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(54) Titre : POLYCARBONATE OU POLYESTERCARBONATE CONTENANT DES AZURANTS OPTIQUES
(54) Title: A POLYCARBONATE OR POLYESTER CARBONATE COMPRISING AN OPTICAL BRIGHTENER

(57) Abrégé/Abstract:
The invention relates to compositions comprising a polymer selected from the group of polycarbonates and polyester carbonates and comprising a compound with an optical brightener action.

A polycarbonate or polyester carbonate containing optical brighteners

Abstract

The present invention concerns compositions containing a polymer selected from the group consisting of polycarbonate and polyester carbonate and containing a compound that acts as an optical brightener.

A polycarbonate or polyester carbonate containing optical brighteners

The present invention concerns compositions containing a polymer selected from the group consisting of polycarbonate and polyester carbonate and containing at least one compound that acts as an optical brightener.

Optical brighteners in polymers are known. The activity of a particular optical brightener depends on the polymer in which it is used. The combination of a particular polymer and a particular optical brightener must therefore go well with one another. The present invention provides new optical brighteners for polycarbonates and polyester carbonates.

WO 98/19862 discloses two-layer sheets made from polymers containing optical brighteners and UV absorbers in one of the two layers.

Hostalux® KCB is an optical brightener. Hostalux® KCB is 1,4-bis-(2-benzoxazolyl) naphthaline. It is available from Clariant GmbH, Frankfurt am Main, Germany. The use of Hostalux® KCB in TiO_2-containing powder coatings is described in WO 01/18130.

The use of Hostalux® KCB in white pigment-containing printing papers is described in JP-A 2001-010210 and in JP-A 03-065948.

The use of Hostalux® KCB in combination with other optical brighteners in PVC or EVA is described in EP-A 0 791 680.

The use of Hostalux® KCB in combination with other optical brighteners in polyesters is described in EP-A 0 240 461 and in Helvetica Chimica Acta (1978), 61, pages 488 to 500.

The use of Hostalux® KCB in combination with other optical brighteners in polyesters and polyamides is described in EP-A 0 136 259 and in EP-A 0 044 996 and in DE-A 19 55 310.

The use of Hostalux® KCB in combination with other optical brighteners in PVC is described in DE-A 33 13 332.

The use of Hostalux® KCB in combination with other optical brighteners in textiles is described in DE-A 26 29 703.

The use of Hostalux® KCB in polyester films is described in DE-A 38 18 986.

The use of Hostalux® KCB in laminated PVC films is described in DE-A 21 33 16.0.

Leukopur® EGM is an optical brightener. Leukopur® EGM is 7-(2H-naphtho[1,2-d]triazol-2-yl)-3-phenyl-2H-1-benzopyran-2-one. It is available from Clariant GmbH, Frankfurt am Main, Germany. The use of Leukopur® EGM in "UV-detecting compositions" is described in JP-A 01-169327.

The use of Leukopur® EGM together with other optical brighteners in polyolefins is described in WO 02/31035.

The use of Leukopur® EGM together with other optical brighteners in PVC is described in DE-A 33 13 332.

The use of Leukopur® EGM in PVC is described in JP-A 040 46 348.

The use of Leukopur® EGM in polyester fibres is described in JP-A 02-033321 and in JP-A 570 56 516 and in JP-A 620 48 690.

The use of Leukopur® EGM in acrylic fibres is described in JP-A 011 92 816.

The use of Leukopur® EGM in greenhouse films is described in DE-A 38 18 986.

The use of Leukopur® EGM in polystyrene is described in US-A 4 404 300.

Brochures published by the manufacturer of Hostalux® KCB and Leukopur® EGM (for example "Technical Information Hostalux® KCB" published by Clariant GmbH, Frankfurt am Main, Germany) mention a number of applications. Polycarbonate is not mentioned. PVC, PS, PE, PP, cellulose acetate and EVA are mentioned.

Hostalux® KSB is a known optical brightener for polycarbonate. Hostalux® KSB is 2-[4-[2-[4-(2-benzoxazolyl)phenyl]ethenyl]phenyl]-5-methyl benzoxazole. It is available from Clariant GmbH, Frankfurt am Main, Germany. The use of Hostalux® KSB in polycarbonate is described in JP-A 2002-003710 and in JP-A 2001-214049 and in JP-A 10-316873 and in DE-A 197 24 638.

