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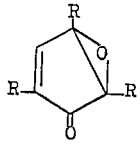
EPOXIDE COMPOUNDS AND PHOTOCHROMIC COMPOSITIONS CONTAINING THE SAME

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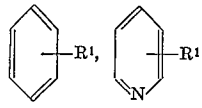
No Drawing. Filed Oct. 1, 1963, Ser. No. 312,850
14 Claims. (Cl. 96—90)

This invention relates to a novel group of photochromic compounds. More particularly, this invention relates to a novel group of compounds characterized by their ability to change and retain their color upon subjection to visible and ultraviolet light. Still more particularly, this invention relates to a novel group of photochromic compounds having the formula

(I)



wherein R is



or a lower alkyl radical and R^1 is hydrogen, a straight or branched lower alkoxy, a straight or branched lower alkyl, a nitro, a cyano, a halo, or an alkoxy carbonyl radical. Still more particularly, this invention relates to various novel compositions of matter comprising various materials having dispersed throughout the body thereof at least one of said photochromic compounds represented by Formula I, above.

Photochromic compounds are well known in the art, as is the usage thereof for such applications as temporary data storage devices, reflectants for incident high-intensity radiation and the like. No photochromic compounds, however, to my knowledge, have been produced which undergo a change of color upon contact with light of one wavelength and remain in this colored state indefinitely until contacted with light of another wavelength. Generally, these prior art photochromic compounds become colored or change color upon subjection to ultraviolet light and automatically revert to their original color when they are removed from the ultraviolet light or stored in the dark.

Generally, these compounds change their color also when exposed to ordinary sunlight and revert back to their original color upon removal thereof from the rays of the sun. Various other materials, however, change color only when subjected to a certain degree of irradiation, and as such, sunlight will not affect them. High intensity radiation, such as 10–25 cal./cm.^{2}/sec. or more is necessary in regard to these compounds, while sunlight (0.2 cal./cm.^{2}/sec.) will affect the former.

The failure of these known photochromic materials to retain their color for more than a few minutes after being subjected to ultraviolet light seriously detracts from their applicability for many commercial and industrial uses. Of prime importance is the need for compounds of this type which can be utilized for permanent or long-period information storage.

I have now found a novel group of photochromic compounds which fulfill the desired need for active ingredients in such articles as permanent information storage devices and the like. These novel compounds are weakly colored and undergo light-induced color change and intensification when subjected to light of one wavelength

and can only be reversed to their original color by subjection to light of a different wavelength. This unusual and desirable property enables these compounds to be utilized in various applications wherein retention of light-induced color is necessary. These novel compounds are represented by Formula I, above.

The compounds also may be used to produce variable transmission devices which must not be thermally bleached or activated. These compounds, in the form of films, castings, moldings, etc., of various materials can also be used for information storage devices, memory systems, computer applications and the like. They may further be used for a direct recording of information by use of a moving or intensity modulated ultraviolet light beam. In this application, the resultant image may be indefinitely preserved in the dark and then may be erased with visible light or, conversely, the compounds can be incorporated in the more highly colored state and visible light can be used to "write the message." They may also be used in computers, rapid recording graph paper and photographic point paper.

It is therefore an object of the present invention to provide a novel group of photochromic materials.

It is a further object of the present invention to provide a novel group of photochromic materials represented by Formula I, above, and characterized by their ability to change and retain their color upon subjection to light.

It is a further object of the present invention to provide novel compositions of matter comprising various materials having dispersed throughout the body thereof at least one of said photochromic compounds represented by Formula I, above.

These and other objects will become more apparent to those skilled in the art by reading the more detailed description of my invention set forth hereinbelow.

PHOTOCHROMISM

Molecules or complexes which undergo reversible photo-induced color changes are termed photochromic systems. That is to say, in the absence of activating radiation, the system has a single stable electronic configuration with a characteristic absorption spectrum. When the system is contacted with a certain wavelength range of light the absorption spectrum for the system changes drastically, but when the light source is removed, the system either spontaneously reverts to its original state or as is shown for the first time in my invention, can be converted to its original state with a different wavelength range of light.

Photochromism has been observed in inorganic and organic compounds both in solution and solid state. Although the exact mechanism of color change varies in each individual system, in many inorganic systems it can be related to one of two possible reaction schemes. The first process is the alteration of the force field around the nucleus of a coordination compound by photo-initiated dissociation, ligand exchange, or isomerization. This alteration can lead to a marked change in the light absorption properties of a molecule.

The second fundamental photo-electronic mechanism generally considered as producing photochromism is electron delocalization. This mechanism is rapidly reversible in organic molecules and therefore usually produces no colored intermediate. However, in inorganic crystals, photoinitiated electron delocalization from an impurity can lead to a colored state in which the electron is either trapped by a crystal defect to form a color center or otherwise reacts with the crystal host to leave the system in a colored state.

There are three major factors which govern the behavior of a photochromic system.

A. ABSORPTION OF INCIDENT RADIATION

According to the quantum theory, each absorbed quantum creates one activated molecule and only absorbed radiation can produce a chemical change. Variables which control the number of photons absorbed include the concentration and extinction coefficient of the photochrome, the screening coefficients of other components of the system, and the wavelengths of the incident radiation.

B. QUANTUM YIELD

All excited molecules will not undergo transformation to the colored form, so that the quantum yield will generally be less than unity. Various deactivating processes which compete for the excited molecules include fluorescence, phosphorescence, permanent chemical change and thermal release.

C. THE REVERSE REACTION

In both the forward and reverse reactions, the concentration of the colored form is dependent on the time period, the intensity and the wavelengths of the light, the kinetics of the reverse reactions, and temperature of the reactions. The kinetics for the reverse reaction will normally be controlling, however some reverse reactions are thermally sensitive and are accelerated by irradiation or heating. In the absence of a non-photochemical reverse reaction, the concentration of the colored form is dependent only on the period, the intensity and the wavelengths of the irradiation.

By the terms "photochromic compound," "photochromic substance" or "photochromic material," as used in the instant disclosure, is meant compounds, substances or materials which change their transmission or reflectance upon being subjected to ultraviolet or visible light and subsequently revert to their original state upon subjection thereof to a different wavelength of light.

THE PHOTOCHROMIC COMPOUNDS

As heretofore enumerated, the photochromic compounds of the instant invention are represented by Formula I, above. These compounds undergo color change from white or pale yellow to red upon subjection to ultraviolet light of wavelengths from about 2000 to about 4000 angstroms and remain highly colored in the dark indefinitely. They then can be reverted to their original color by subjection to visible light of from about 4000 to 6500 angstroms. The compounds of the instant invention are colorless to pale yellow oils and are generally prepared and used without purification due to their instability toward hydroxylic solvents.

