Dark Blue Gum

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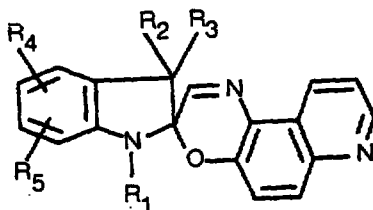
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Claims

1. A photochromic compound represented by the following formula:

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wherein

(a) R₁ is selected from the group consisting of C₁—C₈ alkyl, phenyl, phen(C₁—C₄)alkyl, allyl and mono- and disubstituted phenyl, said phenyl substituents being selected from C₁—C₄ alkyl and C₁—C₅ alkoxy;

(b) R₂ and R₃ are each selected from the group consisting of C₁—C₅ alkyl, phenyl, C₁—C₄ alkyl and C₁—C₅ alkoxy mono- and disubstituted phenyl, benzyl or combine to form a cyclic ring selected from the group consisting of an alicyclic ring containing from 6 to 8 carbon atoms (including the spiro carbon atoms), norbornyl and adamantyl, and

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(c) R₄ and R₅ are each selected from the group consisting of hydrogen, C₁—C₅ alkyl, halogen, C₁—C₅ alkoxy, nitro, cyano and C₁—C₈ alkoxy carbonyl.

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2. A photochromic compound of claim 1, characterized in that

(a) R₁ is selected from the group consisting of C₁—C₄ alkyl, phenyl and benzyl,

(b) R₂ and R₃ are each selected from C₁—C₅ alkyl,

(c) and R₄ and R₅ are each selected from the group consisting of hydrogen, C₁—C₂ alkyl, chlorine, bromine, and C₁—C₅ alkoxy.

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3. A photochromic compound of claim 1, characterized in that R₁, R₂ and R₃ are methyl, and R₄ and R₅ are hydrogen.

4. A photochromic compound of claim 1, characterized in that R₁, R₂ and R₃ are methyl, R₄ is methoxy and R₅ is hydrogen.

5. A photochromic compound of claim 1, characterized in that R₁, R₂, R₃ and R₄ are methyl and R₅ is chloro.

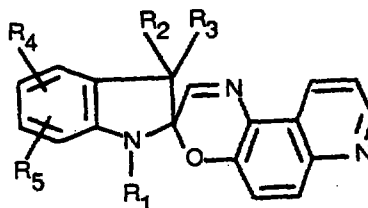
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6. A photochromic compound of claim 1, characterized in that R_1 , R_2 , R_3 , R_4 and R_5 are methyl.
7. A photochromic compound of claim 1, characterized in that R_1 , R_2 , R_4 , R_5 are methyl and R_3 is ethyl.
8. The photochromic compound 1,3,5,6-tetramethyl-3-ethylspiro-(indoline-2,3'-(3H) pyrido(3,2-f)(1,4) benzoxazine).
9. The photochromic compound 1,3,3,5,6-pentamethylspiro-(indoline-2,3'-(3H) pyrido(3,2-f)(1,4) benzoxazine).
10. The photochromic compound 1,3,4,5-tetramethyl-3-ethylspiro (indoline-2,3'-(3H)pyrido (3,2-f)(1,4) benzoxazine).
11. The photochromic compound 1,3,3,4,5-pentamethylspiro(indoline-2,3'-(3H)pyrido (3,2-f)(1,4) benzoxazine).
12. A photochromic article comprising a solid transparent polymerized organic host material containing a photochromatic amount of a photochromic compound, characterized in that said compound is represented by the formula

