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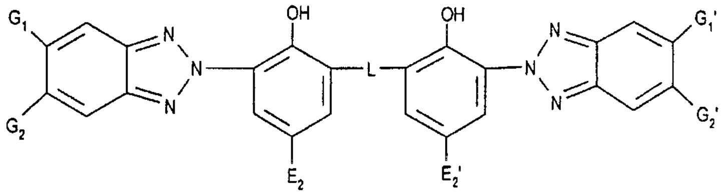
(54) Title: STABILIZED ADHESIVE COMPOSITIONS CONTAINING HIGHLY SOLUBLE, RED-SHIFTED, PHOTOSTABLE BENZOTRIAZOLE UV ABSORBERS AND LAMINATED ARTICLES DERIVED THEREFROM



(IIIc)

(57) Abstract

Adhesive compositions are rendered stable against degradation caused by ultraviolet light through the incorporation of selected highly soluble, red-shifted, photostable benzotriazole UV absorbers which absorb light strongly in the 350 to 400 nm range. Also suitable are 2-(2-hydroxy-3-α-cumyl-5-tert-octylphenyl)-2H-benzotriazole and 2-(2-hydroxy-3-α-cumyl-5-tert-butylphenyl)-2H-benzotriazole in combination with the red shifted benzotriazoles. A further subject of the invention are novel asymmetrical bisbenzotriazoles of formula (IIIc) where G_2' is perfluoroalkyl of 1 to 12 carbon atoms, preferably CF_3, and where G_2 does not contain said group are red-shifted and due to the asymmetry are particularly soluble and useful in a host of applications including automotive coatings, thermoplastics and especially in adhesive compositions, themselves useful in solar panels and other laminate structures. All these UV absorbers exhibit excellent photostability and are highly soluble in adhesive formulations. The laminated articles derived from these compositions include, for example, solar control films, films and glazings, UV absorbing glasses and glass coatings, windscreens, retroreflective sheetings and signs, solar reflectors, optical films and the like.

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STABILIZED ADHESIVE COMPOSITIONS CONTAINING HIGHLY SOLUBLE, RED-SHIFTED, PHOTOSTABLE BENZOTRIAZOLE UV ABSORBERS AND LAMINATED ARTICLES DERIVED THEREFROM

This invention pertains to stabilized adhesive compositions containing an effective amount of a benzotriazole UV absorber having enhanced solubility, durability and absorption in the 350 to 400 nm range. Also subject of the invention are stabilized adhesive compositions containing an effective amount of a benzotriazole substituted in the ortho position of the hydroxyphenyl ring by α-cumyl or phenyl, such as 2-(2-hydroxy-3-α-cumyl-5-tert-octylphenyl)-2H-benzotriazole having enhanced solubility and durability. A further subject of the invention pertains to novel asymmetrical bisbenzotriazole compounds which are red-shifted, and are particularly soluble due to that asymmetry and which are useful in a host of end-use applications.

Background of the Invention

Adhesives are made up of various components such as polymers, tackifiers, waxes and oils. Adhesive formulations based on these ingredients are susceptible to degradation. The consequences of degradation are discoloration, loss of elongation, loss of tensile strength, loss of tack and change in viscosity, molecular weight and molecular weight distribution. Degradation can be caused by prolonged exposure to sunlight. Sunlight contains invisible ultraviolet (UV) radiation with wavelengths between 290 and 400 nm. This radiation is responsible for the initiation of photodegradation.

Absorption of UV light by chromophores present in the adhesive formulation transforms the chromophores into their excited states which can undergo further undesired reactions. Some polymers contain strongly absorbing chromophores as a major part of their structures. Other polymers contain unintentional impurities such as ketones and hydroperoxide moieties and catalyst residues which act as chromophores. Absorption of UV radiation by these chromophores eventually results in bond cleavage, chain scission and/or crosslinking reactions.

Photostabilization of adhesives can be achieved by the addition of UV absorbers which convert the absorbed energy into harmless heat. An ideal UV absorber should be extremely photostable and have strong absorption over the UV range from 290 to 400 nm, but particularly the range of 350 to 400 nm. Classes of UV absorbers include the salicylates, cyanoacrylates, malonates, oxanilides, benzophenones, s-triazines and benzotriazoles.

Salicylates, cyanoacrylates, malonates and oxanilides absorb UV light primarily at the lower wavelengths of the UV range. These compounds have little to no absorption in the range of 350 to 400 nm which make them unsuitable for the instant applications. Benzophenones absorb over the lower half of the UV range, and they tend to be prone to yellowing upon light exposure due to photodegradation. Recently, it has been shown photochemically that benzophenones decompose prematurely in ethylene-vinyl acetate encapsulants which lead to the production of polyenic chromophores. This color generation from light yellow to brown is not only highly undesirable and unsightly in adhesive systems, but also can result in a loss of adhesive properties. By contrast, selected benzotriazole UV absorbers are particularly useful because of their increased photostability.

Some polymers such as polycarbonates, polyesters and aromatic polyurethanes contain strongly absorbing chromophores as a major and integral part of their structures. Poly(ethylene terephthalate) (PET) and poly(ethylene 2,6-naphthalenedicarboxylate) (PEN) are particular examples the latter of which absorbs into the red UV region and especially need red-shifted benzotriazoles for UV protection. U.S. Patent No. 5,294,473 and WO 98/34981 teach the use of coatings containing UV absorbers including some benzotriazoles in stabilizing PEN films. Adding an adhesive UV screening layer containing the benzotriazoles, especially those described in the instant invention, further protects such polymers in multilayered constructions and articles.

The description, preparation and uses of the 2H-benzotriazole UV absorbers are described in United States Patent Nos. 3,004,896; 3,055,896; 3,072,585; 3,074,910; 3,189,615; 3,230,194; 4,127,586; 4,226,763; 4,278,589; 4,315,848; 4,383,863; 4,675,352; 4,681,905 and 4,853,471.

Selected benzotriazoles with just hydrogen or halogen at the 5-position of the benzo ring are photostable and soluble in adhesive formulations. One such benzotriazole is 2-(2-hydroxy-3-α–cumyl-5-tert-octylphenyl)-2H-benzotriazole as described in United States Patent Nos. 5,554,760; 5,563,242; 5,574,166 and 5,607,987. These patents are incorporated herein by reference. While the absorbance of this benzotriazole is not red-shifted toward longer UV wavelengths, it is very photostable and is amazingly soluble in adhesives making it especially well-suited for the instant applications.

Although benzotriazoles with just hydrogen at the 5-position of the benzo ring are photostable and useful in adhesive formulations, they lack a red-shifted absorbance toward longer UV wavelengths which would be most useful in giving added protection to the substrates. United States Patent Nos. 5,319,091 and 5,410,071 described the preparation of benzotriazoles substituted at the 5-position of the benzo ring with alkyl- or aryl-sulfonyl moieties. It is taught in United States Patent No. 5,280,124 that by introducing a higher alkyl or aryl sulfoxide or sulfone at the 5-position of the benzo ring of the benzotriazole, the resulting benzotriazole exhibits enhanced absorption in the near visible range (over 350 nm). Such sulfone substituted products were shown to be useful in automotive coatings applications. Additionally such an electron withdrawing group dramatically increases the photostability of these benzotriazole UV absorbers in automotive coatings. Quite surprisingly, these red-shifted benzotriazoles and particularly the asymetric substituted ones are amazingly soluble in adhesives making them especially well-suited for the instant applications.

It is known in the art that the concomitant use of a hindered amine light stabilizer with a UV absorber such as a benzotriazole provides excellent stabilization in many polymer compositions as summarized by G. Berner and M. Rembold, "New Light Stabilizers for High Solids Coatings", Organic Coatings and Science and Technology, Vol. 6, Dekkar, New York, pp 55-85.

The benzotriazole UV absorbers represent a special class of commercial UV absorbers as described above. Only a few references refer to substitution on the benzo ring by an aryl or alkyl sulfoxide or sulfonyl moiety.

United States Patent No. 3,218,332 discloses benzotriazoles substituted at the 5-position of the benzo ring by a lower alkyl sulfonyl moiety. However, this patent deals with putting reactable groups, namely alkenyl groups, at the 3-position on the phenyl ring and is of little relevance to the instant application. United States Patent Nos. 5,268,450 and 5,319,091 disclose polymer compositions and a process for the production of substituted aryl thio and aryl sulfonyl benzotriazoles which are covalently bound to polymers, such as poly(phenylene sulfide), RYTON®, Phillips Petroleum. United States Patent No. 5,280,124 discloses benzotriazoles with only higher alkyl or aryl sulfinyl or sulfonyl moieties at the 5-position of the benzo ring which are useful for protecting thermoset automotive coatings.

Japanese Patent No. 92-352228 discloses the use of 5-ethylsulfonyl benzotriazoles with the 3-position of the phenyl ring being unsubstituted or substituted by methyl for the UV protection of dust proof poly(vinyl chloride) resin films. These compounds when studied in the instant adhesive compositions were found to be quite insoluble and totally useless for the instant adhesive compositions. By contrast, when a tertiary alkyl group is inserted at the 3-position of the phenyl ring, the solubility of the thus substituted benzotriazole in adhesive composition is surprisingly enhanced.

The instant in 5 position substituted compounds exhibit enhanced broadened absorption characteristics particularly in the long wavelength UV region (over 350 nm) when compared with compounds of the prior art. Additionally, the instant compounds have surprising and unexpectedly high solubility in adhesives making them especially well suited for use in adhesive formulations.

Bisbenzotriazoles such as 2,2'-methylene-bis[4-tert-octyl-6-(2H-benzotriazolyl-2-yl)phenol], TINUVIN® 360 (Ciba) are described in United States Patent No. 5,299,521. While useful, these compounds are not red-shifted.

German 1,670,951 describes generically both symmetrical and asymmetrical alkylene-bisbenzotriazoles, but specifically only some symmetical bisbenzotriazoles which are outside of the scope of the instant claims. None of the compounds described in German 1,670,951 are substituted by a perfluroalkyl moiety, such as by CF_3.

United States Patent No. 4,812,498 describes symmetrical bisbenzotriazoles as stabilizers for polycarbonate resins. The bisbenzotriazoles are symmetrical in structure, do not contain perfluoroalkyl moieties, and are clearly outside the scope of the instant compounds.

EP 924,203 A1 describes bisbenzotriazole compounds each containing a polymerizable moiety and polymers made therefrom. None of these prior art bisbenzotriazoles is red-shifted or contains a perfluoroalkyl group. The instant compounds are clearly distinguished from these prior bisbenzotriazoles.

The effect of UV light on laminated articles that are exposed to the sun or other sources of UV light are of great concern to the manufacturers of such articles. Over time, constant or repeated exposure to UV light can result in dye and/or pigment fade for dyes and/or pigments used in such articles and in the degradation or breakdown of the adhesives, polymers or other materials used in the construction of the articles. The aforementioned fading and degradation shorten the useful life of the articles in question, making protection from UV light exposure an issue of great importance to the manufacturers of such articles.

Molecules known as UV absorbers are generally known in the art. However, due to the differences discussed above between the various UV absorber classes, it is the benzotriazoles and articles containing them which will be discussed here. Due to the incompatibility and low solubility of certain benzotriazoles, a need exists for selected benzotriazoles that are highly soluble and which would provide added protection in the 350 to 400 nm region of the ultraviolet. T. Nagashima et al., J. Non-Cryst. Solids, 178 (1994), 182, report recently ultraviolet light (UV) shielding glass, which is UV absorbing over the range of long wavelengths (320-400 nm) to avoid sunburn effects, has become an important issue because of the possible hazard of skin cancer due to depletion of the ozone layer."

In addition, articles which incorporate the selected benzotriazoles of the instant invention are useful in protecting interior structures, textiles and fabrics from UV induced photodegradation such as in automotive applications.

International application WO 97/32225 describes the use of PEN films having reflective and polarizing elements for use as optical films.

United States Patent No. 5,770,114 discloses stabilized compositions containing soluble benzotriazoles that are used in electrochromic devices. However, these benzotriazoles lack the red-shifted absorption at the 350 to 400 nm region.

Articles which would benefit from the incorporation of the instant, highly soluble, photostable and red-shifted benzotriazoles include, but are not limited to:

(a) Retroreflective Sheets and Signs and Conformable Marking Sheets as seen in WO 97/42261; and United States Patent No. 5,387,458 which is incorporated herein by reference;

(b) Solar Control Films of Various Construction as seen in British 2,012,668; European 355,962; and United States Patent Nos. 3,290,203; 3,681,179; 3,776,805 and 4,095,013 which are incorporated herein by reference;

(c) Corrosion Resistant Silver Mirrors and Solar Reflectors as seen in United States Patent No. 4,645,714 which is incorporated herein by reference;

(d) Reflective Print Labels as seen in United States Patent No. 5,564,843 which is incorporated herein by reference;

(e) UV Absorbing Glasses and Glass Coatings as seen in United States Patent Nos. 5,372,889; 5,426,204; 5,683,804 and 5,618,626 which are incorporated herein by reference;

(f) Electrochromic Devices as seen in European 752,612 A1; and United States Patent Nos. 5,239,406; 5,523,877 and 5,770,114 which are incorporated herein by reference;

(g) Films/Glazings as seen in WO 92/01557; Japanese Nos. 75-33286; 93-143668; 95-3217 and 96-143831; and United States Patent No. 5,643,676 which is incorporated herein by reference;

(h) Windscreens and Intermediate Layers as seen in Japanese Nos. 80-40018; 90-192118; 90-335037; 90-335038; 92-110128 and 94-127591; and United States Patent No. 5,618,863 which is incorporated herein by reference; and

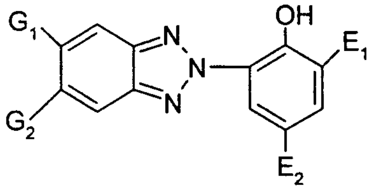
(i) Optical Films as seen in WO 97/32225; and United States Patent Nos. 4,871,784 and 5,217,794 which are incorporated herein by reference.

Detailed Disclosure

One subject of the present invention is a stabilized adhesive composition, suitable for use as an adhesive layer in a laminated article or multilayer construction, which comprises

(a) an adhesive; and

(b1) a highly soluble, red-shifted, photostable benzotriazole of formula I, II or III



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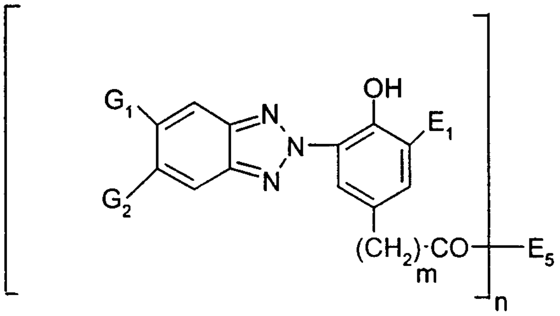

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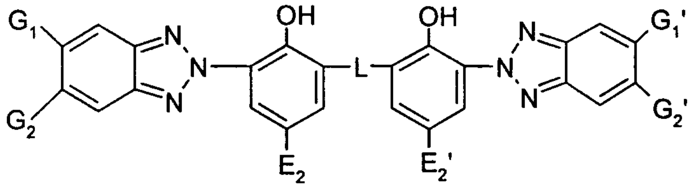


(III) or

(b2) a highly soluble and photostable benzotriazole which is 2-(2-hydroxy-3-α-cumyl-5-tert-octylphenyl)-2H-benzotriazole or 2-(2-hydroxy-3-α-cumyl-5-tert-butylphenyl)-2H-benzotriazole; or

a combination of the compounds of (b1) and (b2);
wherein

G_1 and G_1' are independently hydrogen or halogen,

G_2 and G_2' are independently halogen, nitro, cyano, perfluoroalkyl of 1 to 12 carbon atoms, $-COOG_3$, $-P(O)(C_6H_5)_2$, $-CO-G_3$, $-CO-NH-G_3$, $-CO-N(G_3)_2$, $-N(G_3)-CO-G_3$, E_3SO- or E_3SO_2-; or G_2' is also hydrogen,

G_3 is hydrogen, straight or branched chain alkyl of 1 to 24 carbon atoms, straight or branched chain alkenyl of 2 to 18 carbon atoms, cycloalkyl of 5 to 12 carbon atoms, phenylalkyl of 7 to 15 carbon atoms, phenyl, or said phenyl or said phenylalkyl substituted on the phenyl ring by 1 to 4 alkyl of 1 to 4 carbon atoms,

G_6 is perfluoroalkyl of 1 to 12 carbon atoms,

G_7 is hydrogen or perfluoroalkyl of 1 to 12 carbon atoms,

E_1 is hydrogen, straight or branched chain alkyl of 1 to 24 carbon atoms, straight or branched chain alkenyl of 2 to 24 carbon atoms, cycloalkyl of 5 to 12 carbon atoms, phenylalkyl of 7 to 15 carbon atoms, phenyl, or said phenyl or said phenylalkyl substituted on the phenyl ring by 1 to 4 alkyl of 1 to 4 carbon atoms; or E_1 is alkyl of 1 to 24 carbon atoms substituted by one or two hydroxy groups,

E_2 and E_2' are independently straight or branched alkyl chain of 1 to 24 carbon atoms, straight or branched chain alkenyl of 2 to 18 carbon atoms, cycloalkyl of 5 to 12 carbon atoms, phenylalkyl of 7 to 15 carbon atoms, phenyl, or said phenyl or said phenylalkyl substituted on the phenyl ring by one to three alkyl of 1 to 4 carbon atoms; or E_2 and E_2' are independently said alkyl of 1 to 24 carbon atoms or said alkenyl of 2 to 18 carbon atoms substituted by one or more -OH, $-OCOE_{11}$, $-OE_4$, -NCO, $-NH_2$, $-NHCOE_{11}$, $-NHE_4$ or $-N(E_4)_2$, or mixtures thereof, where E_4 is straight or branched chain alkyl of 1 to 24 carbon atoms; or said alkyl or said alkenyl interrupted by one or more -O-, -NH- or $-NE_4-$ groups or mixtures thereof and which can be unsubstituted or substituted by one or more -OH, $-OE_4$ or $-NH_2$ groups or mixtures thereof;

n is 1 or 2,

when n is 1, E_5 is OE_6 or NE_7E_8, or

E_5 is $-PO(OE_{12})_2$, $-OSi(E_{11})_3$ or $-OCO-E_{11}$,

or straight or branched chain C_1-C_{24}alkyl which is interrupted by -O-, -S- or $-NE_{11}$ and which can be unsubstituted or substituted by -OH or $-OCO-E_{11}$, C_5-C_{12} cycloalkyl which is unsubstituted or substituted by -OH, straight chain or branched C_2-C_{18}alkenyl which is unsubstituted or substituted by -OH, C_7-C_{15}aralkyl, $-CH_2-CHOH-E_{13}$ or glycidyl,

E_6 is hydrogen, straight or branched chain C_1-C_{24}alkyl which is unsubstituted or substituted by one or more OH, OE_4 or NH_2 groups, or $-OE_6$ is $-(OCH_2CH_2)_wOH$ or $-(OCH_2CH_2)_wOE_{21}$where w is 1 to 12 and E_{21} is alkyl of 1 to 12 carbon atoms,

E_7 and E_8 are independently hydrogen, alkyl of 1 to 18 carbon atoms, straight or branched chain C_3-C_{18}alkyl which is interrupted by -O-, -S- or $-NE_{11}-$, C_5-C_{12}cycloalkyl, C_6-C_{14}aryl or C_1-C_3hydroxylalkyl, or E_7 and E_8 together with the N atom are a pyrrolidine, piperidine, piperazine or morpholine ring,

E_5 is $-X-(Z)_p-Y-E_{15}$

wherein

X is -O- or $-N(E_{16})-$,

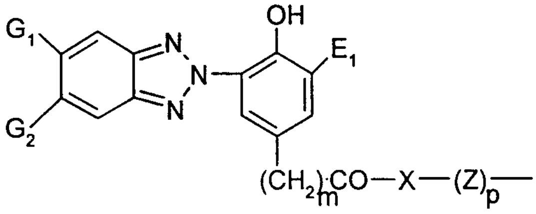
Y is -O- or $-N(E_{17})-$,

Z is C_2-C_{12}-alkylene, C_4-C_{12}-alkylene interrupted by one to three nitrogen atoms, oxygen atoms or a mixture thereof, or is C_3-C_{12}-alkylene, butenylene, butynylene, cyclohexylene or phenylene, each substituted by a hydroxyl group,

m is zero, 1 or 2,

p is 1, or p is also zero when X and Y are $-N(E_{16})-$ and $-N(E_{17})-$, respectively,

E_{15} is a group $-CO-C(E_{18})=C(H)E_{19}$ or, when Y is $-N(E_{17})-$, forms together with E_{17} a group -CO-CH=CH-CO-, wherein E_{18} is hydrogen or methyl, and E_{19} is hydrogen, methyl or $-CO-X-E_{20}$, wherein E_{20} is hydrogen, C_1-C_{12}-alkyl or a group of the formula

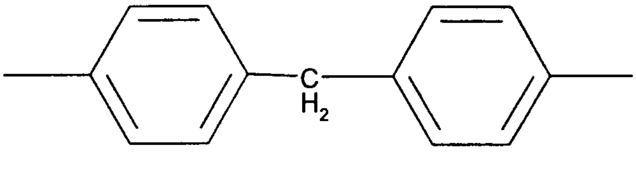


wherein the symbols E_1, G_2, X, Z, m and p have the meanings defined above, and E_{16} and E_{17} independently of one another are hydrogen, C_1-C_{12}-alkyl, C_3-C_{12}-alkyl interrupted by 1 to 3 oxygen atoms, or is cyclohexyl or C_7-C_{15}aralkyl, and E_{16} together with E_{17} in the case where Z is ethylene, also forms ethylene,

when n is 2, E_5 is one of divalent radicals -O-E_9-O- or -N(E_{11})-E_{10}-N(E_{11})- ,

E_9 is C_2-C_8alkylene, C_4-C_8alkenylene, C_4alkynylene, cyclohexylene, straight or branched chain C_4-C_{10}alkylene which is interrupted by -O- or by -CH_2-CHOH-CH_2-O-E_{14}-O-CH_2-CHOH-CH_2-,

E_{10} being straight or branched chain C_2-C_{12}alkylene which may be interrupted by -O-, cyclohexylene, or



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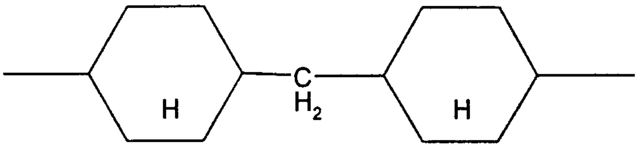
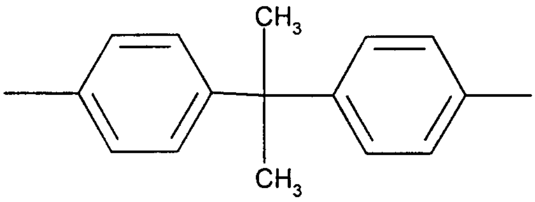


or E_{10} and $E_{11}$with the two nitrogen atoms form a piperazine ring,

E_{14} is straight or branched chain C_2-C_8alkylene, straight or branched chain C_4-C_{10}alkylene which is interrupted by -O-, cycloalkylene, arylene or



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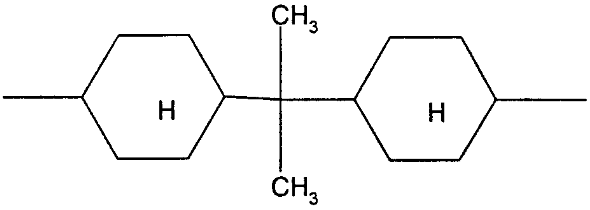


where E_7 and E_8 are independently hydrogen, alkyl of 1 to 18 carbon atoms or E_7 and E_8 together are alkylene of 4 to 6 carbon atoms, 3-oxapentamethylene, 3-iminopentamethylene or 3-methyliminopentamethylene,

E_{11} is hydrogen, straight or branched chain C_1-C_{18}alkyl, C_5-C_{12}cycloalkyl, straight or branched chain C_2-C_{18}alkenyl, C_6-C_{14}aryl or C_7-C_{15}aralkyl,

E_{12} is straight or branched chain C_1-C_{18}alkyl, straight or branched chain C_3-C_{18}alkenyl, C_5-C_{10}cycloalkyl, C_6-C_{16}aryl or C_7-C_{15}aralkyl,

E_{13} is H, straight chain or branched C_1-C_{18}alkyl which is substituted by $-PO(OE_{12})_2$, phenyl which is unsubstituted or substituted by OH, C_7-C_{15}aralkyl or $-CH_2OE_{12}$,

E_3 is alkyl of 1 to 20 carbon atoms, hydroxyalkyl of 2 to 20 carbon atoms, alkyl substituted by alkoxycarbonyl of 2 to 9 carbon atoms, alkenyl of 3 to 18 carbon atoms, cycloalkyl of 5 to 12 carbon atoms, phenylalkyl of 7 to 15 carbon atoms, aryl of 6 to 10 carbon atoms or said aryl substituted by one or two alkyl of 1 to 4 carbon atoms or 1,1,2,2-tetrahydroperfluoroalkyl where the perfluoroalkyl moiety is of 6 to 16 carbon atoms, and

L is alkylene of 1 to 12 carbon atoms, alkylidene of 2 to 12 carbon atoms, benzylidene, p-xylylene, a,a,a',a'-tetramethyl-m-xylylene or cycloalkylidene.

