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(54) Title: PHOTOCHROMIC PRESSURE SENSITIVE ADHESIVE COMPOSITIONS

(57) Abstract: A photochromic pressure sensitive adhesive composition is provided comprised of a pressure sensitive adhesive in combination with a photochromic compound, said photochromic compound being present in said adhesive in an amount sufficient to effect a color change in said adhesive in the presence of a suitable radiation source, and said adhesive not being a styrene-based rubber adhesive.

Photochromic Pressure Sensitive Adhesive Compositions

Background of the Invention

The present invention is directed to photochromic pressure sensitive adhesive compositions which undergo rapid color development or change upon exposure to sunlight or UV-radiation. The compositions may display a wide range of colors ranging from blue, yellow, burgundy, orange to red, or any combination of such, where the color change is reversible. The compositions have particular applicability in connection with laminates or optical displays in which the photochromic effect may be used with advantage.

Photochromic compounds are well-known and have wide application in areas such as tinted optical materials such as windows, eyewear, optical display screens, etc. A durable and layered photochromic film having a gas barrier film layer is disclosed in published U.S. Patent application 2001/0009721. Also, JP 09227845; K. Tadashi, et al is directed to rubber-based photochromic adhesive compositions where the photochromic compound renders the normally translucent adhesive visible for ease of application.

The following U.S. patents disclose various photochromic dyes and their applications (mainly in the ophthalmic applications), each herein incorporated by reference: 6,316,570; 6,296,785; 6,268,055; 6,187,444; 6,153,126; 6,149,841; 6,106,744; 6,068,797; 6,060,001; 6,022,497; 5,981,634; 5,955,520; 5,879,592; 5,869,658; 5,808,063; 5,770,115; 5,723,072; 5,708,064; 5,698,141; 5,552,090; 5,395,567; 5,340,857; 5,330,686; 5,244,602; 5,200,116;

5,185,390; 5,130,353; 5,066,818; 4,994,208; 4,986,934; 4,980,089; 4,936,995; 4,931,221; 4,931,220; 4,931,219; 4,909,963; 4,880,667; 4,816,584; 4,792,224; 4,720,547; 4,637,698; 4,634,767; 4,831,142; 4,785,097; 4,634,767; each assigned to PPG Industries, Inc.; 6,080,338; 6,022,495; 5,753,146; 5,744,070; 5,674,432; 5,645,767; 5,637,262; 5,624,757; 5,585,042; 5,578,252; 5,565,147; 5,466,398; 5,464,567; 5,458,815; 5,451,344; 5,405,958; 5,391,327; 5,384,077; 5,369,158; 5,274,132; 5,238,981; each assigned to Transitions Optical, Inc.; and 5,730,908; 5,242,624; 5,225,563; 5,225,113; 5,186,867; 5,180,524; 5,171,636; 5,110,922; and 5,055,576 each assigned to Enichem Synthesis S.P.A.

The present invention provides the following advantages, among others:

(1) The rapid response kinetics of photochromic dyes in the present invention provides ultra-fast color development or change compared with other existing photochromic designs, which is a distinctive advantage for the applications where rapid switch of color is desired or favored, such as ophthalmic lenses, optical memories and switches;

(2) The composition of the present invention can be tailor-made to achieve different colors and color intensity. The colors cover a wide range from blue, yellow, burgundy, orange to red, or any of these combinations;

(3) The benefits of pressure sensitive adhesives afford the present invention convenience in use and handling, repositioning, replacement, etc.;

(4) The photochromic pressure sensitive adhesive compositions may comprise optically clear adhesives that feature high tack, good strippability, low VOC outgassing and low extractable ions; and

(5) The adhesive composition may be formulated and a barrier of backing film provided to effectively protect the photochromic dyes from damaging UVB, residual acid, oxygen and/or moisture, and consequently improve the performance and life time of the photochromic dyes.

