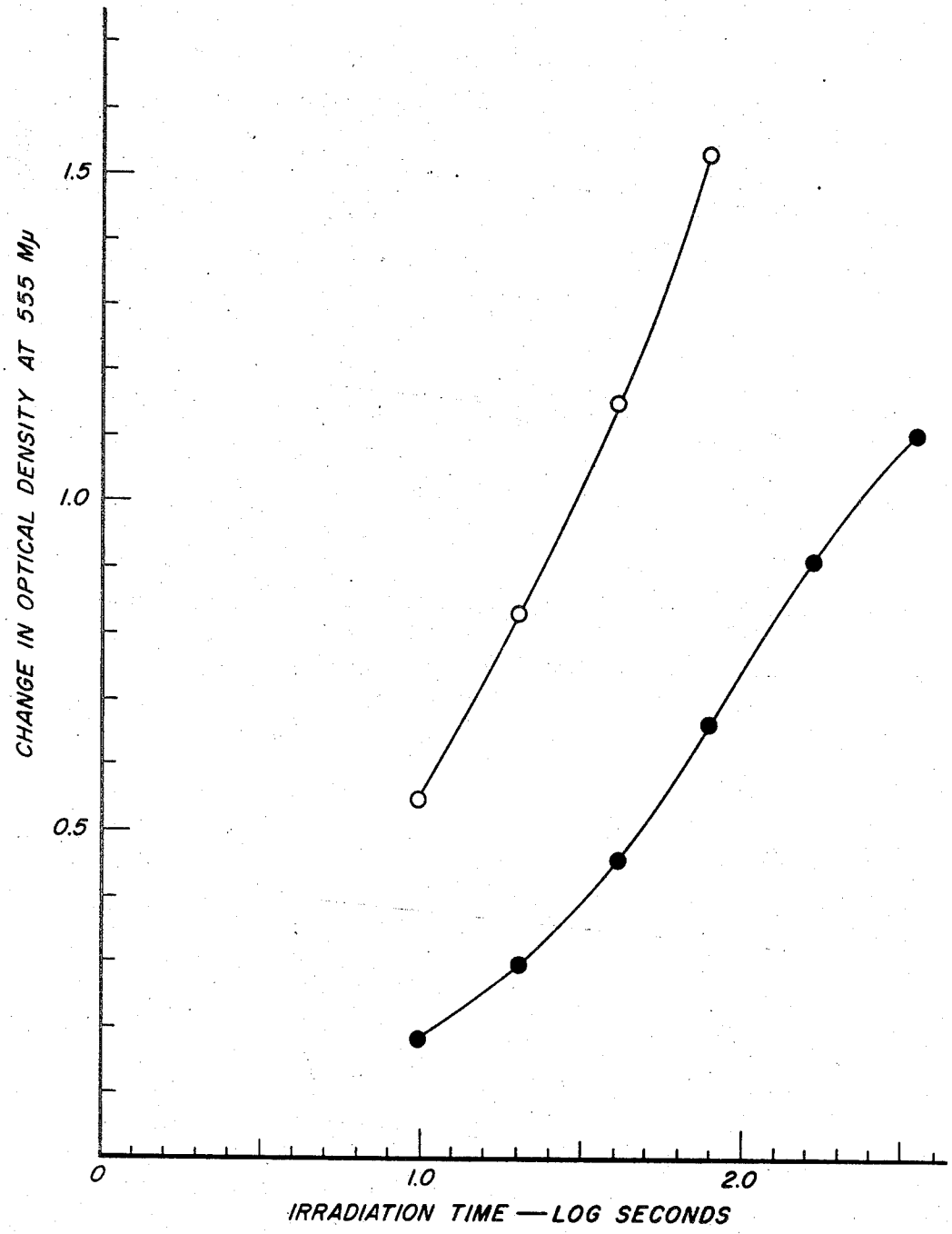
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PHOTOCHROMIC COMPOSITIONS IN A LAURYL METHACRYLATE POLYMERIC BINDER

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PHOTOCHROMIC COMPOSITIONS IN A LAURYL METHACRYLATE POLYMERIC BINDER

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U.S. Cl. 252—300 3 Claims

ABSTRACT OF THE DISCLOSURE

Photochromic compositions comprising a polymer of lauryl methacrylate having dispersed throughout the body thereof various benzospiropyran compounds are described.