Uvitex® OB is a known optical brightener for polycarbonate. Uvitex® OB is 2,2'-(2,5-thiophenediyl)bis[5-(1,1-dimethylethyl) benzoxazole. It is available from Ciba Spezialchemie, Lampertheim, Germany. The use of Uvitex® OB in polycarbonate is described in JP-A 2002-003710 and in JP-A 2000-191918 and in JP-A 072 33 314.

Polycarbonate and polyester carbonate are often used in products that are exposed to weathering. It is therefore important that plastics containing polycarbonate and polyester carbonate have good weathering resistance. The weathering resistance of plastics also depends on the additives (for example optical brighteners) that are used in the plastics.

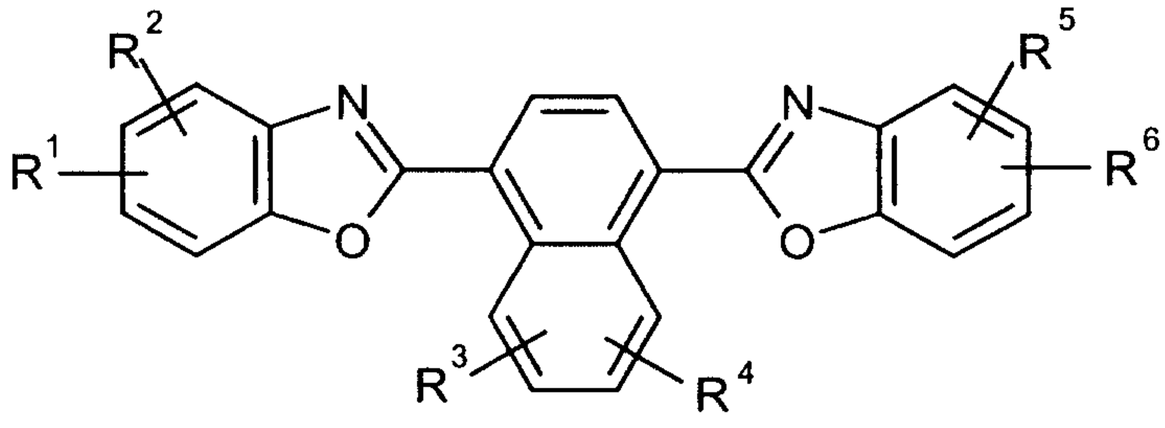
The known optical brighteners for polycarbonate and for polyester carbonate have the disadvantage of not being adequately resistant to weathering.

The object of the present invention is therefore to provide optical brighteners for polycarbonate and for polyester carbonate that have good weathering resistance.

This object is achieved by a composition containing

a) a polymer selected from the group consisting of polycarbonate and polyester carbonate and

b) an OB compound selected from the group consisting of a compound according to formula I,



(1)

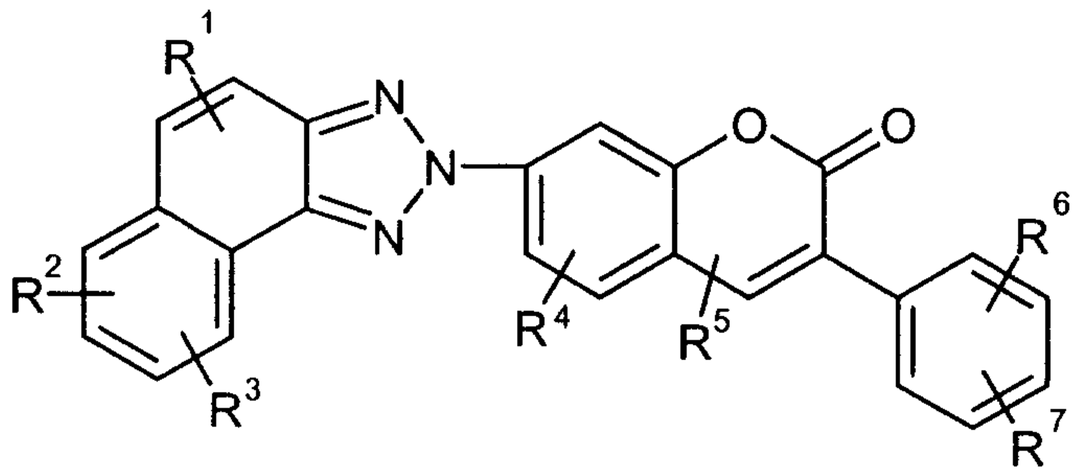
wherein

R^1, R^2, R^5 and R^6 mutually independently stand for H, alkyl, aryl, heteroaryl or halogen,