The viscoelastic nature of pressure sensitive adhesives provides "free volume" in the adhesive matrix, which enables enhanced photochromic performance of the photochromic dyes. Compared with other existing photochromic materials including photochromic plastics or glass, coating and ink, the presence of higher amounts of free volume in the design of the present invention effectively improves the kinetics of the photochromism through facilitating the geometric rearrangement of the photochromic dyes. As a result, upon exposure to sunlight or UV-radiation and removal of the exposure, the pressure sensitive adhesive system allows color change between the ground state and excited states of photochromic dyes in a fast and reversible manner.

Detailed Description of the Drawings

Figure 1 is a cross-sectional view of an adhesive tape comprised of the photochromic pressure sensitive adhesive of the present invention.

Figure 2 is a cross-sectional view of another embodiment of an adhesive tape comprised of the photochromic pressure sensitive adhesive of the present invention.

Detailed Description of the Invention

The present invention is directed to a pressure sensitive adhesive composition that remains pressure sensitive and tacky at and above room temperature. The adhesive composition comprises a low concentration of photochromic compounds such as naphthopyran or oxazine organic compounds, which produce rapid color development or change when exposed to sunlight or UV-radiation. More specifically, such photochromic compounds may include azobenzene compounds, thioindigo compounds, spiropyran compounds, fulgide compounds, triphenylmethane compounds, spirooxazine compounds, viologen compounds, and salicyldineanil compounds, etc.

The color intensity increases continuously with increased exposure time and reaches maximum color intensity or saturation typically within ten seconds. Different color and color intensity can be pre-designed by adjusting the formulation of the composition. The color change may, for example, range from blue, yellow, burgundy, orange to red, or any of these combinations, depending upon the identity of the photochromic compound(s) employed.

The color change process of the photochromic pressure sensitive adhesive composition is reversible; i.e., the color intensity immediately starts to decrease if the radiation exposure is removed or blocked. As is the nature of

photochromic dyes, the fading process occurs much slower than the darkening process.

A variety of photochromic dyes may be employed in the practice of the present invention. Upon exposure to suitable radiation such as ultraviolet radiation, the photochromic compound absorbs at wavelengths in the visible range. For instance, the absorption of red photons from white light leaves a blue color. Upon removal of the radiation source, the net observation is a return to a colorless state. The life of the photochromic reaction depends upon many factors, including the amount of the photochromic compound employed in the composition, the intensity and length of the UV exposure, whether any stabilizers are present in the composition, and the type of adhesive which is used as the matrix material. Ultraviolet absorbers can also be employed to extend the life of the photochromic material, but their presence will also diminish the intensity of the color.

The presence of free radicals such as oxygen, oxidizers such as peroxide, acids and high energy ultraviolet may diminish the stability of the photochromic compounds. Protective agents such as antioxidants, UV stabilizers, free radical scavengers, color neutralizing agents, etc. may be used to protect against such free radicals. It is also preferred to employ a backing film which has a low oxygen permeability to minimize the effect of oxygen on the long term stability of the composition.

The photochromic compounds may be admixed with the pressure sensitive adhesive by any conventional method, such as by physical admixing,

extruding, casting, etc. Such compounds are generally stable at temperatures in the range of 180 to 240°C for short periods of time without degradation, and may thus be admixed or combined with the pressure sensitive adhesive under conditions of elevated temperature as may be required.

The identity of the pressure sensitive adhesive used in the present invention is not critical and may comprise a variety of adhesives, including but not limited to adhesives such as polyvinyl ethers, acrylic adhesives, poly-alpha-olefins, and silicone adhesives, as well as blends thereof, with the proviso that the adhesive is not a styrene-based rubber adhesive.

Polyvinyl ether pressure sensitive adhesives generally comprise blends of vinyl methyl ether , vinyl ethyl ether or vinyl iso-butyl ether, or homopolymers of vinyl ethers and acrylates. Acrylic pressure sensitive adhesives may comprise, for example, a C_{3-12} alkyl ester component and a polar component such as (meth)acrylic acid, N-vinyl pyrrolidone, etc. Such adhesives may be tackified. Poly-alpha-olefins adhesives comprise an optionally crosslinked C_{3-18} poly(alkene) polymer, which is either self-tacky or may include a tackifier. Silicone pressure sensitive adhesives comprise a polymer or gum constituent and a tackifying resin.