Examples of compounds which are represented by Formula I and are therefore subject of the present invention are

2,3-epoxy-2,3,5-triphenylcyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(o-methylphenyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(m-methylphenyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(p-methylphenyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(o-ethylphenyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(m-ethylphenyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(p-ethylphenyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(o-propylphenyl)cyclopent-4-en-1-one,
2,3-epoxy 2,3,5-tris(m-propylphenyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(p-propylphenyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(o-butylphenyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(m-butylphenyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(p-butylphenyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(o-sec-butylphenyl)cyclopent-4-en-1-one,

2,3-epoxy-2,3,5-tris(m-sec-butylphenyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(p-sec-butylphenyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(o-isopropylphenyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(m-isopropylphenyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(p-isopropylphenyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(o-nitrophenyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(m-nitrophenyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(p-nitrophenyl)cyclopent-4-en-1-one,
2,3,epoxy-2,3,5-tris(o-cyanophenyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(m-cyanophenyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(p-cyanophenyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(o-chlorophenyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(m-chlorophenyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(p-chlorophenyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(o-bromophenyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(m-bromophenyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(p-bromophenyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-trimethylcyclopent-4-en-1-one,
2,3-epoxy-2,3,5-triethylcyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tripropylcyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tributylcyclopent-4-en-1-one,
2,3-epoxy-2,3,5-triisopropylcyclopent-4-en-1-one,
2,3-epoxy-2,3,5-triisobutylcyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tri-sec-butylcyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tri-tert-butylcyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tripyridylcyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(o-methoxyphenyl)cyclopent-4-en-1-one.
2,3-epoxy-2,3,5-tris(m-methoxyphenyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(p-methoxyphenyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(o-ethoxyphenyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(m-ethoxyphenyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(p-ethoxyphenyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(o-propoxyphenyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(m-propoxyphenyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(p-propoxyphenyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(o-butoxyphenyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(m-butoxyphenyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(p-butoxyphenyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(o-tert-butoxyphenyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(m-tert-butoxyphenyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(p-tert-butoxyphenyl)cyclopent-4-en-1-one,
2,3-epoxy2,3,5-tris(o-sec-butoxyphenyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(m-sec-butoxyphenyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(p-sec-butoxyphenyl)cyclopent-4-en-1-one,

2,3-epoxy-2,3,5-tris(o-isopropoxyphenyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(m-isopropoxyphenyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(p-isopropoxyphenyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(o-iodophenyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(m-iodophenyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris-(p-iodophenyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(o-fluorophenyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(m-fluorophenyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(p-fluorophenyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(o-methoxycarbonyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(m-methoxycarbonyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(p-methoxycarbonyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(o-ethoxycarbonyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(m-ethoxycarbonyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(p-ethoxycarbonyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(o-butoxycarbonyl)cyclopent-4-en-1-one,
2,3,-epoxy-2,3,5-tris(m-butoxycarbonyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(p-butoxycarbonyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(o-tert-butoxycarbonyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(m-tert-butoxycarbonyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(p-tert-butoxycarbonyl)cyclopent-4-en-1-one,
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2,3-epoxy-2,3,5-tris(4-methoxy-2-pyridyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(5-methoxy-2-pyridyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(6-methoxy-2-pyridyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(3-ethoxy-2-pyridyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(4-ethoxy-2-pyridyl)cyclopent-3-en-1-one,
2,3-epoxy-2,3,5-tris(5-ethoxy-2-pyridyl)cyclopent-4-en-1-one,
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2,3-epoxy-2,3,5-tris(4-methoxy-3-pyridyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(5-methoxy-3-pyridyl)cyclopent-4-en-1-one,

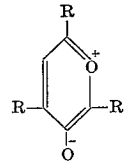
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2,3-epoxy-2,3,5-tris(2-propoxy-4-pyridyl)cyclopent-4-en-1-one,
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2,3-epoxy-2,3,5-tris(3-sec-butoxy-2-pyridyl)cyclopent-4-en-1-one,
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2,3-epoxy-2,3,5-tris(2-methyl-3-pyridyl)cyclopent-4-en-1-one,
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2,3-epoxy-2,3,5-tris(2-sec-butyl-4-pyridyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(3-isopropyl-4-pyridyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(3-ethyl-2-pyridyl)cyclopent-4-en-1-one,
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2,3-epoxy-2,3,5-tris(6-isobutyl-2-pyridyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(3-nitro-2-pyridyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(4-nitro-2-pyridyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(5-nitro-2-pyridyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(6-nitro-2-pyridyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(2-nitro-3-pyridyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(4-nitro-3-pyridyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(5-nitro-3-pyridyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(6-nitro-3-pyridyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(2-nitro-4-pyridyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(3-nitro-4-pyridyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(3-cyano-2-pyridyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(4-cyano-2-pyridyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(5-cyano-2-pyridyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(6-cyano-2-pyridyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(2-cyano-3-pyridyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(4-cyano-3-pyridyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(5-cyano-3-pyridyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(6-cyano-3-pyridyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(2-cyano-4-pyridyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(3-cyano-4-pyridyl)cyclopent-4-en-1-one,

2,3-epoxy-2,3,5-tris(3-chloro-2-pyridyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(4-chloro-2-pyridyl)cylopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(5-chloro-2-pyridyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(6-chloro-2-pyridyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(3-bromo-2-pyridyl)cyclopent-4-en-1-one,
2,3,-epoxy-2,3,5-tris(4-bromo-2-pyridyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(5-bromo-2-pyridyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(6-bromo-2-pyridyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(3-fluoro-2-pyridyl)cyclopent-4-en 1-one,
2,3-epoxy-2,3,5-tris(4-fluoro-2-pyridyl)cyclopent-4-en-1-one,
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2,3-epoxy-2,3,5-tris(6-fluoro-2-pyridyl)cyclopent-4-en-1-one,
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2,3-epoxy-2,3,5-tris(5-iodo-2-pyridyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(6-iodo-2-pyridyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(2-chloro-3-pyridyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(4-chloro-3-pyridyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(5-chloro-3-pyridyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(6-chloro-3-pyridyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(2-bromo-3-pyridyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(4-bromo-3-pyridyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(5-bromo-3-pyridyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(6-bromo-3-pyridyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(2-iodo-3-pyridyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(4-iodo-3-pyridyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(5-iodo-3-pyridyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(6-iodo-3-pyridyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(2-fluoro-3-pyridyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(4-fluoro-3-pyridyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(5-fluoro-3-pyridyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(6-fluoro-3-pyridyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(2-chloro-4-pyridyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(3-chloro-4-pyridyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(2-iodo-4-pyridyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(3-iodo-4-pyridyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(2-fluoro-4-pyridyl)cyclopent-4-en-1-one,

2,3-epoxy-2,3,5-tris(3-fluoro-4-pyridyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(2-bromo-4-pyridyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(3-bromo-4-pyridyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(3-methoxycarbonyl-2-pyridyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(4-ethoxycarbonyl-2-pyridyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(5-propoxycarbonyl-2-pyridyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(6-butoxycarbonyl-2-pyridyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(2-methoxycarbonyl-3-pyridyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(4-ethoxycarbonyl-3-pyridyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(5-isopropoxycarbonyl-3-pyridyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(6-sec-butoxycarbonyl-3-pyridyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(2-tert-butoxycarbonyl-4-pyridyl)cyclopent-4-en-1-one,
2,3-epoxy-2,3,5-tris(3-isobutoxycarbonyl-4-pyridyl)cyclopent-4-en-1-one,
2,3-epoxy-2-methyl-3,5-diphenylcyclopent-4-en-1-one,
2,3-epoxy-2-ethyl-3,5-diphenylcyclopent-4-en-1-one,
2,3-epoxy-2-ethyl-3,5-bis(o-nitrophenyl)cyclopent-4-en-1-one,
2,3-epoxy-5-butyl-2,3-dipyridylcyclopent-4-en-1-one,
2,3-epoxy-2-o-chlorophenyl-3,5-bis(3-ethoxy-2-pyridyl)-cyclopent-4-en-1-one,
2,3-epoxy-2-ethyl-3,5-bis(2-nitro-4-pyridyl)cyclopent-4-en-1-one, and the like.

