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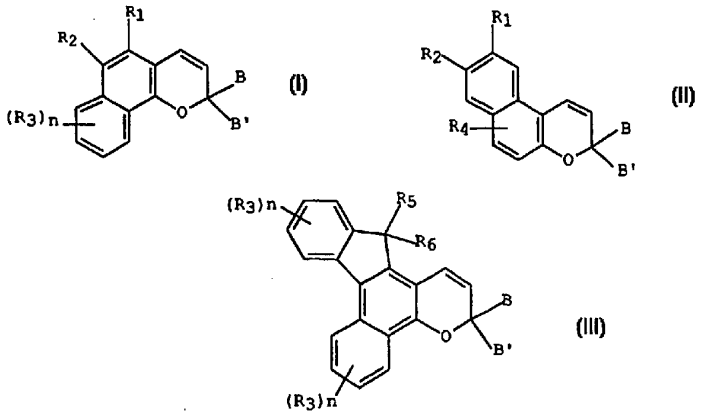


(57) Abstract

Described are novel photochromic polymerizable polyalkoxylated naphthopyran compounds, examples of which are certain 2H–naphtho[1,2–b]pyrans, 3H–naphtho[2,1–b]pyrans and indeno[2,1–f]naphtho[1,2–b]pyrans each having at least one polyalkoxylated substituent of from 1 to 50 alkoxy units per substituent which is end–capped with a polymerizable group. Specific substituents are also present on the naphtho, indeno and pyrano portions of the compounds. These compounds may be represented by graphic formulae (I), (II) or (III). Also described are various substrates, e.g., paper, glass, polymeric organic materials, etc., that contain or that are coated with such compounds. Optically clear articles such as contact lenses or other plastic transparencies that incorporate the novel naphthopyran compounds or combinations thereof with complementary photochromic compounds, e.g., certain other naphthopyrans, indenonaphthopyrans, benzopyrans, oxazine–type compounds, etc., are also described.

POLYMERIZABLE POLYALKOXYLATED NAPHTHOPYRANS

DESCRIPTION OF THE INVENTION

The present invention relates to certain novel naphthopyran compounds. More particularly, this invention relates to photochromic polymerizable polyalkoxylated naphthopyran compounds and to compositions and articles containing such novel photochromic compounds. When exposed to electromagnetic radiation containing ultraviolet rays, such as the ultraviolet radiation in sunlight or the light of a mercury lamp, many photochromic compounds exhibit a reversible change in color. When the ultraviolet radiation is discontinued, such a photochromic compound will return to its original color or colorless state.

Various classes of photochromic compounds have been synthesized and suggested for use in applications in which a sunlight-induced reversible color change or darkening is desired. U.S. Patent 3,567,605 (Becker) describes a series of pyran derivatives, including certain benzopyrans and naphthopyrans. U.S. Patent No. 5,458,814 describes photochromic 2,2-di-substituted-5,6-substituted-2H-naphtho[1,2-b]pyran compounds primarily for use in lenses and other plastic transparencies. These compounds have an acceptable fade rate in addition to a high activated intensity and a high coloration rate. U.S. Patent No. 5,585,042 discloses 3,3-di-substituted-8-substituted-3H-naphtho[2,1-b]pyran compounds for similar uses. These compounds exhibit an improved solar response, a higher activating wavelength than unsubstituted naphthopyrans, and an acceptable bleach or fade rate. U.S. Patent 5,645,767 describes photochromic indeno[2,1-f]naphtho[1,2-b]pyrans having a high activated intensity, an acceptable fade rate and high coloration rate.

Japanese Patent JP-5098252 (Derwent Abstract) discloses a photochromic material containing a polymerisable

substituent which is obtained by homo-polymerising or co-polymerising. The resultant material exhibits acceptable fatigue and chemical resistance properties for use in optical devices. Japanese Patent JP-8176139 (Derwent Abstract) discloses photochromic materials for use in lenses which exhibit acceptable fade rates.

International Patent Application WO 97/05213 describes a photochromic monomer having a photochromic dye moiety bonded to an organic spacer group which terminates with a polymerizable group. It is reported that when the photochromic monomer is incorporated into a cross-linking polymerizable casting composition, the photochromic material has a reduced sensitivity to temperature.

Although 3H-naphtho[2,1-b]pyrans, 2H-naphtho[1,2-b]pyrans and indeno[2,1-f]naphtho[1,2-b]pyrans of good intensity and reasonable fade are currently available, it is desirable to modify certain properties of the photochromic compound, such as the fade and/or activation rate, saturated optical density, sensitivity to elevated temperatures, fatigue rate and/or the formation of residual color, without changing its activated color. Modifications to such properties may be done to match the same properties of complementary photochromic compounds or to enable the use of such compounds in coatings, thin films or in rigid plastic matrices wherein the activation/fade kinetics of photochromic compounds are frequently slowed.

In accordance with the present invention, there have been discovered novel photochromic compounds; namely, certain 2H-naphtho[1,2-b]pyrans, 3H-naphtho[2,1-b]pyrans and indeno[2,1-f]naphtho[1,2-b]pyrans, that have at least one polyalkoxylated substituent terminated with a polymerizable group. Appropriate selection of the polyalkoxylated group, e.g., chain length and the number and nature of the alkoxy

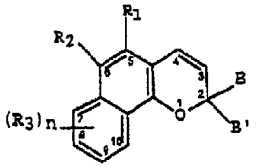
groups, and the polymerizable group enables modification of the aforementioned properties. Incorporation of a polymerizable group in the photochromic compound enables homopolymerization or co-polymerization of the compound with appropriate polymerizable compounds, and can reduce or prevent leaching of the photochromic compound from the polymer matrix into which it is incorporated. Depending on the location of the polymerizable polyalkoxylated substituent, certain other substituents may also be present on the naphtho, pyrano and indeno portions of the aforedescribed compounds.

DETAILED DESCRIPTION OF THE INVENTION

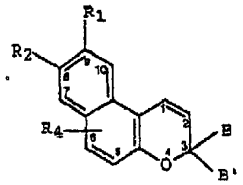
In accordance with the present invention, it has been discovered that certain properties, e.g., fade rate, activation rate, saturated optical density, fatigue rate, sensitivity to temperature, i.e., temperature dependency, and the formation of residual color in polymerizates, of selected photochromic 2H-naphtho[1,2-b]pyrans, 3H-naphtho[2,1-b]pyrans and indeno[2,1-f]naphtho[1,2-b]pyrans may be modified by including at least one polymerizable polyalkoxylated substituent on such compounds. The polymerizable polyalkoxylated substituent may have from 1 to 50 alkoxy units and may be located on the naphtho or indeno portion and/or on the pyrano portion of the naphthopyran.

The naphthopyrans of the present invention also may have certain other substituents. Specifically, the 2H-naphthopyrans may have substituents at the 5 and 6 positions and may have additional substituents at the 7, 8, 9 and 10 positions; the 3H naphthopyrans may have substituents at the 8 and 9 positions and may have additional substituents at the 5 and 6 positions; and the indeno-fused naphthopyrans may have certain substituents at the 5, 6, 7, 8, 9, 10, 11, 12 or 13 positions. The aforedescribed naphthopyrans may be

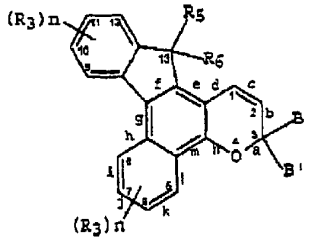
represented by graphic formulae I, II and III in which the internal numbers 1 through 13 identify the ring atoms of the naphthopyrans and letters a through n represent the sides of the naphthopyran rings. In the definition of the substituents shown in the following graphic formulae I, II and III, like symbols have the same meaning unless stated otherwise.



I



II or



III

In graphic formulae I, II and III, R_1, R_3, R_4, R_5 or R_6 is the group R; R_2 is the group R or a mono R-substituted phenyl; provided that there is at least one R group or mono R-substituted phenyl on the naphtho or indeno portion of the naphthopyran. The R group may be represented by the general formula:

$$-A[(C_2H_4O)_x\ (C_3H_6O)_y\ (C_4H_8O)_z]D$$

wherein -A is -C(O)O, $-CH_2O$ or -O, and D is a polymerizable group, i.e., any functional group capable of participating in a polymerization reaction. Polymer forming methods in which

the compounds of the present invention may participate include radical polymerization, and such other polymerization processes as are described in Ullmann's Encyclopedia of Industrial Chemistry, "Polymerization Processes", Vol. 21A, pp 305 to 428, which disclosure is incorporated herein by reference. The polymerizable groups may be selected from the group consisting of hydroxy, (meth)acryloxy, and epoxy. When there are 2 or more polymerizable groups on the naphthopyran, they may be the same or different

The group, $-(C_2H_4O)_x-$, represents poly(ethylene oxide); $-(C_3H_6O)_y-$, represents poly(propylene oxide); and, $-(C_4H_8O)_z-$, represents poly(butylene oxide). When used in combination, the poly(ethylene oxide), poly(propylene oxide) and poly(butylene oxide) groups of R may be in a random or block order within the R moiety. The letters x, y and z are each a number between 0 and 50 and the sum of x, y and z is between 1 and 50. The sum of x, y and z may be any number that falls within the range of 1 to 50, e.g., 1, 2, 3....50. The sum may also range from any lower number to any higher number within the range of 1 to 50, e.g., 6 to 50, 31 to 50. The numbers for x, y, and z are average values and can be partial numbers, e.g., 9.5.

Alternatively, the substituents R_1, R_2, R_3, R_4, R_5 or R_6 in graphic formulae I, II and III may be a group other than R or mono R-substituted phenyl provided that at least one of such substituents is the R group or mono R-substituted phenyl. R_1 may be hydrogen, C_1-C_3 alkyl or the group, -C(O)W, W being $-OR_7$, $-N(R_8)R_9$, piperidino or morpholino, wherein R_7 is allyl, C_1-C_6 alkyl, phenyl, mono(C_1-C_6)alkyl substituted phenyl, mono(C_1-C_6)alkoxy substituted phenyl, phenyl(C_1-C_3)alkyl, mono(C_1-C_6)alkyl substituted

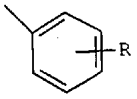
phenyl(C_1-C_3)alkyl, mono(C_1-C_6)alkoxy substituted phenyl(C_1-C_3)alkyl, C_1-C_6 alkoxy(C_2-C_4)alkyl or C_1-C_6 haloalkyl; R_8 and R_9 are each selected from the group consisting of C_1-C_6 alkyl, C_5-C_7 cycloalkyl, phenyl and mono- or di-substituted phenyl, said phenyl substituents being selected from C_1-C_6 alkyl and C_1-C_6 alkoxy, and said halo substituent being chloro or fluoro.

R_2 and each R_3 and R_4 may be selected from the group consisting of hydrogen, C_1-C_6 alkyl, C_3-C_7 cycloalkyl, phenyl, mono- or di-substituted phenyl and the groups $-OR_{10}$ and $-OC(O)R_{10}$, wherein R_{10} is C_1-C_6 alkyl, phenyl(C_1-C_3)alkyl, mono(C_1-C_6)alkyl substituted phenyl(C_1-C_3)alkyl, mono(C_1-C_6)alkoxy substituted phenyl(C_1-C_3)alkyl, C_1-C_6 alkoxy(C_2-C_4)alkyl, C_3-C_7 cycloalkyl or mono(C_1-C_4)alkyl substituted C_3-C_7 cycloalkyl, n is selected from the integers 0, 1 and 2 and said phenyl substituents are the same as for R_1.

R_5 and R_6 may together form an oxo group, a spiro-heterocyclic group containing 2 oxygen atoms and 3 to 6 carbon atoms including the spirocarbon atom, which may be represented by the expression (-O-(C_2-C_5 alkanediyl)-O-), e.g., spiro-1,3-dioxolane-2, spiro-1,3-dioxane-2, etc., or R_5 and R_6 may each be hydrogen, hydroxy, C_1-C_6 alkyl, C_3-C_7 cycloalkyl, allyl, phenyl, mono-substituted phenyl, benzyl, mono-substituted benzyl, chloro, fluoro, the group —C(O)X, wherein X is hydroxy, C_1-C_6 alkyl, C_1-C_6 alkoxy, phenyl, mono-substituted phenyl, amino, mono(C_1-C_6)alkylamino, or di(C_1-C_6)alkylamino, e.g., dimethyl amino, methyl propyl amino, etc., or R_5 and R_6 may each be the group, —OR_{11}, wherein R_{11} is C_1-C_6 alkyl,

phenyl(C_1-C_3)alkyl, mono(C_1-C_6)alkyl substituted phenyl(C_1-C_3)alkyl, mono(C_1-C_6)alkoxy substituted phenyl(C_1-C_3)alkyl, C_1-C_6 alkoxy(C_2-C_4)alkyl, C_3-C_7 cycloalkyl, mono(C_1-C_4)alkyl substituted C_3-C_7 cycloalkyl, C_1-C_6 chloroalkyl, C_1-C_6 fluoroalkyl, allyl, the group, —$CH(R_{12})Y$, wherein R_{12} is hydrogen or C_1-C_3 alkyl and Y is CN, CF_3, or $COOR_{13}$, and R_{13} is hydrogen or C_1-C_3 alkyl, or R_{11} is the group, —C(O)Z, wherein Z is hydrogen, C_1-C_6 alkyl, C_1-C_6 alkoxy, the unsubstituted, mono- or di-substituted aryl groups, phenyl or naphthyl, phenoxy, mono- or di-(C_1-C_6)alkyl substituted phenoxy, mono- or di-(C_1-C_6)alkoxy substituted phenoxy, mono- or di-(C_1-C_6)alkoxy substituted phenoxy, amino, mono(C_1-C_6)alkylamino, di(C_1-C_6)alkylamino, phenylamino, mono- or di(C_1-C_6)alkyl substituted phenylamino, or mono- or di-(C_1-C_6)alkoxy substituted phenylamino, each of the aforedescribed phenyl, benzyl and aryl group substituents being C_1-C_6 alkyl or C_1-C_6 alkoxy.

B is mono R-substituted phenyl represented by the following graphic formula IV:

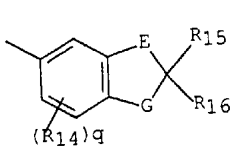


IV

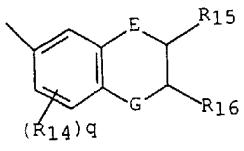
wherein the group R is the same as previously described.