More specifically, the acrylic pressure sensitive adhesive is preferably comprised of a polymer formed from the reaction product of at least one acrylate A monomer and a B monomer different from the A monomer.

The at least one A monomer preferably comprises a monomeric (meth)acrylic acid ester of a non-tertiary alcohol where the alcohol portion has

from 1 to 30 carbon atoms. Exemplary A monomers include but are not limited to esters of acrylic acid or methacrylic acid with non-tertiary alcohols such as 1-butanol, 1-pentanol, 2-pentanol, 3-pentanol, 2-methyl-1-butanol, 1-methyl-1-pentanol, 2-methyl-1-pentanol, 3-methyl-1-pentanol, 2-ethyl-1-butanol, 3,5,5-trimethyl-1-hexanol, 3-heptanol, 2-octanol, 1-decanol, 1-dodecanol, etc. Such monomers are well-known to those skilled in the art. The least one A monomer component (if more than one A monomer is present) will preferably exhibit an average number of carbon atoms in the alcohol portion of the total acrylic or (meth)acrylic acid esters of from 3 to 16.

One or more polymerizable B monomers different from the A monomer may be incorporated in the polymer which B monomer(s) is copolymerizable with the A monomer. Such additional B monomer(s) may be either hydrophilic or hydrophobic.

Exemplary optional B monomers include vinyl monomers having at least one nitrogen atom. Such monomers (each of which exhibit a T_g of >20 °C.) include but are not limited to N-mono-substituted acrylamides such as acrylamide, methacrylamide, N-methylacrylamide, N-ethylacrylamide, N-methylolacrylamide, N-hydroxyethylacrylamide, and diacetone acrylamide; N,N-disubstituted acrylamides such as N,N-dimethylacrylamide, N,N-diethylacrylamide, N-ethyl-N-aminoethyl acrylamide, N-ethyl-N-hydroxyethylacrylamide, N,N-dimethylolacrylamide, and N,N-dihydroxyethylacrylamide, etc.

Other optional B monomers may include, for example, various vinyl monomers such as (meth)acrylic acid, itaconic acid, crotonic acid, methoxyethyl (meth)acrylate, ethyoxyethyl (meth)acrylate, glycerol (meth)acrylate, hydroxyethyl methacrylate, hydroxypropyl methacrylate, beta-carboxyethyl acrylate, vinyl pyrrolidone, vinyl caprolactam and caprolactam acrylate. One or more B monomers may be employed.

Such pressure sensitive adhesives are well known to one of ordinary skill in the art and may be easily selected by such persons for use in the present invention.

The pressure sensitive adhesive composition of the present invention may, for example, be comprised of the following:

a) From about 90 to about 99.95% by weight of a pressure sensitive adhesive or adhesive blend as the base material. Such adhesives include but are not limited to acrylic polymers or copolymers. Exemplary polymer or copolymer compositions may be comprised of, for example, tert-butylmethacrylate, butyl acrylate, glycidyl methacrylate, 2-ethylhexylacylate, hydroxylethylacrylate, isobornyl methacrylate, N-vinylpyrrolidone and vinyl acetate.

b) From about 0.05 to about 10% by weight of a photochromic dye or a blend of two or more photochromic dyes. Such photochromic dyes include but are not limited to organic naphthopyrans and oxazines. Examples of these dyes are Photosol™ photochromic dyes (PPG Industries, Inc.).

c) From about 0 to about 5.0% by weight of an antioxidant. Examples of antioxidants include but are not limited to pentaerythritol tetrakis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate or 2,6-di-tert. butyl -4-methyl phenol.

The photochromic pressure sensitive adhesive composition of the present invention may be used in a variety of end uses with advantage, including but not being limited to the following: removable and replaceable films for ophthalmic applications such as transition lenses and ski goggles; contrast-enhancing and energy-saving film for LCD display to replace the current tint films; UV dosimeter and UV-index indicator; sunlight readable displays; security badges and displays; new types of light detectors, optical switches; low-cost memory device for optical computers and memory-device applications; eyewear; labels; energy efficient window films such as building and automotive windows; etc. In such embodiments, the photochromic pressure sensitive adhesive composition of the present invention may be employed as a thin film bonded to a light transmissive layer together with a backing material or another light transmissive layer.