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25 wherein

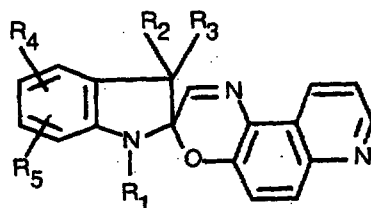
- (a) R_1 is selected from the group consisting of C_1-C_8 alkyl, phenyl, phen(C_1-C_4)alkyl, allyl and mono- and disubstituted phenyl, said phenyl substituents being selected from C_1-C_4 alkyl and C_1-C_5 alkoxy;
- (b) R_2 and R_3 are each selected from the group consisting of C_1-C_5 alkyl, phenyl, C_1-C_4 alkyl and C_1-C_5 alkoxy mono- and disubstituted phenyl, benzyl or combine to form a cyclic ring selected from the group consisting of an alicyclic ring containing from 6 to 8 carbon atoms (including the spiro carbon atom), norbornyl and adamantyl, and
- (c) R_4 and R_5 are each selected from the group consisting of hydrogen, C_1-C_5 alkyl, halogen, C_1-C_5 alkoxy, nitro, cyano and C_1-C_8 alkoxy carbonyl.
13. The photochromic article of claim 12, characterized in that the substituents R of the formula are
- (a) R_1 is selected from the group consisting of C_1-C_4 alkyl, allyl, phenyl and benzyl,
- (b) R_2 and R_3 are each selected from C_1-C_5 alkyl,
- (c) and R_4 and R_5 are each selected from the group consisting of hydrogen, C_1-C_2 alkyl, chlorine, bromine, and C_1-C_5 alkoxy.
14. The photochromic article of claim 12, characterized in that the substituents R of the formula are
- (a) R_1 is selected from the group consisting of C_1-C_4 alkyl, phenyl and benzyl,
- (b) R_2 and R_3 are each selected from C_1-C_5 alkyl,
- (c) and R_4 and R_5 are each selected from the group consisting of hydrogen, C_1-C_2 alkyl, chlorine, bromine and C_1-C_5 alkoxy.
15. The photochromic article of claims 13 or 14, characterized in that the photochromic compound is one wherein R_1 , R_2 , R_4 and R_5 are methyl and R_3 is selected from methyl and ethyl.
16. The photochromic article of claims 12 to 15, characterized in that the transparent host material is selected from the group consisting essentially of polymers of polyol(allyl carbonate), copolymers of polyol(allyl carbonate) and vinyl acetate, polyacrylates, poly(alkylacrylates), cellulose acetate, cellulose triacetate, cellulose acetate propionate, cellulose acetate butyrate, poly(vinyl acetate), poly(vinyl alcohol), polycarbonate, polystyrene, poly(styrene-methylmethacrylate) copolymers, poly(styrene-acrylonitrile) copolymers, and polyvinyl butyral.
17. The photochromic article of claim 16, characterized in that the transparent host material is selected from poly(diethylene glycol bis(allyl carbonate)) and its copolymers with vinyl acetate.
18. The photochromic article of claim 17, characterized in that the copolymer is from 80 to 90 percent diethylene glycol bis(allyl carbonate) and 10 to 20 percent vinyl acetate.
19. The photochromic article of claims 12 to 18, characterized in that the photochromic compound is present in amounts of from 0.05 to 10 weight percent.
20. The photochromic article of claims 12 to 19, characterized in that the photochromic article is a lens.
21. The photochromic article of claim 20, characterized in that the photochromic compound is dispersed across at least one surface of the lens.

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Patentansprüche

1. Photochrome Verbindung der folgenden Formel:



in der

(a) R_1 ausgewählt ist aus der Gruppe bestehend aus C_1 bis C_8 Alkyl, Phenyl, Phen(C_1 bis C_4) Alkyl, Allyl und mono- und disubstituiertem Phenyl, wobei die Substituenten des Phenylrestes aus C_1 bis C_4 Alkyl und C_1 bis C_5 Alkoxy ausgewählt sind;

(b) R_2 und R_3 jeweils ausgewählt sind aus der Gruppe bestehend aus C_1 bis C_5 Alkyl, Phenyl, mit C_1 bis C_4 Alkyl und C_1 bis C_5 Alkoxy mono- und disubstituiertem Phenyl, Benzyl oder einer Kombination, um einen zyklischen Ring enthaltend 6 bis 8 Kohlenstoffatome (einschließlich des Spirokohlenstoffatoms), Norbonyl und Adamantyl, und

(c) R_4 und R_5 jeweils ausgewählt sind aus der Gruppe bestehend aus Wasserstoff, C_1 bis C_5 Alkyl, Halogen, C_1 bis C_5 Alkoxy, Nitro, Cyano und C_1 bis C_8 Alkoxycarbonyl.