B' is selected from the group consisting of:(a) the unsubstituted, mono-, di- and tri-substituted aryl groups, phenyl and naphthyl; (b) the unsubstituted, mono- and di-substituted heteroaromatic groups pyridyl, furanyl, benzofuran-2-yl, benzofuran-3-yl, thienyl, benzothien-2-yl, benzothien-3-yl, dibenzofuranyl, dibenzothienyl, carbazolyl

and fluorenyl, each of said aryl and heteroaromatic substituents in (a) and (b) being selected from the group consisting of hydroxy, aryl, mono(C_1-C_6)alkoxyaryl, di(C_1-C_6)alkoxyaryl, mono(C_1-C_6)alkylaryl, di(C_1-C_6)alkylaryl, chloroaryl, fluoroaryl, C_3-C_7 cycloalkylaryl, C_3-C_7 cycloalkyl, C_3-C_7 cycloalkyloxy, C_3-C_7 cycloalkyloxy(C_1-C_6)alkyl, C_3-C_7 cycloalkyloxy(C_1-C_6)alkoxy, aryl(C_1-C_6)alkyl, aryl(C_1-C_6)alkoxy, aryloxy, aryloxy(C_1-C_6)alkyl, aryloxy(C_1-C_6)alkoxy, mono- and di-(C_1-C_6)alkylaryl(C_1-C_6)alkyl, mono- and di-(C_1-C_6)alkoxyaryl(C_1-C_6)alkyl, mono- and di-(C_1-C_6)alkylaryl(C_1-C_6)alkoxy, mono- and di-(C_1-C_6)alkoxyaryl(C_1-C_6)alkoxy, amino, mono(C_1-C_6)alkylamino, di(C_1-C_6)alkylamino, diarylamino, N-(C_1-C_6)alkylpiperazino, N-arylpiperazino, aziridino, indolino, piperidino, arylpiperidino, morpholino, thiomorpholino, tetrahydroquinolino, tetrahydroisoquinolino, pyrryl, C_1-C_6 alkyl, C_1-C_6 chloroalkyl, C_1-C_6 fluoroalkyl, C_1-C_6 alkoxy, mono(C_1-C_6)alkoxy(C_1-C_4)alkyl, acryloxy, methacryloxy, bromo, chloro and fluoro; (c) the groups represented by the following graphic formulae VA and VB:



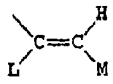
VA



VB

wherein E is carbon or oxygen and G is oxygen or substituted nitrogen, provided that when G is substituted nitrogen, E is

carbon, said nitrogen substituents being selected from the group consisting of hydrogen, C_1-C_6 alkyl and C_2-C_6 acyl; each R_{14} is C_1-C_6 alkyl, C_1-C_6 alkoxy, hydroxy, chloro or fluoro; R_{15} and R_{16} are each hydrogen or C_1-C_6 alkyl; and q is the integer 0, 1 or 2; (d) C_1-C_6 alkyl, C_1-C_6 chloroalkyl, C_1-C_6 fluoroalkyl, and C_1-C_6 alkoxy(C_1-C_4)alkyl; and (e) the group represented by the following graphic formula VC:



VC

wherein L is hydrogen or C_1-C_4 alkyl and M is selected from the unsubstituted, mono-, and di-substituted members of the group consisting of naphthyl, phenyl, furanyl and thienyl, each of said group substituents being C_1-C_4 alkyl, C_1-C_4 alkoxy, fluoro or chloro.

In graphic formulae I, II and III, R_1, R_2, R_3, R_4, R_5 or R_6 may be the same as previously described except that there is at least one R group or mono R-substituted phenyl on the naphthopyran. B and B' may each be selected from the group consisting of the mono R-substituted phenyl represented by graphic formula IV, and the aforedescribed substituents for B' in groups (a), (b), (c), (d) and (e).

Preferably, R_1, R_2, R_3, R_4, R_5, R_6, B and B' are each the same substituents as described in the previous paragraph, provided that in one preferred embodiment there is only one R group or mono R-substituted phenyl on the naphthopyran.

More preferably, R_1, R_3, R_4, R_5 or R_6 is the group R; R_2 is R or a mono R-substituted phenyl. The group, -A, is -C(O). The group, D, is hydroxy or (meth)acryloxy, and most

preferably D is hydroxy. The letters x and y are each a number between 0 and 50, z is 0 and the sum of x and y is between 1 and 50, and most preferably, x is a number between 1 and 50, and y and z are each 0.

Preferably, R_1 is the group, -C(O)W, W being $-OR_7$ or $-N(R_8)R_9$, wherein R_7 is C_1-C_4 alkyl, phenyl, mono(C_2-C_4)alkyl substituted phenyl, mono(C_1-C_4)alkoxy substituted phenyl, phenyl(C_1-C_2)alkyl, mono(C_1-C_4)alkyl substituted phenyl(C_1-C_2)alkyl, mono(C_1-C_4)alkoxy substituted phenyl(C_1-C_2)alkyl, mono(C_1-C_4)alkoxy(C_2-C_3)alkyl or C_1-C_4 haloalkyl; R_8 and R_9 are each selected from the group consisting of C_1-C_4 alkyl, C_5-C_7 cycloalkyl, phenyl and mono- or di-substituted phenyl; the phenyl substituents are C_1-C_4 alkyl or C_1-C_4 alkoxy, and the halo substituents are chloro or fluoro. More preferably, R_7 is a C_1-C_3 alkyl.

Preferably, R_2 and each R_3 and R_4 are selected from the group consisting of hydrogen, C_1-C_3 alkyl, C_3-C_5 cycloalkyl, phenyl, mono- or di-substituted phenyl and the group $-OR_{10}$, wherein R_{10} is C_1-C_4 alkyl, phenyl(C_1-C_2)alkyl, mono(C_1-C_4)alkyl substituted phenyl(C_1-C_2)alkyl, mono(C_1-C_4)alkoxy substituted phenyl(C_1-C_2)alkyl, C_1-C_4 alkoxy(C_2-C_4)alkyl, C_5-C_7 cycloalkyl or mono(C_1-C_3)alkyl substituted C_5-C_7 cycloalkyl, and the phenyl substituents are C_1-C_3 alkyl or C_1-C_3 alkoxy. More preferably, R_2 and each R_3 and R_4 are selected from the group consisting of hydrogen, C_1-C_3 alkyl, phenyl, mono- or di-substituted phenyl and the group $-OR_{10}$, wherein R_{10} is C_1-C_3 alkyl and the phenyl substituents are methyl or methoxy.

Preferably, R_5 and R_6 are each selected from the group consisting of hydrogen, hydroxy, C_1-C_4 alkyl, C_3-C_6 cycloalkyl, chloro, fluoro and the group, —OR_{11}, wherein R_{11} is C_1-C_3 alkyl, phenyl(C_1-C_2)alkyl, mono(C_1-C_3)alkyl substituted phenyl(C_1-C_3)alkyl, mono(C_1-C_3)alkoxy substituted phenyl(C_1-C_3)alkyl, C_1-C_3 alkoxy(C_2-C_4)alkyl, C_1-C_3 chloroalkyl, C_1-C_3 fluoroalkyl, the group, —$CH(R_{12})Y$, wherein R_{12} is hydrogen or C_1-C_2 alkyl and Y is CN or $COOR_{13}$, R_{13} being hydrogen or C_1-C_2 alkyl, or R_{11} is the group, —C(O)Z, wherein Z is hydrogen, C_1-C_3 alkyl, C_1-C_3 alkoxy, phenyl, naphthyl, the mono-substituted aryl groups, phenyl or naphthyl, phenoxy, mono- or di-(C_1-C_3)alkyl substituted phenoxy, mono- or di-(C_1-C_3)alkoxy substituted phenoxy, mono(C_1-C_3)alkylamino, phenylamino, mono- or di-(C_1-C_3)alkyl substituted phenylamino, or mono- or di-(C_1-C_3)alkoxy substituted phenylamino, each of said aryl group substituents being C_1-C_3 alkyl or C_1-C_3 alkoxy. More preferably, R_5 and R_6 are each hydrogen, hydroxy, C_1-C_4 alkyl or the group, —OR_{11}, wherein R_{11} is C_1-C_3 alkyl.

Preferably, B and B' are each selected from the group consisting of: (a) the mono R-substituted group represented by graphic formula IV; (b) phenyl, mono-substituted and di-substituted phenyl; (c) the unsubstituted, mono- and di-substituted heteroaromatic groups furanyl, benzofuran-2-yl, thienyl, benzothien-2-yl, dibenzofuran-2-yl, and dibenzothien-2-yl, each of said phenyl and heteroaromatic substituents in (b) and (c) being selected from the group consisting of hydroxy, aryl, arlyoxy, aryl(C_1-C_3)alkyl, amino, mono(C_1-C_3)alkylamino, di(C_1-C_3)alkylamino, N-

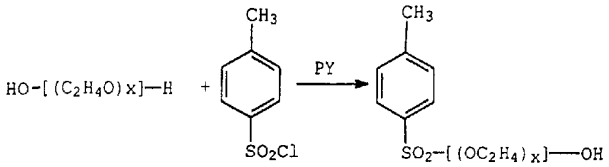
(C_1-C_3)alkylpiperazino, indolino, piperidino, morpholino, pyrryl, C_1-C_3 alkyl, C_1-C_3 chloroalkyl, C_1-C_3 fluoroalkyl, C_1-C_3 alkoxy, mono(C_1-C_3)alkoxy(C_1-C_3)alkyl, chloro and fluoro; (d) the groups represented by graphic formulae VA and VB wherein E is carbon and G is oxygen, R_{14} is C_1-C_3 alkyl or C_1-C_3 alkoxy; R_{15} and R_{16} are each hydrogen or C_1-C_4 alkyl; and q is 0 or 1; (e) C_1-C_4 alkyl; and (f) the group represented by graphic formula VC wherein L is hydrogen or methyl and M is phenyl or mono-substituted phenyl and said phenyl substituent is C_1-C_3 alkyl, C_1-C_3 alkoxy or fluoro.

More preferably, B and B' are each selected from the group consisting of: (a) the group represented by graphic formula IV; (b) phenyl, mono- and di-substituted phenyl, preferably substituted in the meta and/or para positions; (c) the unsubstituted, mono- and di-substituted heteroaromatic groups furanyl, benzofuran-2-yl, thienyl and benzothien-2-yl, each of said phenyl and heteroaromatic substituents in (b) and (c) being selected from the group consisting of hydroxy, C_1-C_3 alkyl, C_1-C_3 alkoxy, phenyl, indolino, fluoro and chloro; (d) the group represented by graphic formulae VA wherein E is carbon and G is oxygen, R_{14} is C_1-C_3 alkyl or C_1-C_3 alkoxy; R_{15} and R_{16} are each hydrogen or C_1-C_3 alkyl; and q is 0 or 1.

Compounds represented by graphic formulae I, II and III may be prepared by the following steps. In Reaction A, an excess of polyethylene glycol represented by general formula VI (wherein x is the same as for group R) or another polyalkylene glycol is reacted with toluenesulfonyl chloride represented by graphic formula VII in the presence of pyridine (PY) at -5°C to produce the hydroxy(polyethoxy)-p-toluenesulfonate represented by graphic formula VIII. See Bradshaw, J. S., et al, "Synthesis of Macrocyclic Acetals

Containing Lipophilic Substituents", Tetrahedron, Vol. 43, No. 19, pp 4271 to 4276, 1987, which disclosure is herein incorporated by reference.

REACTION A

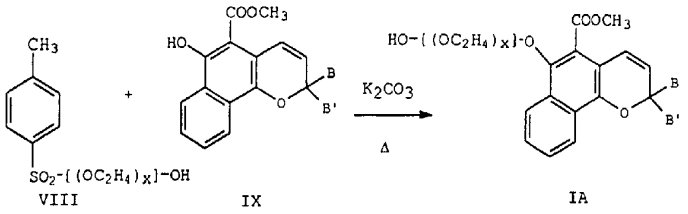


VI VII VIII

In Reaction B, the alkoxylated toluenesulfonate represented by graphic formula VIII is reacted with a naphthopyran represented by graphic formula IX in the presence of anhydrous potassium carbonate, acetone and heat to form the hydroxy end-capped alkoxylated naphthopyran of graphic formula IA. Alternatively, halogenated alkoxylated alcohols may be used in place of the alkoxylated toluenesulfonate to alkylate the hydroxy functionality using the aforementioned reaction conditions. Alkylating reactions are further described in Organic Synthesis, Vol. 31, pages 90-93, John Wiley & Sons, New York, New York.

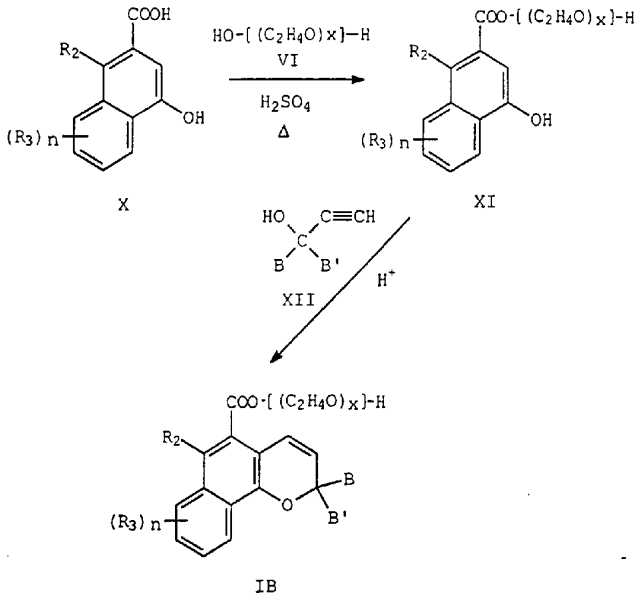
The compound represented by graphic formula IX may be prepared by coupling a substituted naphthol with a propargyl alcohol. This procedure is described in U.S. Patent No. 5,458,814, column 5, line 10 to column 7, line 38. The propargyl alcohol may be prepared according to the methods disclosed in U.S. Patent No. 5,645,767, column 5, line 8 to column 6, line 30. The aforesaid patents are incorporated herein *in toto* by reference.

REACTION B



In Reaction C, a substituted naphthoic acid represented by graphic formula X is reacted with a polyethylene glycol represented by general formula VI using concentrated sulfuric acid and heat to form the alkoxylated naphthol represented by graphic formula XI. In graphic formula X, R_2 and R_3 are as previously defined. The alkoxylated naphthol represented by graphic formula XI is coupled with the propargyl alcohol represented by graphic formula XII to form the alkoxylated naphthopyran represented by graphic formula IB.

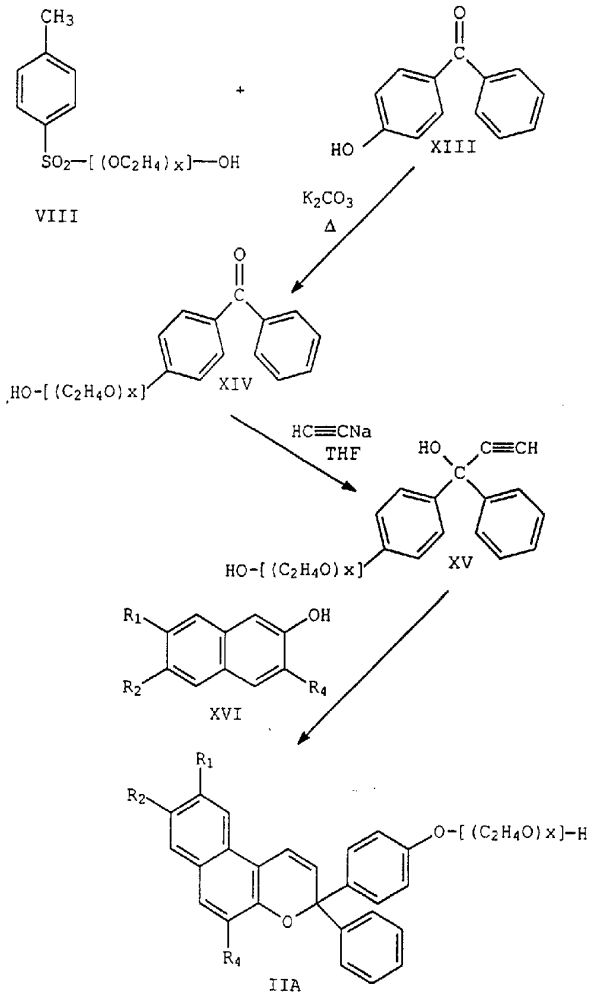
REACTION C



IB

In Reaction D, the alkoxylated toluenesulfonate represented by graphic formula VIII is reacted with a hydroxy substituted benzophenone represented by graphic formula XIII to form the alkoxylated benzophenone represented by graphic formula XIV. The alkoxylated benzophenone is reacted with sodium acetylide in a suitable solvent, such as anhydrous tetrahydrofuran (THF), to form the corresponding propargyl alcohol represented by graphic formula XV. The propargyl alcohol (XV) is coupled with the substituted naphthol of graphic formula XVI to form the alkoxylated naphthopyran represented by graphic formula IIA.