BACKGROUND OF THE INVENTION

The instant invention resides in the field of photochromic compositions. It is more particularly directed to photochromic compositions comprising polymers of lauryl methacrylate which have dispersed throughout the body thereof various benzospiropyrans.

The incorporation of benzospiropyrans into polymeric matrices has been known in the prior art. For example, U.S. Pat. No. 3,212,898 discloses the use of such benzospiropyrans in polyester resins.

While the prior art systems have been found adequate for many service applications, they tend to suffer from the inability to change color very rapidly when subjected to ultraviolet or other light.

SUMMARY

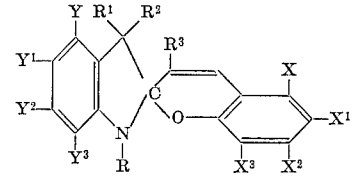
I have now found that the sensitivity of benzospiropyran photochromic compositions, i.e., their rate of color change per unit of exposure, can be materially and drastically increased by incorporating them into a polymer of lauryl methacrylate rather than other polymer systems. The resultant compositions are more easily and rapidly activated in service and therefore enable applications to which they are subjected to be more economically conducted. They are useful in all areas wherein known systems are used, such as data display, signal processing, information storage, photographic dodging, automobile windshields, eyeglass lenses, containers, memory devices, such as optical analogue computers, temporary oscillographs, light switches, optical masks, jewelry, toys, advertising articles and the like.

BRIEF DESCRIPTION OF THE DRAWING

The accompanying drawing is a graphic representation showing the change in optical density at 555 mμ of a composition comprising poly(lauryl methacrylate) and 3% of 1',3',3' - trimethyl - 6' - nitro-8'-methoxy-spiro(2H-1-benzopyran-2,2'-indolene), represented by the open circle (○) and a second composition comprising poly(methyl methacrylate) and 7% of the same spiropyran compound represented by a closed circle (●). Both compositions are in the form of unsupported films, the lauryl film being 1.0 mil thick and the methyl film being 0.7 mil thick. As can be readily seen the poly(lauryl methacrylate) film reaches a higher change in optical density than the poly (methyl methacrylate) film in a shorter irradiation time. Both curves were plotted by recording the optical density change of the two compositions produced in Example 1, below.

DESCRIPTION OF THE INVENTION INCLUDING PREFERRED EMBODIMENTS

The benzospiropyran compounds which are useful as the photochromic additives of the present invention are well known in the prior art and have the general formula:



wherein R, R^1 and R^2 represent the same or different alkyl radicals having 1 to 20 carbon atoms, inclusive, and R^1 and R^2 taken together form a saturated carbocyclic ring, R^3 is hydrogen or an alkyl radical having 1 to 20 carbon atoms, inclusive, X, X^1, X^2, X^3, Y, Y^1, Y^2 and Y^3 represent hydrogen, an alkoxy radical having 1 to 4 carbon atoms, inclusive, a nitro radical or a halogen radical, and the individual pairs Y and Y^1, Y^1 and Y^2, Y^2 and Y^3, X and X^1, X^1 and X^2 or X^2 and X^3, when taken together, form a conjugated aromatic ring.

These compounds are well known in the art as are methods for their preparation. For example, U.S. Pats. Nos. 2,953,454 and 3,022,318 teach various compounds and methods for their preparation, while copending application, Ser. No. 239,334, filed Nov. 21, 1962, now abandoned by Cerreta et al., teaches others, said references hereby being incorporated herein by citation.

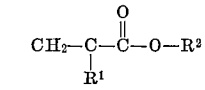
Examples of the compounds which correspond to Formula I include