My novel photochromic compounds can be prepared by contacting the corresponding pyrylium oxide with visible light, preferably of wavelengths greater than 4500 angstroms, until the color thereof substantially disappears. That is to say, by subjecting a compound having the formula

(II)



wherein R is as enumerated above, to visible light, my novel compounds are produced. This transformation occurs thusly:



Utilizing the product obtained by irradiation of 2,4,6-triphenylpyrylium-3-oxide, as an example, the 2,3-epoxy-2,3,5-triphenylcyclopent-4-en-1-one shows infrared carbonyl absorption at 5.78μ, characteristic of unsaturated five-membered ring ketones and ultraviolet absorption in cyclohexane at 231mμ and 288mμ which indicates the above structure. The structure is unambiguously demonstrated by ozonolysis to give a mixture of benzoic acid and oxirane-1,2-dicarboxylic acid. The latter is isolated as its crystalline dimethyl ester. Its structure follows from the appearance of a single ester carbonyl peak in the infrared at 5.75μ, the presence of only o-methyl and aromatic proton peaks in the nuclear magnetic spectrum, and the presence of only phenyl absorption in the ultraviolet specrtum.

The novel compounds of my invention may generally be prepared in solution and may be recovered in any known manner, such as by evaporation etc. They may be also produced in any other manner, any method for the production thereof forming no part of the present invention.

The pyrylium oxides may also be produced by any known method such as, for example, that shown in articles by Suld et al., J. Am. Chem. Soc., volume 83, page 1770, 1963, and volume 84, page 2094, 1962.

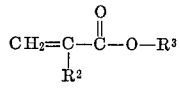
THE NOVEL COMPOSITIONS OF MATTER

The novel compounds represented by Formula I may be incorporated into various materials to produce compositions of matter which are useful for the applications described above and which form part of the present invention. That is to say, my novel photochromic compounds, set forth hereinabove, may be incorporated into such materials as acrylic and methacrylic polymers, styrene polymers, vinyl halide polymers, cyanoethylated cellulosic materials, aminoplast resins, polyester resins and the like. These resultant compositions of matter may be formed into discs, plates, films, foils, castings, and the like, alone or supported on various solid substrates, such as paper, glass and the like, by any known molding, casting, spray-drying etc. technique. Since the color change of my novel photochromic compounds is evidenced in the solid state, the use of laminated articles and/or incapsulated photochromic solutions have been obviated by my novel compositions.

THE ACRYLIC, METHACRYLIC, STYRENE AND VINYL HALIDE POLYMERS

The various esters of acrylic acid and methacrylic acid which may be used to form the polymers comprising the major constituent of my novel photochromic compositions are those having the formula

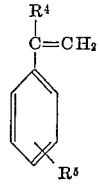
(III)



wherein R^2 is hydrogen or a methyl radical and R^3 is an alkyl radical having from 1 to 6 carbon atoms, inclusive. Compounds which are represented by Formula III 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.

The acrylic and methacrylic acid esters may be polymerized alone or in combination with other ethylenically unsaturated monomers in amounts such that the final polymer has a preponderance of the acrylic or methacrylic acid ester therein, i.e. at least 51%, by weight, based on the total weight of the monomers.

The styrene monomers, which may also be employed in the present invention are those having the formula



wherein R^4 is hydrogen or a lower alkyl radical having 1 to 4 carbon atoms, inclusive, and R^5 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.

These styrene monomers may also be polymerized alone or in combination with other ethylenically unsaturated monomers in amounts equivalent to those set forth hereinabove in regard to the methacrylic and acrylic acid esters.

The vinyl halide monomers which may be used in the present invention are well known in the art and generally vinyl chloride is the most practical for reasons of availability and cost. However, vinyl fluoride has become more important in recent years and its use is also contemplated herein. These vinyl halide polymers may be used as pure homopolymers, however, in as much as commercially available polymeric vinyl halide resins generally are produced containing minor amounts, i.e. up to about 2.0% of copolymeric material, resins of this sort are also applicable herein. Commercially available poly(vinyl chloride) also, for example, may contain about 1.0% or less of other constituents such as vinyl acetate, in copolymeric form. These polymers are also useful herein. These vinyl halides may additionally be employed with varying amounts of comonomers, generally in amounts as indicated above in regard to the esters of acrylic and methacrylic acids.

Examples of applicable comonomeric compounds which may be copolymerized with the acrylates, styrenes and vinyl halides set forth hereinabove in amounts less than about 50%, by weight, based on the total weight of the monomers 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, sebacic, 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 hydrocarbons), 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 tetrachlorostyrenes, -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-para-methyl 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 acryalamide, 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 examples of monomers that can be copolymerized are 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 compati-

bility and copolymerization characteristics of the mixed monomers.

More specific examples of allyl compounds, that can be copolymerized are allyl alcohol, methylallyl alcohol, diallyl carbonate, allyl lactate, allyl alphahydroxyisobutyrate, allyl trichlorosilane, diallyl methylguconate, diallyl tartronate, diallyl tartrate, diallyl mesaconate, the diallyl ester of muconic acid, diallyl chlorophthalate, diallyl dichlorosilane, the diallyl ester of endomethylene tetrahydrophthalic anhydride, triallyl tricarballylate, triallyl cyanurate, triallyl citrate, triallyl phosphate, tetrallyl silane, tetrallyl silicate, hexallyl disiloxane, etc. Other examples of allyl compounds that may be employed are given, for example, in U.S. Patent No. 2,510,503, issued June 6, 1950.

Among the monomers which are preferred for use in carrying our invention into effect are, for example, compounds such as acrylonitrile, and other compounds, e.g., the various substituted acrylonitriles (e.g. methacrylonitrile, 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 CYANOETHYLATED CELLULOSIC MATERIALS

The cyanoethylated cellulosic materials employed in the formation of the novel compositions of the present invention may be prepared from the cellulose of wood pulp or wood fiber after removal of the lignin and the like therefrom. Additionally, α-cellulose flock, regenerated cellulose fibers such as viscose, cotton linters, and natural cellulose materials such as cotton, jute, ramie, and linen may be used in such forms as fibers, yarns, fabrics, raw stock, batting and the like. Additionally, the cellulosic material may be non-fibrous e.g. in the form of felted or webbed materials. The fibrous forms of the cellulose may be employed in woven or knitted condition. It is also within the scope of the present invention to employ methyl cellulose, ethyl cellulose, and the like as the starting material.