C_1-C_{18}alkyl can be linear or branched. Examples are methyl, ethyl, propyl, isopropyl, butyl, 2-butyl, isobutyl, t-butyl, pentyl, 2-pentyl, hexyl, heptyl, octyl, 2-ethylhexyl, t-octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, hexadecyl and octadecyl.

Examples of alkoxy are methoxy, ethoxy, propoxy, isopropoxy, butoxy, isobutoxy, pentoxy, isopentoxy, hexoxy, heptoxy or octoxy.

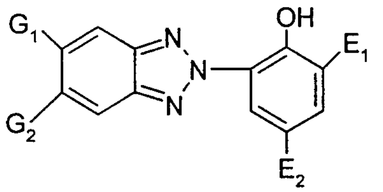
C_2-C_{18}alkenyl is for example ethenyl, propenyl or butenyl, dodecenyl or octoxenyl.

Cycloalkyl having 5 to 12 carbon atoms is for example cyclopentyl, cyclohexyl and cyclooctyl

Phenylalkyl is for example benzyl.

Preferably the benzotriazole (b1) of formula I, II or III and the benzotriazoles (b2) exhibit enhanced durability and low loss of absorbance when exposed to actinic radiation as witnessed by an absorbance loss of less than 0.5 absorbance units after exposure for 893 hours or less than 0.8 absorbance units after exposure for 1338 hours in a Xenon Arc Weather-Ometer.

Preferred is a composition wherein the benzotriazole compound of formula I is



(I)

wherein

G_1 is hydrogen,

G_2 is cyano, chloro, fluoro, CF_3-, -CO-G_3, E_3SO- or E_3SO_2-,

G_3 is straight or branched chain alkyl of 1 to 24 carbon atoms, straight or branched chain alkenyl of 2 to 18 carbon atoms, cycloalkyl of 5 to 12 carbon atoms, phenylalkyl of 7 to 15 carbon atoms, phenyl, or said phenyl or said phenylalkyl substituted on the phenyl ring by 1 to 4 alkyl of 1 to 4 carbon atoms,

E_1 is phenylalkyl of 7 to 15 carbon atoms, phenyl, or said phenyl or said phenylalkyl substituted on the phenyl ring by 1 to 4 alkyl of 1 to 4 carbon atoms,

E_2 is straight or branched alkyl chain of 1 to 24 carbon atoms, straight or branched chain alkenyl of 2 to 18 carbon atoms, cycloalkyl of 5 to 12 carbon atoms, phenylalkyl of 7 to 15 carbon atoms, phenyl, or said phenyl or said phenylalkyl substituted on the phenyl ring by 1 to 3 alkyl of 1 to 4 carbon atoms; or E_2 is said alkyl of 1 to 24 carbon atoms or said alkenyl of 2 to 18 carbon atoms substituted by one or more -OH, $-OCOE_{11}$, $-OE_4$, -NCO, $-NH_2$, $-NHCOE_{11}$, $-NHE_4$ or $-N(E_4)_2$, or mixtures thereof, where E_4 is straight or branched chain alkyl of 1 to 24 carbon atoms; or said alkyl or said alkenyl interrupted by one or more -O-, -NH- or $-NE_4-$ groups or mixtures thereof and which can be unsubstituted or substituted by one or more -OH, $-OE_4$ or $-NH_2$ groups or mixtures thereof;

E_3 is alkyl of 1 to 20 carbon atoms, hydroxyalkyl of 2 to 20 carbon atoms, alkenyl of 3 to 18 carbon atoms, cycloalkyl of 5 to 12 carbon atoms, phenylalkyl of 7 to 15 carbon atoms, aryl of 6 to 10 carbon atoms or said aryl substituted by one or two alkyl of 1 to 4 carbon atoms or 1,1,2,2-tetrahydroperfluoroalkyl where the perfluoroalkyl moiety is of 6 to 16 carbon atoms; or

is a compound of formula I wherein,

G_1 is hydrogen,

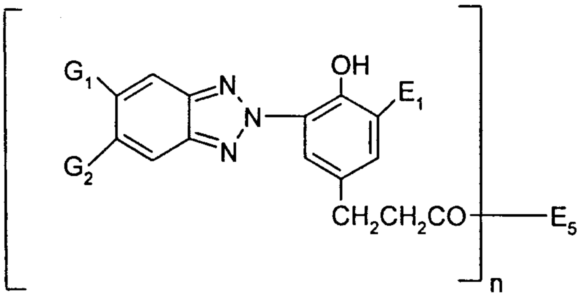
G_2 is chloro, fluoro, CF_3-, E_3SO- or E_3SO_2-,

E_1 is hydrogen or straight or branched alkyl of 1 to 24 carbon atoms,

E_2 is as defined above, and

E_3 is straight or branched chain alkyl of 1 to 7 carbon atoms.

Also preferred is a composition wherein the benzotriazole compound is a compound of formula IIA



(IIA)

wherein

G_1 is hydrogen,

G_2 is is CF_3- or fluoro,

E_1 is hydrogen, straight or branched alkyl of 1 to 24 carbon atoms or phenylalkyl of 7 to 15 carbon atoms,

E_5 is -OE_6 or -NE_7E_8, or

E_5 is -X-$(Z)_p$-Y-E_{15}

wherein

X is -O- or -N(E_{16})-,

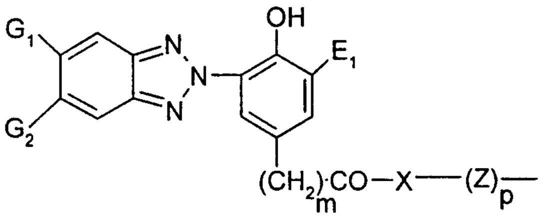
Y is -O- or -N(E_{17})-,

Z is C_2-C_{12}-alkylene, C_4-C_{12}-alkylene interrupted by one to three nitrogen atoms, oxygen atoms or a mixture thereof, or is C_3-C_{12}-alkylene, butenylene, butynylene, cyclohexylene or phenylene, each substituted by a hydroxyl group,

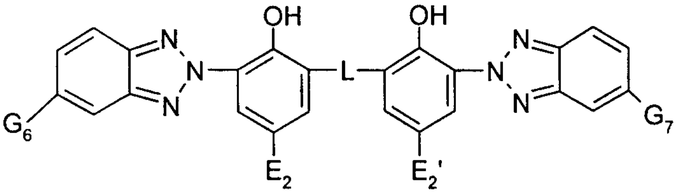
m is 0, 1, 2 or 3,

p is 1, or p is also zero when X and Y are -N(E_{16})- and -N(E_{17})-, respectively,

E_{15} is a group -CO-C(E_{18})=C(H)E_{19} or, when Y is -N(E_{17})-, forms together with E_{17} a group -CO-CH=CH-CO-, wherein E_{18} is hydrogen or methyl, and E_{19} is hydrogen, methyl or -CO-X-E_{20}, wherein E_{20} is hydrogen, C_1-C_{12}-alkyl or a group of the formula.



A further preferred composition is wherein the benzotriazole is a compound of formula IIIA



(IIIA)

wherein

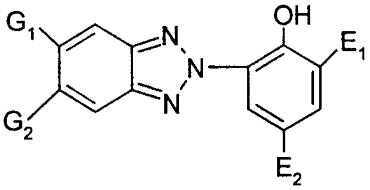
G_6 is CF_3,

G_7 is hydrogen or CF_3,

E_2 and E_2' are independently straight or branched alkyl chain of 1 to 24 carbon atoms, straight or branched chain alkenyl of 2 to 18 carbon atoms, cycloalkyl of 5 to 12 carbon atoms, phenylalkyl of 7 to 15 carbon atoms, phenyl, or said phenyl or said phenylalkyl substituted on the phenyl ring by 1 to 3 alkyl of 1 to 4 carbon atoms; and

L is alkylene of 1 to 12 carbon atoms, alkylidene of 2 to 12 carbon atoms, benzylidene, p-xylylene, a,a,a',a'-tetramethyl-m-xylylene or cycloalkylidene.

More prefered is a composition wherein the benzotriazole is a compound of formula I



(I)

wherein

G_1 is hydrogen,

G_2 is CF_3-,

E_1 is phenylalkyl of 7 to 15 carbon atoms, phenyl, or said phenyl or said phenylalkyl substituted on the phenyl ring by 1 to 4 alkyl of 1 to 4 carbon atoms,

E_2 is straight or branched alkyl chain of 1 to 24 carbon atoms, straight or branched chain alkenyl of 2 to 18 carbon atoms, cycloalkyl of 5 to 12 carbon atoms, phenylalkyl of 7 to 15 carbon atoms, phenyl, or said phenyl or said phenylalkyl substituted on the phenyl ring by

1 to 3 alkyl of 1 to 4 carbon atoms; or E_2 is said alkyl of 1 to 24 carbon atoms or said alkenyl of 2 to 18 carbon atoms substituted by one or more -OH, -OCOE_{11}, -NH_2 or -NHCOE_{11}, or mixtures thereof, or said alkyl or said alkenyl interrupted by one or more -O- and which can be unsubstituted or substituted by one or more -OH; or

is a compound of formula I
wherein,

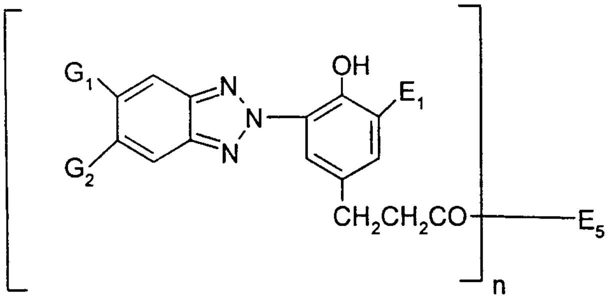
G_1 is hydrogen,

G_2 is CF_3-,

E_1 is hydrogen, straight or branched alkyl of 1 to 24 carbon atoms or phenylalkyl of 7 to 15 carbon atoms, and

E_2 is as defined above.

Also more preferred is a composition wherein the benzotriazole is a compound of formula IIA



(IIA)

wherein

G_1 is hydrogen,

G_2 is CF_3-,

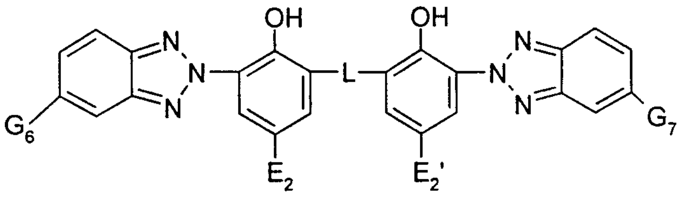
E_1 is hydrogen, straight or branched alkyl of 1 to 24 carbon atoms or phenylalkyl of 7 to 15 carbon atoms,

E_5 is -OE_6 or -NE_7E_8 where

E_6 is hydrogen, straight or branched chain C_1-C_{24}alkyl which is unsubstituted or substituted by one or more OH groups, or $-OE_6$ is $-(OCH_2CH_2)_wOH$ or $-(OCH_2CH_2)_wOE_{21}$where w is 1 to 12 and E_{21} is alkyl of 1 to 12 carbon atoms, and

E_7 and E_8 are independently hydrogen, alkyl of 1 to 18 carbon atoms, straight or branched chain C_3-C_{18}alkyl which is interrupted by -O-, -S- or $-NE_{11}-$, C_5-C_{12}cycloalkyl, C_6-C_{14}aryl or C_1-C_3hydroxylalkyl, or E_7 and E_8 together with the N atom are a pyrrolidine, piperidine, piperazine or morpholine ring.

Particularly preferred is a composition wherein the benzotriazole is a compound of formula IIIA



(IIIA)

wherein

G_6 is CF_3,

G_7 is hydrogen or CF_3,

E_2 and E_2' are independently straight or branched alkyl chain of 1 to 24 carbon atoms, straight or branched chain alkenyl of 2 to 18 carbon atoms, cycloalkyl of 5 to 12 carbon atoms, phenylalkyl of 7 to 15 carbon atoms, phenyl, or said phenyl or said phenylalkyl substituted on the phenyl ring by 1 to 3 alkyl of 1 to 4 carbon atoms; and

L is methylene.

Most preferred is a composition wherein the benzotriazole is

(a) 5-trifluoromethyl-2-(2-hydroxy-3-α–cumyl-5-tert-octylphenyl)-2H-benzotriazole;
(b) 5-trifluoromethyl-2-(2-hydroxy-5-tert-octylphenyl)-2H-benzotriazole;
(c) 5-trifluoromethyl-2-(2-hydroxy-3,5-di-tert-octylphenyl)-2H-benzotriazole;
(d) 2,2'-methylene-bis[6-(5-trifluoromethyl-2H-benzotriazol-2-yl)-4-tert-octyl

phenol];

(e) methylene-2-[4-tert-octyl-6-(2H-benzotriazol-2-yl)phenol]2'-[4-tert-octyl-6-(5-trifluoromethyl-2H-benzotriazol-2-yl)phenol];

(f) 3-(5-trifluoromethyl-2H-benzotriazol-2-yl)-5-tert-butyl-4-hydroxyhydrocinnamic acid;

(g) methyl 3-(5-trifluoromethyl-2H-benzotriazol-2-yl)-5-tert-butyl-4-hydroxyhydro cinnamate;

(h) isooctyl 3-(5-trifluoromethyl-2H-benzotriazol-2-yl)-5-tert-butyl-4-hydroxyhydro cinnamate;

(i) 5-trifluoromethyl-2-[2-hydroxy-5-(3-hydroxypropyl)phenyl]-2H-benzotriazole;

(j) 5-butylsulfonyl-2-(2-hydroxy-3-α–cumyl-5-tert-octylphenyl)-2H-benzotriazole;

(k) 5-octylsulfonyl-2-(2-hydroxy-3,5-di-α–cumylphenyl)-2H-benzotriazole;

(l) 5-dodecylsulfonyl-2-(2-hydroxy-3,5-di-tert-butylphenyl)-2H-benzotriazole;

(m) 5-octylsulfonyl-2-(2-hydroxy-3,5-di-tert-octylphenyl)-2H-benzotriazole;

(n) 5-trifluoromethyl-2-(2-hydroxy-3-α–cumyl-5-tert-butylphenyl)-2H-benzotriazole;

(o) 5-trifluoromethyl-2-(2-hydroxy-3-α-cumyl-5-nonylphenyl)-2H-benzotriazole;

(p) 5-trifluoromethyl-2-[2-hydroxy-3-α-cumyl-5-(2-hydroxyethyl)phenyl]-2H-benzo triazole;

(q) 5-trifluoromethyl-2-[2-hydroxy-3-α-cumyl-5-(3-hydroxypropyl)phenyl]-2H-benzo triazole;

(r) 5-trifluoromethyl-2-(2-hydroxy-3,5-di-tert-amylphenyl)-2H-benzotriazole;

(s) 5-trifluoromethyl-2-(2-hydroxy-3,5-di-tert-butylphenyl)-2H-benzotriazole;

(t) 5-trifluoromethyl-2-(2-hydroxy-3-dodecyl-5-methylphenyl)-2H-benzotriazole;

(u) 5-trifluoromethyl-2-[2-hydroxy-3-tert-butyl-5-(3-hydroxypropyl)phenyl)-2H-benzotriazole;

(v) 5-trifluoromethyl-2-[2-hydroxy-3-tert-butyl-5-(2-hydroxyethyl)phenyl]-2H-benzo triazole;

(w) 5-trifluoromethyl-2-[2-hydroxy-5-(2-hydroxyethyl)phenyl]-2H-benzotriazole;

(x) 5-trifluoromethyl-2-(2-hydroxy-3,5-di-α–cumylphenyl)-2H-benzotriazole;

(y) 5-fluoro-2-(2-hydroxy-3,5-di-α–cumylphenyl)-2H-benzotriazole;

(z) 5-butylsulfonyl-2-(2-hydroxy-3,5-di-α–cumylphenyl)-2H-benzotriazole;

(aa) 5-butylsulfonyl-2-(2-hydroxy-3,5-di-tert-butylphenyl)-2H-benzotriazole;

(bb) 5-butylsulfonyl-2-(2-hydroxy-3,5-di-tert-octylphenyl)-2H-benzotriazole;

(cc) 5-phenylsulfonyl-2-(2-hydroxy-3,5-di-tert-butylphenyl)-2H-benzotriazole; or
(dd) 5-chloro-2-(2-hydroxy-3,5-di-α–cumylphenyl)-2H-benzotriazole.

Particularly preferred is a composition wherein the benzotriazole is

(a) 5-trifluoromethyl-2-(2-hydroxy-3-α–cumyl-5-tert-octylphenyl)-2H-benzotriazole;
(b) 5-trifluoromethyl-2-(2-hydroxy-5-tert-octylphenyl)-2H-benzotriazole;
(c) 5-trifluoromethyl-2-(2-hydroxy-3,5-di-tert-octylphenyl)-2H-benzotriazole;
(g) methyl 3-(5-trifluoromethyl-2H-benzotriazol-2-yl)-5-tert-butyl-4-hydroxy hydrocinnamate;
(j) 5-butylsulfonyl-2-(2-hydroxy-3-α–cumyl-5-tert-octylphenyl)-2H-benzotriazole;
(n) 5-trifluoromethyl-2-(2-hydroxy-3-α–cumyl-5-tert-butylphenyl)-2H-benzotriazole;
(s) 5-trifluoromethyl-2-(2-hydroxy-3,5-di-tert-butylphenyl)-2H-benzotriazole;
(x) 5-trifluoromethyl-2-(2-hydroxy-3,5-di-α–cumylphenyl)-2H-benzotriazole;
(aa) 5-butylsulfonyl-2-(2-hydroxy-3,5-di-tert-butylphenyl)-2H-benzotriazole; or
(cc) 5-phenylsulfonyl-2-(2-hydroxy-3,5-di-tert-butylphenyl)-2H-benzotriazole.

Preferably the amount of benzotriazole of component (b1) or (b2) is from 0.1 to 20%, more preferably from 1 to 10% and most preferably from 2 to 5% by weight based on the adhesive composition.

Preferably the relative amount of (b1) to (b2) by weight is from 75:25 to 25:75, more preferably 50:50.

Preferably the adhesive of component (a) is selected from the group consisting of the pressure sensitive adhesives, the rubber-based adhesives, the solvent or emulsion based adhesives, the hot melt adhesives and natural-product based adhesives.

Suitable resins are selected from the group consisting of the polyurethanes, polyacrylics, epoxys, phenolics, polyimides, poly(vinyl butyral), polycyanoacrylates, polyacrylates, ethylene/acrylic acid copolymers and their salts (ionomers), silicon polymers, poly(ethylene/vinyl acetate), atatic polypropylene, styrene-diene copolymers, polyamides, hydroxyl-terminated polybutadiene, polychloroprene, thermosets, urea-formaldehyde polymers, poly(vinyl acetate), carboxylated styrene/butadiene copolymers and poly(vinyl alcohol).

Preferably the adhesive composition is present in a laminated or multilayer construction.

Preferably the laminated or multilayer construction is selected from the group consisting of

(a) retroreflective sheets and signs and conformable marking sheets;
(b) solar control films of various construction;
(c) corrosion resistant silver mirrors and solar reflectors;
(d) reflective print labels;
(e) UV absorbing glasses and glass coatings;
(f) electrochromic devices;
(g) films/glazings;
(h) windscreens and intermediate layers; and
(i) optical films.

More preferably the laminated or multilayer construction is selected from the group consisting of

(a) retroreflective sheets and signs and conformable marking sheets;
(b) solar control films of various construction;
(e) UV absorbing glasses and glass coatings;
(g) films/glazings; and
(h) windscreens and intermediate layers.

Most preferably the laminated or multilayer construction is selected from the group consisting of
(b) a solar control films of various construction; and
(h) windscreens and intermediate layers.

Preference is given to a composition wherein the adhesive of component (a) is a resin selected from the group consisting of
(i) polyurethanes;
(ii) polyacrylics;

(iii) epoxys;
(iv) phenolics;
(v) polyimides;
(vi) poly(vinyl butyral);
(vii) polycyanoacrylates;
(viii) polyacrylates;
(ix) ethylene/acrylic acid copolymers and their salts (ionomers);
(x) silicon polymers;
(xi) poly(ethylene/vinyl acetate);
(xii) atatic polypropylene;
(xiii) styrene-diene copolymers;
(xiv) polyamides;
(xv) hydroxyl-terminated polybutadiene;
(xvi) polychloroprene;
(xvii) poly(vinyl acetate);
(xviii) carboxylated styrene/butadiene copolymers;
(xix) poly(vinyl alcohol); and
(xx) polyesters.