2. Photochrome Verbindung nach Anspruch 1, dadurch gekennzeichnet, daß

(a) R_1 ausgewählt ist aus der Gruppe bestehend aus C_1 bis C_4 Alkyl, Phenyl und Benzyl,

(b) R_2 und R_3 jeweils ausgewählt sind aus C_1 bis C_5 Alkyl,

(c) und R_4 und R_5 jeweils sind aus der Gruppe bestehend aus Wasserstoff, C_1 bis C_2 Alkyl, Chlor, Brom und C_1 bis C_5 Alkoxy.

3. Photochrome Verbindung nach Anspruch 1, dadurch gekennzeichnet, daß R_1 , R_2 und R_3 Methyl und R_4 und R_5 Wasserstoff sind.

4. Photochrome Verbindung nach Anspruch 1, dadurch gekennzeichnet, daß R_1 , R_2 und R_3 Methyl, R_4 Methoxy und R_5 Wasserstoff sind.

5. Photochrome Verbindung nach Anspruch 1, dadurch gekennzeichnet, daß R_1 , R_2 , R_3 und R_4 Methyl und R_5 Chlor sind.

6. Photochrome Verbindung nach Anspruch 1, dadurch gekennzeichnet, daß R_1 , R_2 , R_3 , R_4 und R_5 Methyl sind.

7. Photochrome Verbindung nach Anspruch 1, dadurch gekennzeichnet, daß, R_1 , R_2 , R_4 , R_5 Methyl und R_3 Ethyl sind.

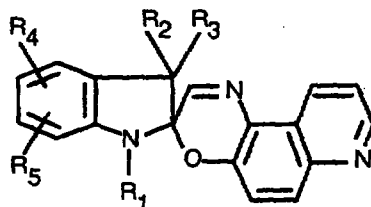
8. Photochrome Verbindung dadurch gekennzeichnet, daß sie 1,3,5,6-Tetramethyl-3-ethylspiro(indolin-2,3'-(3H)pyrido(3,2-f)(1,4)benzoxazin) ist.

9. Photochrome Verbindung dadurch gekennzeichnet, daß sie 1,3,3,5,6-Pentamethylspiro(indolin-2,3'-(3H)pyrido(3,2-f)(1,4)benzoxazin) ist.

10. Photochrome Verbindung dadurch gekennzeichnet, daß sie 1,3,4,5-Tetramethyl-3-ethylspiro(indolin-2,3'-(3H)pyrido(3,2-f)(1,4)benzoxazin) ist.

11. Photochrome Verbindung dadurch gekennzeichnet, daß sie 1,3,3,4,5-Pentamethylspiro(indolin-2,3'-(3H)pyrido(3,2-f)(1,4)benzoxazin) ist.

12. Photochromer Gegenstand, enthaltend ein festes, transparentes polymers organisches Grundmaterial, enthaltend eine photochromatische Menge einer photochromen Verbindung, dadurch gekennzeichnet, daß die Verbindung die folgende Formel



aufweist, in der

(a) R_1 ausgewählt ist aus der Gruppe bestehend aus C_1 bis C_8 Alkyl, Phenyl, Phen(C_1 bis C_4) Alkyl, Allyl und mono- und disubstituiertem Phenyl, wobei die Substituenten des Phenylrestes aus C_1 bis C_4 Alkyl und C_1 bis C_5 Alkoxy ausgewählt sind;

(b) R_2 und R_3 jeweils ausgewählt sind aus der Gruppe bestehend aus C_1 bis C_5 Alkyl, Phenyl, mit C_1 bis C_4 Alkyl und C_1 bis C_5 Alkoxy mono- und disubstituiertem Phenyl, Benzyl oder einer Kombination, um einen zyklischen Ring auszubilden, bestehend aus der Gruppe aus einem alizyklischen Ring enthaltend 6 bis 8 Kohlenstoffatome (einschließlich des Spirokohlenstoffatoms), Norbonyl und Adamantyl, und



(c) R_4 und R_5 jeweils ausgewählt sind aus der Gruppe bestehend aus Wasserstoff, C_1 bis C_5 Alkyl, Halogen, C_1 bis C_5 Alkoxy, Nitro, Cyano und C_1 bis C_8 Alkoxy-carbonyl.