Cyanoethylation of cellulosic materials is well known in the art and is generally carried out by reacting the natural or regenerated cellulosic material with acrylonitrile in various ways. The physical properties of the resultant products vary with the nature of the cellulosic material, its molecular weight, the method of treatment and the like. However, said properties are affected most noticeably by the extent to which the cellulosic material has been cyanoethylated.

The cyanoethylation of the cellulosic material is usually defined in one of two ways, i.e. either by its nitrogen content, expressed in weight percent of nitrogen, or by a decimal fraction representing the number of cyanoethyl groups introduced per anhydroglucose unit. This decimal fraction is usually referred to as the "degree of substitution." Complete cyanoethylation of cellulose generally corresponds to a nitrogen content of about 13.1% or slightly above, and a degree of substitution of about 3. A nitrogen content of at least 10% and a corresponding degree of substitution of about 2.3 is generally present in the most commonly available materials.

At low degrees of substitution, that is, a degree of substitution up to about 2, cyanoethylation does not greatly alter the solubility or the physical appearance of the cellulose, i.e. the fibrous characteristics thereof are generally retained. However, as the degree of substitution increased progressively above 2, the fibrous characteristics of the cellulose gradually diminish and resemblances of the product to a thermoplastic resin, become increasingly apparent. Additionally, the product develops a solubility in certain organic solvents which the cellulosic material did not have.

As mentioned above, substantially any cellulosic material can be utilized in the production of my novel compositions of the present invention. Cellulose, and some chemically related compounds, are structurally polymers of anhydroglucose, and different polymers are generally classed in terms of the number of anhydroglucose units in a molecule. Chemically, an anhydroglucose unit is a trihydric alcohol, one hydroxyl group being a primary hydroxyl and the other two being secondary. Celluloses are predominately 1 to 4 unit polymers, the number of polymerized units usually being referred to as the degree of polymerization.

As with any other polymer, each cellulosic polymer is a mixture of polymers of different molecular weight and it is the average degree of polymerization which determines the classification of the ultimate product. The celluloses used in the present invention generally have a degree of polymerization of at least about 2000, although those celluloses having degrees of polymerization below 2000 are also useful herein. The viscose rayons for example, have a degree of polymerization of from about 250 to 350. Natural cotton has a degree of polymerization of about 850 to 1000 and many wood pulp derivatives have a degree of polymerization in excess of 1000. All these celluloses however, may be used in the practice of the present invention.

The cyanoethylation procedures used to form the starting compositions of the present invention do not form part of the instant invention and any known procedure for achieving this result may be employed. One such method is shown for example, in U.S. Patent No. 2,332,049. Additional procedures are shown in the following U.S. patents: 2,375,847, 2,840,446, 2,786,736, 2,860,946, 2,812,999 and these patents are hereby incorporated herein by reference. In general, the procedure for preparing the cyanoethylated celluloses involves reacting a cellulosic material with acrylonitrile in the presence of an alkali and precipitating and washing the resultant cyanoethylated product. Generally, the amount of acrylonitrile which is used is 10 to 20 times the amount of cellulosic material being treated. The particular alkali employed is not critical and such materials as potassium hydroxide and sodium hydroxide may be used. A good general procedure is to employ about 2.5 to about 7.0 weight percent of alkali, based on the weight of the cellulosic material.

THE AMINOPLAST RESINS

The aminoplast resins employed in the practice of the present invention are synthetic resins prepared by the condensation reaction of an amino (including imino) or amido (including imido) compound with an aldehyde. Resinous condensates of this type, as well as methods for their preparation, have been shown innumerable times in the prior art, and adequate disclosures of them may be found in, for example, U.S. Patent Nos. 2,917,357; 2,310,004 and 2,328,592 to Widmer et al. and 2,260,239 to Talbot. The present invention is concerned particularly with aminoplast resins of the type wherein one or more aminotriazines containing at least two amidogen groups, each having at least one aldehyde reactable hydrogen atom attached to the amidogen nitrogen atom, e.g., melamine, have been reacted with an aldehyde, such as formaldehyde, to yield a thermosetting resinous condensate, i.e., one which has been carried to an intermediate stage of condensation whereby it remains as a resinous material soluble or readily dispersible in aqueous systems while also remaining capable of being converted, under suitable conditions of heat and pressure, to a substantially insoluble and infusible form.

Melamine is the preferred aminotriazine reactant for preparing the heat-curable or potentially heat-curable partially polymerized aminotriazine-aldehyde resinous reaction products which are used in the practice of the present invention, but other aminotriazines, e.g., mono-, di- and tri-substituted melamines, such as the mono-, di- and trimethylmelamines, and the like, guanamines, such as

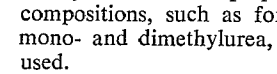
formoguanamine, acetoguanamine, benzoguanamine, and the like, as well as mixtures of aminotriazines, may be utilized as reactants. Similarly, formaldehyde, preferably in aqueous solution, is the preferred aldehyde reactant, but other aldehydes, e.g. acetaldehyde, propionaldehyde, butyraldehyde, benzaldehyde, and the like, or compounds engendering aldehydes, e.g., paraformaldehyde, hexamethylenetetramine, and the like, may also be employed. The properties desired in the finished product and economic considerations are among the elements which will determine the choice of the particular aminotriazine and aldehyde employed.

The mol ratio of aldehyde to aminotriazine in such resinous reaction products is not critical, and may be within the order of from about 1.5:1 to about 4:1, respectively, depending on the nature of the starting materials and the characteristics desired in the final product, but it is preferred that the mol ratio be within the order of from about 2:1 to about 3:1, respectively.

Conventional reaction conditions are observed in preparing the aminotriazine-aldehyde resins, i.e., the aldehyde and aminotriazine may be heat-reacted at temperatures ranging from about 40° C. to reflux temperature, i.e., about 100° C., for periods of time ranging from about 30 to 120 minutes, at a pH ranging from about 7.0 to 10, preferably in an aqueous medium. Any substance yielding acidic or alkaline aqueous solutions may be used to regulate the pH, for example, alkaline materials such as alkali metal or alkaline earth metal oxides, e.g., sodium, potassium or calcium hydroxide or sodium or potassium carbonate; mono-, di-, or tri-alkylamines, e.g., ethanolamine, triethylamine or triethanolamine; alkylene polyamines or polyalkylene polyamines, e.g., 3,3'-iminobisproplyamine, and the like.

Other amido or imido compounds having at least two aldehyde-reactable hydrogen atoms attached to amidogen nitrogen atoms may also be used in preparing the aminoplast resins used in the present invention. For example, urea and those of its derivatives which have been commonly used in the preparation of aminoplast resinous compositions, such as for example the alkylureas, e.g., mono- and dimethylurea, halourea and the like may be used.