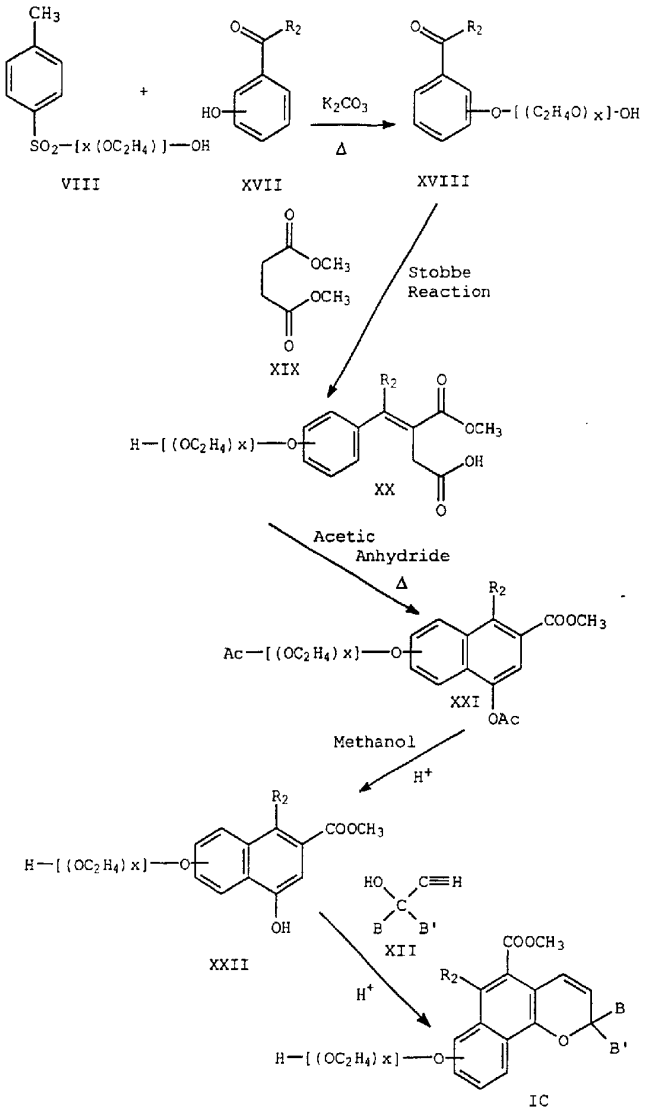
REACTION D



In Reaction E, the hydroxy end-capped alkoxylated toluenesulfonate represented by graphic formula VIII is reacted with a hydroxy substituted acetophenone, benzophenone or benzaldehyde represented by graphic formula XVII to form

the corresponding alkoxylated acetophenone, benzophenone or benzaldehyde. The compound of graphic formula XVIII is reacted with an ester of succinic acid such as dimethyl succinate represented by graphic formula XIX. Addition of the reactants to a solvent, e.g., toluene, containing potassium t-butoxide or sodium hydride as the base, yields the Stobbe condensation half ester represented by graphic formula XX. The half ester (XX) undergoes cyclodehydration in the presence of acetic anhydride to form the alkoxylated acetoxynaphthalene represented by graphic formula XXI. This product is reacted with hydrochloric acid (H^+) and an anhydrous alcohol such as anhydrous methanol to form the corresponding naphthol represented by graphic formula XXII. The naphthol (XXII) is coupled with a propargyl alcohol represented by graphic formula XII to form the alkoxylated naphthopyran represented by graphic formula IC.

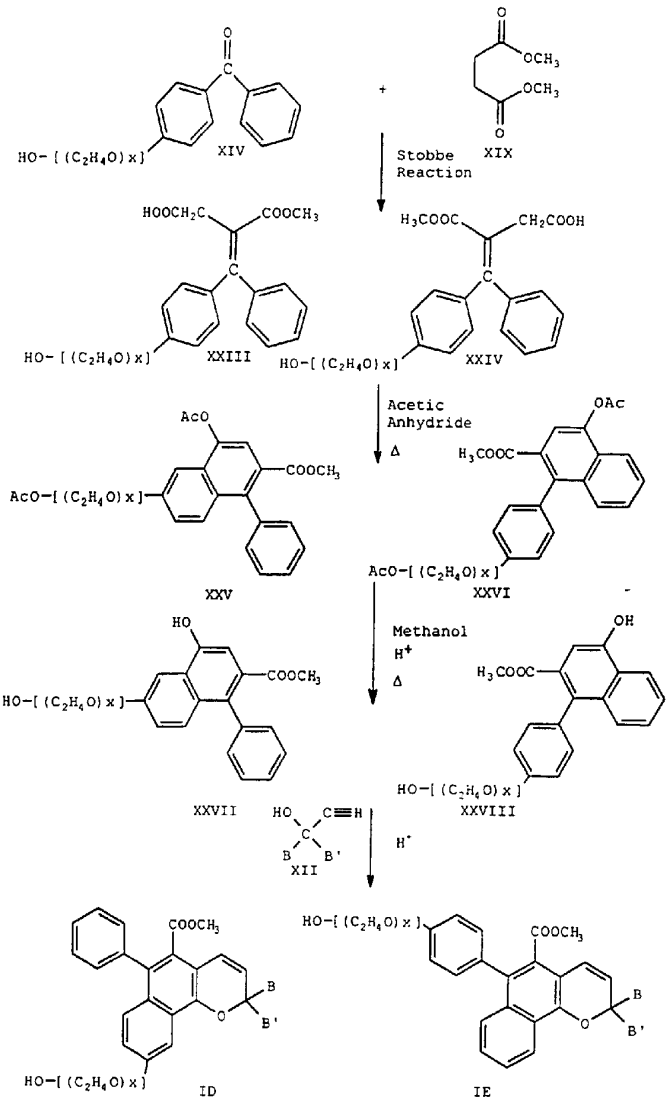
REACTION E



In Reaction F, the alkoxylated benzophenone represented by graphic formula XIV is reacted with an ester of

succinic acid such as dimethyl succinate represented by graphic formula XIX. Addition of the reactants to a solvent, e.g., toluene, containing potassium t-butoxide or sodium hydride as the base, yields the Stobbe condensation half esters represented by graphic formulae XXIII and XXIV. The half esters undergo cyclodehydration in the presence of acetic anhydride to form the alkoxylated acetoxynaphthalenes represented by graphic formulae XXV and XXVI. These products are reacted with hydrochloric acid (H^+) and an anhydrous alcohol such as anhydrous methanol to form the corresponding naphthols represented by graphic formulae XXVII and XXVIII. The naphthols are coupled with propargyl alcohol represented by graphic formula XII to form the hydroxy end-capped alkoxylated naphthopyrans represented by graphic formula ID and IE.

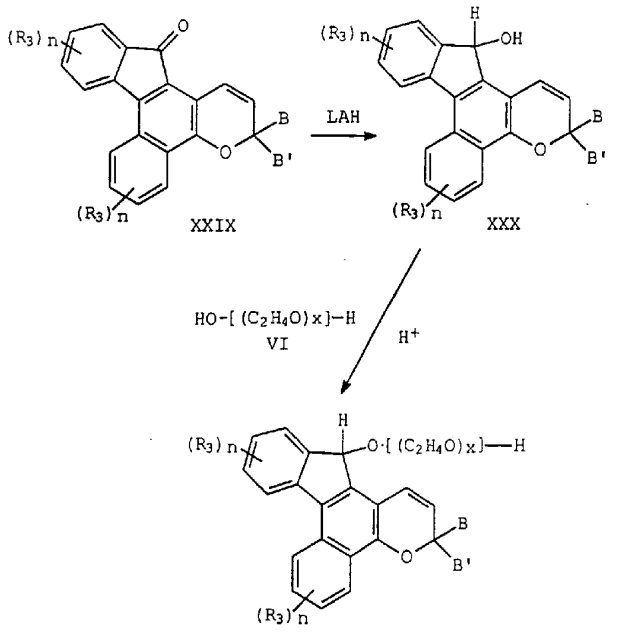
REACTION F



In Reaction G, the compound represented by graphic formula XXIX is reduced with lithium aluminum hydride (LAH) to produce the compound represented by graphic formula XXX.

Procedures for preparing the compound of graphic formula XXIX are disclosed in the afore-referenced U.S. Patent 5,645,767. A polyethylene glycol represented by general formula VI (wherein x is the same as for group R) is reacted with the compound of graphic formula XXX using an acid (H^+) to form the hydroxy end-capped alkoxylated indeno-fused naphthopyran of graphic formula IIIA.

REACTION G



IIIA

Reactions B, C, D, E, F and G produce polymerizable naphthopyrans having an end-capped hydroxy group which may be used in reactions to form polyurethane polymers. These hydroxy end-capped naphthopyrans may be reacted with an acrylate, e.g., ethyl methacrylate, in the presence of a

catalytic amount of an acid to produce an acryloxy, e.g., methacryloxy, end-capped naphthopyran or with epichlorohydrin in the presence of a base to produce an epoxy end-capped naphthopyran.

The polymerizable polyalkoxylated naphthopyran compounds represented by graphic formulae I, IA, IB, IC, ID, IE, II, IIA, III and IIIA may be used in those applications in which organic photochromic substances may be employed, such as optical lenses, e.g., vision correcting ophthalmic lenses, contact lenses and plano lenses, face shields, goggles, visors, camera lenses, windows, automotive windshields, aircraft and automotive transparencies, e.g., T-roofs, sidelights and backlights, plastic films and sheets, textiles and coatings, e.g., coating compositions. As used herein, coating compositions are defined herein to include polymeric coating compositions prepared from materials such as polyurethanes, epoxy resins and other resins used to produce synthetic polymers; paints, i.e., a pigmented liquid or paste used for the decoration, protection and/or the identification of a substrate; and inks, i.e., a pigmented liquid or paste used for writing and printing on substrates, which include paper, glass, ceramics, wood, masonry, textiles, metals and polymeric organic materials. Coating compositions may be used to produce polymeric coatings on optical elements, verification marks on security documents, e.g., documents such as banknotes, passport and drivers' licenses, for which authentication or verification of authenticity may be desired.

Depending on the extent of alkoxylation and the polymerizable group used, the photochromic compounds of the present invention may be soluble in water, i.e., soluble in the amount of at least 1 gram per liter. The water solubility of some of the photochromic compounds of the present invention

offers handling and processing advantages not achieved by water insoluble photochromic compounds. In particular, the use of hazardous organic solvents as carriers for photochromic compounds is avoided. Also avoided is the use of such solvents in cleaning excess photochromic material from the surface of polymeric substrates after an imbibition or transfer process.

The 2H-naphtho-[1,2-b]pyrans represented by graphic formula I exhibit color changes from colorless to colors ranging from yellow to red/purple. The 3H-naphtho[2,1-b]pyrans represented by graphic formula II exhibit color changes from colorless to colors ranging from yellow to orange and red. The indeno[2,1-f]naphtho[1,2-b]pyrans represented by graphic formulae III exhibit color changes from colorless to colors ranging from orange to blue/gray.

Examples of contemplated naphthopyrans within the scope of the invention are the following:

(a) 2,2-bis(4-methoxyphenyl)-5-(2-hydroxyethoxycarbonyl)-6-phenyl-[2H]-naphtho[1,2-b]pyran;

(b) 2,2-bis(4-methoxyphenyl)-5-(2-(2-hydroxyethoxy)ethoxycarbonyl)-6-phenyl-[2H]-naphtho[1,2-b]pyran;

(c) 2,2-bis(4-methoxyphenyl)-5-(2-(2-(2-hydroxy-ethoxy)ethoxy)ethoxycarbonyl)-6-phenyl-[2H]naphtho[1,2-b]pyran;

(d) 2,2-bis(4-methoxyphenyl)-5-(2-(2-(2-(2-hydroxyethoxy)ethoxy)ethoxy)ethoxycarbonyl)-6-phenyl-[2H]-naphtho[1,2-b]pyran;

(e) 2,2-bis(4-methoxyphenyl)-5-methoxycarbonyl-6-(2-hydroxyethoxy)ethoxy-[2H]-naphtho[1,2-b]pyran;

(f) 2-(4-(2-(2-hydroxyethoxy)ethoxy)ethoxyphenyl)-2-phenyl-5-methoxycarbonyl-6-methyl-9-methoxy-[2H]-naphtho[1,2-b]pyran;

(g) 2,2-bis(4-methoxyphenyl)-5-methoxycarbonyl-6-phenyl-9-(2-hydroxyethoxy)-[2H]-naphtho[1,2-b]pyran;

(h) 2,2-bis(4-methoxyphenyl)-5-methoxycarbonyl-6-(4-(2-hydroxyethoxy)phenyl)-[2H]-naphtho[1,2-b]pyran;

(i) 2-phenyl-2-(4-(2-(2-methylprop-2-enoyloxy)ethoxy)phenyl)-5-(methoxycarbonyl)-6-(2-(2-methylprop-2-enoxyloxy)ethoxy)-[2H]-naphtho[1,2-b]pyran;

(j) 2,2,6-triphenyl-5-(2-(2-(2-(2-methylprop-2-enoxyloxy)ethoxy)ethoxy)ethoxycarbonyl)-[2H]-naphtho[1,2-b]pyran; and

(k) 2,2,6-triphenyl-5-(2-(2-(2-(oxiran-2-ylmethoxy)ethoxy)ethoxy)ethoxycarbonyl)-[2H]-naphtho[1,2-b]pyran.

It is contemplated that the photochromic naphthopyrans of the present invention may each be used alone, in combination with other naphthopyrans of the present invention, or in combination with one or more other appropriate complementary organic photochromic materials, i.e., organic photochromic compounds having at least one activated absorption maxima within the range of between about 400 and 700 nanometers (or substances containing the same) and which color when activated to an appropriate hue.