More preferably the adhesive is a resin selected from the group consisting of the polyurethanes, polyacrylics, epoxy resins, phenolics, polyimides, poly(vinyl butyral), poly(vinyl alcohol), ethylene/vinyl acetate copolymers, polyolefins, natural rubber, styrene/butadiene rubber, polyacrylates, thermosets, vinyl polymers, urea-formaldehyde polymers, styrene polymers and polycyanoacrylates.

Another preferred embodiment is wherein the adhesive of component (a) is a resin selection from the group consisting of poly(vinyl butyral), ethylene/vinyl acetate copolymers, polyacrylics, polyacrylates, natural rubber, polycyanoacrylates, poly(vinyl alcohol), styrene/butadiene rubber, phenolics, urea-formaldehyde polymers, epoxy resins, vinyl polymers, polyurethanes and styrene block copolymers.

Particularly preferred is a composition wherein the adhesive of component (a) is a resin selected from the group consisting of
poly(vinyl butyral), ethylene/vinyl acetate copolymers, polyacrylics, polyacrylates, natural

rubber, polycyanoacrylates, poly(vinyl alcohol), styrene/butadiene rubber, phenolics, vinyl polymers, polyurethanes and styrene block copolymers.

Most preferred is a composition wherein the adhesive of component (a) is a polyacrylate.

The instant adhesive stabilized by a benzotriazole may also optionally contain from 0.01 to 10% by weight; preferably from 0.025 to 5% by weight, and most preferably from 0.1 to 3% by weight of additional coadditives such as antioxidants, other UV absorbers, hindered amines, phosphites or phosphonites, hydroxylamines, nitrones, benzofuran-2-ones, thiosynergists, polyamide stabilizers, metal stearates, nucleating agents, fillers, reinforcing agents, lubricants, emulsifiers, dyes, pigments, optical brighteners, flame retardants, antistatic agents, blowing agents and the like.

The stabilizers of the instant invention may readily be incorporated into the adhesive compositions by conventional techniques, at any convenient stage prior to the manufacture of shaped articles therefrom. For example, the stabilizer may be mixed with the polymer in dry powder form, or a suspension or emulsion of the stabilizer may be mixed with a solution, suspension, or emulsion of the polymer.

Examples of coadditives are given below.

1. Antioxidants

1.1. Alkylated monophenols, for example,

2,6-di-tert-butyl-4-methylphenol
2-tert-butyl-4,6-dimethylphenol
2,6-di-tert-butyl-4-ethylphenol
2,6-di-tert-butyl-4-n-butylphenol
2,6-di-tert-butyl-4-i-butylphenol
2,6-di-cyclopentyl-4-methylphenol
2-(α-methylcyclohexyl)-4,6-dimethylphenol
2,6-di-octadecyl-4-methylphenol
2,4,6-tri-cyclohexylphenol

2,6-di-tert-butyl-4-methoxymethylphenol

1.2. Alkylated hydroquinones, for example,

2,6-di-tert-butyl-4-methoxyphenol
2,5-di-tert-butyl-hydroquinone
2,5-di-tert-amyl-hydroquinone
2,6-diphenyl-4-octadecyloxyphenol

1.3. Hydroxylated thiodiphenyl ethers, for example,

2,2'-thio-bis-(6-tert-butyl-4-methylphenol)
2,2'-thio-bis-(4-octylphenol)
4,4'-thio-bis-(6-tert-butyl-3-methylphenol)
4,4'-thio-bis-(6-tert-butyl-2-methylphenol)

1.4. Alkylidene-bisphenols, for example,

2,2'-methylene-bis-(6-tert-butyl-4-methylphenol)
2,2'-methylene-bis-(6-tert-butyl-4-ethylphenol)
2,2'-methylene-bis-[4-methyl-6-(α–methylcyclohexyl)-phenol]
2,2'-methylene-bis-(4-methyl-6-cyclohexylphenol)
2,2'-methylene-bis-(6-nonyl-4-methylphenol)
2,2'-methylene-bis-[6-(α–methylbenzyl)-4-nonylphenol]
2,2'-methylene-bis-[6-(α,α–dimethylbenzyl)-4-nonylphenol]
2,2'-methylene-bis-(4,6-di-tert-butylphenol)
2,2'-ethylidene-bis-(4,6-di-tert-butylphenol)
2,2'-ethylidene-bis-(6-tert-butyl-4-isobutylphenol)
4,4'-methylene-bis-(2,6-di-tert-butylphenol)
4,4'-methylene-bis-(6-tert-butyl-2-methylphenol)
1,1-bis-(5-tert-butyl-4-hydroxy-2-methylphenyl)-butane
2,6-di-(3-tert-butyl-5-methyl-2-hydroxybenzyl)-4-methylphenol
1,1,3-tris-(5-tert-butyl-4-hydroxy-2-methylphenyl)-butane
1,1-bis-(5-tert-butyl-4-hydroxy-2-methylphenyl)-3-n-dodecylmercaptobutane

ethyleneglycol bis-[3,3-bis-(3'-tert-butyl-4'-hydroxyphenyl)-butyrate]
di-(3-tert-butyl-4-hydroxy-5-methylphenyl)-dicyclopentadiene
di-[2-(3'-tert-butyl-2'-hydroxy-5'-methyl-benzyl)-6-tert-butyl-4-methylphenyl] terephthalate.

1.5. Benzyl compounds, for example,

1,3,5-tri-(3,5-di-tert-butyl-4-hydroxybenzyl)-2,4,6-trimethylbenzene
di-(3,5-di-tert-butyl-4-hydroxybenzyl) sulfide
3,5-di-tert-butyl-4-hydroxybenzyl-mercapto-acetic acid isooctyl ester
bis-(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl)dithiol terephthalate
1,3,5-tris-(3,5-di-tert-butyl-4-hydroxybenzyl) isocyanurate
1,3,5-tris-(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl) isocyanurate
3,5-di-tert-butyl-4-hydroxybenzyl-phosphoric acid dioctadecyl ester
3,5-di-tert-butyl-4-hydroxybenzyl-phosphoric acid monoethyl ester, calcium-salt

1.6. Acylaminophenols, for example,

4-hydroxy-lauric acid anilide
4-hydroxy-stearic acid anilide
2,4-bis-octylmercapto-6-(3,5-tert-butyl-4-hydroxyanilino)-s-triazine
octyl-N-(3,5-di-tert-butyl-4-hydroxyphenyl)-carbamate

1.7. Esters of b-(3,5-di-tert-butyl-4-hydroxyphenyl)-propionic acid with monohydric or polyhydric alcohols, for example,

methanol
octadecanol
1,6-hexanediol
neopentyl glycol
thiodiethylene glycol
triethanolamine
diethylene glycol
triethylene glycol
pentaerythritol
tris-hydroxyethyl isocyanurate
di-hydroxyethyl oxalic acid diamide
triisopropanolamine

1.8. Esters of b-(5-tert-butyl-4-hydroxy-3-methylphenyl)-propionic acid with monohydric or polyhydric alcohols, for example,

methanol
octadecanol
1,6-hexanediol
neopentyl glycol
thiodiethylene glycol
triethanolamine
diethylene glycol
triethylene glycol
pentaerythritol
tris-hydroxyethyl isocyanurate
di-hydroxyethyl oxalic acid diamide
triisopropanolamine

1.9. Amides of b-(3,5-di-tert-butyl-4-hydroxyphenyl)-propionic acid for example,

N,N'-di-(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)-hexamethylenediamine
N,N'-di-(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)-trimethylenediamine
N,N'-di-(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)-hydrazine

1.10 Diarylamines, for example,
diphenylamine, N-phenyl-1-naphthylamine, N-(4-tert-octylphenyl)-1-naphthylamine, 4,4'-di-tert-octyl-diphenylamine, reaction product of N-phenylbenzylamine and 2,4,4-trimethylpentene, reaction product of diphenylamine and 2,4,4-trimethylpentene, reaction product of N-phenyl-1-naphthylamine and 2,4,4-trimethylpentene.

2. UV absorbers and light stabilizers

2.1. 2-(2'-Hydroxyphenyl)-benzotriazoles, for example, the 5'-methyl-, 3',5'-di-tert-butyl-, 5'-tert-butyl-, 5'-(1,1,3,3-tetramethylbutyl)-, 5-chloro-3',5'-di-tert-butyl-, 5-chloro-3'-tert-butyl-5'-methyl-, 3'-sec-butyl-5'-tert-butyl-, 4'-octoxy, 3',5'-di-tert-amyl-, 3',5'-bis-(α,α-dimethylbenzyl), 3'-tert-butyl-5'-(2-(omega-hydroxy-octa-(ethyleneoxy)carbonyl-ethyl)-, 3'-dodecyl-5'-methyl-, and 3'-tert-butyl-5'-(2-octyloxycarbonyl)ethyl-, and dodecylated-5'-methyl derivatives.

2.2. 2-Hydroxy-benzophenones, for example, the 4-hydroxy-, 4-methoxy-, 4-octoxy, 4-decyloxy-, 4-dodecyloxy-, 4-benzyloxy, 4,2',4'-trihydroxy- and 2'-hydroxy-4,4'-dimethoxy derivatives.

2.3. Esters of optionally substituted benzoic acids for example, phenyl salicylate, 4-tert-butylphenyl salicylate, octylphenyl salicylate, dibenzoylresorcinol, bis-(4-tert-butylbenzoyl)-

resorcinol, benzoylresorcinol, 3,5-di-tert-butyl-4-hydroxybenzoic acid 2,4-di-tert-butylphenyl ester and 3,5-di-tert-butyl-4-hydroxybenzoic acid hexadecyl ester.

2.4. Acrylates, for example, α–cyano-b,b-diphenylacrylic acid ethyl ester or isooctyl ester, α-carbomethoxy-cinnamic acid methyl ester, α–cyano-β-methyl-p-methoxy-cinnamic acid methyl ester or butyl ester, α–carbomethoxy-p-methoxy-cinnamic acid methyl ester, N-(b-carbomethoxy-b-cyanovinyl)-2-methyl-indoline.

2.5. Nickel compounds, for example, nickel complexes of 2,2'-thio-bis-[4-(1,1,3,3-tetramethylbutyl)-phenol], such as the 1:1 or 1:2 complex, optionally with additional ligands such as n-butylamine, triethanolamine or N-cyclohexyl-diethanolamine, nickel dibutyldithiocarbamate, nickel salts of 4-hydroxy-3,5-di-tert-butylbenzylphosphonic acid monoalkyl esters, such as of the methyl, ethyl or butyl ester, nickel complexes of ketoximes such as of 2-hydroxy-4-methyl-phenyl undecyl ketoxime, nickel complexes of 1-phenyl-4-lauroyl-5-hydroxy-pyrazole, optionally with additional ligands.

2.6. Sterically hindered amines, for example bis-(2,2,6,6-tetramethylpiperidyl) sebacate, bis-(1,2,2,6,6-pentamethylpiperidyl) sebacate, n-butyl-3,5-di-tert.butyl-4-hydroxybenzyl malonic acid bis-(1,2,2,6,6-pentanemethylpiperidyl)ester, condensation product of 1-hydroxyethyl-2,2,6,6-tetramethyl-4-hydroxypiperidine and succinic acid, condensation product of N,N'-(2,2,6,6-tetramethylpiperidyl)-hexamethylenediamine and 4-tert-octylamino-2,6-dichloro-s-triazine, tris-(2,2,6,6-tetramethylpiperidyl)-nitrilotriacetate, tetrakis-(2,2,6,6-tetramethyl-4-piperidyl) 1,2,3,4-butanetetracarboxylate, 1,1'(1,2-ethanediyl)-bis-(3,3,5,5-tetramethylpiperazinone), bis(1-octyloxy-2,2,6,6-tetramethylpiperidin-4-yl) sebacate.

2.7. Oxalic acid diamides, for example, 4,4'-di-octyloxy-oxanilide, 2,2'-di-octyloxy-5,5'-di-tert-butyl-oxanilide, 2,2'-di-dodecyloxy-5,5'-di-tert-butyl-oxanilide, 2-ethoxy-2'-ethyl-oxanilide, N,N'-bis (3-dimethylaminopropyl)-oxalamide, 2-ethoxy-5-tert-butyl-2'-ethyloxanilide and its mixture with 2-ethoxy-2'-ethyl-5,4'-di-tert-butyloxanilide and mixtures of ortho- and para-methoxy- as well as of o- and p-ethoxy-disubstituted oxanilides.

2.8. Hydroxyphenyl-s-triazines, for example 2,6-bis-(2,4-dimethylphenyl)-4-(2-hydroxy-4-octyloxyphenyl)-s-triazine; 2,6-bis-(2,4-dimethylphenyl)-4-(2,4-dihydroxyphenyl)-s-triazine; 2,4-bis(2,4-dihydroxyphenyl)-6-(4-chlorophenyl)-s-triazine; 2,4-bis[2-hydroxy-4-(2-hydroxyethoxy)phenyl]-6-(4-chlorophenyl)-s-triazine; 2,4-bis[2-hydroxy-4-(2-hydroxy-4-(2-hydroxyethoxy)phenyl]-6-(2,4-dimethylphenyl)-s-triazine; 2,4-bis[2-hydroxy-4-(2-hydroxyethoxy)-phenyl]-6-(4-bromophenyl)-s-triazine; 2,4-bis[2-hydroxy-4-(2-acetoxyethoxy)phenyl]-6-(4-chlorophenyl)-s-triazine, 2,4-bis(2,4-dihydroxyphenyl)-6-(2,4-dimethylphenyl)-s-triazine.

3. Metal deactivators, for example, N,N'-diphenyloxalic acid diamide, N-salicylal-N'-salicyloylhydrazine, N,N'-bis-salicyloylhydrazine, N,N'-bis-(3,5-di-tert-butyl-4-hydroxyphenyl-propionyl)-hydrazine, 3-salicyloylamino-1,2,4-triazole, bis-benzylidene-oxalic acid dihydrazide.

4. Phosphites and phosphonites, for example, triphenyl phosphite, diphenylalkyl phosphites, phenyldialkyl phosphites, tri-(nonylphenyl) phosphite, trilauryl phosphite, trioctadecyl phosphite, di-stearyl-pentaerythritol diphosphite, tris-(2,4-di-tert-butylphenyl) phosphite, di-isodecylpentaerythritol diphosphite, di-(2,4,6-tri-tert-butylphenyl)-pentaerythritol diphosphite, di-(2,4-di-tert-butyl-6-methylphenyl)-pentaerythritol diphosphite, di-(2,4-di-tert-butylphenyl)pentaerythritol diphosphite, tristearyl-sorbitol triphosphite, tetrakis-(2,4-di-tert-butylphenyl) 4,4'-diphenylylenediphosphonite.

5. Compounds which destroy peroxide, for example, esters of b-thiodipropionic acid, for example the lauryl, stearyl, myristyl or tridecyl esters, mercapto-benzimidazole or the zinc salt of 2-mercaptobenzimidazole, zinc dibutyl-dithiocarbamate, dioctadecyl disulfide, pentaerythritol tetrakis-(b-dodecylmercapto)-propionate.

6. Hydroxylamines, for example, N,N-dibenzylhydroxylamine, N,N-diethylhydroxylamine, N,N-dioctylhydroxylamine, N,N-dilaurylhydroxylamine, N,N-ditetradecylhydroxylamine, N,N-dihexadecylhydroxylamine, N,N-dioctadecylhydroxylamine, N-hexadecyl-N-octadecyl-hydroxylamine, N-heptadecyl-N-octadecylhydroxylamine, N,N-dialkylhydroxylamine derived from hydrogenated tallow amine.

7. Nitrones, for example, N-benzyl-alpha-phenyl nitrone, N-ethyl-alpha-methyl nitrone, N-octyl-alpha-heptyl nitrone, N-lauryl-alpha-undecyl nitrone, N-tetradecyl-alpha-tridecyl nitrone, N-hexadecyl-alpha-pentadecyl nitrone, N-octadecyl-alpha-heptadecylnitrone, N-hexadecyl-alpha-heptadecyl nitrone, N-octadecyl-alpha-pentadecyl nitrone, N-heptadecyl-alpha-heptadecyl nitrone, N-octadecyl-alpha-hexadecyl nitrone, nitrone derived from N,N-

dialkylhydroxylamine derived from hydrogenated tallow amine.

8. Polyamide stabilizers, for example copper salts in combination with iodides and/or phosphorus compounds and salts of divalent manganese.

9. Basic co-stabilizers, for example, melamine, polyvinylpyrrolidone, dicyandiamide, triallyl cyanurate, urea derivatives, hydrazine derivatives, amines, polyamides, polyurethanes, alkali metal salts and alkaline earth metal salts of higher fatty acids for example Ca stearate, Zn stearate, Mg stearate, Na ricinoleate and K palmitate, antimony pyrocatecholate or zinc pyrocatecholate.

10. Nucleating agents, for example, 4-tert-butyl-benzoic acid, adipic acid, diphenylacetic acid.

11. Fillers and reinforcing agents, for example, calcium carbonate, silicates, glass fibers, asbestos, talc, kaolin, mica, barium sulfate, metal oxides and hydroxides, carbon black, graphite.

12. Other additives, for example, plasticizers, lubricants, emulsifiers, pigments, optical brighteners, flameproofing agents, anti-static agents, blowing agents and thiosynergists such as dilauryl thiodipropionate or distearyl thiodipropionate.

13. Benzofuranones and indolinones, for example those disclosed in US-A-4325863, US-A-4338244 or US-A-5175312, or 3-[4-(2-acetoxyethoxy)phenyl]-5,7-di-tert-butyl-benzofuran-2-one, 5,7-di-tert-butyl-3-[4-(2-stearoyloxyethoxy)phenyl]benzofuran-2-one, 3,3'-bis[5,7-di-tert-butyl-3-(4-[2-hydroxyethoxy]phenyl)benzofuran-2-one], 5,7-di-tert-butyl-3-(4-ethoxyphenyl)-benzofuran-2-one, 3-(4-acetoxy-3,5-dimethylphenyl)-5,7-di-tert-butyl-benzofuran-2-one, 3-(3,5-dimethyl-4-pivaloyloxyphenyl)-5,7-di-tert-butyl-benzofuran-2-one.

The co-stabilizers, with the exception of the benzofuranones listed under 13, are added for example in concentrations of 0.01 to 10%, relative to the total weight of the material to be stabilized.

Further preferred compositions comprise, in addition to components (a) and (b) further additives, in particular phenolic antioxidants, light stabilizers or processing stabilizers.

Particularly preferred additives are phenolic antioxidants (item 1 of the list), sterically hindered amines (item 2.6 of the list), phosphites and phosphonites (item 4 of the list), UV absorbers (item 2 of the list) and peroxide-destroying compounds (item 5 of the list).

Additional additives (stabilizers) which are also particularly preferred are benzofuran-2-ones, such as described, for example, in US-A-4 325 863, US-A-4,338 244 or US-A-5175312.

The phenolic antioxidant of particular interest is selected from the group consisting of n-octadecyl 3,5-di-tert-butyl-4-hydroxyhydrocinnamate, neopentanetetrayl tetrakis(3,5-di-tert-butyl-4-hydroxyhydrocinammate), di-n-octadecyl 3,5-di-tert-butyl-4-hydroxybenzylphosphonate, 1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl)isocyanurate, thiodiethylene bis(3,5-di-tert-butyl-4-hydroxyhydrocinnamate), 1,3,5-trimethyl-2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl)benzene, 3,6-dioxaoctamethylene bis(3-methyl-5-tert-butyl-4-hydroxyhydrocinnamate), 2,6-di-tert-butyl-p-cresol, 2,2'-ethylidene-bis(4,6-di-tert-butylphenol), 1,3,5-tris(2,6-dimethyl-4-tert-butyl-3-hydroxybenzyl)isocyanurate, 1,1,3,-tris(2-methyl-4-hydroxy-5-tert-butylphenyl)butane, 1,3,5-tris[2-(3,5-di-tert-butyl-4-hydroxyhydrocinnamoyloxy)ethyl]isocyanur ate, 3,5-di-(3,5-di-tert-butyl-4-hydroxybenzyl)mesitol, hexamethylene bis(3,5-di-tert-butyl-4-hydroxyhydrocinnamate), 1-(3,5-di-tert-butyl-4-hydroxyanilino)-3,5-di(octylthio)-s-triazine, N,N'-hexamethylene-bis(3,5-di-tert-butyl-4-hydroxyhydrocinnamamide), calcium bis(ethyl 3,5-di-tert-butyl-4-hydroxybenzyl-phosphonate), ethylene bis[3,3-di(3-tert-butyl-4-hydroxyphenyl)butyrate], octyl 3,5-di-tert-butyl-4-hydroxybenzylmercaptoacetate, bis(3,5-di-tert-butyl-4-hydroxyhydrocinnamoyl)hydrazide, N,N'-bis[2-(3,5-di-tert-butyl-4-hydroxyhydrocinnamoyloxy)-eth yl]-oxamide, 2,4-bis(octylthiomethyl)-6-methylphenol, and 2,4-bis(octylthiomethyl)-6-tert-butylphenol.

A most preferred phenolic antioxidant is neopentanetetrayl tetrakis(3,5-di-tert-butyl-4-hydroxyhydrocinnamate), n-octadecyl 3,5-di-tert-butyl-4-hydroxyhydrocinnamate, 1,3,5-trimethyl-2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl)benzene, 1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl)isocyanurate, 2,6-di-tert-butyl-p-cresol, 2,2'-ethylidene-bis(4,6-di-tert-butylphenol), 2,4-bis(octylthiomethyl)-6-methylphenol or 2,4-bis(octylthiomethyl)-6-tert-butylphenol.