The properties of the thermosetting aminoplast resins can be further modified, if desired, by incorporating various other substances into the aminotriazine-aldehyde resin. Included among such substances are plasticizers such as the α-alkyl-D-glucosides, e.g., α-methyl-D-glucoside, disclosed in U.S. Patent No. 2,773,848 to Lindenfelser, methylol derivatives corresponding to the general formula:



wherein R^3 represents an alkyl, aryl or aralkyl group, R^4 represents a hydrogen atom or an alkyl, alkylol, aryl or acyl group, and X represents, $-SO_2-$ or

e.g., N-methylol p-toluenesulfonamide (which may be formed in situ by the addition of p-toluenesulfonamide to an amidogen-formaldehyde reaction mixture) and the like, or combinations of these glucosides and methylol derivatives, e.g., a mixture of α-methyl-D-glucoside and p-toluenesulfonamide, as disclosed in U.S. Patent No. 2,773,788 to Magrane et al.

The aminoplast resinous molding materials may be prepared by first impregnating a fibrous filler, such as chopped α-cellulose, with an aminoplast resin, containing the benzospiropyran photochromic compound, in syrup form, drying the impregnated material to a low volatile content, usually in the order of about 10% or less, converting the dried material to a fine, fluffy powder while blending it with various commonly employed additives, such as curing catalysts, pigments, mold lubricants, and the like, and finally densifying and granulating the powdered molding composition, thus converting it to a form especially suited for commercial molding techniques and to which my novel photochromic materials may be added.

In such techniques, the common practice is to first shape the granular molding composition into a preformed article which approximates the shape the article will assume in its final form. This pre-forming step may be carried out either in a press or mold specifically designed for pre-forming or in a conventional molding press, either with or without the application of heat, to result in a preformed article whose resin content either remains uncured or becomes only partially cured, thus providing for the subsequent application of a decorative overlay, if desired after the addition of the photochromic material. Decorative overlays comprising a single sheet or foil of high grade α-cellulose paper or similar fibrous material impregnated with a thermosetting aminoplast resin are usually employed to provide a decorative effect to relatively flat molded pieces and are ordinarily not used with deep-draw molded articles. The pre-formed article is of a somewhat porous nature, and should contain slightly more resinous material than will be retained by the article when it assumes its final molded form. This is to insure that the mold used in the final molding operation will be substantially filled, with the usual provision being made for a small amount of flashing.

Ordinarily, the pre-formed article, either with or without a decorative overlay, is then placed in a molding press and molded, under suitable conditions of heat and pressure, to its final molded form.

THE POLYESTER RESINS

The polyester resins employed in the practice of the present invention may be either thermoplastic or thermosetting. They are all relatively well known in the art and are prepared by reacting polycarboxylic acids, or their anhydrides, with polyhydric alcohols. The thermosetting polyesters are prepared using a procedure wherein at least one of the reactive components contains α,β-ethylenic unsaturation. By following this procedure, resinous, essentially linear esterification or condensation products containing a plurality of ethylenically unsaturated linkages distributed along the backbones of their polymer chains are produced.

The use of α,β-ethylenically unsaturated polycarboxylic acids provides a convenient method of introducing ethylenic unsaturation into the polyester resins. It is preferred to employ α,β-ethylenically unsaturated dicarboxylic acids, such as maleic, fumaric, citraconic, γ,γ-dimethylcitraconic, mesaconic, itaconic, α-methylitaconic, γ-methylitaconic, tetraconic, and the like, as well as mixtures thereof, but minor amounts of α,β-ethylenically unsaturated polycarboxylic acids containing three or more carboxyl groups, such as aconitic acid and the like, together with the particular α,β-ethylenically unsaturated dicarboxylic acid or acids chosen, may also be used.

Whenever available, the anhydrides of any of the aforementioned α,β-ethylenically unsaturated polycarboxylic acids may be substituted for said acids in whole or in part.

Any of the large class of polyhydric alcohols ordinarily used in preparing reactive polyester resins may be employed in the practice of the present invention. While dihydric alcohols, and especially saturated aliphatic diols, are preferred as co-reactants in the preparation of the polyester resins, it is not mandatory that all of the polyol used be of this type, in that small amounts, e.g., usually up to about 10% of the total equivalents of hydroxyl groups present in the esterification mixture, of polyols having more than two hydroxyl groups may also be employed. Among the dihydric alcohols which may

be employed are saturated aliphatic diols such as ethylene glycol, propylene glycol, butylene glycol, diethylene glycol, dipropylene glycol, triethylene glycol, tetraethylene glycol, butanediol-1,2, butanediol-1,3, butanediol-1,4, pentanediol-1,2, pentanediol-1,3, pentanediol-1,4, pentanediol-1,5, hexanediol-1,2, hexanediol-1,3, hexanediol-1,4, hexanediol-1,5, hexanediol-1,6, neopentyl glycol and the like, as well as mixtures thereof. Among the polyols having more than two hydroxyl groups which may be employed in minor amounts, together with the above-mentioned diols, are saturated aliphatic polyols such as glycerol, trimethylol ethane, trimethylol propane, pentaerythritol, dipentaerythritol, arabitol, xylitol, dulcitol, adonitol, sorbitol, mannitol, and the like, as well as mixtures thereof.

In forming the thermoplastic polyester resins useful herein, the above alcohols are reacted with non-polymerizable polycarboxylic acids, i.e., acids which are saturated or which contain only benzenoid unsaturation, such as oxalic, malonic, succinic, glutaric, adipic, pimelic, suberic, azelaic, sebacic, malic, tartaric, tricarballylic, citric, phthalic, isophthalic, terephthalic, cyclohexanedicarboxylic, endomethylenetetrahydrophthalic, and the like, as well as mixtures thereof.

These saturated acids may be used alone to form thermoplastic resins or in combination with the above-mentioned unsaturated acids in the formation of thermosetting resins in order to impart many beneficial properties thereto. For example, non-polymerizable polycarboxylic acids having only two carboxyl groups, and no other reactive substituents, may be employed to impart a desirable degree of flexibility which may not be achieved by the use of the α,β-ethylenically unsaturated polycarboxylic acids alone. Where such non-polymerizable polycarboxylic acids are employed, the amount thereof should constitute at least about 20% but not more than about 80% of the total equivalents of carboxyl groups present in the esterification mixture. Preferably, such non-polymerizable polycarboxylic acids may be employed in amounts ranging from about 25% to about 75% of the total equivalents of carboxyl groups present in the esterification mixture.

Halogenated unsaturated polycarboxylic acids may also be employed in the preparation of the thermosetting polyester resins of the present invention for purposes of imparting various desirable properties thereto as mentioned above in regard to the saturated acids. Examples of halogenated acids which may be used include monochloro- and monobromomaleic, monochloro- and monobromofumaric, monochloro- and monobromomalonic, dichloro- and dibromomalonic, monochloro- and monobromosuccinic, α,β-dichloro- and dibromosuccinic, hexachloroendomethylenetetrahydrophthalic, and the like, as well as mixtures thereof. Whenever available, the anhydrides of any of these halogenated acids may also be substituted therefore in whole or in part.