The complementary organic photochromic materials may include other polymerizable photochromic compounds, such as those disclosed in U.S. Patents 4,719,296; 5,166,345; 5,236,958; 5,252,742; 5,359,085; and 5,488,119. Further examples of complementary organic photochromic compounds include other naphthopyrans and indenonaphthopyrans, chromenes and oxazines, substituted 2H-phenanthro[4,3-b]pyran and 3H-

phenanthro[1,2-b]pyran compounds, benzopyran compounds having substituents at the 2-position of the pyran ring and mixtures of such photochromic compounds. Such photochromic compounds are described in U.S. Patents 3,562,172; 3,567,605; 3,578,602; 4,215,010; 4,342,668; 4,816,584; 4,818,096; 4,826,977; 4,880,667; 4,931,219; 5,066,818; 5,238,981; 5,274,132; 5,384,077; 5,405,958; 5,429,774; 5,458,814, 5,466,398; 5,514,817; 5,552,090; 5,552,091; 5,565,147; 5,573,712; 5,578,252; 5,637,262; 5,645,767; 5,656,206; 5,658,500; 5,658,501; 5,674,432 and 5,698,141. Spiro(indoline)pyrans are also described in the text, Techniques in Chemistry, Volume III, "Photochromism", Chapter 3, Glenn H. Brown, Editor, John Wiley and Sons, Inc., New York, 1971.

Other complementary photochromic substances contemplated are metal-dithiozonates, e.g., mercury dithizonates which are described in, for example, U.S. Patent 3,361,706; and fulgides and fulgimides, e.g., the 3-furyl and 3-thienyl fulgides and fulgimides, which are described in U.S. Patent 4,931,220 at column 20, line 5 through column 21, line 38.

The disclosures relating to such photochromic compounds in the aforedescribed patents are incorporated herein, *in toto*, by reference. The photochromic articles of the present invention may contain one photochromic compound or a mixture of photochromic compounds, as desired.

The photochromic compounds of the present invention may be associated with a polymeric organic host material or other substrate by various means. They may be incorporated, i.e., dissolved and/or dispersed, into the host material, polymerized with other components of the host material, and/or incorporated into a coating applied to a substrate, e.g., a

polymeric coating applied to one surface of the polymeric organic host material.

Other than where otherwise indicated, all numbers expressing values, such as, wavelengths, quantities of ingredients or reaction conditions used herein are to be understood as modified in all instances by the term "about".

Each of the photochromic substances described herein may be used in amounts (or in a ratio) such that an organic host material or substrate to which the photochromic compounds or mixture of compounds is associated, exhibits a desired resultant color, e.g., a substantially neutral color when activated with unfiltered sunlight, i.e., as near a neutral color as possible given the colors of the activated photochromic compounds. Neutral gray and neutral brown colors are preferred. Further discussion of neutral colors and ways to describe colors may be found in U.S. Patent 5,645,767 column 12, line 66 to column 13, line 19.

The amount of the photochromic naphthopyrans to be applied to or incorporated into a coating composition or host material is not critical provided that a sufficient amount is used to produce a photochromic effect discernible to the naked eye upon activation. Generally such amount can be described as a photochromic amount. The particular amount used depends often upon the intensity of color desired upon irradiation thereof and upon the method used to incorporate or apply the photochromic compounds. Typically, the more photochromic compound applied or incorporated, the greater is the color intensity up to a certain limit.

The relative amounts of the aforesaid photochromic compounds used will vary and depend in part upon the relative intensities of the color of the activated species of such compounds, the ultimate color desired and the method of

application to the host material or substrate. Generally, the amount of total photochromic compound incorporated into or applied to a photochromic optical host material may range from about 0.05 to about 1.0, e.g., from 0.1 to about 0.45, milligrams per square centimeter of surface to which the photochromic compound is incorporated or applied. The amount of photochromic material incorporated into a coating composition may range from 0.1 to 40 weight percent based on the weight of the liquid coating composition.

The photochromic naphthopyrans of the present invention may be associated with the host material by various methods described in the art. See, for example, column 13, lines 40 to 58 of U.S. Patent 5,645,767. Aqueous or organic solutions of the photochromic compounds may be used to incorporate the photochromic compounds into a polymeric organic host material or other materials such as textiles and polymeric coating compositions. Polymeric coating compositions may be applied to the substrate using a coating process such as that described in U.S. Patent 3,971,872, the disclosure of which is incorporated herein by reference.

Application of the polymeric coating may be by any of the methods used in coating technology such as, for example, spray coating, spin coating, spread coating, curtain coating, dip coating, casting or roll-coating and methods used in preparing overlays, such as the method of the type described in U.S. Patent 4,873,029, which is incorporated herein by reference. The application method selected also depends on the thickness of the cured coating. Coatings having a thickness ranging from 1 to 50 microns may be applied by conventional methods used in coating technology. Coatings of a thickness greater than 50 microns may require molding methods typically used for overlays.

The host material will usually be transparent, but may be translucent or even opaque. The host material need only be pervious to that portion of the electromagnetic spectrum, which activates the photochromic substance, i.e., that wavelength of ultraviolet (UV) light that produces the open or colored form of the substance and that portion of the visible spectrum that includes the absorption maximum wavelength of the substance in its UV activated form, i.e., the open form. Preferably, the host color should not be such that it masks the color of the activated form of the photochromic compounds, i.e., so the change in color is readily apparent to the observer. Compatible tints may be applied to the host material as described in U.S. Patent 5,645,767 in column 13, line 59 to column 14, line 3.

Most preferably, the polymeric organic host material is a solid transparent or optically clear material, e.g., materials suitable for optical applications, such as plano, ophthalmic and contact lenses, windows, automotive transparencies, e.g., windshields, aircraft transparencies, plastic sheeting, polymeric films, etc.

Examples of polymeric organic host materials which may be used with the photochromic compounds described herein include: polymers, i.e., homopolymers and copolymers, of the bis(allyl carbonate) monomers, diethylene glycol dimethacrylate monomers diisopropenyl benzene monomers, ethoxylated bisphenol A dimethacrylate monomers, ethylene glycol bismethacrylate monomers, poly(ethylene glycol) bismethacrylate monomers, ethoxylated phenol bismethacrylate monomers, alkoxylated polyhydric alcohol acrylate monomers, such as ethoxylated trimethylol propane triacrylate monomers, urethane acrylate monomers, such as those described in U.S. Patent 5,373,033, and vinylbenzene monomers, such as those

described in U.S. Patent 5,475,074 and styrene; polymers, i.e., homopolymers and copolymers, of polyfunctional, e.g., mono-, di- or multi-functional, acrylate and/or methacrylate monomers, poly(C_1-C_{12} alkyl methacrylates), such as poly(methyl methacrylate), poly(oxyalkylene)dimethacrylate, poly(alkoxylated phenol methacrylates), cellulose acetate, cellulose triacetate, cellulose acetate propionate, cellulose acetate butyrate, poly(vinyl acetate), poly(vinyl alcohol), poly(vinyl chloride), poly(vinylidene chloride), polyurethanes, polythiourethanes, thermoplastic polycarbonates, polyesters, poly(ethylene terephthalate), polystyrene, poly(alpha methylstyrene), copoly(styrene-methyl methacrylate), copoly(styrene-acrylonitrile), polyvinylbutyral and polymers, i.e., homopolymers and copolymers, of diallylidene pentaerythritol, particularly copolymers with polyol (allyl carbonate) monomers, e.g., diethylene glycol bis(allyl carbonate), and acrylate monomers, e.g., ethyl acrylate, butyl acrylate. Further examples of polymeric organic host materials are disclosed in the U.S. Patent 5,753,146, column 8, line 62 to column 10, line 34, which disclosure is incorporated herein by reference.

Transparent copolymers and blends of transparent polymers are also suitable as host materials. Preferably, the host material or substrate for the photochromic polymeric coating composition is an optically clear polymerized organic material prepared from a thermoplastic polycarbonate resin, such as the carbonate-linked resin derived from bisphenol A and phosgene, which is sold under the trademark, LEXAN; a polyester, such as the material sold under the trademark, MYLAR; a poly(methyl methacrylate), such as the material sold under the trademark, PLEXIGLAS; polymerizates of a polyol(allyl carbonate) monomer, especially diethylene glycol

bis(allyl carbonate), which monomer is sold under the trademark CR-39, and polymerizates of copolymers of a polyol (allyl carbonate), e.g., diethylene glycol bis(allyl carbonate), with other copolymerizable monomeric materials, such as copolymers with 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, and copolymers with a polyurethane having terminal diacrylate functionality, as described in U.S. Patents 4,360,653 and 4,994,208; and copolymers with aliphatic urethanes, the terminal portion of which contain allyl or acrylyl functional groups, as described in U.S. Patent 5,200,483; poly(vinyl acetate), polyvinylbutyral, polyurethane, polythiourethanes, polymers of members of the group consisting of diethylene glycol dimethacrylate monomers, diisopropenyl benzene monomers, ethoxylated bisphenol A dimethacrylate monomers, ethylene glycol bismethacrylate monomers, poly(ethylene glycol) bismethacrylate monomers, ethoxylated phenol bismethacrylate monomers and ethoxylated trimethylol propane triacrylate monomers; cellulose acetate, cellulose propionate, cellulose butyrate, cellulose acetate butyrate, polystyrene and copolymers of styrene with methyl methacrylate, vinyl acetate and acrylonitrile.

More particularly, contemplated is use of the photochromic naphthopyrans of the present invention with optical organic resin monomers used to produce optically clear coatings and polymerizates, i.e., materials suitable for optical applications, such as for example lenses, i.e., plano, ophthalmic and contact lenses. Optically clear polymerizates may have a refractive index that may range from about 1.48 to about 1.75, e.g., from about 1.495 to about 1.66.

Specifically contemplated are polymerizates of optical resins sold by PPG Industries, Inc. under the CR- designation, e.g., CR-307 and CR-407, and polymerizates prepared for use as hard or soft contact lenses. Methods for producing both types of contact lenses are disclosed in U.S. Patent 5,166,345, column 11, line 52, to column 12, line 52, which disclosure is incorporated herein by reference.

The present invention 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

STEP 1

Ethylene glycol, 10 milliliters (mL), and concentrated sulfuric acid, 0.1 gram, were added to a reaction flask containing 1-phenyl-4-hydroxy-2-naphthoic acid, 0.5 gram. The 1-phenyl-4-hydroxy-2-naphthoic acid used, was produced by the process described in Steps 1-4 of Example 1 in U.S. Patent 5,645,767. The reaction mixture was heated to and maintained at 90°C for approximately 24 hours. After cooling to room temperature, the reaction mixture was poured slowly into 100 mL of water with vigorous mixing. A yellowish-white solid precipitated. The solid was filtered, washed with copious amounts of water and air dried to obtain 0.52 gram of product. A nuclear magnetic resonance (NMR) showed the product to have a structure consistent with 1-phenyl-2-(2-hydroxyethoxycarbonyl)-4-naphthol.

STEP 2

1-Phenyl-2-(2-hydroxyethoxycarbonyl)-4-naphthol, from Step 1 and 1.1 equivalents of 1,1-bis(4-methoxyphenyl)-2-

propyn-1-ol were added to a reaction flask. Toluene, 100 mL, was added and the reaction mixture was stirred at room temperature. A catalytic amount of dodecylbenzene sulfonic acid (approximately 50 milligrams (mg)) was added, and the resulting brownish-red mixture was stirred at room temperature for 3 hours. The toluene layer was separated and washed carefully with saturated sodium bicarbonate solution. After removing the solvent, toluene, under vacuum, a brownish-red oil was obtained. The oil was purified using silica-gel column chromatography. The eluant was a 1:1.5 mixture of ethyl acetate:hexane. A reddish-brown oil was isolated which foamed upon drying under vacuum. NMR analysis showed the product to have a structure consistent with 2,2-bis(4-methoxyphenyl)-5-(2-hydroxyethoxycarbonyl)-6-phenyl-[2H]-naphtho[1,2-b]pyran.

EXAMPLE 2

STEP 1

The procedure of Step 1 of Example 1 was followed except for the following: diethylene glycol was used in place of ethylene glycol; the reaction mixture was poured into water and extracted with ethyl acetate; the ethyl acetate extracts were combined and dried over anhydrous sodium sulfate; and the solvent, ethyl acetate, was removed under vacuum. The desired product was recovered as a light yellow oil. NMR analysis showed the product to have a structure consistent with 1-phenyl-2-(2-(2-hydroxyethoxy)-ethoxycarbonyl)-4-naphthol.

STEP 2

The procedure of Step 2 of Example 1 was followed using the product of Step 1 of this Example 2; and a 1:1 mixture of ethyl acetate:hexane was the eluant. The desired

product was isolated as a reddish-brown oil. NMR analysis showed the product to have a structure consistent with 2,2-bis(4-methoxyphenyl)-5-(2-(2-hydroxyethoxy)-ethoxycarbonyl)-6-phenyl-[2H]-naphtho[1,2-b]pyran.

EXAMPLE 3

STEP 1

The procedure of Step 1 of Example 2 was followed except for the following: triethylene glycol was used in place of diethylene glycol; the reaction mixture was heated for four hours at approximately 180°C; chloroform was used in place of ethyl acetate; and the separated organic layer was washed with water, 200 mL, aqueous sodium bicarbonate, 200 mL, and finally with dilute aqueous hydrochloric acid, 200 mL. The resulting oil, approximately 5 grams, containing 1-phenyl-2-(2-(2-(2-hydroxyethoxy)ethoxy)ethoxycarbonyl)-4-naphthol was used in the next step without further purification.

STEP 2

The product of Step 1 and 1,1-bis(4-methoxyphenyl)-2-propyn-1-ol, 5 grams, were added to a reaction flask containing 200 mL of toluene and stirred. A catalytic amount of p-toluenesulfonic acid (about 100 mg) was added. The resulting mixture was heated on a steam bath at about 100°C for 1.5 hours, cooled to room temperature and stirred overnight. The solvent, toluene, was removed under vacuum. The resulting residue was dissolved into a minimal amount of a chloroform:ethylacetate eluant (3:1 on a volume basis) and chromatographed in a silica gel column yielding 3.5 grams of an oil recovered as an expanded foam. NMR analysis showed the product to have a structure consistent with 2,2-bis(4-

methoxyphenyl)-5-(2-(2-(2-hydroxy-ethoxy)ethoxy)ethoxy-carbonyl)-6-phenyl-[2H]naphtho[1,2-b]pyran.

EXAMPLE 4

STEP 1

The procedure of Step 1 of Example 2 was followed except that tetraethylene glycol was used in place of diethylene glycol. NMR analysis showed the product to have a structure consistent with 1-phenyl-2-(2-(2-(2-(2-hydroxy-ethoxy)ethoxy)ethoxy)ethoxycarbonyl)-4-naphthol.

STEP 2

The procedure of Step 2 of Example 1 was followed using the product of Step 1 of this Example 4; and a 4:1 mixture of ethyl acetate:hexane was the eluant. The desired product was isolated as a reddish-brown oil. NMR analysis showed the product to have a structure consistent with 2,2-bis(4-methoxyphenyl)-5-(2-(2-(2-(2-hydroxyethoxy)ethoxy)ethoxy)ethoxycarbonyl)-6-phenyl-[2H]-naphtho[1,2-b]pyran.