1',3',3'-trimethyl-5',6-dinitro-spiro(2H-1-benzopyran-2,2'-indoline),
1',3',3'-trimethyl-5',6-dinitro-8-methoxy-spiro(2H-1-benzopyran-2,2'-indoline),
1',3',3'-trimethyl-5',8-dinitro-6-methoxy-spiro(2H-1-benzopyran-2,2'-indoline),
1',3',3'-tributyl-8-chloro-6'-butoxy-spiro(2H-1-benzopyran-2,2'-indoline),
1'-octyl-3'-methyl-3'-ethyl-3-propyl-4',7-diethoxyspiro (2H-1-benzopyran-2,2'-indoline),
1',3',3'-tristearyl-3-butyl-5,6-benzo-6'-fluoro-spiro(2H-1-benzopyran-2,2'-indoline),
1',3',3'-trimethyl-6-nitro-6',7'-benzo-spiro(2H-1-benzopyran-2,2'-indoline),
1',3',3'-triethyl-7-bromo-4',7'-dimethoxy-spiro(2H-1-benzopyran-2,2'-indoline),
1',3',3'-trimethyl-6-nitro-spiro(2H-1-benzopyran-2,2'-indoline),
1',3',3'-trimethyl-8-nitro-spiro(2H-1-benzopyran-2,2'-indoline),
1',3',3'-trimethyl-6-nitro-8-methoxy-spiro(2H-1-benzopyran-2,2'-indoline),
1',3',3'-trimethyl-5-nitro-8-methoxy-spiro(2H-1-benzopyran-2,2'-indoline),
1',3',3'-trimethyl-6-chloro-8-nitro-spiro(2H-1-benzopyran-2,2'-indoline),
1'-methyl-3'-cyclohexyl-5,8-dichloro-5'-methoxy-7'-iodo - spiro(2H - 1-benzopyran-2,2'-indoline), and the like.

The amount of photochromic material incorporated into the lauryl methacrylate polymer is not critical and depends generally upon the intensity of the color of the composition desired upon irradiation thereof, i.e., the more compound

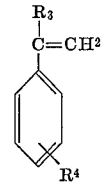
added, the greater the color intensity. However, an amount of photochromic material ranging from about 0.01% to about 20%, by weight, preferably about 0.05% to about 5.0%, by weight, based on the weight of the lauryl methacrylate being polymerized or lauryl methacrylate polymer, may be used.

The lauryl methacrylate may be used alone as a homopolymer or in conjunction with up to 50%, by weight, of a comonomer, such as those having the formula:

(II) 

wherein R^1 is hydrogen or a methyl radical and R^2 is an alkyl radical having from 1 to 6 carbon atoms, inclusive. Compounds which are represented by Formula II and consequently may be used in the present invention include methyl acrylate, ethyl acrylate, n-propyl acrylate, isopropyl acrylate, n-butyl acrylate, isobutyl acrylate, t-butyl acrylate, amyl acrylate, hexyl acrylate, methyl methacrylate, ethyl methacrylate, n-propyl methacrylate, isopropyl methacrylate, n-butyl methacrylate, isobutyl methacrylate, t-butyl methacrylate, amyl methacrylate, hexyl methacrylate and the like.

Styrene monomers may also be copolymerized with the lauryl methacrylate, including those having the formula:

(III) 

wherein R^3 is hydrogen or a lower alkyl radical having 1 to 4 carbon atoms, inclusive, and R^4 is hydrogen, a lower alkyl radical having 1 to 4 carbon atoms, inclusive, or a halogen radical. Suitable monomers represented by this formula include styrene, methyl styrene, ethyl styrene, propyl styrene, butyl styrene, chloro styrene, bromo styrene, fluoro styrene, iodo styrene, α-methyl styrene, α-ethyl styrene, α-butyl styrene, α-methyl methylstyrene, α-methyl ethylstyrene, α-butyl ethylstyrene, α-ethyl chlorostyrene, α-propyl iodostyrene and the like.