The hindered amine compound of particular interest is selected from the group consisting of bis(2,2,6,6-tetramethylpiperidin-4-yl) sebacate, bis(1,2,2,6,6-pentamethylpiperidin-4-yl) sebacate, di(1,2,2,6,6-pentamethylpiperidin-4-yl) (3,5-di-tert-butyl-4-hydroxybenzyl)butylmalonate, 4-benzoyl-2,2,6,6-tetramethylpiperidine, 4-stearyloxy-2,2,6,6-tetramethylpiperidine, 3-n-octyl-7,7,9,9-tetramethyl-1,3,8-triaza-spiro[4.5]decane-2,4-dio ne, tris(2,2,6,6-tetramethylpiperidin-4-yl) nitrilotriacetate, 1,2-bis(2,2,6,6-tetramethyl-3-oxopiperazin-4-yl)ethane, 2,2,4,4-tetramethyl-7-oxa-3,20-diaza-21-oxodispiro[5.1.11.2] heneicosane, polycondensation product of 2,4-dichloro-6-tert-octylamino-s-triazine and 4,4'-hexamethylenebis(amino-2,2,6,6-tetramethylpiperidine), polycondensation product of 1-(2-hydroxyethyl)-2,2,6,6-tetramethyl-4-hydroxypiperidine and succinic acid, polycondensation product of 4,4'-hexamethylenebis-(amino-2,2,6,6-tetramethylpiperidine) and 1,2-dibromoethane, tetrakis(2,2,6,6-tetramethylpiperidin-4-yl) 1,2,3,4-butanetetracarboxylate, tetrakis(1,2,2,6,6-pentamethylpiperidin-4-yl) 1,2,3,4-butanetetracarboxylate, polycondensation product of 2,4-dichloro-6-morpholino-s-triazine and 4,4'-hexamethylenebis(amino-2,2,6,6-tetramethylpiperidine), N,N',N'',N'''-tetrakis[(4,6-bis(butyl-1,2,2,6,6-pentamethylpiperidin-4-yl)-amino-s-triazin-2-yl]-1,10-diamino-4,7-diazadecane, mixed [2,2,6,6-tetramethylpiperidin-4-yl/b,b,b',b'-tetramethyl-3,9-(2,4,8 ,10-tetraoxaspiro[5.5]-undecane) diethyl] 1,2,3,4-butanetetracarboxylate, mixed [1,2,2,6,6-pentamethylpiperidin-4-yl/b,b,b',b'-tetramethyl-3,9-(2,4,8,10-tetraoxaspiro[5. 5]undecane)diethyl]1,2,3,4-butanetetracarboxylate, octamethylene bis(2,2,6,6-tetramethylpiperidin-4-carboxylate), 4,4'-ethylenebis(2,2,6,6-tetramethylpiperazin-3-one), N-2,2,6,6-tetramethylpiperidin-4-yl-n-dodecylsuccinimide, N-1,2,2,6,6-pentamethylpiperidin-4-yl-n-dodecylsuccinimide, N-1-acetyl-2,2,6,6-tetramethylpiperidin-4-yln-dodecylsuccinimide, 1-acetyl3-dodecyl-7,7,9,9-tetramethyl-1,3,8-triazaspiro[4.5]decane-2,4-dione, di-(1-octyloxy-2,2,6,6-tetramethylpiperidin-4-yl) sebacate, di-(1-cyclohexyloxy-2,2,6,6-tetramethylpiperidin-4-yl) succinate, 1-octyloxy-2,2,6,6-tetramethyl-4-hydroxy-piperidine, poly-{[6-tert-octylamino-s-triazin-2,4-diyl][2-(1-cyclohexyloxy-2,2,6,6-tetramethylpiperidin-4-yl)imino-hexamethylene-[4-(1-cyclohexyloxy-2,2,6,6-tetramethylpiperidin-4-yl)imino], 2,4,6-tris[N-(1-cyclohexyloxy-2,2,6,6-tetramethylpiperidin-4-yl)-n-butylamino]-s-triazine, 2-(2-hydroxyethyl)amino-4,6-bis[N-(1-cyclohexyloxy-2,2,6,6-tetramethylpiperidin-4-yl)-n-butylamino]-s-triazine, 1,2-bis(3,3,5,5-

tetramethylpiperazin-2-on-1-yl)ethane, 1,3,5-tris{N-cyclohexyl-N-[2-(3,3,5,5-tetramethylpiperazin-2-on-1-yl)ethyl]amino}-s-triazine, 1,3,5-tris{N-cyclohexyl-N-[2-(3,3,4,5,5-pentaamethylpiperazin-2-on-1-yl)ethyl]amino}-s-triazine, reaction of 2-4 equivalents of 2,4-bis[(1-cyclohexyloxy-2,2,6,6-tetramethylpiperidin-4-yl)butylamino]-6-chloro-s-triazine with 1 equivalent of N,N'-bis(3-aminopropyl)ethylenediamine, bis[1-(2-hydroxy-2-methylpropoxy)-2,2,6,6-tetramethylpiperidin-4-yl] sebacate, mixture of bis[1-(2-hydroxy-2-methylpropoxy)-2,2,6,6-tetramethylpiperidin-4-yl] glutarate and bis[1-(2-hydroxy-2-methylpropoxy)-2,2,6,6-tetramethylpiperidin-4-yl] adipate, 4-hydroxy-1-(2-hydroxy-2-methylpropoxy)-2,2,6,6-tetramethylpiperidine and 4-octadecyloxy-1-(2-hydroxy-2-methylpropoxy)-2,2,6,6-tetramethylpiperidine.

A most preferred hindered amine compound is bis(2,2,6,6-tetramethylpiperidin-4-yl) sebacate, bis(1,2,2,6,6-pentamethylpiperidin-4-yl) sebacate, di(1,2,2,6,6-pentamethylpiperidin-4-yl) (3,5-di-tert-butyl-4-hydroxybenzyl)butylmalonate, the polycondensation product of 1-(2-hydroxyethyl)-2,2,6,6-tetramethyl-4-hydroxypiperidine and succinic acid, the polycondensation product of 2,4-dichloro-6-tert-octylamino-s-triazine and 4,4'-hexamethylenebis(amino-2,2,6,6-tetramethylpiperidine), N,N',N'',N'''-tetrakis[(4,6-bis(butyl-(1,2,2,6,6-pentamethylpiperidin-4-yl)amino)- s-triazine-2-yl]-1,10-diamino-4,7-diazadecane. di-(1-octyloxy-2,2,6,6-tetramethylpiperidin-4-yl) sebacate, di-(1-cyclohexyloxy-2,2,6,6-tetramethylpiperidin-4-yl) succinate, 1-octyloxy-2,2,6,6-tetramethyl-4-hydroxy-piperidine, poly-{[6-tert-octylamino-s-triazin-2,4-diyl][2-(1-cyclohexyloxy-2,2,6,6-tetramethyl-piperidin-4-yl)imino-hexamethylene-[4-(1-cyclohexyloxy-2,2,6,6-tetramethylpiperidin-4-yl)imino], 2,4,6-tris[N-(1-cyclohexyloxy-2,2,6,6-tetramethylpiperidin-4-yl)-n-butylamino]-s-triazine, 2-(2-hydroxyethyl)amino-4,6-bis[N-(1-cyclohexyloxy-2,2,6,6-tetramethylpiperidin-4-yl)-n-butylamino]-s-triazine, 1,2-bis(3,3,5,5-tetramethylpiperazin-2-on-1-yl)ethane, 1,3,5-tris{N-cyclohexyl-N-[2-(3,3,5,5-tetramethylpiperazin-2-on-1-yl)ethyl]amino}-s-triazine, 1,3,5-tris{N-cyclohexyl-N-[2-(3,3,4,5,5-pentaamethylpiperazin-2-on-1-yl)ethyl]amino}-s-triazine, reaction of 2-4 equivalents of 2,4-bis[(1-cyclohexyloxy-2,2,6,6-tetramethylpiperidin-4-yl)butylamino]-6-chloro-s-triazine with 1 equivalent of N,N'-bis(3-aminopropyl)ethylenediamine, bis[1-(2-hydroxy-2-methylpropoxy)-2,2,6,6-tetramethylpiperidin-4-yl] sebacate, mixture of bis[1-(2-hydroxy-2-methylpropoxy)-2,2,6,6-tetramethylpiperidin-4-yl] glutarate and bis[1-(2-hydroxy-2-methylpropoxy)-2,2,6,6-tetramethylpiperidin-4-yl] adipate, 4-hydroxy-1-(2-hydroxy-2-methylpropoxy)-2,2,6,6-tetramethylpiperidine or 4-octadecyloxy-1-(2-hydroxy-2-methylpropoxy)-2,2,6,6-tetramethylpiperidine.

The instant composition can additionally contain another UV absorber selected from the group consisting of the benzotriazoles, s-triazines, the oxanilides, the hydroxybenzophenones, benzoates and the α–cyanoacrylates.

The following optional components are often also present in adhesive formulations and are presented here for illustrative purposes only and are not meant to limit the total adhesive compositions in any way. These optional components include plasticizers, adhesion promoters, waxes, petroleum waxes, elastomers, tackifier resins, oils, resins, polymers, rosin, modified rosin or rosin derivatives, hydrocarbon resins, terpene resins, paraffin wax, microcrystalline wax, synthetic hard wax and/or polyethylene wax. The amounts of these coadditives are those normally used in adhesive formulations.

Although in the instant invention, the instant benzotriazoles are intended for use in the adhesive and the adhesive layers of the laminated or multilayer articles, it is clear that the same beneficial UV absorption protection would be afforded to the articles if said benzotriazoles are also incorporated into the other layers of the articles, e.g. polymeric films with any dye or pigment present therein, whether by direct incorporation, by coextrusion or by migration from the adhesive layer into said other layer(s).

These polymers are those selected from the group consisting of

(1) polyolefins;
(2) mixtures of polyolefins;
(3) copolymers of monoolefins and diolefins or other vinyl monomers;
(4) polystyrene, poly(p-methylstyrene) or poly(α-methylstyrene);
(5) copolymers of styrene or α-methylstyrene with dienes or acrylic derivative;
(6) graft copolymers of styrene or α-methylstyrene;
(7) halogen containing polymers;
(8) polymers derived from a,b-unsaturated acids and derivatives thereof;
(9) copolymers of monomers of (8) with each other or other unsaturated monomers;
(10) polymers derived from unsaturated alcohols and amines or the acyl derivatives or acetals thereof;
(11) polyacetals such as polyoxymethylene and those polyoxymethylenes which

contain ethylene oxide as a comonomer, polyacetals modified with thermoplastic polyurethanes, acrylates or MBS;

(12) polyurethanes;

(13) polyamides and copolyamides from diamines and dicarboxylic acids and/or from aminocarboxylic acids or the corresponding lactams;

(14) polyureas or polyimides;

(15) polyesters derived from dicarboxylic acids and diols and/or from hydroxycarboxylic acids or the corresponding lactones, especially poly(ethylene terephthalate) (PET) and poly(ethylene 2,6-naphthalenedicarboxylate) (PEN);

(16) polycarbonates and polyester carbonates;

(17) polysulfones and polyether sulfones;

(18) crosslinked polymers derived from aldehydes on the one hand and phenols, ureas and melamines on the other hand;

(19) unsaturated polyester resins derived from copolyesters of saturated and unsaturated dicarboxylic acids with polyhydric alcohols and vinyl compounds as crosslinking agents;

(20) crosslinkable acrylic resins derived from substituted acrylates;

(21) blends of the aforementioned polymers;

(22) polysiloxanes;

(23) polyketimines in combination with unsaturated acrylic polyacetoacetate resins or with unsaturated acrylic resins;

(24) radiation curable compositions containing ethylenically unsaturated monomers or oligomers and a polyunsaturated aliphatic oligomer; and

(25) ionomers (copolymers of ethylene/acrylic acid and their salts).

Additionally, the instant adhesives particularly when the adhesive is poly(vinyl butyral) may be inserted between two (or more) layers of glass such as in an automobile windshield.

A further subject of the invention is a stabilized adhesive composition, suitable for use as an adhesive layer in a laminated article or multilayer construction, which comprises

(a) an adhesive; and

(b) a combination of

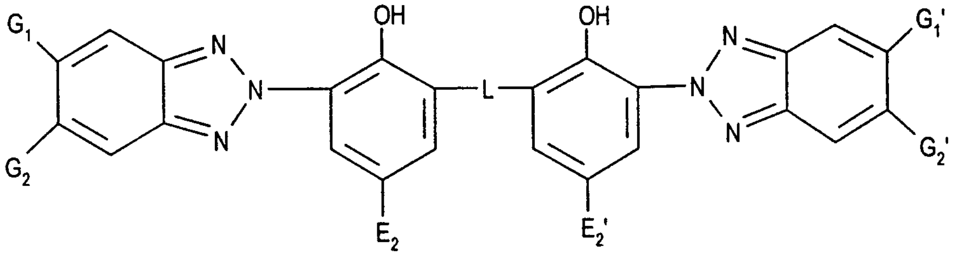
(1) a highly photostable benzotriazole which is 2-(2-hydroxy-3,5-di-α-cumylphenyl)-2H-benzotriazole or a red-shifted benzotriazole which is 5-chloro-2-(2-hydroxy-3,5-di-tert-butylphenyl)-2H-benzotriazole or 5-chloro-2-(2-hydroxy-3-tert-butyl-5-methylphenyl)-2H-benzotriazole each of which has relatively low solubility in some adhesives; and

(2) a solubilizing amount of a second benzotriazole having high solubility in said adhesives and selected from the group consisting of 2-(2-hydroxy-3,5-di-tert-butylphenyl)-2H-benzotriazole, 2-(2-hydroxy-3,5-di-tert-amylphenyl)-2H-benzotriazole, 2-(2-hydroxy-5-tert-octylphenyl)-2H-benzotriazole, 2-(2-hydroxy-3-sec-butyl-5- tert-butylphenyl)-2H-benzotriazole, 2-(2-hydroxy-3-α-cumyl-5-tert-octylphenyl)-2H-benzotriazole or 2-(2-hydroxy-3-α-cumyl-5-tert-butylphenyl)-2H-benzotriazole.

Preferably the benzotriazole mixture in component (b) exhibits enhanced durability and low loss of absorbance when exposed to actinic radiation as witnessed by an absorbance loss of less than 0.5 absorbance units after exposure for 893 hours or less than 0.8 absorbance units after exposure for 1338 hours in a Xenon Arc Weather-Ometer.

The definitions and preferences with respect to the adhesives apply also for the afore mentioned stabilized adhesive composition.

Yet another subject of the present invention is a compound of formula IIIc



(IIIc)

wherein

G_1 and G_1' are independently hydrogen or halogen;

G_2 is halogen, nitro, cyano, $-COOG_3$, $-P(O)(C_6H_5)_2$, $-CO-G_3$, $-CO-NH-G_3$, $-CO-N(G_3)_2$, $-N(G_3)-CO-G_3$, E_3S-, E_3SO- or E_3SO_2-;

G_2' is perfluoroalkyl of 1 to 12 carbon atoms;

G_3 is hydrogen, straight or branched chain alkyl of 1 to 24 carbon atoms, straight or branched chain alkenyl of 2 to 18 carbon atoms, cycloalkyl of 5 to 12 carbon atoms, phenylalkyl of 7 to 15 carbon atoms, phenyl, or said phenyl or said phenylalkyl substituted on the phenyl ring by 1 to 4 alkyl of 1 to 4 carbon atoms;

E_2 and E_2' are independently straight or branched alkyl chain of 1 to 24 carbon atoms, straight or branched chain alkenyl of 2 to 18 carbon atoms, cycloalkyl of 5 to 12 carbon atoms, phenylalkyl of 7 to 15 carbon atoms, phenyl, or said phenyl or said phenylalkyl substituted on the phenyl ring by one to three alkyl of 1 to 4 carbon atoms; or E_2 and E_2' are independently said alkyl of 1 to 24 carbon atoms or said alkenyl of 2 to 18 carbon atoms substituted by one or more -OH, $-OCOE_{11}$, $-OE_4$, -NCO, $-NH_2$, $-NHCOE_{11}$, $-NHE_4$ or $-N(E_4)_2$, or mixtures thereof, where E_4 is straight or branched chain alkyl of 1 to 24 carbon atoms; or said alkyl or said alkenyl interrupted by one or more -O-, -NH- or $-NE_4-$ groups or mixtures thereof and which can be unsubstituted or substituted by one or more -OH, $-OE_4$ or $-NH_2$ groups or mixtures thereof; or E_2 and E_2' are independently $-(CH_2)_m-CO-E_5$; or E_2 and E_2' are independently a group of the formula

$$-(CH_2)_m-CO-X-(Z)_p-Y-E_{15}$$

wherein

E_5 is $-OE_6$ or $-NE_7E_8$, or

E_5 is $-PO(OE_{12})_2$, $-OSi(E_{11})_3$ or $-OCO-E_{11}$,

or straight or branched chain C_1-C_{24}alkyl which is interrupted by -O-, -S- or $-NE_{11}$ and which can be unsubstituted or substituted by -OH or $-OCO-E_{11}$, C_5-C_{12} cycloalkyl which is unsubstituted or substituted by -OH, straight chain or branched C_2-C_{18}alkenyl which is unsubstituted or substituted by -OH, C_7-C_{15}aralkyl, $-CH_2-CHOH-E_{13}$ or glycidyl,

E_6 is hydrogen, straight or branched chain C_1-C_{24}alkyl which is unsubstituted or substituted by one or more OH, OE_4 or NH_2 groups, or $-OE_6$ is $-(OCH_2CH_2)_wOH$ or $-(OCH_2CH_2)_wOE_{21}$where w is 1 to 12 and E_{21} is alkyl of 1 to 12 carbon atoms,

E_7 and E_8 are independently hydrogen, alkyl of 1 to 18 carbon atoms, straight or branched chain C_3-C_{18}alkyl which is interrupted by -O-, -S- or $-NE_{11}-$, C_5-C_{12}cycloalkyl, C_6-C_{14}aryl or C_1-C_3hydroxylalkyl, or E_7 and E_8 together with the N atom are a pyrrolidine, piperidine, piperazine or morpholine ring,

X is -O- or $-N(E_{16})-$,
Y is -O- or $-N(E_{17})-$,
Z is C_2-C_{12}-alkylene, C_4-C_{12}-alkylene interrupted by one to three nitrogen atoms, oxygen atoms or a mixture thereof, or is C_3-C_{12}-alkylene, butenylene, butynylene, cyclohexylene or phenylene, each substituted by a hydroxyl group,

m is zero, 1 or 2,

p is 1, or p is also zero when X and Y are $-N(E_{16})-$ and $-N(E_{17})-$, respectively,

E_{15} is a group $-CO-C(E_{18})=C(H)E_{19}$ or, when Y is $-N(E_{17})-$, forms together with E_{17} a group -CO-CH=CH-CO-, wherein E_{18} is hydrogen or methyl, and E_{19} is hydrogen, methyl or $-CO-X-E_{20}$, wherein E_{20} is hydrogen or C_1-C_{18}-alkyl;

E_{16} and E_{17} independently of one another are hydrogen, C_1-C_{18}-alkyl, C_3-C_{12}-alkyl interrupted by 1 to 3 oxygen atoms, or is cyclohexyl or C_7-C_{15}aralkyl, and E_{16} together with E_{17} in the case where Z is ethylene, also forms ethylene,

E_{11} is hydrogen, straight or branched chain C_1-C_{18}alkyl, C_5-C_{12}cycloalkyl, straight or branched chain C_2-C_{18}alkenyl, C_6-C_{14}aryl or C_7-C_{15}aralkyl;

E_{12} is straight or branched chain C_1-C_{18}alkyl, straight or branched chain C_3-C_{18}alkenyl, C_5-C_{10}cycloalkyl, C_6-C_{16}aryl or C_7-C_{15}aralkyl;

E_{13} is hydrogen, straight chain or branched C_1-C_{18}alkyl which is substituted by -$PO(OE_{12})_2$, phenyl which is unsubstituted or substituted by OH, C_7-C_{15}aralkyl or -CH_2OE_{12};

E_3 is alkyl of 1 to 20 carbon atoms, hydroxyalkyl of 2 to 20 carbon atoms, alkyl substituted by alkoxycarbonyl of 2 to 9 carbon atoms, alkenyl of 3 to 18 carbon atoms, cycloalkyl of 5 to 12 carbon atoms, phenylalkyl of 7 to 15 carbon atoms, aryl of 6 to 10 carbon atoms or said aryl substituted by one or two alkyl of 1 to 4 carbon atoms or 1,1,2,2-tetrahydroperfluoroalkyl where the perfluoroalkyl moiety is of 6 to 16 carbon atoms; and

L is alkylene of 1 to 12 carbon atoms, alkylidene of 2 to 12 carbon atoms, benzylidene, p-xylylene, $\alpha,\alpha,\alpha',\alpha'$-tetramethyl-m-xylylene or cycloalkylidene.

These compounds are novel and clearly distinct from the prior art because they are asymmetrically subsituted by a perfluoroalkyl moiety in one ring, and the other ring is substituted by a different electron withdrawing moiety.

Preferred is a compound of formula IIIc wherein

G_1 and G_1' are each hydrogen,
G_2 is chloro, phenylsulfonyl or phenylthio,
G_2' is CF_3,
E_2 and E_2' are independently straight or branched alkyl chain of 1 to 24 carbon atoms, straight or branched chain alkenyl of 2 to 18 carbon atoms, cycloalkyl of 5 to 12 carbon atoms, phenylalkyl of 7 to 15 carbon atoms, phenyl, or said phenyl or said phenylalkyl substituted on the phenyl ring by 1 to 3 alkyl of 1 to 4 carbon atoms; and

L is alkylene of 1 to 12 carbon atoms, alkylidene of 2 to 12 carbon atoms, benzylidene, p-xylylene, $\alpha,\alpha,\alpha',\alpha'$-tetramethyl-m-xylylene or cycloalkylidene.

More preferred is a compound of formula IIIc wherein

G_1 and G_1' are each hydrogen,
G_2 is chloro, phenylsulfonyl or phenylthio,
G_2' is CF_3,

E_2 and E_2' are independently straight or branched alkyl chain of 1 to 24 carbon atoms, straight or branched chain alkenyl of 2 to 18 carbon atoms, cycloalkyl of 5 to 12 carbon atoms, phenylalkyl of 7 to 15 carbon atoms, phenyl, or said phenyl or said phenylalkyl substituted on the phenyl ring by 1 to 3 alkyl of 1 to 4 carbon atoms; and

L is methylene.

Most preferred are the following compounds

(a) methylene-2-[4-tert-butyl-6-(5-phenylsulfonyl-2H-benzotriazol-2-yl)phenol]-2'-[4-tert-octyl-6-(5-trifluoromethyl-2H-benzotriazol-2-yl)phenol];
(b) methylene-2-[4-tert-butyl-6-(5-chloro-2H-benzotriazol-2-yl)phenol]-2'-[4-tert-octyl-6-(5-trifluoromethyl-2H-benzotriazol-2-yl)phenol]; or
(c) methylene-2-[4-tert-butyl-6-(5-phenylthio-2H-benzotriazol-2-yl)phenol]-2'-[4-tert-octyl-6-(5-trifluoromethyl-2H-benzotriazol-2-yl)phenol].

The compounds of formula IIIc are also very useful as stabilizers in an adhesive composition.

Consequently a further subject of the invention is a stabilized adhesive composition, suitable for use as an adhesive layer in a laminated article or multilayer construction, which comprises

(a) an adhesive; and

(b) a highly soluble, red-shifted, photostable benzotriazole of formula IIIc.

The definitions and preferences with respect to the adhesives apply also for the afore mentioned stabilized adhesive composition. The compounds of formula IIIc are particularly suitable for this application since they combine a red shifted absorption with a very good solubility.

Yet another subject of the invention is a composition stabilized against thermal, oxidative or light-induced degradation which comprises,

(a) an organic material subject to thermal, oxidative or light-induced degradation,

and

(b) an effective stabilizing amount of a compound of formula IIIc.

Preferably the organic material is a natural, semi-synthetic, synthetic, thermoplastic or crosslinked polymer.

More preferably, the polymer is a polyolefin or polycarbonate, especially polyethylene or polypropylene; most especially polypropylene; or the polymer is a styrenic, ABS, a nylon, a polyester such as poly(ethylene terephthalate) or poly(butylene terephthalate), a polyurethane, an acrylate, a rubber modified styrenic, poly(vinyl chloride), poly(vinyl butyral), polyacetal (polyoxymethylene), poly(ethylene naphthalenedicarboxylate), or other blends or copolymers such as poly(ethylene/1,4-cyclohexylenedimethylene terephthalate) PETG or an ionomer.