EXAMPLE 5

2,2-Bis(4-methoxyphenyl)-5-methoxycarbonyl-6-hydroxy-[2H]-naphtho[1,2-b]pyran (Example 1 of U.S. Patent 5,458,814), 3.7 grams, 2-(2-chloroethoxy)ethanol, 5 grams, sodium iodide, 1.2 grams, and anhydrous potassium carbonate, 1.4 grams, were added to a reaction flask containing 40 ml of N,N-dimethylformamide. The reaction mixture was stirred under a nitrogen atmosphere and heated to and maintained at 80°C for four hours. The reaction mixture was cooled to room temperature, and ethyl acetate, 250 mL, and then water, 300 mL, were added to it. The aqueous layer was separated and

extracted with ethyl acetate three times, each with 150 mL. The ethyl acetate extracts were combined and washed carefully with water , three times, each with 300 mL, and then dried over anhydrous sodium sulfate. Removal of the solvent, ethyl acetate, under vacuum yielded a red oil. The oil was dissolved in a minimal amount of chloroform and chromatographed on a silica-gel column using a mixture, based on percent volume, of 50% chloroform, 40% ethyl acetate, and 10% hexane as the eluant. A red oil, 2.1 grams, was isolated which foamed upon drying under vacuum. NMR analysis showed the product to have a structure consistent with 2,2-bis(4-methoxyphenyl)-5-methoxycarbonyl-6-(2-hydroxyethoxy)ethoxy-[2H]-naphtho[1,2-b]pyran.

EXAMPLE 6

STEP 1

4-Hydroxybenzophenone, 19.8 grams, sodium iodide, 4.5 grams, and anhydrous potassium carbonate, 27.6 grams, were added to a reaction flask containing 50 mL of N,N-dimethylformamide. The reaction mixture was stirred under a nitrogen atmosphere and heated to 100°C. A solution of 2-(2-(2-chloroethoxy)ethoxy)-ethanol, 18.5 grams, in 20 ml of N,N-dimethylformamide was added dropwise over a one hour period. Afterwards, the reaction temperature was maintained at 100°C for three hours. The reaction mixture was cooled to room temperature. Ethyl acetate, 300 mL, and then 400 mL of water were added to the reaction mixture. The aqueous layer was separated and extracted with ethyl acetate, two times, each with 150 mL. The ethyl acetate extracts were combined and washed carefully with water, two times with 300 mL each time, and then dried over anhydrous sodium sulfate. Solvent removal under vacuum yielded a light yellow liquid. NMR analysis

showed the product to have a structure consistent with 4-(2-(2-hydroxyethoxy)ethoxy)ethoxy benzophenone. This product was utilized in the next step without further purification.

STEP 2

The product of Step 1, 13.2 grams, and N,N-dimethylformamide saturated with acetylene, 150 mL, was added to a reaction flask. The reaction mixture was stirred using a mechanical stirrer at room temperature under a nitrogen atmosphere. Sodium acetylide in xylene/mineral oil, 28 grams of an 18 weight percent suspension, was added to the reaction flask over a thirty minute period while stirring. After three hours, the reaction mixture was added slowly to 1200 mL of distilled water. The water layer was separated and washed with 300 mL of hexane and extracted with ethyl acetate, three times with 250 mL each time. The ethyl acetate extracts were combined, washed with water, and dried over anhydrous sodium sulfate. The remaining solvents were removed under vacuum to yield a dark brown oil. NMR analysis showed the product to have a structure consistent with 1-(4-(2-(2-hydroxy-ethoxy)ethoxy)ethoxyphenyl)-1-phenyl-2-propyn-1-ol. This product was utilized in the next step without further purification.

STEP 3

The procedure of Step 2 of Example 1 was followed except for the following: the product of Step 2 of this Example and 1-methyl-2-methoxycarbonyl-6-methoxy-4-naphthol were used; and the eluant used was a mixture, based on percent volume, of 50% ethyl acetate, 45% chloroform and 5% hexane. NMR analysis showed the product to have a structure consistent

with 2-(4-(2-(2-hydroxyethoxy)ethoxy)ethoxyphenyl)-2-phenyl-5-methoxycarbonyl-6-methyl-9-methoxy-[2H]-naphtho[1,2-b]pyran.

EXAMPLE 7

STEP 1

4-Hydroxybenzophenone (19.8 grams) and 15 grams of anhydrous potassium carbonate were added to a reaction flask containing 80 mL of N,N-dimethylformamide. The reaction mixture was stirred under a nitrogen atmosphere and heated to 100°C. A solution of 2-bromoethanol (26.3 grams) in 20 mL of N,N-dimethylformamide was added dropwise over a fifteen minute period. After overnight stirring at 100°C, the heating was stopped and the reaction mixture was cooled to room temperature. The reaction mixture was poured slowly accompanied by vigorous stirring into 800 mL of water. A white, pasty solid precipitated out. The solid was filtered and 500 mL of ethyl acetate (500 mL) was added to dissolve the product. The ethyl acetate solution was washed twice with water (300 mL), and then once with saturated sodium chloride solution (400 mL). The solvent, ethyl acetate, was removed under vacuum to obtain 22 grams of a white solid. A nuclear magnetic resonance (NMR) showed the product to have a structure consistent with 4-(2-hydroxyethoxy)-benzophenone. This product was utilized in the next step without further purification.

STEP 2

Potassium t-butoxide (9 grams) was added to a reaction flask containing 50 mL of toluene. A solution containing 4-(2-hydroxyethoxy)-benzophenone (12 grams) and dimethyl succinate (8.3 grams) in 100 mL of toluene was added dropwise over a thirty minute period to the reaction flask

accompanied by mechanical stirring. The resulting brownish-red solution was heated to reflux temperature under a nitrogen atmosphere. After two hours, the heating was stopped and the reaction mixture was cooled to room temperature. Water (300 mL) was added to the reaction mixture. The aqueous layer was separated and washed once with 200 mL of ethyl acetate. The aqueous layer was neutralized with dilute hydrochloric acid, and then extracted three times with ethyl acetate (200 mL) each time. The combined ethyl acetate extracts were washed once with saturated sodium chloride solution (200 mL), dried over anhydrous sodium sulfate, and then the solvent was removed under vacuum to yield 14.4 grams of a dark brown oil. Mass spectroscopic analysis showed the oil to contain the cis and trans isomers of 4-phenyl-4-(4-(2-hydroxyethoxy)phenyl)-3-methoxycarbonyl-3-butenoic acid as the major product. This product was utilized in the next step without further purification.

STEP 3

The mixture of isomers (14.1 grams) from Step 2 was added to a reaction flask containing 30 mL of acetic anhydride and 2.3 grams of sodium acetate. The reaction mixture was heated at reflux temperature under a nitrogen atmosphere. After four hours, the heating was stopped and the reaction mixture was cooled to room temperature. The following were added carefully to the reaction mixture in the order listed: ethyl acetate (300 mL), water (100 mL) and saturated sodium bicarbonate solution (100 mL). The remaining acid was neutralized with solid sodium bicarbonate. The ethyl acetate layer was separated and washed with 300 mL of saturated sodium bicarbonate solution, followed by 200 mL of saturated sodium chloride solution. After drying

over anhydrous sodium sulfate, the solvent was removed under vacuum to obtain 12.8 grams of a brown oil containing 1-phenyl-2-methoxycarbonyl-4-acetoxy-6-(2-acetoxyethoxy)-naphthalene and 1-(4-(2-acetoxyethoxy)phenyl)-2-methoxycarbonyl-4-acetoxy-naphthalene. This product was utilized in the next step without further purification.

STEP 4

The brown oil (12.2 grams) from Step 3 was added to a reaction flask containing 200 mL of methanol. Concentrated hydrochloric acid (1 mL) was added and the reaction mixture was heated at reflux temperature under a nitrogen atmosphere. After five hours, the heating was stopped and the reaction mixture was cooled to room temperature. The solvent was removed under reduced pressure to yield 11.3 grams of a reddish-brown oil containing 1-phenyl-2-methoxycarbonyl-6-(2-hydroxyethoxy)-4-naphthol and 1-(4-(2-hydroxyethoxy)phenyl)-2-methoxycarbonyl-4-naphthol. This product was utilized in the next step without further purification.

STEP 5

The reddish-brown oil (0.7 gram) from Step 4 was added to a reaction flask containing 40 mL of toluene. The mixture was heated to dissolve the reddish-brown oil, and then 0.55 gram of 1,1-bis(4-methoxyphenyl)-2-propyn-1-ol was added to the reaction flask. A catalytic amount (approximately 20 mg) of dodecylbenzenesulfonic acid was added, and the resulting brownish-red mixture was stirred at room temperature under a nitrogen atmosphere. The stirring was stopped after two hours. The toluene layer was separated and washed carefully with saturated sodium bicarbonate solution. After removing the solvent under vacuum, a brownish-red oil was

obtained. The oil was purified using preparatory thin layer chromatography on a silica-gel plate. The desired photochromic products were isolated as red oils. When the isolated products on silica gel plates were exposed to ultraviolet radiation (265 Nm), both formed a deeper red color. This activated color faded back to the original color after removal of the UV radiation source. Nuclear magnetic resonance (NMR) showed the first product to have a structure consistent with 2,2-bis(4-methoxyphenyl)-5-methoxycarbonyl-6-phenyl-9-(2-hydroxyethoxy)-[2H]-naphtho[1,2-b]pyran, and the second product to have a structure consistent with 2,2-bis(4-methoxyphenyl)-5-methoxycarbonyl-6-(4-(2-hydroxyethoxy)-phenyl)-[2H]-naphtho[1,2-b]pyran.

COMPARATIVE EXAMPLE 1 (CE 1)

CE 1 is 2,2-bis(4-methoxyphenyl)-5-methoxycarbonyl-6-phenyl[2H]naphtho[1,2-b]pyran. It may be prepared by following the procedure described for Example 1 of U.S. Patent 5,458,814 using 1-phenyl-4-hydroxy-2-naphthoate in place of methyl-4-dihydroxy-2-naphthoate.

COMPARATIVE EXAMPLE 2 (CE 2)

CE 2 is 2,2-bis(4-methoxyphenyl)-5-methoxycarbonyl-6-methoxy-[2H]-naphtho[1,2-b]pyran. It may be prepared by following the procedure described for Example 2 of U.S. Patent 5,458,814.

COMPARATIVE EXAMPLE 3 (CE 3)

CE 3 is 2-(4-methoxyphenyl)-2-phenyl-5-methoxycarbonyl-6-methyl-9-methoxy-[2H]-naphtho[1,2-b]pyran. This compound was prepared using the procedure described for Step 2 of Example 5 of U.S. Patent 5,458,814 except that 1-

methyl-2-methoxycarbonyl-6-methoxy-4-naphthol was used in place of methyl-1,4-dihydroxy-2-naphthoate.

EXAMPLE 8

PART A

Testing was done with the photochromic compounds described in the Examples and the Comparative Examples in the following manner. A quantity of photochromic compound calculated to yield a 1.5×10^{-3} molal solution was added to a flask containing 50 grams of a monomer blend of 4 parts ethoxylated bisphenol A dimethacrylate (BPA 2EO DMA), 1 part poly(ethylene glycol) 600 dimethacrylate, and 0.033 weight percent 2,2'-azobis(2-methyl propionitrile) (AIBN). The photochromic compound was dissolved into the monomer blend by stirring and gentle heating, if necessary. After a clear solution was obtained, it was poured into a flat sheet mold having the interior dimensions of 2.2 mm x 6 inches (15.24 cm) x 6 inches (15.24 cm). The mold was sealed and placed in a horizontal air flow, programmable oven programmed to increase the temperature from 40°C to 95°C over a 5 hour interval, hold the temperature at 95°C for 3 hours, lower it to 60°C over a 2 hour interval and then hold it at 60°C for 16 hours. After the mold was opened, the polymer sheet was cut using a diamond blade saw into 2 inch (5.1 centimeters) test squares.

Part B

The photochromic test squares prepared in Part A were tested for photochromic response on an optical bench. Prior to testing on the optical bench, the photochromic test squares were conditioned, i.e., exposed to 365 nanometer ultraviolet light for about 15 minutes to activate the photochromic compounds and then placed in a 76°C oven for

about 15 minutes to bleach or inactivate the photochromic compounds. The test squares were then cooled to room temperature, exposed to fluorescent room lighting for at least 2 hours and then kept covered for at least 2 hours prior to testing on an optical bench maintained at 72°F (22.2°C). The bench was fitted with a 250 watt Xenon arc lamp, a remote controlled shutter, a copper sulfate bath acting as a heat sink for the arc lamp, a Schott WG-320 nm cut-off filter which removes short wavelength radiation; neutral density filter(s) and a sample holder in which the square to be tested was inserted. The power output of the optical bench, i.e., the dosage of light that the sample lens would be exposed to, was calibrated with a photochromic test square used as a reference standard. This resulted in a power output ranging from 0.15 to 0.20 milliWatts per square centimeter (mW/cm^2). Measurement of the power output was made using a GRASEBY Optronics Model S-371 portable photometer (Serial #21536) with a UV-A detector (Serial #22411) or comparable equipment. The UV-A detector was placed into the sample holder and the light output was measured. Adjustments to the power output were made by increasing or decreasing the lamp wattage or by adding or removing neutral density filters in the light path.

A monitoring, collimated beam of light from a tungsten lamp was passed through the square at a small angle (approximately 30°) normal to the square. After passing through the square, the light from the tungsten lamp was directed to a detector through Spectral Energy Corp. GM-200 monochromator set at the previously determined visible lambda max of the photochromic compound being measured. The output signals from the detector were processed by a radiometer.

Change in optical density (ΔOD) was determined by inserting a test square in the bleached state into the sample

holder, adjusting the transmittance scale to 100%, opening the shutter from the Xenon lamp to provide ultraviolet radiation to change the test square from the bleached state to an activated (i.e., darkened) state, measuring the transmittance in the activated state, and calculating the change in optical density according to the formula: $\Delta OD=\log(100/\%Ta)$, where %Ta is the percent transmittance in the activated state and the logarithm is to the base 10.

The optical properties of the photochromic compounds in the test squares are reported in Table 1. When comparing results, Comparative Example 1 is the corresponding compound of, i.e., should be compared to, Examples 1-4, CE 2 should be compared to Example 5 and CE 3 should be compared to Example 6. In each comparison, the Comparative Example compound has the same structure as the Example compound except for the hydroxy end-capped polyalkoxylated substituent. The Δ OD/Min, which represents the sensitivity of the photochromic compound's response to UV light, was measured over the first five (5) seconds of UV exposure, then expressed on a per minute basis. The saturation optical density (Δ OD@ Saturation) was taken under identical conditions as the Δ OD/Min, except UV exposure was continued for 15 minutes. The lambda max (Vis) is the wavelength in nanometers (nm) in the visible spectrum at which the maximum absorption of the activated (colored) form of the photochromic compound in a test square occurs. The lambda max (Vis) wavelength was determined by testing the photochromic test square polymerizates of Part A in a Varian Cary 3 UV-Visible spectrophotometer. The Bleach Rate (T 1/2) is the time interval in seconds for the absorbance of the activated form of the photochromic compound in the test squares to reach one

half the highest absorbance at room temperature (72°F, 22.2°C) after removal of the source of activating light.