Examples of other applicable comomeric compounds which may be copolymerized with the lauryl methacrylate include the unsaturated alcohol esters, more particularly the allyl, methallyl, crotyl, 1-chloroallyl, 2-chloroallyl, cinnamyl, vinyl, methvinyl, 1-phenylallyl, butenyl, etc., esters of saturated and unsaturated aliphatic and aromatic monobasic and polybasic acids such, for instance, as acetic, propionic, butyric, valeric, caproic, crotonic, oxalic, malonic, succinic, glutaric, adipic, pimelic suberic, azelaic, sebasic, citraconic, mesaconic, itaconic, acetylene, dicarboxylic, aconitic, benzoic, phenylacetic, phthalic, terephthalic, benzoylphthalic, etc., acids; the saturated monohydric alcohol esters, e.g., the methyl, ethyl, propyl, isopropyl, butyl, sec.-butyl, amyl, etc.; esters of ethylenically unsaturated aliphatic monobasic and polybasic acids, illustrative examples of which appear above, vinyl cyclic compounds (including monovinyl aromatic hydrcarbons), e.g., styrene, o-, m-, and p-chlorostyrenes, -bromostyrenes, -fluorostyrenes, -methylstyrenes, -ethylstyrenes, -cyanostyrenes, the various poly-substituted styrenes such for example, as the various di-, tri-, and tetra-chlorostyrenes, -bromostyrenes, -fluorostyrenes, -methylstyrenes, -ethylstyrenes, -cyanostyrenes, etc., vinyl naphthalene, vinylcyclohexane, vinyl furane, vinyl pyridine, vinyl dibenzofuran divinyl benzene, trivinyl benzene, allyl benzene, diallyl benzene, N-vinyl carbazole, the various allyl cyanostyrenes, the various alpha-substituted styrenes and alpha-substituted ring-substituted styrenes, e.g., alpha-methyl styrene, alpha-methyl-paramethyl styrene, etc.; unsaturated ethers, e.g., ethyl vinyl ether, diallyl ether, ethyl methallyl ether, etc.; unsaturated amides, for instance, N-allyl caprolactam, acrylamide, and N-substituted acrylamides, e.g., N-methylol acrylamide, N-allyl acrylamide, N-methyl acrylamide, N-phenyl acrylamide, etc.; unsaturated ketones, e.g., methyl vinyl ketone, methyl allyl ketone, etc.; methylene malonic esters, e.g., methylene methyl malonate, etc.; ethylene; unsaturated polyhydric alcohol (e.g., butenediol, etc.) esters of saturated and unsaturated aliphatic and aromatic, monobasic and polybasic acids.

Other exmples of monomers that can be copolymerized with lauryl methacrylate include the vinyl halides, more particularly vinyl fluoride, vinyl chloride, vinyl bromide and vinyl iodide, and the various vinylidene compounds, including the vinylidene halides, e.g., vinylidene chloride, vinylidene bromide, vinylidene fluoride and vinylidene iodide, other comonomers being added if needed in order to improve the compatibility and copolymerization characteristics of the mixed monomers.

Among the monomers which are preferred for use in carrying my invention into effect are, for example, compounds such as acrylonitrile, and other compounds, e.g., the various substituted acrylonitriles (e.g., methylacrylonitrile, ethacrylonitrile, phenylacrylonitrile, etc.), the various N-substituted acrylamides and alkacrylamides, for instance, N-dialkyl acrylamides and methacrylamides, e.g., N-dimethyl, -diethyl, -dipropyl, -dibutyl, etc., acrylamides and methacrylamides and the like.

The photochromic spiropyrans may be incorporated into the lauryl methacrylate polymer after the polymer is formed, by, for example, dissolving both components in a common solvent, or by adding the spiropyran during the polymer production.

The actual polymerization process employed during which the photochromic material may be completely and uniformly dispersed throughout the lauryl methacrylate polymer during polymerization is not critical, and generally any known process for the polymerization of the monomer may be employed. The exact process used in each instance is governed by the photochromic material which is to be incorporated into the resulting polymer. For example, a polymerization process should be selected which does not require the use of any material, substance, compound or condition which will neutralize or react with the photochromic material, thereby nullifying the reversible color change ability of the photochromic compound. In other words, if any material in a predominant excess, such as an acid catalyst or other functional compound, or a chain length regulator such as a mercaptan, is a necessary ingredient of the polymerization process, that process cannot be used to produce the compositions of the present invention, since spiropyrans are sensitive to these ingredients. The use of polymerization systems of this kind cause a decrease in the ability of the spiropyran to reverse its color.

The same is true of processes necessitating conditions of high temperature etc. wherein the organic spiropyran is destroyed. A polymerization method which may be used for example, comprises conducting the polymerization in the presence of a free-radical generating catalyst (and a polymerization regulator) at temperatures of from about 10° C. to 90° C. Any known free-radical generating catalyst which initiates the polymerization of the lauryl methacrylate may be used. Suitable catalysts include, for example, the organic peroxides such as methyl ethyl ketone peroxide, benzoyl peroxide; the hydroperoxides such as cumene hydroperoxide; the persulfate type compounds such as potassium persulfate, or catalysts such as azobisisobutyronitrile and the like. Additionally, such catalysts as lauroyl peroxide, 2,5-dimethyl-2,5-di(t-butylperoxy)hexane, the dialkyl peroxides, e.g., diethyl peroxide, dipropyl peroxide, dilauryl peroxide, dioleyl peroxide, distearyl peroxide, di(tertiary-butyl)peroxide and di(terti-