and wherein

R^3 and R^4 mutually independently stand for H, alkyl, aryl, heteroaryl or halogen,

and a compound according to formula 2,



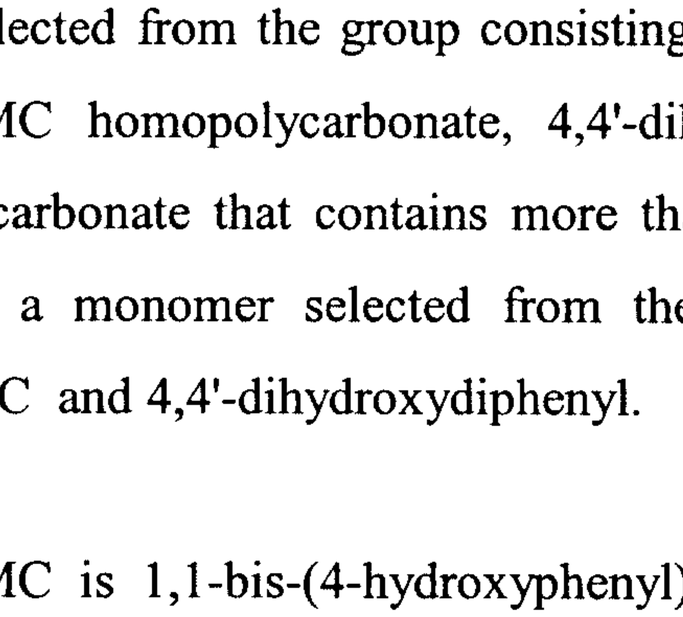
(2)

wherein

R^1, R^2, R^3, R^4, R^5, R^6 and R^7 mutually independently stand for H, alkyl, aryl, heteroaryl, halogen or cyano.

A particular embodiment of the present invention is this composition, wherein the polymer is selected from the group consisting of bisphenol A homopolycarbonate, bisphenol TMC homopolycarbonate, 4,4'-dihydroxydiphenyl homopolycarbonate and a copolycarbonate that contains more than 50 mol% repeat units, which are derived from a monomer selected from the group consisting of bisphenol A, bisphenol TMC and 4,4'-dihydroxydiphenyl.

Bisphenol TMC is 1,1-bis-(4-hydroxyphenyl)-3,3,5-trimethylcyclohexane and has the following formula (Me stands for a methyl group):



The cited polycarbonates can additionally contain:

10-40 mol% 4,4'-dihydroxydiphenyl,

60-90 mol% bisphenol A,

0-30 mol% bisphenol TMC.

A particular embodiment of the present invention is the composition wherein the polymer is bisphenol A homopolycarbonate.

In a particular embodiment of the present invention the OB compound has the formula 1 wherein R^1, R^2, R^5 and R^6 mutually independently stand for H, C_1 to C_{20} alkyl, C_1 to C_{20} aryl, C_1 to C_{20} heteroaryl or halogen, and wherein R^3 and R^4 mutually independently stand for H, C_1 to C_{20} alkyl, C_1 to C_{20} aryl, C_1 to C_{20} heteroaryl or halogen.

In a particular embodiment of the present invention the OB compound has the formula 1 wherein R^1, R^2, R^3 R^4, R^5 and R^6 equal H.

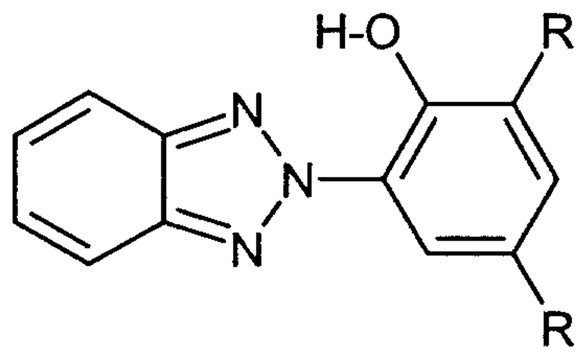
In a particular embodiment of the present invention the OB compound has the formula 2 wherein R^1, R^2, R^3, R^4, R^5, R^6 and R^7 mutually independently stand for H, C_1 to C_{20} alkyl, C_1 to C_{20} aryl, C_1 to C_{20} heteroaryl, halogen or cyano.