Part C

Further testing was done with the photochromic compounds described in the Examples and the Comparative Examples in the following manner. 0.608 Millimole of each photochromic compound was dissolved in 1.264 grams of N-methyl pyrrolidone (NMP). The resulting photochromic solutions of Comparative Examples 1-3 were each added to 4.0 grams of Polyurethane Coating Composition (PCC) A. PCC A is substantially the same formulation as Example 5 in co-pending U.S. Patent Application Serial No. 09/083,376, filed May 22, 1998, except that PCC A does not contain Photochromics No. 1 and 2, TINUVIN 292 stabilizer and additional NMP but it does contain 2.8 weight percent γ-glycidoxypropyltrimethoxysilane, available as SILQUEST A-187 from OSI Specialties, Inc.

The resulting photochromic solutions of Examples 1-6 were each added to 4.387 grams of PCC-B. PCC B is substantially the same as PCC A except that it contains an additional 10 weight percent of VESTANAT B 1358. The additional amount of VESTANAT B 1358 was added to maintain an NCO:OH ratio of 1.2:1.0 since the photochromic compounds of Examples 1-6 contributed additional hydroxyl groups.

Part D

The solutions prepared in Part C were applied via a spincoating method to lenses prepared from CR-39® monomer. The lenses were 76 millimeters in diameter, 2 millimeters thick and were obtained from SOLA Optical USA. Prior to application of the coating, each lens was immersed for 3 minutes in an aqueous potassium hydroxide solution having a

normality of about 2.4 that was maintained at a temperature of 55°C and then rinsed with deionized water twice, by immersion for 3 minutes each time and then rinsed with isopropyl alcohol and air dried. The immersion steps were conducted in a Branson Ultrasonic Model 5200 sonicator. Approximately 200 milligrams of solution was dispensed onto each lens that was spinning at 2000 rpm. The coated lenses were cured for 40 minutes in a convection oven maintained at 140°C.

Part E

The photochromic coated lenses prepared in Part D were subjected to microhardness testing using a Fischerscope HCV, Model H-100 available from Fischer Technology, Inc. The microhardness, measured in Newtons per mm^2, of the coated lenses was determined under the conditions of a 100 milliNewton load, 30 load steps and 0.5 second pauses between load steps. Each lens was tested 3 times after the samples were stored in an enclosed chamber having a humidity of less than or equal to 50 percent, e.g., 30 percent, for at least 12 hours before each Fischer microhardness test. The numerical average of those test results is listed in Table 2.

Part F

The photochromic coated lenses prepared in Part D were tested for photochromic response using the procedure described in Part B except for the following: test sample exposure times were increased from 15 to 20 minutes and from 2 to 3 hours, the power output of the optical bench was adjusted to 0.67 mW/cm^2 measurements were made when the optical bench temperature was 72°F (22°C) and 95°F (35°C). When the temperature of 72°F (22°C) was used, the lenses were activated for 45 minutes and the ΔOD was measured after the first 30

seconds and then after 45 minutes. When the temperature of 95°F (35°C) was used, the lenses were activated for 25 minutes and the ΔOD was measured after the first 30 seconds and then after 25 minutes.

The photochromic response data collected when the optical bench temperature was 72°F (22°C) and 95°F (35°C) was also used to determine the temperature dependency of the Example compounds compared to the Comparative Examples. These results are reported in Table 3. The temperature dependence (TD) is calculated by using the following formula:

$$\frac{\Delta OD\ 72°F - \Delta OD\ 95°F}{\text{Average } (\Delta OD\ 72°F + \Delta OD\ 95°F)}$$

Fatigue testing was conducted on the coated lenses by exposing the samples to solar simulated radiation in a Weather-Ometer, Model No. Ci 4000 made by the Atlas Electric Devices Co. Immediately prior to exposure in the Weather-Ometer, the coated lenses were stored for 1 hour in a dark chamber maintained at 40°C and 45% relative humidity. In the Weather-Ometer, the lenses were kept for 65 hours at a temperature of 50°C and relative humidity of 70% and were exposed to a source of 340 Nm radiation at a dosage level of 0.25 mW/cm^2.

The Percent Fatigue was determined by measuring on the optical bench the difference between the change in optical density (ΔOD) of the test lenses before and after fatiguing in the Weather-Ometer and calculating the percent reduction in optical density that the difference represents. Prior to testing on the optical bench, the test lenses were conditioned using the aforedescribed conditioning step. The Percent Fatigue was measured for a specific wavelength using a 520 ± 15

nm band pass filter. Testing on the optical bench was done at a temperature of 100°F with an exposure interval of 90 sec and a dosage of 1.86 mW/cm^2.

The Δb* color values were also determined for the test lenses by subtracting the initial b* color values of the CIELAB color space from the b* values measured after 65 hours of fatigue at 122°F (50°C). The b* color values of the CIELAB color space were collected under the conditions of a D_{65} illuminant and a 10 degree observer on a Hunter Ultrascan XE color spectrophotometer. The control of the test conditions and acquisition of data was handled by the Labtech Notebook Pro software and the recommended I/O board. The results of the Fatigue and Δb* color value testing are listed in Table 4. The results of the photochromic response testing at 72°F and at 95°F are reported in Tables 5 and 6, respectively.

TABLE 1

Example Number	(λ) max (VIS)	ΔOD/MIN Sensitivity	ΔOD@ Saturation	Bleach Rate (T 1/2)
1	521	0.21	0.19	46
2	521	0.25	0.19	42
3	523	0.22	0.19	40
4	520	0.22	0.21	43
5	513	0.32	0.67	115
6	515	0.14	0.6	272
CE 1	518	0.18	0.22	56
CE 2	512	0.29	0.77	136
CE 3	515	0.18	0.71	279

The results of Table 1 show that the Bleach Rate (T½) of the Example compounds was faster than that of the corresponding Comparative Example compounds, i.e., the T½ of

each of Examples 1-4 was faster than that of CE 1, the T½ of Example 5 was faster than that of CE 2 and the T½ of Example 6 was faster than that of CE 3. In a comparison of the other parameters tested, the results from the Examples and corresponding Comparative Examples were very similar. The results of Table 1 are for Example compounds that were not polymerized into the sample matrix.

Table 2

Example Number	Microhardness Newtons per mm^2
1	118
2	118
3	116
4	110
5	122
6	115
CE 1	88
CE 2	90
CE 3	89

The results in Table 2 show that the coatings made with the polymerizable naphthopyrans of Examples 1-6 were harder than those made with the non-polymerizable Comparative Examples 1-3.

Table 3

Example Number	Temperature Dependency
1	0.58
2	0.66
3	0.63
4	0.68
5	0.54
6	0.57
CE 1	0.78
CE 2	0.64
CE 3	0.63

The results in Table 3 show that each of the polymerizable Examples 1-6 has a lower value for Temperature Dependency than their corresponding Comparative Examples. This means that the Example Compounds showed less of a decrease in the Δ Optical Density vis-a-vis their corresponding Comparative Example Compounds when comparing test results at 95°F to 72°F.

Table 4

Example Number	Percent Fatique	Δb*
1	15	2.6
2	14	2.8
3	19	2.7
4	16	2.5
5	38	7.1
6	48	5.3
CE 1	26	4.7
CE 1**	9	2.7
CE 2	94	2.6
CE 3	77	8.7

**Comparative Example 1 with 1.8 weight percent of TINUVIN 144 a hindered amine light stabilizer (HALS) available from Ciba Geigy.

The results of Table 4 show that the coatings prepared with the polymerizable Example Compounds 1-4 and 6 demonstrated less fatigue and a lower Δb* color value than the coatings prepared with their corresponding Comparative Examples 1 and 3, respectively. The results for Example Compound 5 as compared to corresponding CE 2 showed less fatigue but a higher Δb*. Coatings prepared with Examples 1-4 had Δb* color values approximately equal to that of a coating prepared with CE 1** containing HALS.

Table 5

Example Number	ΔOD at 30 seconds	ΔOD@ Saturation	Bleach Rate (T 1/2)
1	0.10	0.42	281
2	0.13	0.47	207
3	0.13	0.46	189
4	0.16	0.51	140
5	0.25	1.28	430
6	0.19	1.41	901
CE 1	0.29	0.64	62
CE 2	0.38	1.29	176
CE 3	0.34	1.61	441

The results of Table 5 (photochromic response at 72°F) show that the ΔOD at saturation is lower and there is a decrease in the rate of bleaching, i.e., an increase in the $T_{½}$ for each of the coatings containing polymerizable Example 1-6

compounds as compared to their corresponding Comparative Examples except for the ΔOD of Example 5 which is roughly equal to that of Comparative Example 2. Also shown by the results is a progressive decrease in the T½ and a progressive increase in ΔOD values for coatings containing Examples 1, 2, 3 and 4. These examples have the same photochromic base compound with varying chain lengths of 1, 2, 3 and 4 ethoxy units, respectively.

Table 6

Example Number	ΔOD at 30 seconds	ΔOD@ Saturation	Bleach Rate (T 1/2)
1	0.08	0.23	95
2	0.11	0.24	58
3	0.11	0.24	55
4	0.14	0.25	37
5	0.24	0.73	118
6	0.18	0.78	211
CE 1	0.22	0.28	16
CE 2	0.35	0.66	48
CE 3	0.31	0.84	106

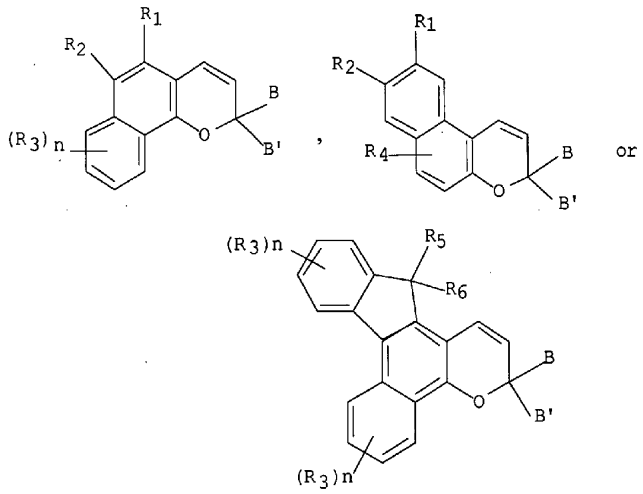
The results of Table 6 (photochromic response at 95°F) show that the ΔOD at saturation is slightly lower and there is an increase in the T½ for the coatings containing polymerizable Example compounds 1-4 and 6 as compared to their corresponding Comparative Examples. The ΔOD of Example 5 is slightly higher than that of corresponding Comparative Example 2. The aforementioned progressive trend with increasing ethoxy chain length of Examples 1-4 is also evident in these results. There is also less of a difference between the ΔOD

of the coating containing Example 4 and the Comparative Example 1 coating at 95°F *vis-à-vis* the same coatings tested at 72°F.

The present invention has been described with reference to specific details of particular embodiments thereof. It is not intended that such details be regarded as limitations upon the scope of the invention except insofar as to the extent that they are included in the accompanying claims.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A naphthopyran compound represented by the following graphic formulae:



wherein,

(a) one of R_1, R_2, R_3, R_4, R_5 or R_6 is the group R or R_2 is a mono-R-substituted phenyl, the group R is represented by the formula:

$-A[(OC_2H_4)_x\ (OC_3H_6)_y\ (OC_4H_8)_z]D$ or

$-[(C_2H_4O)_x\ (C_3H_6O)_y\ (C_4H_8O)_z]D$

wherein -A- is -C(O)- or $-CH_2-$, D is a polymerizable group, x, y and z are each a number between 0 and 50, and the sum of x, y and z is between 0 and 50; provided that there is at least one R group or mono-R-substituted phenyl on said naphthopyran and that such substituents which are not said R group or mono-R-substituted phenyl are chosen from;

(b) R_1 is hydrogen, C_1-C_3 alkyl or the group, -C(O)W, W being $-OR_7$, $-N(R_8)R_9$, piperidino or morpholino, wherein R_7 is allyl, C_1-C_6 alkyl, phenyl, mono(C_1-C_6)alkyl substituted phenyl, mono(C_1-C_6)alkoxy substituted phenyl,

phenyl(C_1-C_3)alkyl, mono(C_1-C_6)alkyl substituted phenyl(C_1-C_3)alkyl, mono(C_1-C_6)alkoxy substituted phenyl(C_1-C_3)alkyl, C_1-C_6 alkoxy(C_2-C_4)alkyl or C_1-C_6 haloalkyl; R_8 and R_9 are each selected from the group consisting of C_1-C_6 alkyl, C_5-C_7 cycloalkyl, phenyl, mono-substituted phenyl and di-substituted phenyl, said phenyl substituents being C_1-C_6 alkyl or C_1-C_6 alkoxy, and said halo substituent being chloro or fluoro;

(c) R_2 is selected from the group consisting of hydrogen, C_1-C_6 alkyl, C_3-C_7 cycloalkyl, phenyl, mono-substituted phenyl, di-substituted phenyl and the groups $-OR_{10}$ and $-OC(O)R_{10}$, wherein R_{10} is C_1-C_6 alkyl, phenyl(C_1-C_3)-alkyl, mono(C_1-C_6)alkyl substituted phenyl(C_1-C_3)alkyl, mono(C_1-C_6)alkoxy substituted phenyl(C_1-C_3)alkyl, C_1-C_6 alkoxy(C_2-C_4)alkyl, C_3-C_7 cycloalkyl or mono(C_1-C_4)alkyl substituted C_3-C_7 cycloalkyl, and n is selected from the integers 0, 1 and 2 and said phenyl substituent being C_1-C_6 alkyl or C_1-C_6 alkoxy;

(d) each R_3 and R_4 are selected from the group consisting of hydrogen, C_1-C_6 alkyl, C_3-C_7 cycloalkyl, phenyl, mono-substituted phenyl, di-substituted phenyl and the groups $-OR_{10}$ and $-OC(O)R_{10}$, wherein R_{10} is C_1-C_6 alkyl, phenyl(C_1-C_3)-alkyl, mono(C_1-C_6)alkyl substituted phenyl(C_1-C_3)alkyl, mono(C_1-C_6)alkoxy substituted phenyl(C_1-C_3)alkyl, C_1-C_6 alkoxy(C_2-C_4)alkyl, C_3-C_7 cycloalkyl or mono(C_1-C_4)alkyl substituted C_3-C_7 cycloalkyl, and n is selected from the integers 0, 1 and 2;

(e) R_5 and R_6 together form an oxo group, a spiro heterocyclic group having 2 oxygen atoms and from 3 to 6 carbon atoms including the spirocarbon atom; or R_5 and R_6 independent of each other hydrogen, hydroxy, C_1-C_6 alkyl,