The invention is described in connection with the following examples, which are provided solely for purposes of illustration and are not intended to limit the invention.

Example

Six photochromic pressure sensitive adhesive compositions are provided and coated on 3-mil Melinex® 453 polyester film and dried at 150°F to produce

pressure sensitive adhesive compositions. The photochromic compound is admixed with the pressure sensitive adhesive composition by dissolving the photochromic dye and Irganox 1010 in toluene and blending with an acrylic adhesive (Gelva 788) to yield the compositions set forth in Table 1 below:

Table 1

Sample No.	1	2	3	4	5	6
Photochromic dye	A	B	C	D	E	F
Dye amount (g)	0.42	0.44	0.42	0.44	0.39	0.42
Adhesive (g)	43.4	46.6	40.7	47.1	39.9	65.0
Irganox 1010 (g)	0.19	0.15	0.14	0.15	0.13	0.14
Toluene (g)	7.4	8.8	7.7	8.1	8.0	7.5

Note: The photochromic dyes A-F employed in Samples 1-6 are (A) Photosol 5-3, (B) Photosol 02-65, (C) Photosol 7-106, (D) Photosol 336-72, (E) Photosol 5-83, (F) Photosol 7-49 (each from PPG).

The pressure sensitive films prepared above were tested for photochromic response under sunlight exposure outdoors. The compositions were found to undergo acceptable darkening and fading under different periods of exposure.

The photochromic pressure sensitive adhesive is easily produced through solution coating. The adhesive composition is prepared by mixing the photochromic dye, adhesive and additives such as antioxidant in a solvent or a mixture of solvents, which include but are not limited to ethyl acetate, toluene, vinyl acetate and methyl ethyl ketone. The adhesive solution is subsequently coated on an optically clear backing film 1 followed by drying the solvent and laminating with a release liner 3 with the photochromic pressure sensitive

adhesive layer 5 sandwiched therebetween. The construction of the pressure sensitive adhesive tape is illustrated in Figure 1.

The pressure sensitive adhesives used in the present invention include but are not limited to solvent-based, hot-melt, emulsion and liquid adhesive systems (which can be cured at a second stage).

The backing film used in the construction shown in Figure 1 is preferably a plastic film with the following optical properties: Light Transmission not smaller than 75% at and above 330 nm and Haze not greater than 0.5% (ASTM D1003). A variety of films may be employed including but not limited to polyethylene terephthalate, polyvinyl chloride, polyethylene, polypropylene, and cellulose acetate. For applications where the substrate itself is optically clear and can be exposed to UV radiation (such as glass plates, etc.), alternative backing materials may be used such as metal, foam, paper and pigmented plastics. The adhesive provides high tack, high adhesion and good strippability on a wide range of substrate materials such as glass, plastics and metal.

Another alternative construction design is to use two release liners to produce transfer photochromic adhesive film. Such transfer films can be used to bond two substrate materials, at least one of which is optically clear to permit U.V. radiation to pass through the film.

Multiple layer constructions (Figure 2) may be used to produce photochromic pressure sensitive adhesive tapes disclosed in the present invention. This construction design is particularly suitable to applications

where a photochromic effect is desired for thick adhesive tapes. Despite that UV radiation does not afford deep penetration, the first thin layer of pressure sensitive adhesive 5 produces the maximum photochromic performance, while the second layer of pressure sensitive adhesive 7 can be tailor-made to produce good bonding and conformability to various substrate materials. A carrier layer 9 is placed therebetween. When a release liner 3 is used in the replacement of the backing film 1, this multiple layer construction is also particularly useful for bonding two substrate materials, which are very different in nature and chemistry and at least one is optically clear.

WHAT IS CLAIMED IS:

1. A photochromic pressure sensitive adhesive composition comprised of a pressure sensitive adhesive in combination with a photochromic compound, said photochromic compound being present in said adhesive in an amount sufficient to effect a color change in said adhesive in the presence of a suitable radiation source, and said adhesive not being a styrene-based rubber adhesive.