Particularly preferred is a composition wherein the polymer is a polyester.

Preferably the polyester is poly(ethylene terephthalate), poly(butylene terephthalate) or poly(ethylene naphthalenedicarboxylate), or copolymer poly(ethylene/1,4-cyclohexylene-dimethylene terephthalate) PETG.

A further preferred polymer is a copolymer of ethylene/acrylic acid or an alkali metal, alkaline earth metal or transition metal salt thereof (an ionomer).

Also preferred is a composition wherein the polymer is is a polyolefin or polycarbonate.

In particular the polyolefin is polyethylene or polypropylene, most preferably polypropylene.

The composition stabilized against thermal, oxidative or light-induced degradation may additionally contain an effective stabilizing amount of at least one other UV absorber selected from the group consisting the benzotriazoles, the s-triazines, hydroxy-benzophenones, the α-cyanoacrylates, the oxanilides and benzoates.

Preferred are the 2-hydroxyphenyl-2H-benzotriazoles which are selected from the group consisting of

2-(2-hydroxy-5-methylphenyl)-2H-benzotriazole;
2-(2-hydroxy-3,5-di-tert-butylphenyl)-2H-benzotriazole;
2-(2-hydroxy-5-tert-butylphenyl)-2H-benzotriazole;
2-(2-hydroxy-5-tert-octylphenyl)-2H-benzotriazole;
5-chloro-2-(2-hydroxy-3,5-di-tert-butylphenyl)-2H-benzotriazole;
5-chloro-2-(2-hydroxy-3-tert-butyl-5-methylphenyl)-2H-benzotriazole;
2-(2-hydroxy-3-sec-butyl-5-tert-butylphenyl)-2H-benzotriazole;
2-(2-hydroxy-4-octyloxyphenyl)-2H-benzotriazole;
2-(2-hydroxy-3-dodecyl-5-methylphenyl)-2H-benzotriazole;
2-(2-hydroxy-3,5-di-tert-amylphenyl)-2H-benzotriazole;
2-[2-hydroxy-3,5-di(α,α-dimethylbenzyl)phenyl]-2H-benzotriazole;
2-[2-hydroxy-3-(α,α-dimethylbenzyl)-5-tert-octylphenyl]-2H-benzotriazole;
2-{2-hydroxy-3-tert-butyl-5-[2-(omega-hydroxy-octa(ethyleneoxy)carbonyl)ethyl]-phenyl}-2H-benzotriazole; and
2-{2-hydroxy-3-tert-butyl-5-[2-(octyloxy)carbonyl)ethyl]phenyl}-2H- benzotriazole.

In particular the other benzotriazole is

2-(2-hydroxy-3,5-di-tert-amylphenyl)-2H-benzotriazole;
2-[2-hydroxy-3,5-di(α,α-dimethylbenzyl)phenyl]-2H-benzotriazole;
2-[2-hydroxy-3-(α,α-dimethylbenzyl)-5-tert-octylphenyl]-2H-benzotriazole;
2-{2-hydroxy-3-tert-butyl-5-[2-(omega-hydroxy-octa(ethyleneoxy)carbonyl)ethyl]-phenyl}-2H-benzotriazole;
5-chloro-2-(2-hydroxy-3,5-di-tert-butylphenyl)-2H-benzotriazole;
5-chloro-2-(2-hydroxy-3-tert-butyl-5-methylphenyl)-2H-benzotriazole;
2-(2-hydroxy-5-tert-octylphenyl)-2H-benzotriazole; or
2-{2-hydroxy-3-tert-butyl-5-[2-(octyloxy)carbonyl)ethyl]phenyl}-2H- benzotriazole.

The composition stabilized against thermal, oxidative or light-induced degradation may also contain an effective stabilizing amount of a hindered amine.

In another preferred embodiment of the instant invention, the organic material is a resin selected from the group consisting of a thermoset acrylic melamine resin, an acrylic urethane resin, an epoxy carboxy resin, a silane modified acrylic melamine, an acrylic resin with carbamate pendant groups crosslinked with melamine or an acrylic polyol resin crosslinked with melamine containing carbamate groups.

Most preferably, the resin is a thermoset acrylic melamine resin or an acrylic urethane resin.

In yet another preferred embodiment of the invention, the organic material is a recording material.

The recording materials according to the invention are suitable for pressure-sensitive copying systems, photocopying systems using microcapsules, heat-sensitive copying systems, photographic materials and ink jet printing.

The recording materials according to the invention are distinguished by an unexpected improvement in quality, especially with regard to the fastness to light.

The recording materials according to the invention have the construction known for the particular use. They consist of a customary carrier, for example, paper or plastic film, which has been coated with one or more layers. Depending on the type of material, these layers contain the appropriate necessary components, in the case of photographic materials, for example, silver halide emulsions, dye couplers, dyes and the like. Material particularly suitable for ink jet printing has a layer particularly absorptive for ink on a customary carrier. Uncoated paper can also be employed for ink jet printing. In this case the paper acts at the same time as the carrier material and as the ink-absorbent layer. Suitable material for ink jet printing is, for example, described in United States Patent No. 5,073,448 which is incorporated herein by reference.

The recording material can also be transparent as, for example, in the case of projection films.

The compounds of formula IIIc can be incorporated into the carder material as early as the production of the latter, in the production of paper, for example, being added to the paper pulp. A second method of application is to spray the carder material with an aqueous solution of compounds of formula IIIc or to add the compounds to the coating composition.

Coating compositions intended for transparent recording materials suitable for projection cannot contain any particles which scatter light, such as pigments and fillers.

The dye-binding coating composition can contain a number of other additives, for example, antioxidants, light stabilizers (including also UV absorbers which do not fall under the scope of the UV absorbers of this invention), viscosity improvers, fluorescent brighteners, biocides and/or antistatic agents.

The coating composition is usually prepared as follows: the water-soluble components, for example, the binder, are dissolved in water and stirred together; the solid components, for example, fillers and other additives already described, are dispersed in this aqueous medium; and disperison is advantageously carried out by means of devices, for example, ultrasonic systems, turbine stirrers, homogenizers, colloid mills, bead mills, sand mills, high-speed stirrers and the like. The compounds of formula IIIc can be easily incorporated into the coating composition.

The recording material according to this invention preferably contains 1 to 5000 mg/m^2, in particular 50-1200 mg/m^2, of a compound of formula IIIc.

As already mentioned, the recording materials according to the invention embrace a wide field. The compounds of formula IIIc can, for example, be employed in pressure-sensitive copying systems. They can be introduced either into the paper in order to protect the micro-encapsulated dye precursors there from light, or into the binder of the developer layer in order to protect the dyes formed there.

Photocopying systems using light-sensitive microcapsules which are developed by means of pressure are described in United States Patent Nos. 4,416,966; 4,483,912; 4,352,200; 4,535,050; 4,535,463; 4,551,407; 4,562,137 and 4,608,330; and also in EP-A 139,479; EP-A 162,664; EP-A 164,931; EP-A 237,024; EP-A 237,025 and EP-A 260,129. In all these systems, the compounds can be put into the dye-receiving layer. The compounds can, however, also be put into the donor layer in order to protect the color formers from light.

Photographic materials which can be stabilized are photographic dyes and layers containing such dyes or precursors thereof, for example, photographic paper and films. Suitable materials are, for example, described in United States Patent No. 5,364,749 which is incorporated herein by reference. The compounds of formula IIIc act here as a UV filter against electrostatic flashes. In color photographic materials, couplers and dyes are also protected against photochemical decomposition.

The instant compounds of formula IIIc can be used for all types of color photographic materials. For example, they can be employed for color paper, color reversal paper, direct-positive color material, color negative film, color positive film, color reversal film and the like. They are preferably used inter alia for photographic color material which contains a reversal substrate or form positives.

Color-photographic recording materials usually contain, on a support, a blue-sensitive and/or a green-sensitive and/or a red-sensitive silver halide emulsion layer and, if desired, a protection layer, with the instant compounds being, preferably, either in the green-sensitive or the red-sensitive layer or in a layer between the green-sensitive and the red-sensitive layer or in a layer on top of the silver halide emulsion layers.

The compounds of formula IIIc can also be employed in recording materials based on the principles of photopolymerization, photoplasticization or the rupture of microcapsules, or in cases where heat-sensitive and light-sensitive diazonium salts, leuko dyes having an oxidizing agent or dye lactones having Lewis acids are used.

Furthermore, the instant compounds can be employed in recording materials for dye diffusion transfer printing, thermal wax transfer printing and non-matrix printing and for use with electrostatic, electrographic, electrophoretic, magnetographic and laser-electrophotographic printers and pen-plotters. Of the above, recording materials for dye diffusion transfer printing are preferred, for example, as described in EP-A 507,734.

The instant compounds of formula IIIc can also be employed in inks, preferably for ink jet printing, for example, as described in United States Patent No. 5,098,477 which is incorporated herein by reference.

The compounds exhibit superior hydrolytic stability, handling and storage stability as well as good resistance to extractability when present in a stabilized composition.

The instant benzotriazoles are made by conventional methods for preparing such compounds. The usual procedure involves the diazotization of a substituted o-nitroaniline followed by coupling the resultant diazonium salt with a substituted phenol and reduction of the azobenzene intermediate to the corresponding desired benzotriazole. The starting materials for these benzotriazoles are largely items of commerce or can be prepared by normal methods of organic synthesis.

The following examples illustrate the instant invention.

Examples A: Use of Benzotriazoles

Example A1

UV Absorption Spectra

Various instant benzotriazoles substituted on the phenyl ring with a 3-α–cumyl moiety and a 5-tert-octyl group and have a maximum absorbance value and the given wavelength as seen below. The UV spectra are measured in ethyl acetate solution at approximately 20 mg/L concentration.

Compound*	λ max (nm)	absorbance at 375 (nm)
A	345	0.28
B	352	0.40
C	348	0.33
D	362	0.50
E	358	0.42
F	357	0.59
G	354	0.41

*A is 2-(2-hydroxy-3-α–cumyl-5-tert-octylphenyl)-2H-benzotriazole.
B is 5-chloro-2-(2-hydroxy-3-α–cumyl-5-tert-octylphenyl)-2H-benzotriazole.
C is 5-trifluoromethyl-2-(2-hydroxy-3-α–cumyl-5-tert-octylphenyl)-2H-benzotriazole.
D is 5-phenylsulfonyl-2-(2-hydroxy-3-α–cumyl-5-tert-octylphenyl)-2H-benzotriazole.
E is 5-methoxycarbonyl-2-(2-hydroxy-3-α–cumyl-5-tert-octylphenyl)-2H-benzotriazole.
F is 5-butylsulfonyl-2-(2-hydroxy-3,5-di-tert-butylphenyl)-2H-benzotriazole.
G is methyl 3-(5-trifluoromethyl-2H-benzotriazol-2-yl)-5-tert-butyl-4-hydroxyhydrocinnamate.

Example A2

UV Absorption Spectra

The maximum absorbance value and the given wavelength of various blends of benzotriazoles are determined as seen below. The UV spectra are measured in ethyl acetate solution at approximately 20 mg/L concentration.

Mixture of Compounds*	λ max (nm)	absorbance at 375 (nm)
B	349	0.39
C	352	0.46

B is 1:3 mixture by weight of 2-(2-hydroxy-3,5-di-α-cumylphenyl)-2H-benzotriazole (TINUVIN® 900, Ciba) and 5-trifluoromethyl-2-(2-hydroxy-3-α-cumyl-5-tert-octylphenyl)-2H-benzotriazole.

C is 1:3 mixture by weight of 5-chloro-2-(2-hydroxy-3,5-di-tert-butylphenyl)-2H-benzotriazole (TINUVIN® 327, Ciba) and 5-trifluoromethyl-2-(2-hydroxy-3-α-cumyl-5-tert-octylphenyl)-2H-benzotriazole.

Example A3

Benzotriazole Solubility in Adhesive

To measure this solubility a number of structurally different benzotriazoles are added to a typical adhesive GELVA® 263 (Solutia) which is a 44.5% solution of a polyacrylate in a mixture of ethyl acetate and hexane. The polyacrylate is a copolymer of methyl methacrylate, 2-ethylhexyl methacrylate and glycidyl methacrylate.

The test benzotriazole is dissolved in 5 mL of ethyl acetate, toluene or a mixture of ethyl acetate and toluene. To the solution is added 5 g of GELVA® 263 and 2-3 mL of the resulting solution is placed into individual watch glasses. Solubility is then evaluated based upon observed crystallization once the solvent has evaporated. Observations start after several hours and then continue over a period of several weeks.

The solubility values given in the table below are approximate maximum concentrations where no sign of subsequent crystallization is evident. Solubilities are reported in weight of total benzotriazole added to GELVA® 263 as is. From these data it clear that the instant benzotriazoles are considerably more soluble in adhesives (in this case GELVA® 263) than many benzotriazoles of the prior art. The use of many benzotriazoles in adhesives has been limited in the past by the limited solubility and compatibility of some benzotriazole compounds. By using the instant benzotriazoles, the use levels can be increased substantially to add greatly increased stabilization protection which is further augmented by the photostability and the red-shiftedness of the instant benzotriazoles.

Compound*	Trade Name or Class	Solubility without Crystallization (%)
A	5-ethylsulfonyl	< 1
B	TINUVIN/ 900	2.0
C	TINUVIN/ 327	2.0
D	5-butylsulfonyl	4.0
E	5-CF_3	4.0
F	5,5'-CF_3	4.0
G	5-butylsulfonyl	8.0
H	5-CF_3	8.0
I	5-CF_3	8.0
J	5-methoxycarbonyl-methylsulfinyl	8.0
K	5-phenylsulfonyl	11.3
L	5-phenylsulfonyl	11.3
M	5-CF_3	22.6
N	5-CF_3	22.6
O	5-CF_3	22.6

P	TINUVIN® 928	22.6
Q	5-chloro	22.6

*A is 5-ethylsulfonyl-2-(2-hydroxy-5-methylphenyl)-2H-benzotriazole.

B is 2-(2-hydroxy-3,5-di-α–cumylphenyl)-2H-benzotriazole.

C is 5-chloro-2-(2-hydroxy-3,5-di-tert-butylphenyl)-2H-benzotriazole.

D is 5-butylsulfonyl-2-(2-hydroxy-3,5-di-tert-butylphenyl)-2H-benzotriazole.

E is 5-trifluoromethyl-2-(2-hydroxy-3,5-di-α–cumylphenyl)-2H-benzotriazole.

F is 2,2'-methylene-bis[6-(5-trifluoromethyl-2H-benzotriazol-2-yl)-4-tert-octylphenol].

G is 5-butylsulfonyl-2-(2-hydroxy-3-α–cumyl-5-tert-octylphenyl)-2H-benzotriazole;

H is 5-trifluoromethyl-2-(2-hydroxy-5-tert-octylphenyl)-2H-benzotriazole;

I is methyl 3-(5-trifluoromethyl-2H-benzotriazol-2-yl)-5-tert-butyl-4-hydroxyhydrocinnamate.

J is 5-methoxycarbonylmethylsulfinyl-2-(2-hydroxy-3,5-di-tert-butylphenyl)-2H-benzotriazole.

K is methyl 3-(5-phenylsulfonyl-2H-benzotriazol-2-yl)-5-tert-butyl-4-hydroxyhydrocinnamate.

L is 5-phenylsulfonyl-2-(2-hydroxy-3,5-di-tert-butylphenyl)-2H-benzotriazole.

M is 5-trifluoromethyl-2-(2-hydroxy-3-α–cumyl-5-tert-octylphenyl)-2H-benzotriazole.

N is 5-trifluoromethyl-2-(2-hydroxy-3,5-di-tert-octylphenyl)-2H-benzotriazole.

O is 5-trifluoromethyl-2-(2-hydroxy-3-α–cumyl-5-tert-butylphenyl)-2H-benzotriazole.

P is 2-(2-hydroxy-3-α–cumyl-5-tert-octylphenyl)-2H-benzotriazole.

Q is 5-chloro-2-(2-hydroxy-3-α–cumyl-5-tert-butylphenyl-2H-benzotriazole.

Example A4

Solubility in Adhesive of Benzotriazole Blends

Following the procedure of Example 3, the solubility in GELVA® 263 (Solutia) of various mixtures of benzotriazoles is determined. The results are seen in the table below.

Mixture of Compounds*	Solubility without Crystallization (%)
A	22.6
B	22.6

C	22.6
D	22.6

*A is 3:1 mixture by weight of 2-(2-hydroxy-3-α-cumyl-5-tert-octylphenyl)-2H-benzotriazole (TINUVIN® 928, Ciba) and 5-trifluoromethyl-2-(2-hydroxy-3-α-cumyl-5-tert-octylphenyl)-2H-benzotriazole.

B is 1:3 mixture by weight of 2-(2-hydroxy-3,5-di-α-cumylphenyl)-2H-benzotriazole (TINUVIN® 900, Ciba) and 5-trifluoromethyl-2-(2-hydroxy-3-α-cumyl-5-tert-octylphenyl)-2H-benzotriazole.

C is 1:3 mixture by weight of 5-chloro-2-(2-hydroxy-3,5-di-tert-butylphenyl)-2H-benzotriazole (TINUVIN® 327, Ciba) and 5-trifluoromethyl-2-(2-hydroxy-3-α-cumyl-5-tert-octylphenyl)-2H-benzotriazole.

D is 3:1 mixture by weight of 2-(2-hydroxy-3-α–cumyl-5-tert-octylphenyl)-2H-benzotriazole (TINUVIN® 928, Ciba) and 5-chloro-2-(2-hydroxy-3,5-di-tert-butylphenyl)-2H-benzotriazole (TINUVIN® 327, Ciba).

Example A5

Weathering Experiments

To ascertain the effect of durability and loss rate of various benzotriazole test compounds, the following test is carried out on adhesive compositions in selected articles.

GELVA® 263 (Solutia) adhesive is described in Example 3. A biaxially oriented poly(ethylene terephthalate) (PET) film is obtained from United States Plastics.

The GELVA® 263 is reduced 50% by dilution with ethyl acetate to a final resin solids content of 23%. The test compound is dissolved in the GELVA® 263 solution and samples are prepared in duplicate. The formulations seen in the table below are based on total coating solids. Approximately 8 micron coatings are applied to 1.5 inch glass discs for each formulation using a Headway Research Inc. Photo Resist Spinner (Model EC101DT) operating at 5000 rpm for 10 seconds. All formulations receive the same 80°C x 3 minute bake in a Hereaus model LUT 6050F oven operating at 3 air changes/minute.

Since the adhesive remains tacky even after baking a direct thickness measurement is not possible. Indirect film thickness is determined by creating an adhesive sandwich between to layers of PET film and comparing its thickness versus two PET sheets without adhesive using magnetic induction methodology.

The spin coating conditions are thus obtained. Further, since the spin coating conditions are not changed for applying the adhesive onto the glass, very little if any thickness variations are expected. After curing it in an oven, a layer of PET (ca 2 mils) is placed over the adhesive and pressed down.

Absorbance spectra are collected using a Perkin Elmer Lambda 19 Spectrophotometer running UVWINLAB software. Absorbance data are collected from 400-300 nm every half nanometer at a speed of 240 nm/minute and a slit width of 2 nm.

Weathering is done at a controlled irradiance at 6500 W. The cycle is as follows: 3.8 hours straight irradiance with no water spray, followed by one hour darkness. In the light cycle, the black panel temperature is controlled at 89°C. The chamber (dry bulb) temperature is 62°C in the light cycle. The relative humidity in the light cycle is in the range of 50-55% and in the dark cycle 95%. The chamber (dry bulb) temperature is 38°C in the dark cycle.

The test samples are placed in a Xenon Arc Weather-O-meter with the glass facing the Xenon lamp to emulate articles such as solar films. UV spectra are obtained at about 250 hour intervals. UV spectra are obtained at 500 hours and the samples are rotated to insure that all samples receive similar weathering conditions.

To follow the loss of the UV absorber from the adhesive composition, UV spectra measured initially and after weathering. The UV spectrophotometer measure absorbance linearly up to 5.5 absorbance units using a reference beam attenuation technique.

It is assumed that the degradation products for the UV absorber do not contribute to the UV spectrum. This is tested by following the ratio of absorbance of the band at 300 nm and the band at about 340 nm. The ratio does not change upon weathering the sample. This suggests that the UV spectrum of the weathered films correspond to the amount of UV absorber remaining in the film with very little if any contribution to the spectrum by the photodegradants.

The results after 893 hours exposure are given in the table below.

Compound(%)*	Initial Absorbance	Final Absorbance	Absorbance Loss
I (8%)	2.998	2.048	0.950
II(10%)	2.810	2.013	0.797
III (5%)	1.561	1.241	0.320
IV(10%)	2.181	1.904	0.277
IV (10%) + V (0.5%)	2.088	1.974	0.114

*% is the weight amount in formulation.

I is 2,2'-dihydroxy-4-methoxybenzophenone.

II is octyl 3-(2H-benzotriazol-2-yl)-5-tert-butyl-4-hydroxyhydrocinnamate.

III is 2-(2-hydroxy-3-α-cumyl-5-tert-octylphenyl)-2H-benzotriazole.

IV is 5-trifluoromethyl-2-(2-hydroxy-3-α-cumyl-5-tert-octylphenyl)-2H-benzotriazole.

V is bis(1-octyloxy-2,2,6,6-tetramethylpiperidin-4-yl) sebacate.

These data clearly show that the instant benzotriazole is especially durable in adhesives as measured by the low loss rate of absorbance values after exposure to actinic radiation. The instant benzotriazoles such as 2-(2-hydroxy-3-α–cumyl-5-tert-octylphenyl)-2H-benzotriazole even though not red-shifted as well as the red-shifted benzotriazoles are far superior to the benzophenones in adhesive compositions. Furthermore, the combination of the benzotriazoles with a hindered amine stabilizer offers quite superior performance. In summary, the instant benzotriazoles combine both great photostability and unexpectedly high solubility in adhesive systems.

Example A6

Weathering Experiments

In an experiment similar to Example 5, GELVA® 263 (Solutia) adhesive described in Example 3, which contains 8% by weight of a test compound, is placed between a sheet of glass and a biaxially oriented film of poly(ethylene terephthalate) (PET) described in Example 4. The structure is then exposed to weathering for 947 hours as described in Example 4.

The results are seen in the table below. Each test sample also contains 0.5% of the hindered amine bis(1-octyloxy-2,2,6,6-tetramethylpiperidin-4-yl) sebacate.

Compound(%)*	Initial Absorbance	Final Absorbance	Absorbance Loss
I (8%)	2.88	2.12	0.76
II(8%)	1.73	1.55	0.18
III(8%)	1.46	1.45	0.01
IV(8%)	1.96	1.59	0.37

*% is the weight amount in formulation.

I is 2,2'-dihydroxy-4-methoxybenzophenone.

II is methyl 3-(5-trifluoromethyl-2H-benzotriazol-2-yl)-5-tert-butyl-4-hydroxyhydrocinnamate.
III is 5-trifluoromethyl-2-(2-hydroxy-3-α-cumyl-5-tert-octylphenyl)-2H-benzotriazole.
IV is 2-(2-hydroxy-3-α–cumyl-5-tert-octylphenyl)-2H-benzotriazole.