13. Photochromer Gegenstand nach Anspruch 12, dadurch gekennzeichnet, daß die Substituenten R der Formel folgende sind:

- 5 (a) R_1 ist ausgewählt aus der Gruppe bestehend aus C_1 bis C_4 Alkyl, Allyl, Phenyl und Benzyl,
 (b) R_2 und R_3 sind jeweils ausgewählt aus C_1 bis C_5 Alkyl,
 (c) und R_4 und R_5 sind jeweils ausgewählt aus der Gruppe bestehend aus Wasserstoff, C_1 bis C_2 Alkyl, Chlor, Brom und C_1 bis C_5 Alkoxy.

14. Photochromer Gegenstand nach Anspruch 12, dadurch gekennzeichnet, daß die Substituenten R der Formel die folgenden sind:

- 10 (a) R_1 ist ausgewählt aus der Gruppe bestehend aus C_1 bis C_4 Alkyl, Phenyl und Benzyl,
 (b) R_2 und R_3 sind jeweils ausgewählt aus C_1 bis C_5 Alkyl,
 (c) und R_4 und R_5 sind jeweils ausgewählt aus der Gruppe bestehend aus Wasserstoff, C_1 bis C_2 Alkyl, Chlor, Brom und C_1 bis C_5 Alkoxy.

15 15. Photochromer Gegenstand nach Ansprüchen 13 oder 14, dadurch gekennzeichnet, daß die Photochrome Verbindung eine solche ist, in der R_1 , R_2 , R_4 und R_5 Methyl sind und R_3 ausgewählt ist aus Methyl und Ethyl.

16. Photochromer Gegenstand nach Ansprüchen 12 bis 15, dadurch gekennzeichnet, daß das transparente Grundmaterial ausgewählt ist aus der Gruppe bestehend im wesentlichen aus Polymeren von Polyol(allylkarbonat), Copolymeren von Polyol(allylkarbonat) und Vinylacetat, Polyacrylaten, Poly(alkylacrylaten), Celluloseacetat, Cellulosetriacetat, Celluloseacetatpropionat, Celluloseacetatbutyrat, Polyvinylacetat, Polyvinylalkohol, Polykarbonat, Polystyrol, Poly(styrol-methylmethacrylat)copolymeren, Poly(styrol-acrylnitril)copolymeren und Polyvinylbutyral.

17. Photochromer Gegenstand nach Anspruch 16, dadurch gekennzeichnet, daß das transparente Grundmaterial ausgewählt ist aus Poly(diethylenglycol-bis-(allylkarbonat)) und seinen Copolymeren mit Vinylacetat.

18. Photochromer Gegenstand nach Anspruch 17, dadurch gekennzeichnet, daß das Copolymer von 80 bis 90% Diethylenglycol bis(allylkarbonat) und 10 bis 20% Vinylacetat enthält.

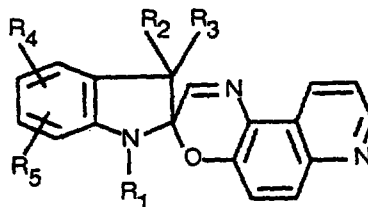
19. Photochromer Gegenstand nach Ansprüchen 12 bis 18, dadurch gekennzeichnet, daß die photochrome Verbindung in Mengen von 0,05 bis 10 Gew.-% vorhanden ist.

20. Photochromer Gegenstand nach Ansprüchen 12 bis 19, dadurch gekennzeichnet, daß der photochrome Gegenstand eine Linse ist.