In a particular embodiment of the present invention the OB compound has the formula 2 wherein R^1, R^2, R^3, R^4, R^5, R^6 and R^7 equal H.

In a particular embodiment of the present invention the composition additionally contains UV absorbers.

Examples of UV absorbers are:

a) Benzotriazole derivatives:

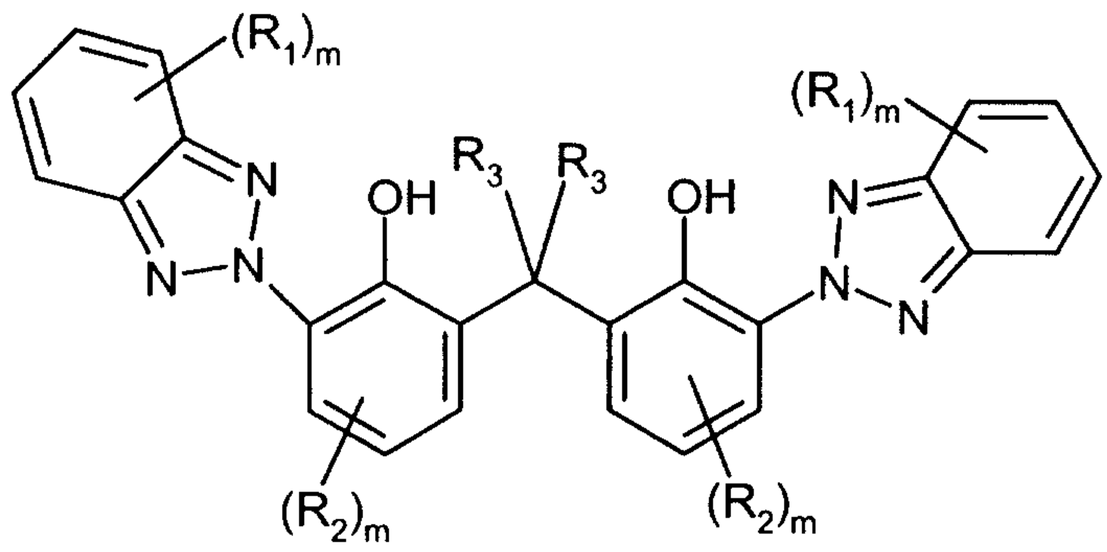


(3)

wherein

R and X are the same or different and are H or alkyl or alkyl aryl,

b) Dimeric benzotriazole derivatives:



(4)