C_3-C_7 cycloalkyl, allyl, phenyl, mono-substituted phenyl, benzyl, mono-substituted benzyl, chloro, fluoro, the group, —C(O)X, wherein X is hydroxy, C_1-C_6 alkyl, C_1-C_6 alkoxy, phenyl, mono-substituted phenyl, amino, mono(C_1-C_6)alkylamino, or di(C_1-C_6)alkylamino; or R_5 and R_6 are each the group, —OR_{11}, wherein R_{11} is C_1-C_6 alkyl, phenyl(C_1-C_3)alkyl, mono(C_1-C_6)alkyl substituted phenyl(C_1-C_3)alkyl, mono(C_1-C_6)alkoxy substituted phenyl(C_1-C_3)alkyl, C_1-C_6 alkoxy(C_2-C_4)alkyl, C_3-C_7 cycloalkyl, mono(C_1-C_4)alkyl substituted C_3-C_7 cycloalkyl, C_1-C_6 chloroalkyl, C_1-C_6 fluoroalkyl, allyl, the group, —$CH(R_{12})Y$, wherein R_{12} is hydrogen or C_1-C_3 alkyl and Y is CN, CF_3, or $COOR_{13}$ and R_{13} is hydrogen or C_1-C_3 alkyl; or R_{11} is the group, —C(O)Z, wherein Z is hydrogen, C_1-C_6 alkyl, C_1-C_6 alkoxy, the unsubstituted, mono-or di-substituted aryl groups phenyl or naphthyl, phenoxy, mono- or di-(C_1-C_6)alkyl substituted phenoxy, mono- or di-(C_1-C_6)alkoxy substituted phenoxy, amino, mono(C_1-C_6)alkylamino, di(C_1-C_6)alkylamino, phenylamino, mono- or di-(C_1-C_6)alkyl substituted phenylamino, or mono- or di-(C_1-C_6)alkoxy substituted phenylamino, each of said phenyl, benzyl and aryl group substituents being C_1-C_6 alkyl or C_1-C_6 alkoxy; and

(f) B and B′ are each selected from the group consisting of:

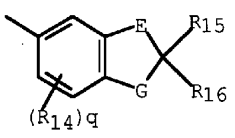
(i) mono-R-substituted phenyl;

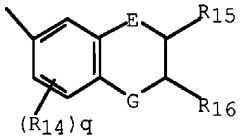
(ii) the unsubstituted, mono-, di- and tri-substituted aryl groups, phenyl and naphthyl;

(iii) the unsubstituted, mono- and di- substituted hetroaromatic groups pyridyl, furanyl, benzofuran-2-yl, benzofuran-3-yl, thienyl, benzothien-2-yl, benzothien-3-yl, dibenzofuranyl, dibenzothienyl, carbazolyl and fluorenyl, each of said aryl and heteroaromatic substituents in (f)(i)

and (iii) being selected from the group consisting of hydroxy, aryl, mono(C_1-C_6)alkoxyaryl, di(C_1-C_6)alkoxyaryl, mono(C_1-C_6)alkylaryl, di(C_1-C_6)alkylaryl, chloroaryl, fluoroaryl, C_3-C_7 cycloalkylaryl, C_3-C_7 cycloalkyl, C_3-C_7 cycloalkyloxy, C_3-C_7 cycloalkyloxy(C_1-C_6)alkyl, C_3-C_7 cycloalkyloxy(C_1-C_6)alkoxy, aryl(C_1-C_6)alkyl, aryl(C_1-C_6)alkoxy, aryloxy, aryloxy(C_1-C_6)alkyl, aryloxy(C_1-C_6)alkoxy, mono- and di-(C_1-C_6)alkylaryl(C_1-C_6)alkyl, mono- and di-(C_1-C_6)alkoxyaryl(C_1-C_6)alkyl, mono- and di-(C_1-C_6)alkylaryl(C_1-C_6)alkoxy, mono- and di-(C_1-C_6)alkoxyaryl(C_1-C_6)alkoxy, amino, mono(C_1-C_6)alkylamino, di(C_1-C_6)alkylamino, diarylamino, N-(C_1-C_6)alkylpiperazino, N-arylpiperazino, aziridino, indolino, piperidino, arylpiperidino, morpholino, thiomorpholino, tetrahydroquinolino, tetrahydroisoquinolino, pyrryl, C_1-C_6 alkyl, C_1-C_6 chloroalkyl, C_1-C_6 fluoroalkyl, C_1-C_6 alkoxy, mono(C_1-C_6)alkoxy(C_1-C_4)alkyl, acryloxy, methacryloxy, bromo, chloro and fluoro;

(iv) the groups represented by the following graphic formulae:



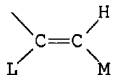


wherein E is carbon or oxygen and G is oxygen or substituted nitrogen, provided that when G is substituted nitrogen, E is carbon, said nitrogen substituents being selected from the group consisting of hydrogen, C_1-C_6 alkyl and C_2-C_6 acyl; each R_{14} is C_1-C_6 alkyl, C_1-C_6 alkoxy,

hydroxy, chloro or fluoro; R_{15} and R_{16} are each hydrogen or C_1-C_6 alkyl; and q is the integer 0, 1 or 2;

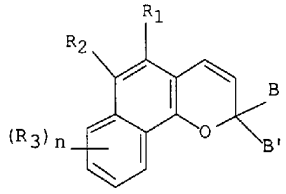
(v) C_1-C_6 alkyl, C_1-C_6 chloroalkyl, C_1-C_6 fluoroalkyl, and C_1-C_6 alkoxy(C_1-C_4)alkyl; and

(vi) the group represented by the following graphic formula:

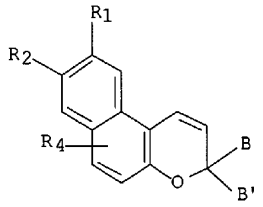


wherein L is hydrogen or C_1-C_4 alkyl and M is selected from the unsubstituted, mono-, and di-substituted members of the group consisting of naphthyl, phenyl, furanyl and thienyl, each of said group substituents being C_1-C_4 alkyl, C_1-C_4 alkoxy, fluoro or chloro.

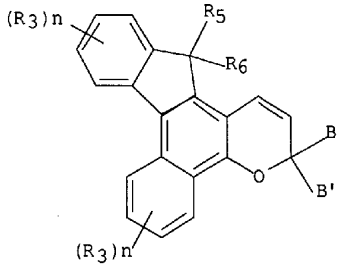
2. The naphthopyran compound of claim 1 represented by the following graphic formulae:



,



or



wherein,

(a) one of R_1, R_2, R_3, R_4, R_5 or R_6 is the group R or R_2 is a mono-R-substitute phenyl, the group R is represented by the formula:

$-A[(OC_2H_4)_x\ (OC_3H_6)_y\ (OC_4H_8)_z]D$ or

$-[(C_2H_4O)_x\ (C_3H_6O)_y\ (C_4H_8O)_z]D$

wherein -A- is -C(O)- or $-CH_2-$, D is a polymerizable group, x, y and z are each a number between 0 and 50, and the sum of x, y and z is between 0 and 50; provided that there is at least one R group or mono-R-substituted phenyl on said naphthopyran and that such substituents which are not said R group or mono-R-substituted phenyl are chosen from;

(b) R_1 is hydrogen, C_1-C_3 alkyl or the group, -C(O)W, W being $-OR_7$, $-N(R_8)R_9$, piperidino or morpholino, wherein R_7 is allyl, C_1-C_6 alkyl, phenyl, mono(C_1-C_6)alkyl substituted phenyl, mono(C_1-C_6)alkoxy substituted phenyl, phenyl(C_1-C_3)alkyl, mono(C_1-C_6)alkyl substituted phenyl(C_1-C_3)alkyl, mono(C_1-C_6)alkoxy substituted phenyl(C_1-C_3)alkyl, C_1-C_6 alkoxy(C_2-C_4)alkyl or C_1-C_6 haloalkyl; R_8 and R_9 are each selected from the group consisting of C_1-C_6 alkyl, C_5-C_7 cycloalkyl, phenyl, mono-substituted phenyl and di-substituted phenyl, said phenyl substituents being C_1-C_6 alkyl or C_1-C_6 alkoxy, and said halo substituent being chloro or fluoro;

(c) R_2 selected from the group consisting of hydrogen, C_1-C_6 alkyl, C_3-C_7 cycloalkyl, phenyl, mono-substituted phenyl, di-substituted phenyl and the groups $-OR_{10}$ and $-OC(O)R_{10}$, wherein R_{10} is C_1-C_6 alkyl, phenyl(C_1-C_3)-alkyl, mono(C_1-C_6)alkyl substituted phenyl(C_1-C_3)alkyl, mono(C_1-C_6)alkoxy substituted phenyl(C_1-C_3)alkyl, C_1-C_6 alkoxy(C_2-C_4)alkyl, C_3-C_7 cycloalkyl or mono(C_1-C_4)alkyl substituted C_3-C_7 cycloalkyl, said phenyl substituent being C_1-C_6 alkyl or C_1-C_6 alkoxy;

(d) each R_3 and R_4 are selected from the group consisting of hydrogen, C_1-C_6 alkyl, C_3-C_7 cycloalkyl, phenyl, mono-substituted phenyl, di-substituted phenyl and the groups -

OR_{10} and $-OC(O)R_{10}$, wherein R_{10} is C_1-C_6 alkyl, phenyl(C_1-C_3)-alkyl, mono(C_1-C_6)alkyl substituted phenyl(C_1-C_3)alkyl, mono(C_1-C_6)alkoxy substituted phenyl(C_1-C_3)alkyl, C_1-C_6 alkoxy(C_2-C_4)alkyl, C_3-C_7 cycloalkyl or mono(C_1-C_4)alkyl substituted C_3-C_7 cycloalkyl, and n is selected from the integers 0, 1 and 2; and

(e) R_5 and R_6 together form an oxo group, a spiro heterocyclic group having 2 oxygen atoms and from 3 to 6 carbon atoms including the spirocarbon atom, or R_5 and R_6 independent of each other is hydrogen, hydroxy, C_1-C_6 alkyl, C_3-C_7 cycloalkyl, allyl, phenyl, mono-substituted phenyl, benzyl, mono-substituted benzyl, chloro, fluoro, the group, —C(O)X, wherein X is hydroxy, C_1-C_6 alkyl, C_1-C_6 alkoxy, phenyl, mono-substituted phenyl, amino, mono(C_1-C_6)alkylamino, or di(C_1-C_6)alkylamino, or R_5 and R_6 are each the group, —OR_{11}, wherein R_{11} is C_1-C_6 alkyl, phenyl(C_1-C_3)alkyl, mono(C_1-C_6)alkyl substituted phenyl(C_1-C_3)alkyl, mono(C_1-C_6)alkoxy substituted phenyl(C_1-C_3)alkyl, C_1-C_6 alkoxy(C_2-C_4)alkyl, C_3-C_7 cycloalkyl, mono(C_1-C_4)alkyl substituted C_3-C_7 cycloalkyl, C_1-C_6 chloroalkyl, C_1-C_6 fluoroalkyl, allyl, the group, —$CH(R_{12})Y$, wherein R_{12} is hydrogen or C_1-C_3 alkyl and Y is CN, CF_3, or $COOR_{13}$ and R_{13} is hydrogen or C_1-C_3 alkyl, or R_{11} is the group, —C(O)Z, wherein Z is hydrogen, C_1-C_6 alkyl, C_1-C_6 alkoxy, the unsubstituted, mono-or di-substituted aryl groups phenyl or naphthyl, phenoxy, mono- or di-(C_1-C_6)alkyl substituted phenoxy, mono- or di-(C_1-C_6)alkoxy substituted phenoxy, amino, mono(C_1-C_6)alkylamino, di(C_1-C_6)alkylamino, phenylamino, mono- or di-(C_1-C_6)alkyl substituted phenylamino, or mono- or di-(C_1-C_6)alkoxy substituted

phenylamino, each of said phenyl, benzyl and aryl group substituents being C_1-C_6 alkyl or C_1-C_6 alkoxy; and

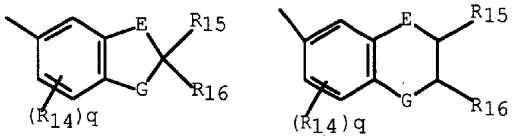
(f) B is a mono-R-substituted phenyl;

(g) B′ is selected from the group consisting of

(i) the unsubstituted, mono-, di- and tri-substituted aryl groups, phenyl and naphthyl;

(ii) the unsubstituted, mono- and di-substituted hetroaromatic groups pyridyl, furanyl, benzofuran-2-yl, benzofuran-3-yl, thienyl, benzothien-2-yl, benzothien-3-yl, dibenzofuranyl, dibenzothienyl, carbazolyl and fluorenyl, each of said aryl and heteroaromatic substituents in (e)(ii) and (ii) being selected from the group consisting of hydroxy, aryl, mono(C_1-C_6)alkoxyaryl, di(C_1-C_6)alkoxyaryl, mono(C_1-C_6)alkylaryl, di(C_1-C_6)alkylaryl, chloroaryl, fluoroaryl, C_3-C_7 cycloalkylaryl, C_3-C_7 cycloalkyl, C_3-C_7 cycloalkyloxy, C_3-C_7 cycloalkyloxy(C_1-C_6)alkyl, C_3-C_7 cycloalkyloxy(C_1-C_6)alkoxy, aryl(C_1-C_6)alkyl, aryl(C_1-C_6)alkoxy, aryloxy, aryloxy(C_1-C_6)alkyl, aryloxy(C_1-C_6)alkoxy, mono- and di-(C_1-C_6)alkylaryl(C_1-C_6)alkyl, mono- and di-(C_1-C_6)alkoxyaryl(C_1-C_6)alkyl, mono- and di-(C_1-C_6)alkylaryl(C_1-C_6)alkoxy, mono- and di-(C_1-C_6)alkoxyaryl(C_1-C_6)alkoxy, amino, mono(C_1-C_6)alkylamino, di(C_1-C_6)alkylamino, diarylamino, N-(C_1-C_6)alkylpiperazino, N-arylpiperazino, aziridino, indolino, piperidino, arylpiperidino, morpholino, thiomorpholino, tetrahydroquinolino, tetrahydroisoquinolino, pyrryl, C_1-C_6 alkyl, C_1-C_6 chloroalkyl, C_1-C_6 fluoroalkyl, C_1-C_6 alkoxy, mono(C_1-C_6)alkoxy(C_1-C_4)alkyl, acryloxy, methacryloxy, bromo, chloro and fluoro;

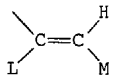
(iii) the groups represented by the following graphic formulae:



wherein E is carbon or oxygen and G is oxygen or substituted nitrogen, provided that when G is substituted nitrogen, E is carbon, said nitrogen substituents being selected from the group consisting of hydrogen, C_1-C_6 alkyl and C_2-C_6 acyl; each R_{14} is C_1-C_6 alkyl, C_1-C_6 alkoxy, hydroxy, chloro or fluoro; R_{15} and R_{16} are each hydrogen or C_1-C_6 alkyl; and q is the integer 0, 1 or 2;

(v) C_1-C_6 alkyl, C_1-C_6 chloroalkyl, C_1-C_6 fluoroalkyl, and C_1-C_6 alkoxy(C_1-C_4)alkyl; and

(vi) the group represented by the following graphic formula:



wherein L is hydrogen or C_1-C_4 alkyl and M is selected from the unsubstituted, mono-, and di-substituted members of the group consisting of naphthyl, phenyl, furanyl and thienyl, each of said group substituents being C_1-C_4 alkyl, C_1-C_4 alkoxy, fluoro or chloro.