21. Photochromer Gegenstand nach Anspruch 20, dadurch gekennzeichnet, daß die photochrome Verbindung mindestens über eine Oberfläche der Linse verteilt dispergiert ist.

Revendications

1. Composé photochromique représenté par la formule suivante:



dans laquelle

50 (a) R_1 est choisi dans le groupe comprenant les radicaux alkyle en C_1 — C_5 , phényle, phén(alkyle en C_1 — C_4), allyl et phényle mono- et disubstitué, lesdits substituants du radical phényle étant choisis parmi les radicaux alkyle en C_1 — C_4 et alcoxy en C_1 — C_5 ;

55 (b) R_2 et R_3 sont chacun choisis dans le groupe comprenant les radicaux alkyle en C_1 — C_5 , phényle, phényle mono- ou disubstitué par un ou deux radicaux alkyl en C_1 — C_4 et alcoxy en C_1 — C_5 , benzyle, ou se combinent pour former un noyau cyclique choisi dans le groupe comprenant un noyau alicyclique contenant de 6 à 8 atomes de carbone (y compris les atomes de carbone spiro) norbornyle et adamantyle, et

(c) R_4 et R_5 sont chacun choisi dans le groupe comprenant l'hydrogène, les radicaux alkyle en C_1 — C_5 , halogéno, alcoxy en C_1 — C_5 , nitro, cyano et (alcoxy en C_1 — C_8) carbonyle.

2. Composé photochromique selon la revendication 1, caractérisé en ce que

60 (a) R_1 est choisi dans le groupe comprenant les radicaux alkyle en C_1 — C_4 , phényle et benzyle,

(b) R_2 et R_3 sont chacun choisis parmi les radicaux alkyle en C_1 — C_5 ,

(c) et R_4 et R_5 sont chacun choisis dans le groupe comprenant l'hydrogène, les radicaux alkyle en C_1 — C_2 , chloro, bromo et alcoxy en C_1 — C_5 .

65 3. Composé photochromique selon la revendication 1, caractérisé en ce que R_1 , R_2 et R_3 sont chacun le radical méthyle, et R_4 et R_5 sont chacun un hydrogène.



4. Composé photochromique selon la revendication 1, caractérisé en ce que R_1 , R_2 et R_3 sont chacun le radical méthyle, R_4 est le radical méthoxy et R_5 est un hydrogène.

5. Composé photochromique selon la revendication 1, caractérisé en ce que R_1 , R_2 , R_3 et R_4 sont chacun le radical méthyle, et R_5 est le radical chloro.

6. Composé photochromique selon la revendication 1, caractérisé en ce que R_1 , R_2 , R_3 , R_4 et R_5 sont chacun le radical méthyle.

7. Composé photochromique selon la revendication 1, caractérisé en ce que R_1 , R_2 , R_4 , R_5 sont chacun le radical méthyle et R_3 est le radical éthyle.

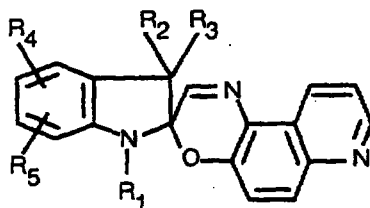
8. Le composé photochromique 1,3,5,6-tétraméthyl-3-éthylspiro-(indoline-2,3'(3H)pyrido(3,2-f)(1,4)-benzoxazine).

9. Le composé photochromique 1,3,3,5,6-pentaméthylspiro(indoline-2,3'(3H)pyrido(3,2-f)(1,4)-benzoxazine).

10. Le composé photochromique 1,3,4,5-tétraméthyl-3-éthylspiro(indoline-2,3'(3H)pyrido(3,2-f)(1,4)-benzoxazine).

11. Le composé photochromique 1,3,3,4,5-pentaméthylspiro(indoline-2,3'(3H)pyrido(3,2-f)(1,4)-benzoxazine).

12. Article photochromique comprenant un matériau hôte organique polymérisé transparent solide, contenant une quantité photochromatique d'un composé photochromique, caractérisé en ce que ledit composé est représenté par la formule



dans laquelle

(a) R_1 est choisi dans le groupe comprenant les radicaux alkyle en C_1-C_8 , phényle, phén(alkyle en C_1-C_4), allyle et phényle mono- et disubstitué, lesdits substituants du radical phényle étant choisis parmi les radicaux alkyle en C_1-C_4 et alcoxy en C_1-C_5 ;