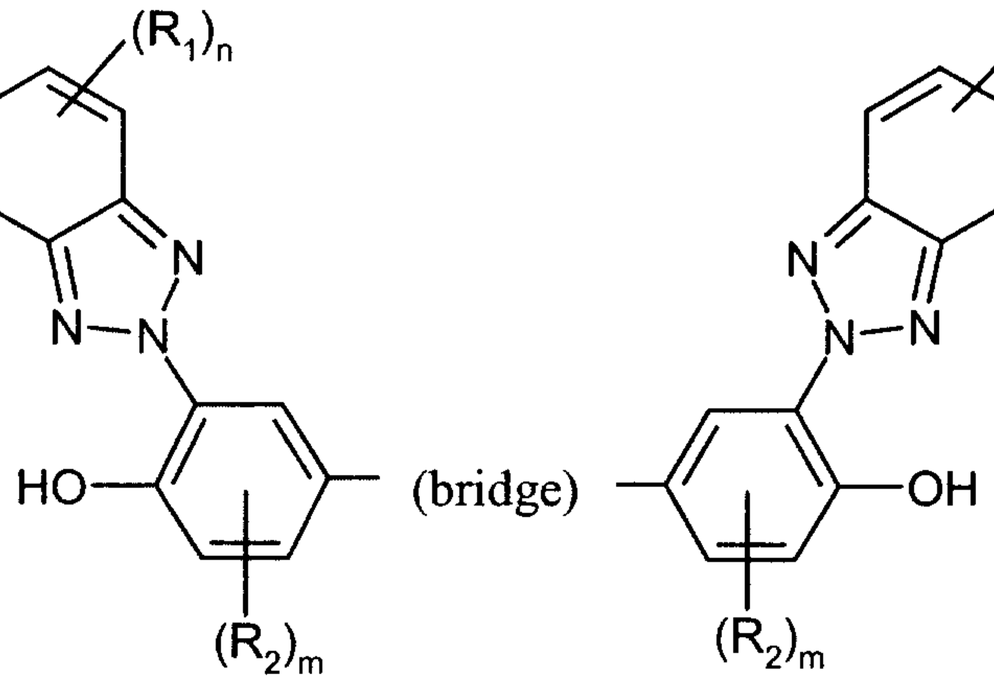
wherein

R^1 and R^2 are the same or different and denote H, halogen, C_1-C_{10} alkyl, C_5-C_{10} cycloalkyl, C_7-C_{13} aralkyl, C_6-C_{14} aryl, $-OR^5$ or $-(CO)-O-R^5$ where R^5 = H or C_1-C_4 alkyl,

R^3 and R^4 are likewise the same or different and denote H, C_1-C_4 alkyl, C_5-C_6 cycloalkyl, benzyl or C_6-C_{14} aryl,

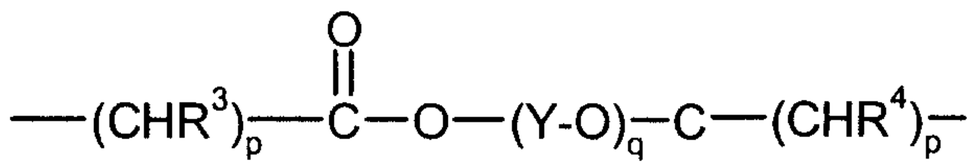
m is 1, 2 or 3 and

n is 1, 2, 3 or 4,



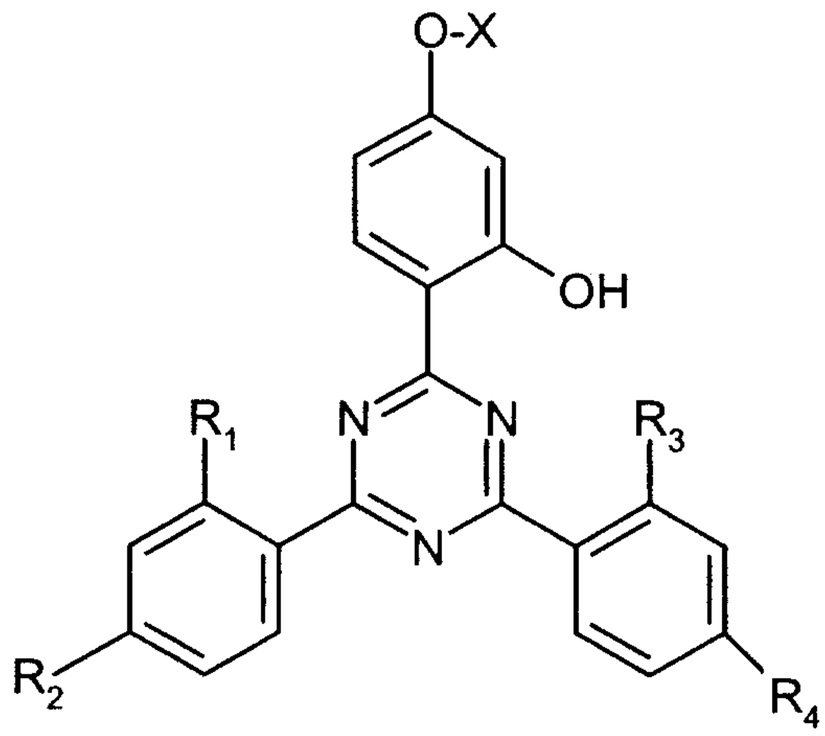
(5)

wherein the bridge denotes



	R^1, R^2, m and n	have the meaning cited for formula (IV), wherein in addition
	p	is a whole number from 0 to 3,
	q	is a whole number from 1 to 10
	Y	is $-CH_2-CH_2-$, $-(CH_2)_3-$, $-(CH_2)_4-$, $-(CH_2)_5-$, $-(CH_2)_6-$ or $CH(CH_3)-CH_2-$ and
	R^3 and R^4	have the meaning cited for formula (II);

c) Triazine derivatives



(6)