These data clearly show that the instant benzotriazoles substituted at the 5-position of the benzo ring with an electron withdrawing moiety or an α-cumyl moiety in the ortho position of phenyl ring are especially durable in adhesives as measured by the low loss rate of absorbance values after exposure to actinic radiation. Additionally, it is seen that the red-shifted benzotriazoles are far superior to the benzophenones in adhesive compositions. Furthermore, the combination of the red-shifted benzotriazoles with a hindered amine stabilizer offers quite superior performance. In summary, the instant red-shifted benzotriazoles combine both great photostability and unexpectedly high solubility in adhesive systems.

Example A7

Windshield Interlayer Assembly

When an adhesive composition containing a benzotriazole UV absorber is placed between two sheets of glass, the assembly resembles a typical windshield. In this confined environment, there is no chance that the benzotriazole stabilizer can escape by volatility since the glass sheets provide a impervious container for the adhesive interlayer. The photostability and durability of the soluble benzotriazole stabilizer is now paramount. Benzotriazole UV absorbers whose structures causes them to be volatile and which precludes their use in other types of applications can be used in such windshield interlayer assemblies with impunity to achieve long lasting and stable windshield structures.

A windshield or windscreen prototype structure is exposed to weathering according to the procedure described in Example 5. The GELVA® 263 (Solutia) adhesive is placed between two sheets of glass and additionally contains 8% by weight of selected test UV absorbers. The structure is then exposed to weathering for 1338 hours as described in Example 5.

The results are seen in the table below. Each test sample contains only a UV absorber and no hindered amine coadditive.

Compound(%)*	Initial Absorbance	Final Absorbance	Absorbance Loss
I (8%)	2.69	0.85	1.84
II(8%)	2.24	1.54	0.70
III(8%)	1.81	1.02	0.79
IV(8%)			0.35

*% is the weight amount in formulation.
I is 2,2'-dihydroxy-4-methoxybenzophenone.
II is 5-trifluoromethyl-2-(2-hydroxy-5-tert-octylphenyl)-2H-benzotriazole.
III is methyl 3-(5-trifluoromethyl-2H-benzotriazol-2-yl)-5-tert-butyl-4-hydroxyhydrocinnamate.
IV is 2-(2-hydroxy-3-α–cumyl-5-tert-octylphenyl)-2H-benzotriazole.

These data clearly show that the instant benzotriazoles substituted at the 5-position of the benzo ring with an electron withdrawing moiety or an α-cumyl moiety in the ortho position of phenyl ring are especially durable in adhesives as measured by the low loss rate of absorbance values after exposure to actinic radiation. Additionally, it is seen that the red-shifted benzotriazoles are far superior to the benzophenones in adhesive compositions. In summary, the instant red-shifted benzotriazoles combine both great photostability and unexpectedly high solubility in adhesive systems.

Example A8

A windshield or windscreen prototype structure as described in Example 7 is exposed to weathering according to the procedure described in Example. The GELVA® 263 (Solutia) adhesive is placed between two sheets of glass and additionally contains 8% by weight of selected test UV absorbers. The structure is then exposed to weathering for 1338 hours as described in Example 5.

The results are seen in the table below. Each test sample also contains 0.5% of the hindered amine bis(1-octyloxy-2,2,6,6-tetramethylpiperidin-4-yl) sebacate.

Compound(%)*	Initial Absorbance	Final Absorbance	Absorbance Loss
I (8%)	3.69	2.89	0.80
II(8%)	2.06	1.85	0.21
III(8%)	1.45	1.21	0.24
IV (8%)	1.84	1.61	0.23
V (8%)	1.34	1.02	0.32

*% is the weight amount in formulation.
I is 2,2'-dihydroxy-4-methoxybenzophenone.
II is 5-trifluoromethyl-2-(2-hydroxy-5-tert-octylphenyl)-2H-benzotriazole.
III is 5-trifluoromethyl-2-(2-hydroxy-3-α-cumyl-5-tert-octylphenyl)-2H-benzotriazole.
IV is methyl 3-(5-trifluoromethyl-2H-benzotriazol-2-yl)-5-tert-butyl-4-hydroxyhydrocinnamate.
V is 5-n-butylsulfonyl-2-(2-hydroxy-3-α–cumyl-5-tert-octylphenyl)-2H-benzotriazole.

These data clearly show that the instant benzotriazoles substituted at the 5-position of the benzo ring with an electron withdrawing moiety are especially durable in adhesives as measured by the low loss rate of absorbance values after exposure to actinic radiation. Additionally, it is seen that the red-shifted benzotriazoles are far superior to the benzophenones in adhesive compositions. Furthermore, the combination of the red-shifted benzotriazoles with a hindered amine stabilizer offers quite superior performance. In summary, the instant red-shifted benzotriazoles combine both great photostability and unexpectedly high solubility in adhesive systems.

Example A9

The instant benzotriazole UV absorbers can be used in film and rigid plastic protective overlaminates for printed matter and photographs providing excellent photostability.

Example A10

The instant benzotriazole UV absorbers can be used in backlit displays to provide excellent long term stabilization.

Example 11

The instant benzotriazole UV absorbers can be used in semi-transparent and opaque window displays, signs and decals wherein a film or rigid plastic graphic is laminated to window glass to provide excellent long term stabilization.

Example A12

The instant benzotriazole UV absorbers can be used in clear/tinted anti-graffiti films used over class, metal or plastic substrates to provide excellent long term stabilization.

Example A13

The instant benzotriazoleUV absorbers can be used in clear anti-lacerative or "security" films used over or between layers of glass or polycarbonate to provide long term stabilization.

Example A14

The instant benzotriazole UV absorbers can be used in decorative and protective films and decals for painted surfaces such as on automobiles, buses, equipment and other exterior products to provide long term stabilization.

Examples B: Preparation and Use of Novel Benzotriazoles of Formula IIIc.

Example B1

5-Trifluoromethyl-2-(2-hydroxy-3-(di-n-butyl-
aminomethyl-5-tert-octylphenyl)-2H-benzotriazole

5-Trifluoromethyl-2-(2-hydroxy-5-tert-octylphenyl)-2H-benzotriazole (40.9 g, 0.104 mol), paraformaldehyde (3.65 g, 0.116 mol) and di-n-butylamine (28.2 g, 0.216 mol) are charged to a pressure reactor at ambient temperature. The reactor is sealed and the temperature is raied to 160°C. The reaction mass is held at 160°C for four hours and then discharged. The reactor is rinsed with toluene. The toluene, amine and water are stripped by rotary evaporation. This crude Mannich product is chromatographed on silica gel using a heptane/ethyl acetate gradient as eluent to remove a trace of unreacted starting benzotriazole intermiediate. The title compound is obtained as a yellow oil in 93% yield after chormatography.

Analysis:

^{1}Hnmr ($CDCl_3$): δ 0.79 (s, 9H); 0.88 (t, 6H); 1.32 (m, 4H); 1.40 (s, 6H); 1.52 (m, 4H); 1.75 (s, 2H); 2.55 (t, 4H); 3.90 (s, 2H); 7.18 (d, 1H); 7.60 (dd, 1H); 7.68 (d, 1H); 8.13 (dd, 1H); 8.35 (d, 1H).

Mass spectrometry: m/z 533 (M + H).

Example B2

Methylene-2-[4-tert-butyl-6-(5-phenylsulfonyl-
2H-benzotriazol-2-yl)phenol]-2'-[4-tert-octyl-
6-(5-trifluoromethyl-2H-benzotriazol-2-yl)phenol]

5-Phenylsulfonyl-2-(2-hydroxy-5-tert-butylphenyl)-2H-benzotriazole (6.8 g, 0.017 mol), sodium methoxide (0.99 g, 0.017 mol) and xylenes (20 g, 0.187 mol) are added to a reaction flask with is then heated to 160°C. The compound prepared in Example B1 (8.93 g, 0.0167 mol) dissolved in 8 g of xylenes is dripped into the reaction mass over a one-hour period. At the end of the addition, the reaction mass is heated to 205°C while distilling off xylene, methanol and di-n-butylamine. After one hour at 205°C, the reaction mass is subjected to a 26" Hg vacuum for three hours, After the vacuum is released, the reaction mass is cooled to 100°C and 50 g of xylenes are added. The solution is then washed with 25 g of 10% aqueous hydrochloric acid. After distilling off the solvent 15.5 g of crude product is obtained. This is chromatographed over silica gel using 15% ethyl acetate in heptane as eluent. The title compound is obtained as a solid in a yield of 6.6 g melting at 95-100°C.

Analysis:

^{1}Hnmr ($CDCl_3$): δ 0.72 (s, 9H); 1.35 (s, 9H); 1.42 (s, 6H); 1.76 (s, 2H); 4.31 (s, 2H); 7.44 (d, 2H); 7.55 (t, 2H); 7.61 (t, 1H); 7.68 (dd, 1H); 7.91 (dd, 1H); 8.03 (d, 2H); 8.04 (d, 1H); 8.08 (d, 1H); 8.31 (d, 1H); 8.32 (d, 2H);, 8.73 (d, 1H); 11.14 (s, 1H); 11.23 (s, 1H).

^{19}Fnmr ($CDCl_3$): -68.9 ppm.

Mass spectrometry: m/z 811 (M + H).

Example B3

Methylene-2-[4-tert-butyl-6-(5-chloro-2H-benzotriazol-2-yl)phenol]-2'-[4-tert-octyl-6-(5-trifluoromethyl-2H-benzotriazol-2-yl)phenol]

Using the procedure of Example B2 with 4.5 g of 5-chloro-2-(2-hydroxy-5-tert-butylphenyl)-2H-benzotriazole instead of the 5-phenylsulfonyl-2-(2-hydroxy-5-tert-butylphenyl)-2H-benzotriazole and keeping the same molar ratios of the reactants the same, 8.67 g of the title compound is obtained having a melting point of 32-44°C.

Analysis:

^{1}Hnmr ($CDCl_3$): δ 0.73 (s, 9H); 1.36 (s, 9H); 1.42 (s, 6H); 1.76 (s, 2H); 4.31 (s, 2H); 7.40 (d, 1H); 7.43 (d, 1H); 7.44 (dd, 1H); 7.68 (dd, 1H); 7.89 (d, 1H); 7.94 (d, 1H); 8.08 (d, 1H); 8.29 (d, 1H); 8.32 (d, 2H); 11.23 (s, 1H); 11.29 (s, 1H).

^{19}Fnmr ($CDCl_3$): -68.9 ppm.

Mass spectrometry: m/z 705 (M + H).

Example B4

Methylene-2-[4-tert-butyl-6-(5-phenylthio-2H-benzotriazol-2-yl)phenol]-2'-[4-tert-octyl-6-(5-trifluoromethyl-2H-benzotriazol-2-yl)phenol]

Using the procedure of Example B2 with 5.67 g of 5-phenylthio-2-(2-hydroxy-5-tert-butylphenyl)-2H-benzotriazole instead of the 5-phenylsulfonyl-2-(2-hydroxy-5-tert-butyl-phenyl)-2H-benzotriazole and keeping the same molar ratios of the reactants the same, 5.97 g of the title compound is obtained having a melting point of 49-65°C.

Analysis:

^{1}Hnmr ($CDCl_3$): δ 0.72 (s, 9H); 1.34 (s, 9H); 1.41 (s, 6H); 1.75 (s, 2H); 4.30 (s, 2H); 7.34-7.52 (m, 3H); 7.37 (d, 1H); 7.39 (dd, 1H); 7.43 (d, 1H); 7.50 (d, 2H); 7.68 (d, 1H); 7.73 (d, 1H); 7.84 (d, 1H); 8.08 (d, 1H); 8.26 (d, 1H); 8.31 (d, 1H); 8.32 (d, 1H); 11.20 (s, 1H); 11.36 (s, 1H).

^{19}Fnmr ($CDCl_3$): -68.9 ppm.

Mass spectrometry: m/z 779 (M + H).

Example B5

2,2'-Methylene-bis[6-(5-phenylsulfonyl-2H-benzotriazol-2-yl)-4-tert-butylphenol]

5-Phenylsulfonyl-2-(2-hydroxy-5-tert-butylphenyl)-2H-benzotriazole (15 g, 0.037 mol), paraformaldehyde (0.63 g, 0.019 mol) and di-n-butylamine (5.0 g, 0.386 mol) are charged to a reactor which is then sealed. The temperature is increased to 110°C at which time sodium methoxide (0.33 g, 0.0069 mol) is added. The reaction mixture is then heated to 205°C and held there for three hours, The reaction mass is then cooled to 110°C and 100 mL of xylenes are added. The reaction mass is neutralized with 10% aqueous hydrochloric acid and the organic phase is twice washed with water. The xylene phase is filtered through a plug of silica gel and is then distilled. The crude Mannich product is recrystallized twice from heptane to yield 8.3 g of the title compound having a melting point of 224-234°C.

Analysis:

^{1}Hnmr ($CDCl_3$): δ 1.40 (s, 18H); 4.30 (s, 2H); 7.50 (d, 2H); 7.55 (t, 4H); 7.61 (t, 4H); 7.91 (dd, 2H); 8.04 (m, 6H); 8.30 (d, 2H); 8.73 (d, 2H); 11.12 (s, 2H).

Mass spectrometry: m/z 827 (M + H).

Example B6

Bisbenzotriazole Solubility in Adhesive

To measure the solubility of the instant bisbenzotriazole UV absorber in an adhesive composition, the compound is added to a typical adhesive GELVA® 263 (Solutia) which is a 44.5% solution of a polyacrylate in a mixture of ethyl acetate and hexane. The polyacrylate is a copolymer of methyl methacrylate, 2-ethylhexyl methacrylate and glycidyl methacrylate.

The test compound is dissolved in 5 mL of ethyl acetate, toluene or a mixture of ethyl acetate and toluene. To the solution is added 5 g of GELVA® 263. 2-3 mL of the resulting solution is place into individual watch glasses. Solubility is then evaluated based upon observed crystallization once the solvent has evaporated. Observations start after several hours and then continue over a period of several weeks.

The solubility values given in the table below are approximate maximum concentrations where no sign of subsequent crystallization is evident. Solubilities are reported in weight of total bisbenzotriazole added to GELVA® 263 as is. From these data, it is clear that some of the instant bisbenzotriazoles are considerably more soluble in adhesives, in this case GELVA® 263, than some bisbenzotriazoles of the prior art. The use of many UV absorbers in adhesive compositions has been limited in the past by the limited solubility and compatibility of some UV absorber compounds.

By using the selected instant bisbenzotriazoles, the use levels for the UV absorber can be raised substantially to add greatly to increased stabilization protection afforded by the instant compound. This is further augmented by the excellent photostability and red-shifted nature of the instant bisbenzotriazoles.

Compound*	Trade Name or Class	Solubility without Crystallization (%)
A	bisbenzotriazole	0.0
B	TINUVIN® 900	2.0
C	TINUVIN® 327	2.0
D	bisbenzotriazole	2.0
E	bisbenzotriazole	4.0
F	bisbenzotriazole	11.0
G	bisbenzotriazole	22.0
H	bisbenzotriazole	22.0

*A is comparative symmetrical bisbenzotriazole compound of Example 5, generically disclosed in German 1,670,951.

B is 2-(2-hydroxy-3,5-di-α-cumylphenyl)-2H-benzotriazole.

C is 5-chloro-2-(2-hydroxy-3,5-di-tert-butylphenyl)-2H-benzotriazole.

D is methylene-2-[4-tert-octyl-6-(2H-benzotriazol-2-yl)phenol]-2'-[4-tert-octyl-6-(5-trifluoromethyl-2H-benzotriazol-2-yl)phenol].
E is 2,2'-methylene-bis[6-(5-trifluoromethyl-2H-benzotriazol-2-yl)-4-tert-octylphenol].
F is instant asymmetrical bisbenzotriazole compound of Example 3.
G is instant asymmetrical bisbenzotriazole compound of Example 2.
H is instant asymmetrical bisbenzotriazole compound of Example 4.

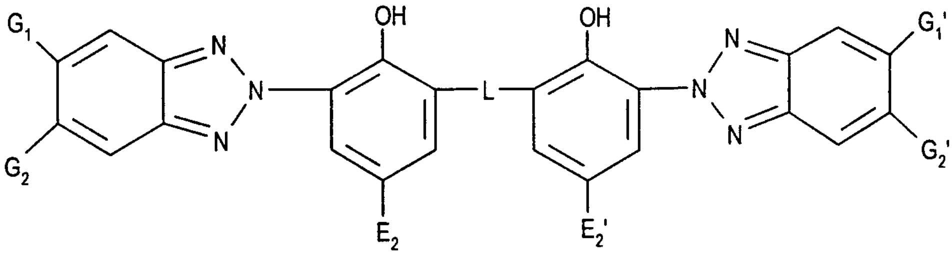
Example B7

Methylene-2-[4-(2-methoxycarbonylethyl)-6-(5-chloro-2H-benzotriazol-2-yl)phenol]-2'-[4-tert-octyl-6-(5-trifluoromethyl-2H-benzotriazol-2-yl)phenol]

Following the general synthetic procedures outlined in Examples B1 and B2, or disclosed in EP 924,203 A1, the title compound is prepared.

Examples B8-B30

Following the general synthetic procedures outlined in Examples 1 and 2, the following compounds of formula I are prepared.



(I)

Ex*	G_2	E_2	E_2'	L	G_3 or E_3
8	F	CH_3	t-Bu	$-CH_2-$	-
9	F	t-Oc	t-Oc	$-CH_2-$	-
10	Cl	Do	CH_3	m-Xy	-
11	Cl	t-Bu	t-Bu	$-CH_2-$	-
12	$PO(Ph)_2$	Do	Do	$-CH_2-$	-
13	$COOG_3$	Cu	Bu	p-Xy	CH_3
14	$COOG_3$	CH_3	CH_3	$-CH_2-$	Octad
15	$COOG_3$	t-Oc	CH_3	$-CH_2-$	Benz
16	$CONHG_3$	$C_{24}H_{49}$	Bu	$-CH_2-$	Bu
17	$CON(G_3)_2$	Do	Hept	$-CH_2-$	Al
18	CN	t-Oc	t-Bu	$-CH_2-$	-
19	CN	Cu	Do	$-CH_2-$	-
20	E_3SO	CH_3	Cu	$-CH_2-$	Bu
21	E_3S	CH_3	t-Bu	$-CH_2-$	Do
22	E_3SO_2	MeOCOEt	t-Bu	$-CH_2-$	Ph
23	E_3SO_2	MeOCOEt	MeOCOEt	$-CH_2-$	Oc

24	E_3SO_2	t-Bu	t-Bu	-CH_2-	HOEt
25	Cl	AlOCOEt	CH_3	-CH_2-	-
26	Cl	OcOCOEt	Oc	-CH_2-	-
27	Cl	AlOCOEt	AlOCOEt	-CH_2-	-
28	Cl	MeAcOEt	CH_3	-CH_2-	-
29	Cl	Do	MeAcOEt	-CH_2-	-
30	Cl	HOPr	HOPr	-CH_2-	-

*G_1 is always hydrogen except in Example 9 where it is F and in Examples 10-11 where it is Cl.

G_1' is always hydrogen except in Example 11 where it is Cl.

G_2' is always CF_3 except in Example 10 where it is C_8F_{17} and in Example 11 where it is C_2F_5.

Al is allyl, AlOCOEt is CH_2=CH-$CH_2$0COCH_2CH_2, Benz is benzyl, Bu is butyl, t-Bu is tert-butyl, Cu is α-cumyl, Do is dodecyl, Hept is heptyl, HOEt is $HOCH_2CH_2$, HOPr is $HOCH_2CH_2CH_2$, MeAcOEt is CH_2=C(CH_3)$COOCH_2CH_2$, MeOCOEt is $CH_3OCOCH_2CH_2$, Oc is octyl, t-Oc is tert-octyl, OcOCOEt is $C_8H_{17}OCOCH_2CH_2$, Octad is octadecyl, Ph is phenyl, m-Xy is α,α,α',α'-tetramethyl-m-xylylene and p-Xy is α,α,α',α'-tetramethyl-p-xylylene.

Example 31

Polycarbonate

The durability of the instant benzotriazoles in thermoplastic substrates is determined by incorporating various test compounds into solvent cast films of polycarbonate resins. The free standing films are mounted into cardboard holders, secured in metal frames and exposed in an Atlas C165 Xenon-arc Weather-Ometer under dry conditions according to ASTM G26 for 1100 and 2200 hour exposure. Loss of UV absorber is determined by monitoring the loss of diagnostic UV absorption as described earlier. Performance is measured by a change in color or the physical integrity of the film.

Polycarbonate flake (LEXAN® 145, General Electric) is dissolved in methylene chloride at room temperature along with between 1 and 3% by weight of test benzotriazole, based on the polycarbonate. Films are cast using a calibrated drawdown bar to prepare 1 mil thick film after drying.

There is an increase in durability obtained with a benzotriazole substituted on the 5-position of the benzo ring with a trifluoromethyl moiety.

Example 32

Pigmented Polyacetal

The following example shows an improvement in color protection of a pigmented polyacetal formulation for a bisbenzotriazole substituted on the 5-position of the benzo ring with a trifluoromethyl moiety.

The test additives are dry blended with polyacetal pellets (DELRIN® 500P NC010, DuPont) using a Turbula mixer. The dry blend is extruded and pelletized using a twin screw extruder at a melt temperature of about 410°F (210°C). The pellets are molded into test plaques (2" x 2" x 0.060") using an injection molder operated at 410-420°F (204-216°C). The plaques are exposed in a Xenon-arc Weather-Ometer according to automotive test procedure SAE J1885. Exposure is measured in terms of the total irradiation, measured in kilojoules per square meter (kJ/m^2). Color change in the exposed samples is determined by measuring the color of the exposed samples compared to the unexposed samples as color difference (ΔE) according to ASTM D2244.

Example 33

Poly(butylene terephthalate)

The following example illustrates the superior performance of a bisbenzotriazole substituted on the 5-position of the benzo ring with a trifluoromethyl group in protecting poly(butylene terephthalate) as measured by gloss retention.

The test additives are dry blended with poly(butylene terephthalate) pellets (VALOX® 315-1001, General Electric) using a Turbula mixer. The dry blends are extruded and pelletized using a twin screw extruder at 465-490°C. The pellets are molded into test plaques (2" x 2" x 0.060") using an injection molder operated at 475-515°F (246-268°C). The plaques are exposed in a Xenon arc Weather-Ometer according to ASTM G26 test method A. Gloss is measure at 60° on the unexposed and exposed samples using a glossmeter according to ASTM D523. Gloss retention % = (gloss exposed sample/gloss of unexposed sample) x 100.

Example 34

Polystyrene

Polystyrene films (crystalline polystyrene obtained from Chevron, free of zinc stearate and mineral oil) are solvent case from solutions in methylene chloride. These films are exposed to UV light as described in Example 31. The samples contain no hindered amine stabilizer and are monitored for color change after 1000 hours exposure, for loss of UV absorber and for physical integrity (cracking or catastrophic film failure).