3. The naphthopyran of claim 1 wherein there is one R group or mono R-substituted phenyl on said naphthopyran.

4. The naphthopyran of claim 1 wherein (a) one of R_1, R_2, R_3, R_4, R_5 or R_6 is the group R or R_2 is a mono-R-substituted phenyl, the group R is represented by the formula:

$-A[(OC_2H_4)_x\ (OC_3H_6)_y\ (OC_4H_8)_z]D$ or

$-[(C_2H_4O)_x\ (C_3H_6O)_y\ (C_4H_8O)_z]D$

wherein -A- is -C(O)- or $-CH_2-$, D is hydroxy or (meth) acryloxy; x and y are each a number between 0 and 50, z is 0 and the sum of x and y is between 1 and 50; provided that there is at least one R group or mono-R-substituted phenyl on said naphthopyran and that such substituents which are not said R group or mono-R-substituted phenyl are chosen from;

(b) R_1 is the group, -C(O)W, W being $-OR_7$ or $-N(R_8)R_9$, wherein R_7 is C_1-C_4 alkyl, phenyl, mono(C_2-C_4)alkyl substituted phenyl, mono(C_1-C_4)alkoxy substituted phenyl, phenyl(C_1-C_2)alkyl, mono(C_1-C_4)alkyl substituted phenyl(C_1-C_2)alkyl, mono(C_1-C_4)alkoxy substituted phenyl(C_1-C_2)alkyl, mono(C_1-C_4)alkoxy(C_2-C_3)alkyl or C_1-C_4 haloalkyl; R_8 and R_9 are each selected from the group consisting of C_1-C_4 alkyl, C_5-C_7 cycloalkyl, phenyl, mono-substituted phenyl and di-substituted phenyl, said phenyl substituents being C_1-C_4 alkyl or C_1-C_4 alkoxy, said halo substituents being chloro or fluoro;

(c) R_2 is selected from the group consisting of hydrogen, C_1-C_3 alkyl, C_3-C_5 cycloalkyl, phenyl, mono-substituted phenyl, di-substituted phenyl and the group $-OR_{10}$, wherein R_{10} is C_1-C_4 alkyl, phenyl(C_1-C_2)alkyl, mono(C_1-C_4)alkyl substituted phenyl(C_1-C_2)alkyl, mono(C_1-C_4)alkoxy substituted phenyl(C_1-C_2)alkyl, C_1-C_4 alkoxy(C_2-C_4)alkyl, C_5-C_7 cycloalkyl or mono(C_1-C_3)alkyl substituted C_5-C_7 cycloalkyl and said phenyl substituents being C_1-C_3 alkyl or C_1-C_3 alkoxy;

(d) each R_3 and R_4 are selected from the group consisting of hydrogen, C_1-C_3 alkyl, C_3-C_5 cycloalkyl, phenyl, mono-

substituted phenyl, di-substituted phenyl and the group $-OR_{10}$, wherein R_{10} is C_1-C_4 alkyl, phenyl(C_1-C_2)alkyl, mono(C_1-C_4)alkyl substituted phenyl(C_1-C_2)alkyl, mono(C_1-C_4)alkoxy substituted phenyl(C_1-C_2)alkyl, C_1-C_4 alkoxy(C_2-C_4)alkyl, C_5-C_7 cycloalkyl or mono(C_1-C_3)alkyl substituted C_5-C_7 cycloalkyl and said phenyl substituents being C_1-C_3 alkyl or C_1-C_3 alkoxy;

(e) R_5 and R_6 independent of each other is selected from the group consisting of hydrogen, hydroxy, C_1-C_4 alkyl, C_3-C_6 cycloalkyl, chloro, fluoro and the group, $—OR_{11}$, wherein R_{11} is C_1-C_3 alkyl, phenyl(C_1-C_2)alkyl, mono(C_1-C_3)alkyl substituted phenyl(C_1-C_3)alkyl, mono(C_1-C_3)alkoxy substituted phenyl(C_1-C_3)alkyl, C_1-C_3 alkoxy(C_2-C_4)alkyl, C_1-C_3 chloroalkyl, C_1-C_3 fluoroalkyl, the group, $—CH(R_{12})Y$, wherein R_{12} is hydrogen or C_1-C_2 alkyl and Y is CN or $COOR_{13}$, and R_{13} is hydrogen or C_1-C_2 alkyl, or R_{11} is the group, —C(O)Z, wherein Z is hydrogen, C_1-C_3 alkyl, C_1-C_3 alkoxy, phenyl, naphthyl, mono-substituted aryl groups, phenyl or naphthyl, phenoxy, mono- or di-(C_1-C_3)alkyl substituted phenoxy, mono- or di-(C_1-C_3)alkoxy substituted phenoxy, mono(C_1-C_3)alkylamino, phenylamino, mono- or di-(C_1-C_3)alkyl substituted phenylamino, or mono- or di-(C_1-C_3)alkoxy substituted phenylamino, and said aryl substituents being C_1-C_3 alkyl or C_1-C_3 alkoxy;

(f) B and B′ are each selected from the group consisting of:

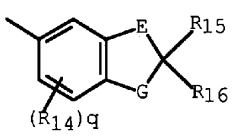
(i) mono R-substituted phenyl;

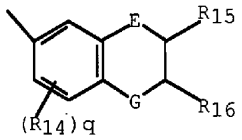
(ii) phenyl, mono-substituted and di-substituted phenyl;

(iii) the unsubstituted, mono- and di-substituted heteroaromatic groups furanyl, benzofuran-2-yl, thienyl, benzothien-2-yl, dibenzofuran-2-yl, and dibenzothien-2-yl,

each of said phenyl and heteroaromatic substituents in (e) (ii) and (iii) being selected from the group consisting of hydroxy, aryl, arlyoxy, aryl(C_1-C_3)alkyl, amino, mono(C_1-C_3)alkylamino, di(C_1-C_3)alkylamino, N-(C_1-C_3)alkylpiperazino, indolino, piperidino, morpholino, pyrryl, C_1-C_3 alkyl, C_1-C_3 chloroalkyl, C_1-C_3 fluoroalkyl, C_1-C_3 alkoxy, mono(C_1-C_3)alkoxy(C_1-C_3)alkyl, chloro and fluoro;

(iv) the groups represented by the following graphic formulae:

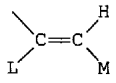




wherein E is carbon and G is oxygen, R_{14} is C_1-C_3 alkyl or C_1-C_3 alkoxy; R_{15} and R_{16} are each hydrogen or C_1-C_4 alkyl; and q is 0 or 1;

(v) C_1-C_4 alkyl; and

(vi) the group represented by the following graphic formula:



wherein L is hydrogen or methyl and M is phenyl or mono-substituted phenyl, said phenyl substituents being C_1-C_3 alkyl, C_1-C_3 alkoxy or fluoro.

5. The naphthopyran of claim 4 wherein:

(a) one of R_1, R_2, R_3, R_4, R_5 or R_6 is the group R or R_2 is a mono-R-substituted phenyl, the group R is represented by the formula:

$-A[(OC_2H_4)_x\ (OC_3H_6)_y\ (OC_4H_8)_z]D$ or

$-[(C_2H_4O)_x\ (C_3H_6O)_y\ (C_4H_8O)_z]D$

wherein -A- is -C(O)- or $-CH_2-$, D is hydroxy; x is a number between 1 and 50, y and z are each 0; provided that there is at least one R group or mono-R-substituted phenyl on said naphthopyran and that such substituents which are not said R group or mono-R-substituted phenyl are chosen from;

(b) R_1 is the group, -C(O)W, wherein W is the group, $-OR_7$, and R_7 is C_1-C_3 alkyl;

(c) R_2 is selected from the group consisting of hydrogen, C_1-C_3 alkyl, phenyl, mono-substituted phenyl, di-substituted phenyl and the group, OR_{10}, wherein R_{10} is C_1-C_3 alkyl and said phenyl substituents being methyl or methoxy;

(d) each R_3 and R_4 are the group R or are selected from the group consisting of hydrogen, C_1-C_3 alkyl, phenyl, mono-substituted phenyl, di-substituted phenyl and the group, OR_{10}, wherein R_{10} is C_1-C_3 alkyl and said phenyl substituents being methyl or methoxy;

(e) R_5 and R_6 independent of each other is hydroxy, C_1-C_4 alkyl, or the group, —OR_{11}, wherein R_{11} is C_1-C_3 alkyl;

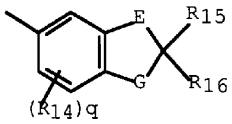
(f) B and B′ are each selected from the group consisting of:

(i) mono R-substituted phenyl;

(ii) phenyl, mono- and di-substituted phenyl;

(iii) the unsubstituted, mono- and di-substituted heteroaromatic groups furanyl, benzofuran-2-yl, thienyl and benzothien-2-yl, each of said phenyl and heteroaromatic substituents in (e) (ii) and (iii) being selected from the group consisting of hydroxy, C_1-C_3 alkyl, C_1-C_3 alkoxy, phenyl, indolino, fluoro and chloro; and

(iv) the group represented by the following graphic formula:



wherein E is carbon and G is oxygen, R_{14} is C_1-C_3 alkyl or C_1-C_3 alkoxy; R_{15} and R_{16} are each hydrogen or C_1-C_3 alkyl; and q is 0 or 1.

6. A naphthopyran compound selected from the group consisting of:

(a) 2,2-bis(4-methoxyphenyl)-5-(2-hydroxyethoxycarbonyl)-6-phenyl-[2H]-naphtho[1,2-b]pyran;

(b) 2,2-bis(4-methoxyphenyl)-5-(2-(2-hydroxyethoxy)ethoxycarbonyl)-6-phenyl-[2H]-naphtho[1,2-b]pyran;

(c) 2,2-bis(4-methoxyphenyl)-5-(2-(2-(2-hydroxy-ethoxy)ethoxy)ethoxycarbonyl)-6-phenyl-[2H]naphtho[1,2-b]pyran;

(d) 2,2-bis(4-methoxyphenyl)-5-(2-(2-(2-(2-hydroxyethoxy)ethoxy)ethoxy)ethoxycarbonyl)-6-phenyl-[2H]-naphtho[1,2-b]pyran;

(e) 2,2-bis(4-methoxyphenyl)-5-methoxycarbonyl-6-(2-hydroxyethoxy)ethoxy-[2H]-naphtho[1,2-b]pyran;

(f) 2-(4-(2-(2-hydroxyethoxy)ethoxy)ethoxyphenyl)-2-phenyl-5-methoxycarbonyl-6-methyl-9-methoxy-[2H]-naphtho[1,2-b]pyran;

(g) 2,2-bis(4-methoxyphenyl)-5-methoxycarbonyl-6-phenyl-9-(2-hydroxyethoxy)-[2H]-naphtho[1,2-b]pyran; and

(h) 2,2-bis(4-methoxyphenyl)-5-methoxycarbonyl-6-(4-(2-hydroxyethoxy)phenyl)-[2H]-naphtho[1,2-b]pyran.

(i) 2-phenyl-2-(4-(2-(2-methylprop-2-enoyloxy)ethoxy)phenyl)-5-(methoxycarbonyl)-6-(2-(2-methylprop-2-enoxyloxy)ethoxy)-[2H]-naphtho[1,2-b]pyran;

(j) 2,2,6-triphenyl-5-(2-(2-(2-(2-methylprop-2-enoxyloxy)ethoxy)ethoxy)ethoxycarbonyl)-[2H]-naphtho[1,2-b]pyran; and

(k) 2,2,6-triphenyl-5-(2-(2-(2-(oxiran-2-ylmethoxy)ethoxy)ethoxy)ethoxycarbonyl)-[2H]-naphtho[1,2-b]pyran.

7. A photochromic article comprising a polymeric organic host material and a photochromic amount of the naphthopyran compound of claim 1.

8. The photochromic article of claim 7 wherein the polymeric organic host material is selected from the group consisting of polyacrylates, polymethacrylates, poly(C_1-C_{12}) alkyl methacrylates, polyoxy(alkylene methacrylates), poly (alkoxylated phenol methacrylates), cellulose acetate, cellulose triacetate, cellulose acetate propionate, cellulose acetate butyrate, poly(vinyl acetate), poly(vinyl alcohol), poly(vinyl chloride), poly(vinylidene chloride), thermoplastic polycarbonates, polyesters, polyurethanes, polythiourethanes, poly(ethylene terephthalate), polystyrene, poly(alpha methylstyrene), copoly(styrene-methylmethacrylate), copoly(styrene-acrylonitrile), polyvinylbutyral and polymers of members of the group consisting of polyol(allyl carbonate) monomers, polyfunctional acrylate monomers, polyfunctional methacrylate monomers, diethylene glycol dimethacrylate monomers, diisopropenyl benzene monomers, alkoxylated polyhydric alcohol monomers and diallylidene pentaerythritol monomers.

9. The photochromic article of claim 8 wherein the polymeric organic material is a homopolymer or copolymer of monomer(s) selected from the group consisting of acrylates, methacrylates, methyl methacrylate, ethylene glycol bis methacrylate, ethoxylated bisphenol A dimethacrylate, vinyl acetate, vinylbutyral, urethane, thiourethane, diethylene glycol bis(allyl carbonate), diethylene glycol dimethacrylate, diisopropenyl benzene, and ethoxylated trimethylol propane triacrylate.

10. The photochromic article of claim 7 wherein the photochromic compound is present in an amount of from 0.05 to 1.0 milligram per square centimeter of polymeric organic host material surface to which the photochromic substance(s) is incorporated or applied.

11. The photochromic article of claim 7 wherein said polymeric organic host material is an optical element.

12. The photochromic article of claim 11 wherein said optical element is a lens.

13. A photochromic article comprising a polymeric organic host material selected from the group consisting of poly(methyl methacrylate), poly(ethylene glycol bismethacrylate), poly(ethoxylated bisphenol A dimethacrylate), thermoplastic polycarbonate, poly(vinyl acetate), polyvinylbutyral, polyurethane and polymers of members of the group consisting of diethylene glycol bis(allyl carbonate) monomers, diethylene glycol dimethacrylate monomers, ethoxylated phenol bismethacrylate monomers, diisopropenyl benzene monomers and ethoxylated trimethylol propane triacrylate monomers, and a photochromic amount of the naphthopyran compound of claim 5.

14. A photochromic article comprising, in combination, a solid substrate and a photochromic amount of each of (a) at least one naphthopyran compound of claim 1, and (b) at least one other organic photochromic compound having at least one activated absorption maxima within the range of between 400 and 700 nanometers.

15. A photochromic article comprising a polymerizate of an optical organic resin monomer and a photochromic amount of the naphthopyran compound of claim 1.

16. The photochromic article of claim 15 wherein the refractive index of the polymerizate is from about 1.48 to about 1.75.

17. The photochromic article of claim 15 wherein the polymerizate is an optical element.

18. The photochromic article of claim 17 wherein said optical element is an ophthalmic lens or a contact lens.

19. A photochromic article comprising, in combination, a solid substrate and on at least one surface thereof a cured coating of a coating composition having a photochromic amount of the naphthopyran compound of claim 1.

20. The photochromic article of claim 19 wherein said coating composition is selected from the group consisting of a polymeric coating composition, paint and ink.

21. The photochromic article of claim 19 wherein the substrate is selected from the group consisting of glass, masonry, textiles, ceramics, metals, wood, paper and polymeric organic materials.

Dated this 26th day of March 2003
TRANSITIONS OPTICAL, INC
By their Patent Attorneys
COLLISON & CO