(b) R_2 et R_3 sont chacun choisis dans le groupe comprenant les radicaux alkyle en C_1-C_8 , phényle, phényle mono- ou disubstitué par un ou deux radicaux alkyle en C_1-C_4 et alcoxy en C_1-C_5 , benzyle, ou se combinent pour former un noyau cyclique choisi dans le groupe comprenant un noyau alicyclique contenant de 6 à 8 atomes de carbone (y compris les atomes de carbone spiro), norbornyle et adamantyle, et

(c) R_4 et R_5 sont chacun choisis dans le groupe comprenant l'hydrogène, les radicaux alkyle en C_1-C_8 , halogéno, alcoxy en C_1-C_5 , nitro, cyano et (alcoxy en C_1-C_5) carbonyle.

13. Article photochromique selon la revendication 12, caractérisé en ce que les substituants R de la formule sont les suivante:

(a) R_1 est choisi dans le groupe comprenant les radicaux alkyle en C_1-C_4 , allyle, phényle et benzyle,

(b) R_2 et R_3 sont chacun choisis parmi les radicaux alkyle en C_1-C_5 ,

(c) et R_4 et R_5 sont chacun choisis dans le groupe comprenant l'hydrogène, les radicaux alkyle en C_1-C_2 , chloro, bromo et alcoxy et C_1-C_5 .

14. Article photochromique selon la revendication 12, caractérisé en ce que les substituants R de la formule sont les suivants:

(a) R_1 est choisi dans le groupe comprenant les radicaux alkyle en C_1-C_4 , phényle et benzyle,

(b) R_2 et R_3 sont chacun choisis parmi les radicaux alkyle en C_1-C_5 ,

(c) et R_4 et R_5 sont chacun choisis dans le groupe comprenant l'hydrogène, les radicaux alkyle en C_1-C_2 , chloro, bromo et alcoxy en C_1-C_5 .

15. Article photochromique selon les revendications 13 ou 13, caractérisé en ce que le composé photochromique est un composé dans lequel R_1 , R_2 , R_4 et R_5 sont chacun le radical méthyle, et R_3 est choisi parmi les radicaux méthyle et éthyle.

16. Article photochromique selon les revendications 12 à 15, caractérisé en ce que le matériau hôte transparent est choisi dans le groupe comprenant essentiellement les polymères de polyol (carbonate d'allyle), les copolymères de polyol (carbonate d'allyle) et d'acétate de vinyle, les polyacrylates, les poly(acrylates d'alkyle), l'acétate de cellulose, le triacétate de cellulose, l'acétopropionate de cellulose, l'acéto-butyrat de cellulose, le poly(acétate de vinyle), le poly(alcool vinylique), les polycarbonates, le polystyrène, les copolymères de styrène et de méthacrylate de méthyle, les copolymères de styrène et d'acrylonitrile et le polyvinylbutyral.

17. Article photochromique selon la revendication 16, caractérisé en ce que le matériau hôte transparent est choisi entre le poly(diéthylèneglycol-bis-(carbonate d'allyle)) et ses copolymères avec l'acétate de vinyle.

18. Article photochromique selon la revendication 17, caractérisé en ce que le copolymère est constitué de 80 à 90 % de diéthylèneglycol-bis-(carbonate d'allyle) et de 10 à 20 % d'acétate de vinyle.



19. Article photochromique selon les revendications 12 à 18, caractérisé en ce que le composé photochromique est présent en des quantités de 0,05 à 10% en poids.

20. Article photochromique selon les revendication 12 à 19, caractérisé en ce que l'article photochromique est une lentille.

5 21. Article photochromique selon la revendication 20, caractérisé en ce que le composé photochromique est dispersé sur au moins une surface de la lentille.

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