Among the halogenated polyols that may be employed are 2,2'-chloromethylpropanediol-1,3, adducts of hexachlorocyclopentadiene with unsaturated polyols, such as butanediols, pentenediols, and the like, and adducts of hexachlorocyclopentadiene with polyols having three or more hydroxyl groups, one of which is etherified with an unsaturated alcohol reactive with hexachlorocyclopentadiene. Among the latter are compounds such as 3-[1,4,5,6,7,7 - hexachlorobicyclo(2.2.1) - 5-hepten-2-yl-oxy]-1,2-propanediol, which is the adduct of hexachlorocyclopentadiene with vinyl glycerol ether, 3-[1,4,5,6,7,7-hexachlorobicyclo(2.2.1) - 5 - hepten - 2 - yl]methoxy-1,2-propanediol, which is the adduct of hexachlorocyclopentadiene with allyl glycerol ether, adducts of hexachlorocyclopentadiene with vinyl and allyl ethers of pentaerythritol, and the like. Mixtures of these halogenated polyols may also be employed, if desired.

The esterification mixtures, from which both the thermoplastic and the thermosetting polyester resins employed in the practice of the present invention are prepared, are generally formulated so as to contain at least a stoichiometric balance between carbonyl and hydroxyl groups. Thus, where a diol and a dicarboxylic acid are employed, they are usually reacted on at least a mol to mol basis. In common commercial practice, a small excess of polyol, usually in the range of from about 5% to about 15% excess, is employed. This is done primarily for economic reasons, i.e. to insure a rapid rate of esterification.

Both types of polyester resins used in the practice of the present invention are formed in the manner customarily observed in the art. Thus, the particular polycarboxylic acid or acids and polyol or polyols employed are reacted at elevated temperatures and atmospheric pressure. Since resinifying reactants of this type are prone to develop undesirable color when in contact with air at elevated temperatures, it is generally considered good practice to conduct the esterification reaction in an inert atmosphere, such as can be obtained by bubbling an inert gas, e.g., carbon dioxide, nitrogen, and the like, through the esterification mixture. The reaction temperature is not critical, thus the reaction will preferably be carried out at a temperature which usually will be just below the boiling point of the most volatile component of the reaction mixture, generally the polyol.

The esterification mixture should be sufficiently reacted so as to ultimately produce a polyester resin having an acid number not appreciably more than about 75. It is preferred to employ polyester resins having acid numbers ranging from about 30 to about 50.

Further details pertaining to the preparation of polyester resins of the types employed in the practice of the present invention are disclosed in U.S. Patent No. 2,255,313 to Ellis, and in U.S. Patents Nos. 2,443,735 to 2,443,741, inclusive, to Kropa and these patents are hereby incorporated into the present application by reference.

The thermosetting polyester resins of the present invention, in combination with the photochromic benzospiropyrans, may be cross-linked by the addition of a suitable cross-linking agent.

The polyester resins are cross-linked by admixing them with monomer compound containing the polymerizable $CH_2{=}C<$ group to give a composition that may be cured to a stable thermoset condition. One may use about 10 parts by weight of the monomeric material to about 90 parts by weight of the polyester resin up to about 60 parts of the monomeric material to about 40 parts of the polyester resin. The preferred embodiment, however, is to use from about 25 parts of the monomeric material to about 35 parts of the monomeric material with about 75 parts to about 65 parts, respectively, of the polyester resin.

The monomeric material containing the polymerizable $CH_2{=}C<$ group which may be used in the practice of the present invention, has a boiling point of at least 60° C. Among the polymerizable monomeric materials that will find use in my invention are those such as styrene, side chain alkyl and halo substituted styrenes such as alpha-methylstyrene, alpha-chlorostyrene, alpha-ethylstyrene and the like or alkyl and halo ring-substituted styrenes such as ortho, meta and paraalkyl styrenes such as o-methylstyrene, p-ethylstyrene, meta-propylstyrene, 2,4-dimethylstyrene, 2,5-diethylstyrene, bromostyrene, chlorostyrene, dichlorostyrene, and the like. Still further, one can make use of the allyl compounds such as diallyl phthalate, tetrachlorodiallyl phthalate, allyl alcohol, methallyl alcohol, allyl acetate, allyl methacrylate, diallyl carbonate, allyl lactate, allyl alphahydroxyisobutyrate, allyl trichlorosilane, allyl acrylate, diallyl malonate, diallyl oxalate, allyl gluconate, allyl methylgluconate, diallyl adipate, diallyl sebacate, diallyl citraconate, the diallyl ester of muconic acid, diallyl itaconate, diallyl chlorophalate, diallyl dichlorosilane, the diallyl ester of endomethylene tetrahydrophthalic anhydride, the diallyl ester of tetrachloro endomethylene tetrahydrophthalic anhy-

dride, triallyl tricarballylate, triallyl aconitate, triallyl cyanurate, triallyl citrate, triallyl phosphate, trimethallyl phosphate, tetraallyl silane, tetraallyl silicate, hexallyl desiloxane and the like. These monomeric materials may be used either singly or in combination with one another.

When the thermosetting polyester resin is combined with the cross-linking monomeric material, it is desirable to incorporate therein a polymerization inhibitor in order to prevent premature gelation of the resinous composition, particularly if it is expected that said composition will be subjected to prolonged periods of storage or if it is expected that it will be subjected to temperatures significantly higher than room temperature. With the polymerization inhibitor, the resinous composition will remain stable at room temperature for months without noticeable deterioration. Amongst the polymerization inhibitors which may be used are any of those which are conventionally known and used in the art such a hydroquinone, benzaldehyde, ascorbic acid, isoascorbic acid, resorcinol, tannin, symmetrical di(beta-naphthyl)-p-phenylene diamine, phenolic resins, sulfur compounds and the like. The concentration of the inhibitor is preferably and as a general rule less than 1% by weight is usually sufficient. However, with the preferred inhibitors, e.g., polyhydric phenols and aromatic amines, one may make use of such small amounts as 0.01%–0.1% by weight.

The thermosetting polyester resins can readily be solidified without benefit of catalyst by the application of heat or by application of heat and pressure. However, in such an operation without benefit of a catalytic agent the time element makes it desirable to incorporate into the composition conventional polymerization catalysts such as the organic superoxides, the alcoholic and acidic peroxides. Among the preferred catalysts are: the acidic peroxides, e.g. benzoyl peroxide, phthalic peroxide, succinic peroxide and benzoyl acetic peroxide; fatty oil acid peroxides, e.g., coconut oil acid peroxides, lauric peroxide, stearic peroxide and oleic peroxide; alcohol peroxides, e.g., tertiary-butyl hydroperoxide, usually called tertiary-butyl peroxide, and terpene oxides, e.g., ascaridole. Still other polymerization catalysts might be used in some instances, e.g., soluble cobalt salts (particularly the linoleate and naphthenate), p-toluene sulfonic acid, aluminum chloride, stannic chloride and boron trifluoride and azobisisobutyronitrile.

As mentioned above, the method used to prepare the polyester resin used in the formation of the novel compositions of the present invention is not critical and any known method may be used. The only criteria which must be followed in adding the photochromic compound to the polyester resin is in regard to the residual acid or anhydride present in the polyester. All acid or anhydride of this nature must first be removed, such as by washing with a basic solution, since acids and anhydrides interfere chemically with the photochromic nature of the added compounds.

It should also be noted that these photochromic compounds, no matter to what media they are being added, should be added before the media is cured or set thermally or otherwise.