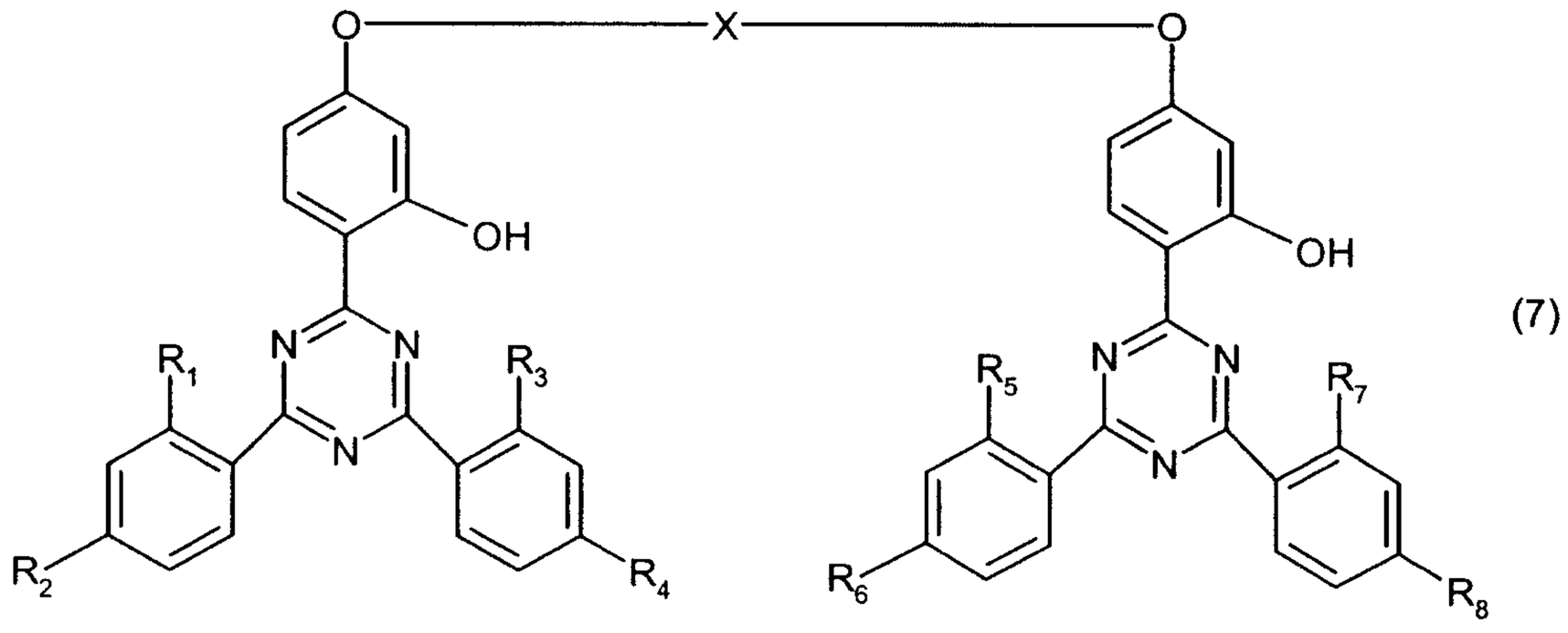
wherein

R^1, R^2, R_3, R_4 in formula (VI) are the same or different and are H or alkyl or CN or halogen and