ary-amyl)peroxide, such peroxides often being designated as ethyl, propyl, lauryl, oleyl, stearyl, tertiary-butyl and tertiary-amyl peroxides; the alkyl hydrogen peroxides, e.g., tertiary-butyl hydrogen peroxide (tertiary-butyl hydroperoxide), tertiary-amyl hydrogen peroxide (tertiary-amyl hydroperoxide), etc.; symmetrical diacyl peroxides, for instance, peroxides which commonly are known under such names as acetyl peroxide, propionyl peroxide, lauroyl peroxide, stearoyl peroxide, malonyl peroxide, succinyl peroxide, phthaloyl peroxide, benzoyl peroxide, etc.; unsymmetrical or mixed diacyl peroxides, e.g., acetyl benzoyl peroxide, propionyl benzoyl peroxide, etc.; terpene oxides, e.g., ascaridole, etc.; and salts of inorganic per-acids, e.g., ammonium persulfate, sodium persulfate, sodium percarbonate, potassium percarbonate, sodium perborate, potassium perborate, sodium perphosphate, potassium perphosphate, etc. Other examples of organic peroxide catalysts which may be employed are the following: tetralin hydroperoxide, tertiary-butyl diperphthalate, tertiary-butyl perbenzoate, 2,4-dichlorobenzoyl peroxide, urea peroxide, caprylyl peroxide, p-chlorobenzoyl peroxide, 2,2-bis(tertiary-butylperoxy)butane, hydroxyheptyl peroxide, the diperoxide of benzaldehyde and the like. Catalyst concentrations ranging from 0.0001 to 5.00 parts, by weight, based on the weight of the monomer employed may advantageously be used.

If emulsion polymerization processes are employed, any available emulsifier may be used, with compounds such as fatty acid soaps, rosin soaps, sodium lauryl sulfate, non-ionic emulsifiers such as polyethoxy alkylated phenols, compounds such as dioctyl sodium sulfosuccinate, dihexyl sodium sulfosuccinate and the like, in amounts ranging from about 1% to 8%, by weight, preferably 4% to 5%, by weight, based on the amount of monomer employed, being exemplary.

The same limitations of procedure must also be placed upon the physical blending techniques when the photochromic material is blended with the lauryl methacrylate polymer utilizing various devices to admix the polymer and the photochromic compounds.

When physical blending of the polymer and photochromic substance is desired, known procedures such as utilizing a ball mill, a tumbler mixer, hot rolls, emulsion blending techniques, Banbury mixers, Waring Blendors and the like are effective. Another procedure which may be employed is known as a devolatilization-extrusion method, wherein separate streams of solutions of the polymer and photochromic material are subjected to mixing, compounding, devolatilization and extrusion in commercially available devices. In the devolatilizer-extruder, the mixture is worked in a chamber under heat and vacuum so that new surfaces of the polymer mixture are continuously and rapidly exposed to vacuum to remove the solvent before extruding the product. The term "devolatilization" as herein employed refers to the step in which the nonpolymeric material is removed from the solution of the polymer. The apparatus which simultaneously devolatilizes and extrudes the material comprises a chamber with one or more screws having a close tolerance with the wall for compounding the material in its passage therethrough, and at least one vacuum chamber for removing the volatile components of the mixture.

The terms "photochromic compound," "photochromic substance" or "photochromic material," as used in the instant disclosure, mean compounds, substances, or materials which change their transmission or reflectance upon being subjected to ultraviolet or visible irradiation and subsequently revert to their original state upon subjection thereof to a different wavelength of radiation, or removal of the initial ultraviolet source.

The compositions of this invention may be further modified with such materials as fillers, dyes, lubricants, plasticizers, colorants, stabilizers, etc. It is also possible to lengthen the life of the composition by incorporating various amounts of an ultraviolet light stabilizer into the compositions. In this manner the photochromic life of the added benzospiropyrans is lengthened by preventing an extraneous amount of ultraviolet light from coming into contact with the photochromic material. When absorbers of this type are added, amounts up to about 20%, by weight, based on the weight of the polymer, may be used.

The following examples are set forth for purposes of illustration only and are not to be construed as limitations on the instant invention. All parts and percentages are by weight unless otherwise specified.