2. The composition of claim 1 wherein said photochromic compound is present in said composition in an amount in the range of from about 0.05 to about 10 % by weight, based on the total weight of the composition.

3. The composition of claim 1 wherein said pressure sensitive adhesive is present in said composition in an amount within the range of about 90 to about 99.5% by weight, based on the total weight of the composition.

4. The composition of claim 1 further comprising a component selected from the group consisting of an antioxidant, UV stabilizer, free radical scavenger, color neutralizing agent, or mixtures thereof.

5. The composition of claim 1 in the form of a film.

6. The composition of claim 5 further comprising a backing film.

7. The composition of claim 1 wherein the pressure sensitive adhesive is selected from the group consisting of polyvinyl ethers, acrylic adhesives, poly-alpha-olefins, silicone adhesives, and mixtures thereof.

8. A laminate having photochromic properties comprised of a layer of a pressure sensitive adhesive in combination with a photochromic compound, said photochromic compound being present in said adhesive in an amount sufficient to effect a color change in said adhesive in the presence of a suitable radiation source, and an optically clear backing layer, and said adhesive not being a styrene-based rubber adhesive.

9. The laminate of claim 8 wherein said backing layer exhibits light transmission not smaller than 75% at and above 330 nm and haze not greater than 0.5% according to ASTM D1003.

10. The laminate of claim 8 wherein said backing layer is comprised of glass or plastic.

11. The laminate of claim 8 wherein said pressure sensitive adhesive layer is placed between two optically clear backing layers.

12. The laminate of claim 8 wherein a second non-optically clear backing layer is employed.

13. The laminate of claim 8 in combination with an LCD display as a display screen.

14. The laminate of claim 11 in the form of a window.

15. The laminate of claim 8 in combination with eye goggles or glasses.

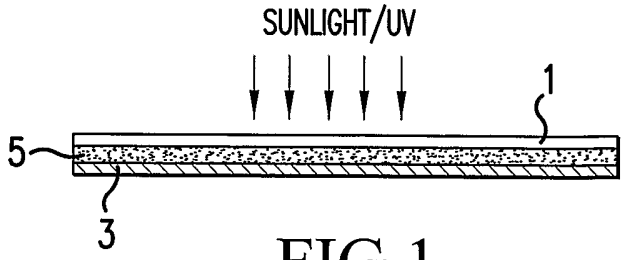

FIG.1

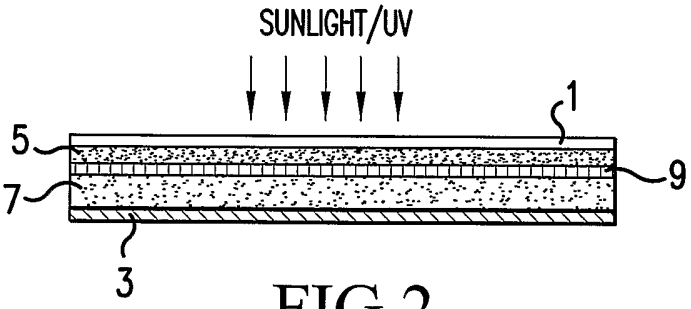

FIG.2

INTERNATIONAL SEARCH REPORT

International application No.
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A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : C08F 16/12, 10/02, 122/14
US CL : 524/560, 570, 588; 523/171, 168

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
U.S. : 524/560, 570, 588; 523/171, 168

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EAST and WEST

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 10330708 A (KK KIROKU SOZAI SOGO KENKYUSHO), 15 December 1998 (15.12.1998), whole document.	1, 2, 3, 7
Y	JP 09227845 A (SONY CHEM CORP.) 02 September 1997 (02.09.1997), whole document.	1-7
Y/P	US 6,461,722 B1 (KITTEL et al) 08 October 2002 (8.10.2002), columns 8, 10, 11.	1-7
A	US 6,319,433 B1 (KOHAN) 20 November 2001 (20.11.2001), whole document.	8-15
A	US 5,914,174 (GUPTA et al) 22 June 1999 (22.06.1999), whole document.	8-15

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:

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