X = alkyl,

d) Triazine derivatives as disclosed in EP-A 1 033 243

e) Dimeric triazine derivatives



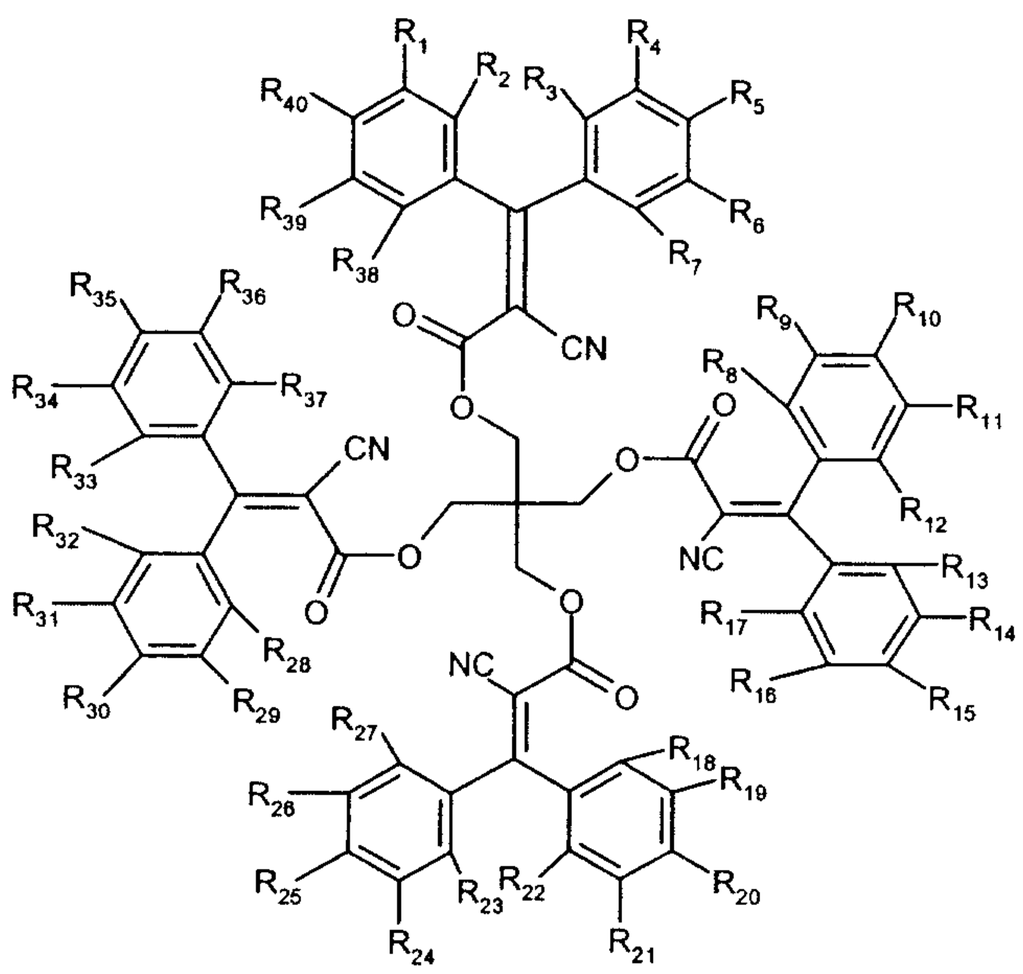
(7)

wherein

R_1, R_2, R_3, R_4, R_5, R_6, R_7, R_8 in formula (VII) are the same or different and are H or alkyl or CN or halogen and

X = alkyl or $-(CH_2CH_2O-)n-C(=O)-$, wherein n is 1 to 20

f) Diaryl cyanoacrylates

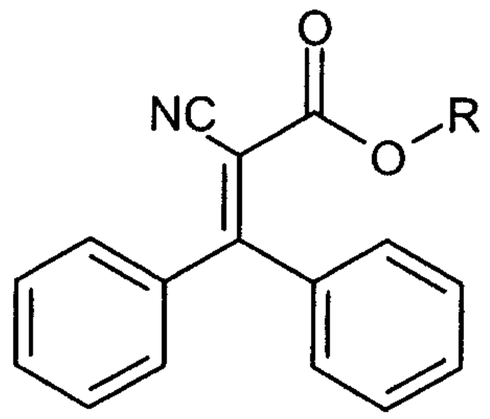


(8)

wherein

R_1 to R_{40} are the same or different and are H, alkyl, CN or halogen,

g) Diaryl cyanoacrylates having formula (IX)



(9)

wherein

R equals C_2 alkyl to C_{10} alkyl or aryl.

Uvinul 3035 where R = C_2H_5 and Uvinul 3039 where R = $CH_2CH(C_2H_5)C_4H_9$ are preferred.

In a particular embodiment of the present invention the composition additionally contains dyes and/or pigments. With regard to pigments, white pigments and light-scattering pigments (inorganic and/or organic) are preferred.