The amount of photochromic material incorporated into the desired media in each instance 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 10%, by weight, preferably about 0.05% to about 5.0%, by weight, based on the weight of the resinous polymer may be used.

In regard to the acrylate, methacrylate, styrene and vinyl halide polymers, the actual polymerization process employed in the production of these polymers is not critical, and generally any known process for the polymerization of the monomeric materials may be employed. The exact process used in each instance is governed more by the monomers being polymerized when any other single feature. One 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, for example, methyl methacrylate, styrene or vinyl chloride, 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, di(tertiary-butyl)-peroxide, tertiary-butyl hydrogen peroxide (tertiary-butyl hydroperoxide), tertiary-amyl hydrogen peroxide, 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: tertiary-butyl perbenzoate, 2,4-dichlorobenzoyl peroxide, 2,2-bis(tertiary-butylperoxy) butane, 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.

When 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.

Physical blending of the media and photochromic substance may be conducted by any known procedure such as by 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 selected media 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 mixture are continuously and rapidly exposed to vacuum to remove the solvent before extruding the product.

The scope of the instant invention is also of such breadth so as to include various formed articles produced from the novel compositions of matter disclosed above. Therefore, such shaped articles as films, foils, fibers, moldings, castings, laminates, and the like form part of the present invention. Specific properties and characteristics of these articles are set forth more fully hereinbelow in regard to the examples listed.

The compositions of this invention may be further modified with such compatible materials as fillers, lubricants, plasticizers, colorants, etc., as mentioned above.

The methods of addition of the photochromic compounds, including those mentioned above, are not critical. Furthermore, it has been found convenient to first incorporate the pyrylium oxide in the desired medium and then irridate with, for example, a 500 watt slide projector fitted with a 4500 angstrom cut-off filter, to produce my novel compositions of matter.

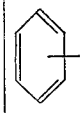
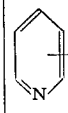
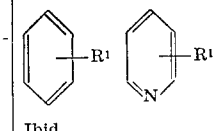
The following examples are set forth for purposes of illustration only and are not to be construed as limitations on the instant invention. All parts and percentages are by weight unless otherwise specified.

Example 1

To a suitable vessel is added a 5% solution of 2,4,6-triphenylpyrylium-3-oxide in benzene. The solution is irradiated, under nitrogen, with a light from a tungsten source, filtered by a 4500 angstrom cut-off filter, until the red color of the solution disappears. The benzene is then removed in vacuum at room temperature. The resultant pale yellow oil is identified as 2,3-epoxy-2,3,5-triphenylcyclopent-4-en-1-one in 99% yield.

Following the procedure of Example 1, various other photochromic compounds were produced. The results obtained are set forth in Table I, below.

TABLE I

Ex.	R	R¹	Solvent
2	Methyl		Benzene.
3	Sec-butyl		Hexane.
4	n-Butyl		Do.
5		o-Methoxy	Benzene.
6	Ibid	p-Propoxy	Do.
7	Ibid	m-Tert-butoxy	Do.
8	Ibid	o-Methyl	Do.
9	Ibid	m-Ethyl	Ether.
10	Ibid	p-n-Butyl	Do.
11	Ibid	o-Nitro	Benzene.
12	Ibid	m-Chloro	Do.
13	Ibid	p-Bromo	Chloroform.
14	Ibid	o-Iodo	Do.
15	Ibid	o-Fluoro	Do.
16	Ibid	m-Cyano	Cyclohexane.
17	Ibid	p-Cyano	Benzene.
18	Ibid	o-Methoxycarbonyl	Do.
19	Ibid	p-Ethoxycarbonyl	Do.
20	Ibid	m-Sec-butoxycarbonyl	Do.
21		Hydrogen	Do.
22	Ibid	3-methoxy-2-*	Ethyl acetate.
23	Ibid	4-ethoxy-2-	Do.
24	Ibid	6-n-butoxy-2-	Do.
25	Ibid	2-methyl-3-	Benzene.
26	Ibid	6-n-propyl-3-	Do.
27	Ibid	4-t-butyl-2-	Do.
28	Ibid	4-nitro-3-	Acetonitrile.
29	Ibid	5-chloro-3-	Do.
30	Ibid	5-bromo-2-	Benzene.
31	Ibid	2-cyano-4-	Do.
32	Ibid	4-methoxycarbonyl-2-	Do.
33	Ibid	6-isopropoxycarbonyl-2-	Do.
34	Ibid	6-n-butyoxycarbonyl-2-	Do.
35	Ibid	4-ethoxycarbonyl-2-	Do.
36	Ethyl		Do.
37	n-Propyl		Do.
38	Isopropyl		Do.
39	t-Butyl		Do.
40		p- and 4-methoxy-2-	Do.
41	Ibid	p- and 6-n-butoxy-2-	Do.
42	Ibid	o- and 5-methyl-3-	Do.
43	Ibid	p- and 6-sec-butyl-3-	Do.
44	Ibid	p- and 2-chloro-4-	Do.
45	Ibid	o- and 3-cyano-4-	Do.
46	Ibid	m- and 5-nitro-2-	Do.
47	Ibid	p- and 4-methoxycarbonyl-2-	Do.
48	Ibid	o- and 6-n-butoxycarbonyl-3-	Do.

*Pyridyl position.

In Examples 1 to 48, irradiation of the solutions of the resulting photochromic compounds with light from a mercury arc, filtered to remove visible radiation, colored the solutions. The colored solutions could not be bleached by heating or allowing them to stand in the dark. Irradiation of the solutions with light from a tungsten source bleached the solutions. The procedure could be repeated many times in each case.

Example 49

100 parts of a benzene solution of poly(methyl methacrylate) (20% solids) and 10 parts of 2,3-epoxy-2,3,5-triphenylcyclopent-4-en-1-one are drawn down on a glass plate and allowed to set for five hours to remove the solvent. The resultant film is substantially colorless and becomes red when irradiated with ultraviolet light from a sunlamp.

Example 50

Red 2,4,6-triphenylpyrylium-3-oxide is dissolved in a 10% poly(methyl methacrylate) solution in methylethyl-ketone. The film dope produced is cast to produce an optical quality film of poly(methyl methacrylate) containing 5% of the oxide after evaporation of the solvent. Irradiation with visible light bleaches the film and no color is formed even when the film is kept in the dark. Irradiation of the film with ultraviolet light from a sunlamp colors the film red.

Example 51

100 parts of polystyrene are added to 200 parts of methylene chloride to form a complete solution thereof. To this solution are added 8.5 parts of 2,3-epoxy-2,3,5-triphenylcyclopent-4-en-1-one. The resultant solution is drawn down on a paper substrate and allowed to dry at room temperature to evaporate the solvent. The resultant paper article is substantially colorless and becomes red when irradiated with ultraviolet light.

Example 52

Following the procedure of Example 50 except that poly(vinyl chloride) is utilized as the polymeric media, a film is produced which is bleached when contacted with visible light and returns to its red color upon subjection to irradiation with ultraviolet light. The color change and subsequent reversion cycle is continued approximately 5000 times with no evidence of decrease of color intensity or rapidity of color change.