Example 35

Poly(methyl methacrylate)

The durability of the instant benzotriazoles in thermoplastic substrates is determined by incorporating various test compounds into solvent cast films of a poly(methyl methacrylate) resin. The free standing films are mounted into cardboard holders, secured in metal frames and exposed in an Atlas C165 Xenon-arc Weather-Ometer under dry conditions according to ASTM G26 for 1100 and 2200 hour exposure. Loss of UV absorber is determined by monitoring the loss of diagnostic UV absorption as described earlier. Performance is measured by a change in color or the physical integrity of the film, or in loss of absorbance of the UV absorber at λmax.

Poly(methyl methacrylate), medium molecular weight, Aldrich, is dissolved in methylene chloride at room temperature along with between 1 and 3% by weight of test benzotriazole, based on the PMMA resin. Films are cast using a calibrated drawdown bar to prepare 1 mil thick film after drying.

There is an increase in durability obtained with a bisbenzotriazole substituted on the 5-position of the benzo ring with a trifluoromethyl moiety.

Example 36

Polyurethane

An acrylic polyol (RK 4037, DuPont) which is 75% solids in methyl amyl ketone is used in these experiments. The molecular weight is 7000-9000 and the OH number is 145. To 595 g of the acrylic polyol are added 26.2 g of butyl acetate, 5.8 g of ethyl acetate and 0.4 g of 50% strength FC 439 (flow control aid, 3M). Bis(1-octylocy-2,2,6,6-tetramethylpiperidin-4-yl) sebacate (0.75 g TINUVIN®123, Ciba), 1% by weight based on resin solids, is added to the mixture. To 2.43 g of the above mixture is added 0.9 g of DESMODUR®N-3390 (Bayer), an aliphatic polyisocyanate, 90% solids. The UV absorber is incorporated into the acrylic polyol component. The polyurethane formed is applied as a coating onto a quartz disc by spin coating at 1000 rpm for two seconds. The wet coating is cured at 260°F (127°C) for 30 minutes.

UV spectra are collected using a λ-9 spectrophotometer from Perkin Elmer every half nm at 120 nm/min using a slit width of 2 nm.

Loss rates are measured from a 1.4 mil coating. The absorbance of the long wavelength UV absorbance band is around 2.3 before weathering. Weathering is done according to SAE J-1960 (exterior automotive weathering conditions): 0.55 watts/sq. in. at 340 nm using inner and outer borosilicate filters, 40' straight irradiance with no water spray; 20' light plus front spray; 60' light and 60' dark plus rear spray (condensation). Black panel temperature in light cycle is 70±2°C and relative humidity of 50-55% in light cycle and 100%

in dark cycle. The loss of long wavelength absorbance band is followed after approximately every 200 hours.

This test shows that the instant bisbenzotriazoles are especially durable in polyurethane films as judged by low loss rates.

Example 37

Poly(vinyl chloride)

Poly(vinyl chloride) (PVC) films of GEON® 27 (Geon Co.) are solvent cast as described in Example 31 in warm tetrahydrofuran (THF) and then exposed in an Atlas C165 Weather-Ometer as described in Example 31.

This test shows that the instant bisbenzotriazoles are especially durable in PVC films as judged by low loss rates.

Example 38

Coating Composition

A high solids thermoset acrylic clear coat is prepared by mixing an experimental acrylic polyol resin and hexamethoxymethylmelamine (Resimene® 747, Monsanto) at a solids ratio of 60/40. The dodecylbenzene sulfonic acid catalyst (Nacure®5225; King Industries) is added at 0.70% by weight. A flow aid Modaflow® (Monsanto) is added at 0.25% by weight to form a model acrylic melamine resin system.

The model clear coat is reduced with xylene to a viscosity of 26-27 second using a Zahn #2 cup and applied via a conventional air spray at 50 psi (3.5 Kg/cm^2) over a 1" x 3" (2.54 cm x 7.62 cm) quartz slide. Cure is achieved by baking the slide for 30 minutes at 260°F (127°C). The clear coat is stabilized with 1% by weight of a hindered amine light stabilizer, bis-(1-octyloxy-2,2,6,6-tetramethylpiperidin-4-yl) sebacate, (TINUVIN® 123, Ciba). The various test benzotriazole UV absorbers are incorporated at the 5 mmol % by weight in the clear coat. The film thickness on the quartz slides range from 1.15 to 1.41 mils (0.029 to 0.036 mm).

The films on the quartz slides are weathered according to the following conditions in Xenon Arc Weather-Ometer with a controlled irradiance at 6500 W, using inner quartz and outer borosilicate S-type filter. The irradiation cycle is as follows: 40 minutes of straight irradiation with no water spray, followed by 20 minutes of light plus front spray, followed by 60 minutes of light irradiation and finally by 60 minutes dart plus rear spray (condensation). The setting is at 0.55 W/M^2 at 340 nm, 1.98 kJ/hour. In the light cycle the black panel temperature is controlled at 70±2°C. The relative humidity in the light cycle is in the range of 50-55% and in the dark cycle 100%. The absorbance of the long wavelength UV band as a function of Xenon arc weathering hours are recorded.

To follow the loss of UV absorbers from the clear coats, UV spectra are measured initially and after weathering at regular time intervals. The UV spectrophotometer measures absorbance linearly up to 5.5 absorbance units using a reference beam attenuation technique.

It is assumed that the degradation products from the UV absorber do not contribute to the UV spectrum. This is tested by following the ratio of absorbance of the band at about 300 nm and the band at about 340 nm. The ratio does not change upon weathering the sample, This suggests that the UV spectrum of the weathered films correspond to the amount of UV absorber remaining in the film with very little if any contribution to the spectrum by photo degradants.

Representative bisbenzotriazole test compounds are incorporated into a high solid thermoset acrylic melamine resin at concentrations between 1.93 and 3% by weight to give equal molar concentrations of the test benzotriazole in equal film thickness and sufficient to give a starting absorbance of approximately 2.0 absorbance units. The test samples are exposed for 2000 hours.

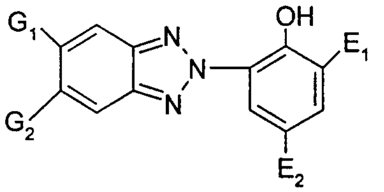
The test shows that the instant bisbenzotriazoles are especially durable in automotive coatings as judged by low loss rates.

Claims

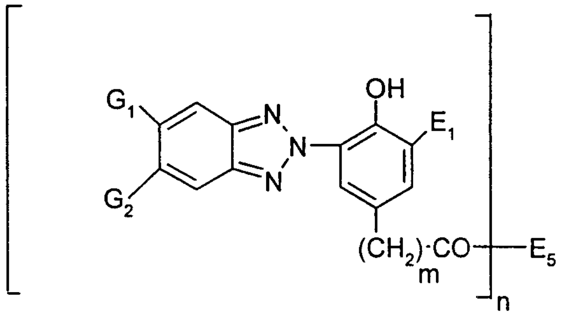
1. A stabilized adhesive composition, suitable for use as an adhesive layer in a laminated article or multilayer construction, which comprises

(a) an adhesive; and

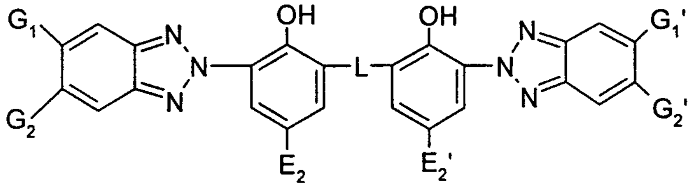
(b1) a highly soluble, red-shifted, photostable benzotriazole of formula I, II or III



(I)



(II)



(III) or

(b2) a highly soluble and photostable benzotriazole which is 2-(2-hydroxy-3-α-cumyl-5-tert-octylphenyl)-2H-benzotriazole or 2-(2-hydroxy-3-α-cumyl-5-tert-butylphenyl)-2H-benzotriazole; or

a combination of the compounds according to (b1) and (b2);
wherein

G_1 and G_1' are independently hydrogen or halogen,

G_2 and G_2' are independently halogen, nitro, cyano, perfluoroalkyl of 1 to 12 carbon atoms, $-COOG_3$, $-P(O)(C_6H_5)_2$, $-CO-G_3$, $-CO-NH-G_3$, $-CO-N(G_3)_2$, $-N(G_3)-CO-G_3$, E_3SO- or E_3SO_2-; or G_2' is also hydrogen,

G_3 is hydrogen, straight or branched chain alkyl of 1 to 24 carbon atoms, straight or branched chain alkenyl of 2 to 18 carbon atoms, cycloalkyl of 5 to 12 carbon atoms, phenylalkyl of 7 to 15 carbon atoms, phenyl, or said phenyl or said phenylalkyl substituted on the phenyl ring by 1 to 4 alkyl of 1 to 4 carbon atoms,

G_6 is perfluoroalkyl of 1 to 12 carbon atoms,

G_7 is hydrogen or perfluoroalkyl of 1 to 12 carbon atoms,

E_1 is hydrogen, straight or branched chain alkyl of 1 to 24 carbon atoms, straight or branched chain alkenyl of 2 to 24 carbon atoms, cycloalkyl of 5 to 12 carbon atoms, phenylalkyl of 7 to 15 carbon atoms, phenyl, or said phenyl or said phenylalkyl substituted on the phenyl ring by 1 to 4 alkyl of 1 to 4 carbon atoms; or E_1 is alkyl of 1 to 24 carbon atoms substituted by one or two hydroxy groups,

E_2 and E_2' are independently straight or branched alkyl chain of 1 to 24 carbon atoms, straight or branched chain alkenyl of 2 to 18 carbon atoms, cycloalkyl of 5 to 12 carbon atoms, phenylalkyl of 7 to 15 carbon atoms, phenyl, or said phenyl or said phenylalkyl substituted on the phenyl ring by one to three alkyl of 1 to 4 carbon atoms; or E_2 and E_2' are independently said alkyl of 1 to 24 carbon atoms or said alkenyl of 2 to 18 carbon atoms substituted by one or more -OH, $-OCOE_{11}$, $-OE_4$, -NCO, $-NH_2$, $-NHCOE_{11}$, $-NHE_4$ or $-N(E_4)_2$, or mixtures thereof, where E_4 is straight or branched chain alkyl of 1 to 24 carbon atoms; or said alkyl or said alkenyl interrupted by one or more -O-, -NH- or $-NE_4-$ groups or mixtures thereof and which can be unsubstituted or substituted by one or more -OH, $-OE_4$ or $-NH_2$ groups or mixtures thereof;

n is 1 or 2,

when n is 1, E_5 is OE_6 or NE_7E_8, or

E_5 is $-PO(OE_{12})_2$, $-OSi(E_{11})_3$ or $-OCO-E_{11}$,

or straight or branched chain C_1-C_{24}alkyl which is interrupted by -O-, -S- or $-NE_{11}$ and which can be unsubstituted or substituted by -OH or $-OCO-E_{11}$, C_5-C_{12} cycloalkyl which is unsubstituted or substituted by -OH, straight chain or branched C_2-C_{18}alkenyl which is unsubstituted or substituted by -OH, C_7-C_{15}aralkyl, $-CH_2-CHOH-E_{13}$ or glycidyl,

E_6 is hydrogen, straight or branched chain C_1-C_{24}alkyl which is unsubstituted or substituted by one or more OH, OE_4 or NH_2 groups, or $-OE_6$ is $-(OCH_2CH_2)_wOH$ or $-(OCH_2CH_2)_wOE_{21}$where w is 1 to 12 and E_{21} is alkyl of 1 to 12 carbon atoms,

E_7 and E_8 are independently hydrogen, alkyl of 1 to 18 carbon atoms, straight or branched chain C_3-C_{18}alkyl which is interrupted by -O-, -S- or $-NE_{11}-$, C_5-C_{12}cycloalkyl, C_6-C_{14}aryl or C_1-C_3hydroxylalkyl, or E_7 and E_8 together with the N atom are a pyrrolidine, piperidine, piperazine or morpholine ring,

E_5 is $-X-(Z)_p-Y-E_{15}$

wherein

X is -O- or $-N(E_{16})-$,

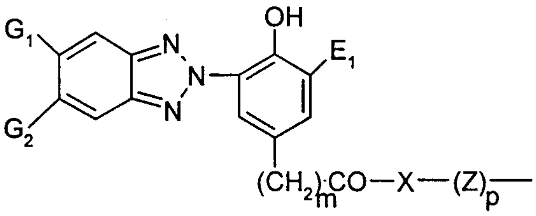
Y is -O- or $-N(E_{17})-$,

Z is C_2-C_{12}-alkylene, C_4-C_{12}-alkylene interrupted by one to three nitrogen atoms, oxygen atoms or a mixture thereof, or is C_3-C_{12}-alkylene, butenylene, butynylene, cyclohexylene or phenylene, each substituted by a hydroxyl group,

m is zero, 1 or 2,

p is 1, or p is also zero when X and Y are $-N(E_{16})-$ and $-N(E_{17})-$, respectively,

E_{15} is a group $-CO-C(E_{18})=C(H)E_{19}$ or, when Y is $-N(E_{17})-$, forms together with E_{17} a group -CO-CH=CH-CO-, wherein E_{18} is hydrogen or methyl, and E_{19} is hydrogen, methyl or $-CO-X-E_{20}$, wherein E_{20} is hydrogen, C_1-C_{12}-alkyl or a group of the formula

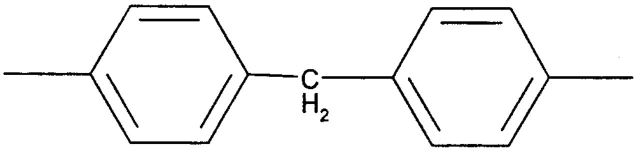


wherein the symbols E_1, G_2, X, Z, m and p have the meanings defined above, and E_{16} and E_{17} independently of one another are hydrogen, C_1-C_{12}-alkyl, C_3-C_{12}-alkyl interrupted by 1 to 3 oxygen atoms, or is cyclohexyl or C_7-C_{15}aralkyl, and E_{16} together with E_{17} in the case where Z is ethylene, also forms ethylene,

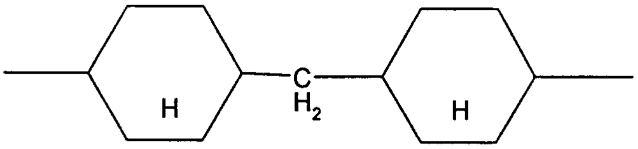
when n is 2, E_5 is one of divalent radicals -O-E_9-O- or -N(E_{11})-E_{10}-N(E_{11})- ,

E_9 is C_2-C_8alkylene, C_4-C_8alkenylene, C_4alkynylene, cyclohexylene, straight or branched chain C_4-C_{10}alkylene which is interrupted by -O- or by -CH_2-CHOH-CH_2-O-E_{14}-O-CH_2-CHOH-CH_2-,

E_{10} being straight or branched chain C_2-C_{12}alkylene which may be interrupted by -O-, cyclohexylene, or

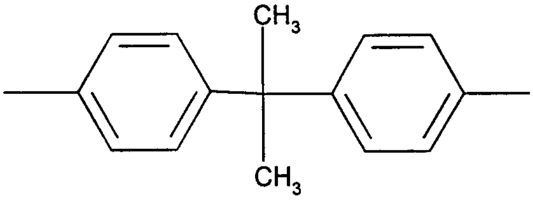


or

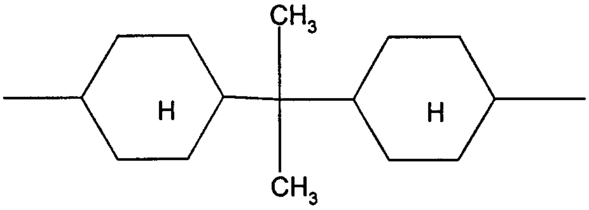


or E_{10} and $E_{11}$with the two nitrogen atoms form a piperazine ring,

E_{14} is straight or branched chain C_2-C_8alkylene, straight or branched chain C_4-C_{10}alkylene which is interrupted by -O-, cycloalkylene, arylene or



or



where E_7 and E_8 are independently hydrogen, alkyl of 1 to 18 carbon atoms or E_7 and E_8 together are alkylene of 4 to 6 carbon atoms, 3-oxapentamethylene, 3-iminopentamethylene or 3-methyliminopentamethylene,

E_{11} is hydrogen, straight or branched chain C_1-C_{18}alkyl, C_5-C_{12}cycloalkyl, straight or branched chain C_2-C_{18}alkenyl, C_6-C_{14}aryl or C_7-C_{15}aralkyl,

E_{12} is straight or branched chain C_1-C_{18}alkyl, straight or branched chain C_3-C_{18}alkenyl, C_5-C_{10}cycloalkyl, C_6-C_{16}aryl or C_7-C_{15}aralkyl,

E_{13} is H, straight chain or branched C_1-C_{18}alkyl which is substituted by -PO(OE_{12})$_2$, phenyl which is unsubstituted or substituted by OH, C_7-C_{15}aralkyl or -CH_2OE_{12},

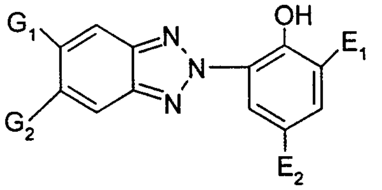
E_3 is alkyl of 1 to 20 carbon atoms, hydroxyalkyl of 2 to 20 carbon atoms, alkyl substituted by alkoxycarbonyl of 2 to 9 carbon atoms, alkenyl of 3 to 18 carbon atoms, cycloalkyl of 5 to 12 carbon atoms, phenylalkyl of 7 to 15 carbon atoms, aryl of 6 to 10 carbon atoms or said aryl substituted by one or two alkyl of 1 to 4 carbon atoms or 1,1,2,2-tetrahydroperfluoroalkyl where the perfluoroalkyl moiety is of 6 to 16 carbon atoms, and

L is alkylene of 1 to 12 carbon atoms, alkylidene of 2 to 12 carbon atoms, benzylidene, p-xylylene, a,a,a',a'-tetramethyl-m-xylylene or cycloalkylidene.

2. A composition according to claim 1, wherein the benzotriazole (b1) of formula I, II or III and the benzotriazoles (b2) exhibit enhanced durability and low loss of absorbance when exposed to actinic radiation as witnessed by an absorbance loss of less than 0.5 absorbance units after exposure for 893 hours or less than 0.8 absorbance units after

exposure for 1338 hours in a Xenon Arc Weather-Ometer.

3. A composition according to claim 1 wherein the benzotriazole compound of formula I is



(I)

wherein

G_1 is hydrogen,

G_2 is cyano, chloro, fluoro, CF_3-, -CO-G_3, E_3SO- or E_3SO_2-,

G_3 is straight or branched chain alkyl of 1 to 24 carbon atoms, straight or branched chain alkenyl of 2 to 18 carbon atoms, cycloalkyl of 5 to 12 carbon atoms, phenylalkyl of 7 to 15 carbon atoms, phenyl, or said phenyl or said phenylalkyl substituted on the phenyl ring by 1 to 4 alkyl of 1 to 4 carbon atoms,

E_1 is phenylalkyl of 7 to 15 carbon atoms, phenyl, or said phenyl or said phenylalkyl substituted on the phenyl ring by 1 to 4 alkyl of 1 to 4 carbon atoms,

E_2 is straight or branched alkyl chain of 1 to 24 carbon atoms, straight or branched chain alkenyl of 2 to 18 carbon atoms, cycloalkyl of 5 to 12 carbon atoms, phenylalkyl of 7 to 15 carbon atoms, phenyl, or said phenyl or said phenylalkyl substituted on the phenyl ring by 1 to 3 alkyl of 1 to 4 carbon atoms; or E_2 is said alkyl of 1 to 24 carbon atoms or said alkenyl of 2 to 18 carbon atoms substituted by one or more -OH, -OCOE$_{11}$, -OE$_4$, -NCO, -NH$_2$, -NHCOE$_{11}$, -NHE$_4$ or -N(E$_4$)$_2$, or mixtures thereof, where E_4 is straight or branched chain alkyl of 1 to 24 carbon atoms; or said alkyl or said alkenyl interrupted by one or more -O-, -NH- or -NE$_4$- groups or mixtures thereof and which can be unsubstituted or substituted by one or more -OH, -OE$_4$ or -NH$_2$ groups or mixtures thereof;

E_3 is alkyl of 1 to 20 carbon atoms, hydroxyalkyl of 2 to 20 carbon atoms, alkenyl of 3 to 18 carbon atoms, cycloalkyl of 5 to 12 carbon atoms, phenylalkyl of 7 to 15 carbon atoms, aryl of 6 to 10 carbon atoms or said aryl substituted by one or two alkyl of 1 to 4 carbon atoms or 1,1,2,2-tetrahydroperfluoroalkyl where the perfluoroalkyl moiety is of 6 to 16 carbon atoms; or

is a compound of formula I wherein,

G_1 is hydrogen,

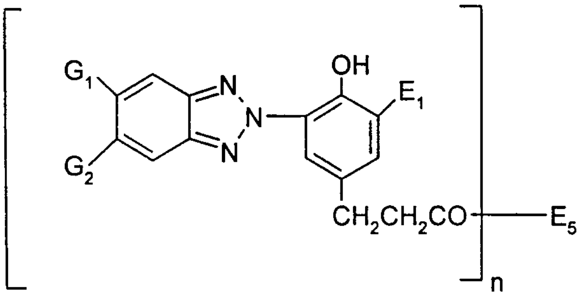
G_2 is chloro, fluoro, CF_3-, E_3SO- or E_3SO_2-,

E_1 is hydrogen or straight or branched alkyl of 1 to 24 carbon atoms,

E_2 is as defined above, and

E_3 is straight or branched chain alkyl of 1 to 7 carbon atoms.

4. A composition according to claim 1 wherein the benzotriazole compound is a compound of formula IIA



(IIA)

wherein

G_1 is hydrogen,

G_2 is is CF_3- or fluoro,

E_1 is hydrogen, straight or branched alkyl of 1 to 24 carbon atoms or phenylalkyl of 7 to 15 carbon atoms,

E_5 is $-OE_6$ or $-NE_7E_8$, or

E_5 is $-X-(Z)_p-Y-E_{15}$

wherein

X is -O- or $-N(E_{16})-$,

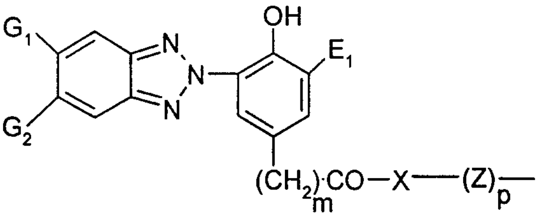
Y is -O- or $-N(E_{17})-$,

Z is C_2-C_{12}-alkylene, C_4-C_{12}-alkylene interrupted by one to three nitrogen atoms, oxygen atoms or a mixture thereof, or is C_3-C_{12}-alkylene, butenylene, butynylene, cyclohexylene or phenylene, each substituted by a hydroxyl group,

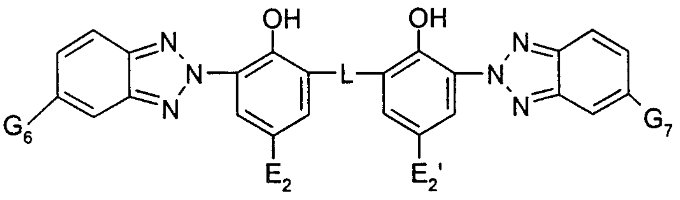
m is 0, 1, 2 or 3,

p is 1, or p is also zero when X and Y are $-N(E_{16})-$ and $-N(E_{17})-$, respectively,

E_{15} is a group $-CO-C(E_{18})=C(H)E_{19}$ or, when Y is $-N(E_{17})-$, forms together with E_{17} a group -CO-CH=CH-CO-, wherein E_{18} is hydrogen or methyl, and E_{19} is hydrogen, methyl or $-CO-X-E_{20}$, wherein E_{20} is hydrogen, C_1-C_{12}-alkyl or a group of the formula.