EXAMPLE 1

To a suitable vessel are added 100 parts of poly(lauryl methacrylate) in toluene representing a solution having an 18% solids content. To this solution are added 3 parts of 1',3',3'-trimethyl-6-nitro-8-methoxy-spiro(2H-1-benzopyran-2,2'-indoline). The mixture is stirred until the spiropyran is dissolved. The resultant solution is then drawn down onto a piece of glass and dried at room temperature for 8 hours to produce a 1.0 mil thick film.

The resultant film is stripped from the glass substrate and irradiated with a 555 mμ wavelength of light. The rate of change in optical density is recorded versus the irradiation time, log seconds. The curve recorded is shown as plotted on the drawing and represented by the open circle.

A similar film (0.7 mil) of poly(methyl methacrylate) containing 7% of the same spiropyran exhibited a slower optical density change after a longer irradiation time than the lauryl methacrylate film under the same conditions of exposure. The plot of the curve recorded testing the methyl methacrylate film is shown on the drawing by a closed circle.

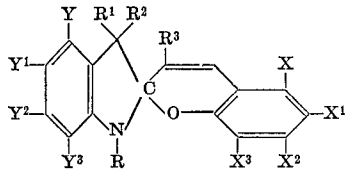
Following the procedure of Example 1, various other spiropyran compounds represented by Formula I are incorporated into various lauryl methacrylate polymers. In each instance, the sensitivity is greater than in known systems. The results are set forth in Table I, below:

TABLE I

	Polymer	Benzopyran compound	Conc. Percent
Example			
2	Lauryl methacrylate/methacrylic acid (95/5) copolymer.	1',3',3'-trimethyl-6-nirto-spiro(2H-1-benzopyran-2,2'-indollne).	1.0
3	Lauryl methacrylate/ethyl acrylate (95/5) copolymer.	1',3',3'-trimethyl-6-chloro-8'-nitro-spiro(2H-1-benzopyran-2,2'-indoline).	2.5
4	Lauryl methacrylate/vinyl benzene (90/10) copolymer.	1',3',3'-trimethyl-5',6'-dinitro-8-methoxy-spiro-(2H-1-benzopyran-2,2'-indoline).	0.50
5	Lauryl methacrylate/styrene/ acrylonitrile (75/15/10) terpolymer.	1',3',3'-tributyl-6-nitro-6',7'-benzo-spiro(2H-1-benzopyran-2,2'-indoline).	0.25
6	Poly(lauryl methacrylate)	1',3',3'-trimethyl-6-nitro-8'-butoxy-spiro(2H-1-benzopyran-2,2'-indoline).	5.0
7	Lauryl methacrylate/styrene (80/20) copolymer.	1',3',3'-trimethyl-5',6'-dinitro-spiro(2H-1-benzopyran-2,2'-indoline).	10.0
8	Lauryl methacrylate/acrylonitrile (50/50) copolymer.	1',3',3'-trimethyl-5'-iodo-spiro-(2H-1-benzopyran-2,2'-indoline).	4.5
9	Poly(lauryl methacrylate)	1',3',3'-trimethyl-7-bromo-4',7'-dimethoxy-spiro(2H-1-benzopyran-2,2'-indoline).	3.0
10	Lauryl methacrylate/vinyl chloride (95/5)copolymer.	1',3',3'-trimethyl-5',8-dinitro-6-ethoxy-spiro(2H-1-benzopyran-2,2'-indoline).	1.5

What is claimed is:

1. A photochromic composition of matter comprising a polymer of lauryl methacrylate containing not more than 50%, by weight, of at least one monoethylenically unsaturated comonomer coplymerizable therewith having uniformly dispersed throughout the body thereof a photochromic amount of a compound having the formula:



wherein R, R^1 and R^2 individually represent an alkyl radical having from 1–4 carbon atoms, inclusive, R^3 is hydrogen or an alkyl radical of 1–4 carbon atoms, inclusive, X, X^1, X^2, X^3, Y, Y^1, Y^2 and Y^3 represent hydrogen, an alkoxy radical of 1–4 carbon atoms, inclusive, a nitro radical or a halogen radical and the individual pairs Y and Y^1, Y^1 and Y^2, Y^2 and Y^3, X and X^1, X^1 and X^2 or X^2 and X^3, when taken together, form a conjugated aromatic ring.

2. A composition according to claim 1 wherein said polymer is poly(lauryl methacrylate).

3. A composition according to claim 1 wherein said compound is 1',3',3'-trimethyl-6-nitro-8-methoxy-spiro-(2H-1-benzopyran-2,2'-indoline).

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96—90