Example 53

100 parts of a powdery commercially available cyanoethylated cellulose (nitrogen content—13%; degree of substitution—2.8) and 10 parts of 2,3-epoxy-2,3,5-triphenylcyclopent-4-en-1-one are added to a ball mill mixer. The ingredients are allowed to thoroughly mix for about 30 minutes. A solution of the mixture is prepared by dissolving it in acetone and a film of the cyanoethylated cellulose mixture is then cast on a glass plate by evaporating the solvent at room temperature. The colorless film becomes red when contacted with ultraviolet light and returns to a colorless state when subjected to visible light.

Example 54

Into a suitable reaction vessel are added 300 parts of acrylonitrile and 12 parts of sodium hydroxide. To this mixture is added 40 parts of water and 0.25 part of isopropyl naphthalene sodium sulfonate, as an emulsifier. The resultant mixture is agitated for ½ hour and 25 parts of white cotton yarn are then added. The temperture is raised to 38° C. and the reaction mixture is thoroughly agitated for one hour. The sodium hydroxide is then neutralized with phosphoric acid and the yarn is washed with water. The nitrogen content is 12.6% and the degree of substitution is 2.8. To the yarn is then added a solution of 15 parts of 2,3-epoxy-2,3,5-triphenylcyclopent-4-en-1-one in benzene. Upon removal of the benzene by evaporation, the yarn turns to dark red when contacted with ultraviolet light and reverts to its white color when subjected to visible light.

Example 55

100 parts of a powdered, commercially available, spray dried melamine-formaldehyde resin (mole ratio of formaldehyde to melamine of 2:1) is added to a ball mill along with 5 parts of 2,4,6-triphenylpyrylium-3-oxide. The ingredients are allowed to thoroughly mix and the resultant admixture is placed into a pre-heated saucer-shaped mold and heated to 155° C. for five minutes. The resultant saucer darkens in color to red when subjected to ultraviolet light and returns to its off-white color upon subjection to visible light.

Example 56

A commercially available polyester resin of maleic anhydride, phthalic anhydride and propylene glycol (15.1/46.2/38.7) is washed three times with an aqueous solution of $NaCO_3$ at 20° C. to rid the polyester of residual anhydride therein. The polyester is then dried over calcium chloride for two hours and to 100 parts of it are added one part of 2,4,6-triphenylpyrylium-3-oxide. To this mixture is then added 61 parts of styrene. The resultant mixture is then poured between glass plates and sealed. The plates are heated for 12 hours at 90° C. and for 1½ hours at 110° C. The resultant polyester casting turns red upon contact thereof with ultraviolet light.

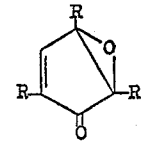
Following the procedures of Examples 49–56, the specific procedure in each instance being governed by the specific polymer media employed, various photochromic additives of the type produced as described hereinabove are added to various polymer substrates. In each instance, the resultant article produced is photochromic and maintains its color until subjected to light of a different wavelength. The results obtained are set forth hereinbelow in Table II.

TABLE II

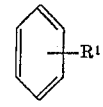
Ex.	Photochromic Additive of Example	Percent	Polymer Media of Example	Color Stability
57	2	10	49	Good.
58	3	8	49	Do.
59	4	7.5	49	Do.
60	5	5	51	Excellent.
61	6	5	51	Do.
62	7	5	51	Do.
63	8	3	52	Good.
64	9	1	52	Do.
65	10	0.1	53	Do.
66	11	0.1	53	Do.
67	12	0.01	55	Do.
68	13	1	55	Do.
69	16	2	56	Excellent.
70	18	5	56	Do.
71	20	8	56	Do.
72	21	10	49	Good.
73	22	10	49	Do.
74	24	7	51	Do.
75	25	4	51	Do.
76	27	2	52	Do.
77	28	2	52	Do.
78	29	5	53	Do.
79	32	10	55	Excellent.
80	34	9	55	Do.
81	36	7	56	Do.
82	39	4	56	Do.
83	40	8.6	49	Good.
84	41	5.8	49	Do.
85	42	0.1	49	Do.
86	43	0.1	49	Do.
87	44	0.01	49	Do.
88	45	10	51	Do.
89	46	5.5	52	Do.
90	47	10	53	Fair.

I claim:

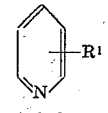
1. A composition of matter comprising a polymeric material having uniformly dispersed throughout the body thereof a photochromic material having the formula



wherein R is selected from the group consisting of a lower alkyl radical, a



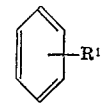
radical, and a



radical and R^1 is selected from the group consisting of hydrogen, a lower alkoxy radical, an alkyl radical, a nitro radical, a cyano radical, a halo radical, and an alkoxy carbonyl radical.

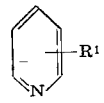
2. A composition according to claim 1 wherein R is a lower alkyl radical.

3. A composition according to claim 1 wherein R is a



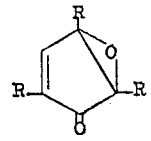
radical.

4. A composition according to claim **1** wherein R is a

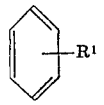


radical.

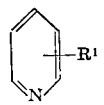
5. A composition of matter comprising a polymeric material selected from the group consisting of acrylic polymers, methacrylic polymers, styrene polymers, vinyl halide polymers, cyanoethylated cellulosic materials, amino-plast resins and polyester resins having uniformly dispersed throughout the body thereof a photochromic material having the formula



wherein R is selected from the group consisting of a lower alkyl radical, a



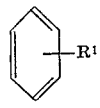
radical, and a



radical and R^1 is selected from the group consisting of hydrogen, a lower alkoxy radical, an alkyl radical, a nitro radical, a cyano radical, a halo radical, and an alkoxy carbonyl radical.

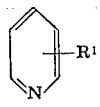
6. A composition according to claim **5** wherein R is a lower alkyl radical.

7. A composition according to claim **5** wherein R is a



radical.

8. A composition according to claim **5** wherein R is a

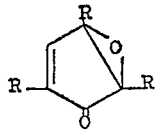


radical.

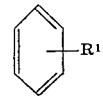
9. A composition according to claim **1** wherein the photochromic material is 2,3-epoxy-2,3,5-triphenylcyclopent-4-en-1-one.

10. A composition according to claim **5** wherein the photochromic material is 2,3-epoxy-2,3,5-triphenylcyclopent-4-en-1-one.

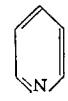
11. A compound having the formula



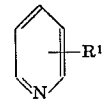
wherein R is selected from the group consisting of a lower alkyl radical, a



radical, a



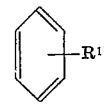
radical, and a



radical and R^1 is selected from the group consisting of a lower alkoxy radical, an alkyl radical, a nitro radical, a cyano radical, a halo radical, and an alkoxy carbonyl radical.

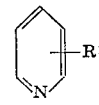
12. A compound according to claim **11** wherein R is a lower alkyl radical.

13. A compound according to claim **11** wherein R is a



radical.

14. A compound according to claim **11** wherein R is a



radical.

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