5. A composition according to claim 1 wherein the benzotriazole is a compound of formula IIIA



(IIIA)

wherein

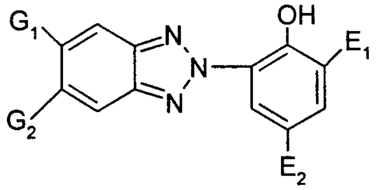
G_6 is CF_3,

G_7 is hydrogen or CF_3,

E_2 and E_2' are independently straight or branched alkyl chain of 1 to 24 carbon atoms, straight or branched chain alkenyl of 2 to 18 carbon atoms, cycloalkyl of 5 to 12 carbon atoms, phenylalkyl of 7 to 15 carbon atoms, phenyl, or said phenyl or said phenylalkyl substituted on the phenyl ring by 1 to 3 alkyl of 1 to 4 carbon atoms; and

L is alkylene of 1 to 12 carbon atoms, alkylidene of 2 to 12 carbon atoms, benzylidene, p-xylylene, a,a,a',a'-tetramethyl-m-xylylene or cycloalkylidene.

6. A composition according to claim 1 wherein the benzotriazole is a compound of formula I



(I)

wherein

G_1 is hydrogen,

G_2 is CF_3-,

E_1 is phenylalkyl of 7 to 15 carbon atoms, phenyl, or said phenyl or said phenylalkyl substituted on the phenyl ring by 1 to 4 alkyl of 1 to 4 carbon atoms,

E_2 is straight or branched alkyl chain of 1 to 24 carbon atoms, straight or branched chain alkenyl of 2 to 18 carbon atoms, cycloalkyl of 5 to 12 carbon atoms, phenylalkyl of 7 to 15 carbon atoms, phenyl, or said phenyl or said phenylalkyl substituted on the phenyl ring by 1 to 3 alkyl of 1 to 4 carbon atoms; or E_2 is said alkyl of 1 to 24 carbon atoms or said alkenyl of 2 to 18 carbon atoms substituted by one or more -OH, $-OCOE_{11}$, $-NH_2$ or $-NHCOE_{11}$, or mixtures thereof, or said alkyl or said alkenyl interrupted by one or more -O- and which can be unsubstituted or substituted by one or more -OH; or

is a compound of formula I
wherein,

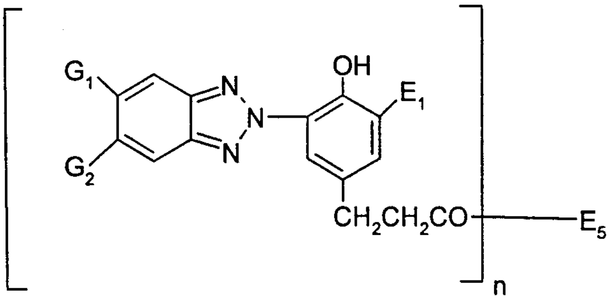
G_1 is hydrogen,

G_2 is CF_3-,

E_1 is hydrogen, straight or branched alkyl of 1 to 24 carbon atoms or phenylalkyl of 7 to 15 carbon atoms, and

E_2 is as defined above.

7. A composition according to claim 1 wherein the benzotriazole is a compound of formula IIA



(IIA)

wherein

G_1 is hydrogen,

G_2 is CF_3-,

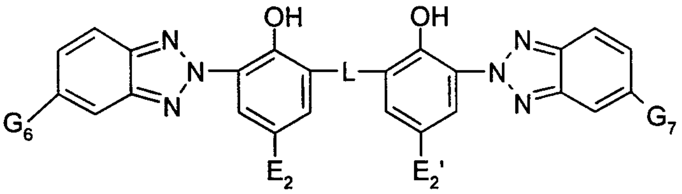
E_1 is hydrogen, straight or branched alkyl of 1 to 24 carbon atoms or phenylalkyl of 7 to 15 carbon atoms,

E_5 is $-OE_6$ or $-NE_7E_8$ where

E_6 is hydrogen, straight or branched chain C_1-C_{24}alkyl which is unsubstituted or substituted by one or more OH groups, or $-OE_6$ is $-(OCH_2CH_2)_wOH$ or $-(OCH_2CH_2)_wOE_{21}$ where w is 1 to 12 and E_{21} is alkyl of 1 to 12 carbon atoms, and

E_7 and E_8 are independently hydrogen, alkyl of 1 to 18 carbon atoms, straight or branched chain C_3-C_{18}alkyl which is interrupted by -O-, -S- or $-NE_{11}$-, C_5-C_{12}cycloalkyl, C_6-C_{14}aryl or C_1-C_3hydroxylalkyl, or E_7 and E_8 together with the N atom are a pyrrolidine, piperidine, piperazine or morpholine ring.

8. A composition according to claim 1 wherein the benzotriazole is a compound of formula IIIA



(IIIA)

wherein

G_6 is CF_3,

G_7 is hydrogen or CF_3,

E_2 and E_2' are independently straight or branched alkyl chain of 1 to 24 carbon atoms, straight or branched chain alkenyl of 2 to 18 carbon atoms, cycloalkyl of 5 to 12 carbon atoms, phenylalkyl of 7 to 15 carbon atoms, phenyl, or said phenyl or said phenylalkyl substituted on the phenyl ring by 1 to 3 alkyl of 1 to 4 carbon atoms; and

L is methylene.

9. A composition according to claim 1 wherein the benzotriazole is

(a) 5-trifluoromethyl-2-(2-hydroxy-3-α–cumyl-5-tert-octylphenyl)-2H-benzotriazole;

(b) 5-trifluoromethyl-2-(2-hydroxy-5-tert-octylphenyl)-2H-benzotriazole;

(c) 5-trifluoromethyl-2-(2-hydroxy-3,5-di-tert-octylphenyl)-2H-benzotriazole;

(d) 2,2'-methylene-bis[6-(5-trifluoromethyl-2H-benzotriazol-2-yl)-4-tert-octylphenol];

(e) methylene-2-[4-tert-octyl-6-(2H-benzotriazol-2-yl)phenol]2'-[4-tert-octyl-6-(5-trifluoromethyl-2H-benzotriazol-2-yl)phenol];

(f) 3-(5-trifluoromethyl-2H-benzotriazol-2-yl)-5-tert-butyl-4-hydroxyhydrocinnamic acid;

(g) methyl 3-(5-trifluoromethyl-2H-benzotriazol-2-yl)-5-tert-butyl-4-hydroxyhydrocinnamate;

(h) isooctyl 3-(5-trifluoromethyl-2H-benzotriazol-2-yl)-5-tert-butyl-4-hydroxyhydrocinnamate;

(i) 5-trifluoromethyl-2-[2-hydroxy-5-(3-hydroxypropyl)phenyl]-2H-benzotriazole;

(j) 5-butylsulfonyl-2-(2-hydroxy-3-α–cumyl-5-tert-octylphenyl)-2H-benzotriazole;

(k) 5-octylsulfonyl-2-(2-hydroxy-3,5-di-α–cumylphenyl)-2H-benzotriazole;
(l) 5-dodecylsulfonyl-2-(2-hydroxy-3,5-di-tert-butylphenyl)-2H-benzotriazole;
(m) 5-octylsulfonyl-2-(2-hydroxy-3,5-di-tert-octylphenyl)-2H-benzotriazole;
(n) 5-trifluoromethyl-2-(2-hydroxy-3-α–cumyl-5-tert-butylphenyl)-2H-benzotriazole;
(o) 5-trifluoromethyl-2-(2-hydroxy-3-α–cumyl-5-nonylphenyl)-2H-benzotriazole;
(p) 5-trifluoromethyl-2-[2-hydroxy-3-α–cumyl-5-(2-hydroxyethyl)phenyl]-2H-benzo triazole;
(q) 5-trifluoromethyl-2-[2-hydroxy-3-α–cumyl-5-(3-hydroxypropyl)phenyl]-2H-benzotriazole;
(r) 5-trifluoromethyl-2-(2-hydroxy-3,5-di-tert-amylphenyl)-2H-benzotriazole;
(s) 5-trifluoromethyl-2-(2-hydroxy-3,5-di-tert-butylphenyl)-2H-benzotriazole;
(t) 5-trifluoromethyl-2-(2-hydroxy-3-dodecyl-5-methylphenyl)-2H-benzotriazole;
(u) 5-trifluoromethyl-2-[2-hydroxy-3-tert-butyl-5-(3-hydroxypropyl)phenyl)-2H-benzotriazole;
(v) 5-trifluoromethyl-2-[2-hydroxy-3-tert-butyl-5-(2-hydroxyethyl)phenyl]-2H-benzo triazole;
(w) 5-trifluoromethyl-2-[2-hydroxy-5-(2-hydroxyethyl)phenyl]-2H-benzotriazole;
(x) 5-trifluoromethyl-2-(2-hydroxy-3,5-di-α–cumylphenyl)-2H-benzotriazole;
(y) 5-fluoro-2-(2-hydroxy-3,5-di-α–cumylphenyl)-2H-benzotriazole;
(z) 5-butylsulfonyl-2-(2-hydroxy-3,5-di-α–cumylphenyl)-2H-benzotriazole;
(aa) 5-butylsulfonyl-2-(2-hydroxy-3,5-di-tert-butylphenyl)-2H-benzotriazole;
(bb) 5-butylsulfonyl-2-(2-hydroxy-3,5-di-tert-octylphenyl)-2H-benzotriazole;
(cc) 5-phenylsulfonyl-2-(2-hydroxy-3,5-di-tert-butylphenyl)-2H-benzotriazole; or
(dd) 5-chloro-2-(2-hydroxy-3,5-di-α–cumylphenyl)-2H-benzotriazole.

10. A composition according to claim 1 wherein the amount of benzotriazole of component (b1) or (b2) is 0.1 to 20% by weight based on the adhesive composition.

11. A composition according to claim 1 wherein the relative amount of (b1) to (b2) by weight is from 75:25 to 25:75.

12. A composition according to claim 1 wherein the adhesive of component (a) is selected from the group consisting of the pressure sensitive adhesives, the rubber-based adhesives, the solvent or emulsion based adhesives, the hot melt adhesives and natural-

product based adhesives.

13. A composition according to claim 1 wherein the adhesive composition is present in a laminated or multilayer construction.

14. A composition according to claim 13 wherein the laminated or multilayer construction is selected from the group consisting of

(a) retroreflective sheets and signs and conformable marking sheets;
(b) solar control films of various construction;
(c) corrosion resistant silver mirrors and solar reflectors;
(d) reflective print labels;
(e) UV absorbing glasses and glass coatings;
(f) electrochromic devices;
(g) films/glazings;
(h) windscreens and intermediate layers; and
(i) optical films.

15. A composition according to claim 1 wherein the adhesive of component (a) is a resin selected from the group consisting of
(i) polyurethanes;
(ii) polyacrylics;
(iii) epoxys;
(iv) phenolics;
(v) polyimides;
(vi) poly(vinyl butyral);
(vii) polycyanoacrylates;
(viii) polyacrylates;
(ix) ethylene/acrylic acid copolymers and their salts (ionomers);
(x) silicon polymers;
(xi) poly(ethylene/vinyl acetate);
(xii) atatic polypropylene;
(xiii) styrene-diene copolymers;
(xiv) polyamides;

(xv) hydroxyl-terminated polybutadiene;
(xvi) polychloroprene;
(xvii) poly(vinyl acetate);
(xviii) carboxylated styrene/butadiene copolymers;
(xix) poly(vinyl alcohol); and
(xx) polyesters.

16. A composition according to claim 15 wherein the adhesive of component (a) is a resin selected from the group consisting of poly(vinyl butyral), ethylene/vinyl acetate copolymers, polyacrylics, polyacrylates, natural rubber, polycyanoacrylates, poly(vinyl alcohol), styrene/butadiene rubber, phenolics, vinyl polymers, polyurethanes and styrene block copolymers.

17. A stabilized adhesive composition, suitable for use as an adhesive layer in a laminated article or multilayer construction, which comprises

(a) an adhesive; and

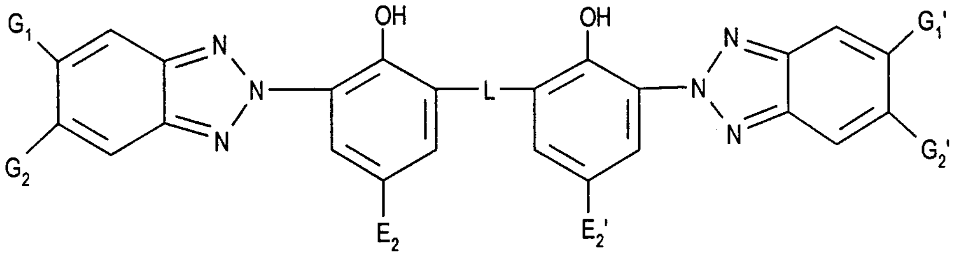
(b) a combination of

(1) a highly photostable benzotriazole which is 2-(2-hydroxy-3,5-di-α–cumylphenyl)-2H-benzotriazole or a red-shifted benzotriazole which is 5-chloro-2-(2-hydroxy-3,5-di-tert-butylphenyl)-2H-benzotriazole or 5-chloro-2-(2-hydroxy-3-tert-butyl-5-methylphenyl)-2H-benzotriazole each of which has relatively low solubility in some adhesives; and

(2) a solubilizing amount of a second benzotriazole having high solubility in said adhesives and selected from the group consisting of 2-(2-hydroxy-3,5-di-tert-butylphenyl)-2H-benzotriazole, 2-(2-hydroxy-3,5-di-tert-amyl-phenyl)-2H-benzotriazole, 2-(2-hydroxy-5-tert-octylphenyl)-2H-benzotriazole, 2-(2-hydroxy-3-sec-butyl-5- tert-butylphenyl)-2H-benzotriazole, 2-(2-hydroxy-3-α–cumyl-5-tert-octylphenyl)-2H-benzotriazole or 2-(2-hydroxy-3-α–cumyl-5-tert-butyl-phenyl)-2H-benzotriazole;

18. A composition according to claim 17 wherein the benzotriazole mixture in component (b) exhibits enhanced durability and low loss of absorbance when exposed to actinic radiation as witnessed by an absorbance loss of less than 0.5 absorbance units after exposure for 893 hours or less than 0.8 absorbance units after exposure for 1338 hours in a Xenon Arc Weather-Ometer.

19. A compound of formula IIIc



(IIIc)

wherein

G_1 and G_1' are independently hydrogen or halogen;

G_2 is halogen, nitro, cyano, $-COOG_3$, $-P(O)(C_6H_5)_2$, $-CO-G_3$, $-CO-NH-G_3$, $-CO-N(G_3)_2$, $-N(G_3)-CO-G_3$, E_3S-, E_3SO- or E_3SO_2-;

G_2' is perfluoroalkyl of 1 to 12 carbon atoms;

G_3 is hydrogen, straight or branched chain alkyl of 1 to 24 carbon atoms, straight or branched chain alkenyl of 2 to 18 carbon atoms, cycloalkyl of 5 to 12 carbon atoms, phenylalkyl of 7 to 15 carbon atoms, phenyl, or said phenyl or said phenylalkyl substituted on the phenyl ring by 1 to 4 alkyl of 1 to 4 carbon atoms;

E_2 and E_2' are independently straight or branched alkyl chain of 1 to 24 carbon atoms, straight or branched chain alkenyl of 2 to 18 carbon atoms, cycloalkyl of 5 to 12 carbon atoms, phenylalkyl of 7 to 15 carbon atoms, phenyl, or said phenyl or said phenylalkyl substituted on the phenyl ring by one to three alkyl of 1 to 4 carbon atoms; or E_2

and E_2' are independently said alkyl of 1 to 24 carbon atoms or said alkenyl of 2 to 18 carbon atoms substituted by one or more -OH, -OCOE$_{11}$, -OE$_4$, -NCO, -NH$_2$, -NHCOE$_{11}$, -NHE$_4$ or -N(E$_4$)$_2$, or mixtures thereof, where E_4 is straight or branched chain alkyl of 1 to 24 carbon atoms; or said alkyl or said alkenyl interrupted by one or more -O-, -NH- or -NE$_4$- groups or mixtures thereof and which can be unsubstituted or substituted by one or more -OH, -OE$_4$ or -NH$_2$ groups or mixtures thereof; or E_2 and E_2' are independently -(CH$_2$)$_m$-CO-E$_5$; or E_2 and E_2' are independently a group of the formula

$$-(CH_2)_m-CO-X-(Z)_p-Y-E_{15}$$

wherein

E_5 is -OE$_6$ or -NE$_7$E$_8$, or

E_5 is -PO(OE$_{12}$)$_2$, -OSi(E$_{11}$)$_3$ or -OCO-E$_{11}$,

or straight or branched chain C_1-C_{24}alkyl which is interrupted by -O-, -S- or -NE$_{11}$ and which can be unsubstituted or substituted by -OH or -OCO-E$_{11}$, C_5-C_{12} cycloalkyl which is unsubstituted or substituted by -OH, straight chain or branched C_2-C_{18}alkenyl which is unsubstituted or substituted by -OH, C_7-C_{15}aralkyl, -CH$_2$-CHOH-E$_{13}$ or glycidyl,

E_6 is hydrogen, straight or branched chain C_1-C_{24}alkyl which is unsubstituted or substituted by one or more OH, OE$_4$ or NH$_2$ groups, or -OE$_6$ is -(OCH$_2$CH$_2$)$_w$OH or -(OCH$_2$CH$_2$)$_w$OE$_{21}$where w is 1 to 12 and E_{21} is alkyl of 1 to 12 carbon atoms,

E_7 and E_8 are independently hydrogen, alkyl of 1 to 18 carbon atoms, straight or branched chain C_3-C_{18}alkyl which is interrupted by -O-, -S- or -NE$_{11}$-, C_5-C_{12}cycloalkyl, C_6-C_{14}aryl or C_1-C_3hydroxylalkyl, or E_7 and E_8 together with the N atom are a pyrrolidine, piperidine, piperazine or morpholine ring,

X is -O- or -N(E$_{16}$)-,

Y is -O- or -N(E$_{17}$)-,

Z is C_2-C_{12}-alkylene, C_4-C_{12}-alkylene interrupted by one to three nitrogen atoms, oxygen atoms or a mixture thereof, or is C_3-C_{12}-alkylene, butenylene, butynylene, cyclohexylene or phenylene, each substituted by a hydroxyl group,

m is zero, 1 or 2,

p is 1, or p is also zero when X and Y are -N(E_{16})- and -N(E_{17})-, respectively,

E_{15} is a group -CO-C(E_{18})=C(H)E_{19} or, when Y is -N(E_{17})-, forms together with E_{17} a group -CO-CH=CH-CO-, wherein E_{18} is hydrogen or methyl, and E_{19} is hydrogen, methyl or -CO-X-E_{20}, wherein E_{20} is hydrogen or C_1-C_{18}-alkyl;

E_{16} and E_{17} independently of one another are hydrogen, C_1-C_{18}-alkyl, C_3-C_{12}-alkyl interrupted by 1 to 3 oxygen atoms, or is cyclohexyl or C_7-C_{15}aralkyl, and E_{16} together with E_{17} in the case where Z is ethylene, also forms ethylene,

E_{11} is hydrogen, straight or branched chain C_1-C_{18}alkyl, C_5-C_{12}cycloalkyl, straight or branched chain C_2-C_{18}alkenyl, C_6-C_{14}aryl or C_7-C_{15}aralkyl;

E_{12} is straight or branched chain C_1-C_{18}alkyl, straight or branched chain C_3-C_{18}alkenyl, C_5-C_{10}cycloalkyl, C_6-C_{16}aryl or C_7-C_{15}aralkyl;

E_{13} is hydrogen, straight chain or branched C_1-C_{18}alkyl which is substituted by -PO(OE_{12})$_2$, phenyl which is unsubstituted or substituted by OH, C_7-C_{15}aralkyl or -CH_2OE_{12};

E_3 is alkyl of 1 to 20 carbon atoms, hydroxyalkyl of 2 to 20 carbon atoms, alkyl substituted by alkoxycarbonyl of 2 to 9 carbon atoms, alkenyl of 3 to 18 carbon atoms, cycloalkyl of 5 to 12 carbon atoms, phenylalkyl of 7 to 15 carbon atoms, aryl of 6 to 10 carbon atoms or said aryl substituted by one or two alkyl of 1 to 4 carbon atoms or 1,1,2,2-tetrahydroperfluoroalkyl where the perfluoroalkyl moiety is of 6 to 16 carbon atoms; and

L is alkylene of 1 to 12 carbon atoms, alkylidene of 2 to 12 carbon atoms, benzylidene, p-xylylene, $\alpha,\alpha,\alpha',\alpha'$-tetramethyl-m-xylylene or cycloalkylidene.

20. A compound of formula IIIc according to claim 19 wherein

G_1 and G_1' are each hydrogen,
G_2 is chloro, phenylsulfonyl or phenylthio,
G_2' is CF_3,

E_2 and E_2' are independently straight or branched alkyl chain of 1 to 24 carbon atoms, straight or branched chain alkenyl of 2 to 18 carbon atoms, cycloalkyl of 5 to 12 carbon atoms, phenylalkyl of 7 to 15 carbon atoms, phenyl, or said phenyl or said phenylalkyl substituted on the phenyl ring by 1 to 3 alkyl of 1 to 4 carbon atoms; and

L is methylene.

21. A composition stabilized against thermal, oxidative or light-induced degradation which comprises,

(a) an organic material subject to thermal, oxidative or light-induced degradation, and

(b) a compound of formula IIIc according to claim 20.

22. A composition according to claim 21 wherein the organic material is a natural, semi-synthetic, synthetic, thermoplastic or crosslinked polymer.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 00/03616

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C09J11/06 B32B7/12 C08K5/00 C08K5/3475

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)
IPC 7 C09J B32B C08K

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 practical, search terms used)

EPO-Internal, PAJ, WPI Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 2 051 672 A (TRANSPARENT PAPER LTD) 21 January 1981 (1981-01-21) claims 1,5 example 1 page 1, column 2, line 95 - line 100 ---	1-8, 10-18, 21,22
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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"&" document member of the same patent family

Date of the actual completion of the international search 2 August 2000	Date of mailing of the international search report 09/08/2000
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer Glanddier, A

Interr   nal Application No
PCT/EP 00/03616

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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