The compositions according to the invention preferably contain 0.0001 to 0.2 wt.%, particularly preferably 0.0003 to 0.1 wt.%, most particularly preferably 0.0005 to 0.05 wt.% of the OB compound.

If the compositions according to the invention contain UV absorbers, then they preferably contain them in the following mass ratio to the OB compound: UV absorber : OB compound = 2000 : 1 to 10 : 1, particularly preferably: UV absorber : OB compound = 1500 : 1 to 50 : 1, most particularly preferably: UV absorber : OB compound = 1000 : 1 to 90 : 1.

In addition to the cited polymer, the compositions according to the invention can also contain other, additional polymers, such that there is a mixture (or blend) of the cited polymer and the other, additional polymers.

The compositions according to the invention preferably contain at least 50, particularly preferably at least 80, most particularly preferably at least 90 wt.% of the cited polymer.

In a particular embodiment, in addition to the cited polymers, the OB compound and optionally UV absorbers, the compositions according to the invention additionally contain only conventional auxiliary substances and additives.

In a particular embodiment, in addition to the cited polymers, the OB compound and optionally UV absorbers, the compositions according to the invention contain no other substances.

The present invention provides the composition described.

The composition according to the invention can be melt processed by injection moulding, extrusion, coextrusion or other methods. Products such as e.g. moulded articles, sheets, profiles and pipes can be obtained in this way. They can be single-layer or multi-layer.

The present invention therefore also provides a product containing the composition according to the invention.

This product can in particular be multi-layer and can contain the composition according to the invention in at least one layer.

This product can be selected in particular from the group consisting of sheet, profile or pipe.

A multi-layer product containing the composition according to the invention in an outer layer is particularly preferred. Multi-layer sheets that can be produced by coextrusion in particular are preferred.

Polycarbonates and polyester carbonates and their production are known.

The compounds according to formula 1 can be produced by known methods. They are disclosed for example in Liebigs Annalen der Chemie 1982, pages 1423 to 1433 and in US-A 3 843 632 and in US-A 3 993 659.

The compound according to formula 1 where $R^1 = R^2 = R^3 = R^4 = R^5 = R^6 = H$ is commercially available from Clariant GmbH, Frankfurt am Main, Germany under the trade name Hostalux® KCB.

The compounds according to formula 2 can be produced by known methods. They are disclosed for example in JP-A 480 37 970 and in JP-A 460 07 388 and in DE-A 19 09 182.

The compound according to formula 2 where $R^1 = R^2 = R^3 = R^4 = R^5 = R^6 = R^7 = H$ is commercially available from Clariant GmbH, Frankfurt am Main, Germany under the trade name Leukopur® EGM.

The compositions according to the invention have numerous advantages. By using the compounds according to the invention as optical brighteners in the same concentration as for optical brighteners of the prior art, the optical properties remain at a good level for longer when the compositions are exposed to weathering. The optically brightening effect likewise remains at a good level for a long time.

In addition, the fluorescence of the optical brighteners in the compositions according to the invention remains visible even after extended weathering periods. The compositions according to the invention therefore appear more attractive to the eye.

In addition, the yellowing of the compositions according to the invention due to weathering is less than in compositions such as are known from the prior art. The compositions according to the invention therefore appear more attractive to the eye.

Examples

1. Production of compounds

Linear bisphenol A polycarbonate (Makrolon® 3108 from Bayer AG, Leverkusen, Germany with a melt flow rate (MFR) according to ISO 1133 of 6.5 g/10 min at 300°C and 1.2 kg loading) was melted on an extruder and mixed (compounded) with 0.25 wt.% Tinuvin® 350 and 0.02 wt.% of the optical brightener cited in Table 1.

Table 1: Optical brightener used

Compound no.	Optical brightener
1	Uvitex® OB
2	Leukopur® EGM
3	Hostalux® KS-N
4	Hostalux® KCB

Compounds 2 and 4 are according to the invention. Compounds 1 and 3 are comparative experiments.

The trade names used stand for the following substances:

Tinuvin® 350 is 2-(2H-benzotriazol-2-yl)-4-(1,1-dimethylethyl)-6-(2-methylpropyl) phenol; it is available from Ciba Spezialchemie, Lampertheim, Germany.

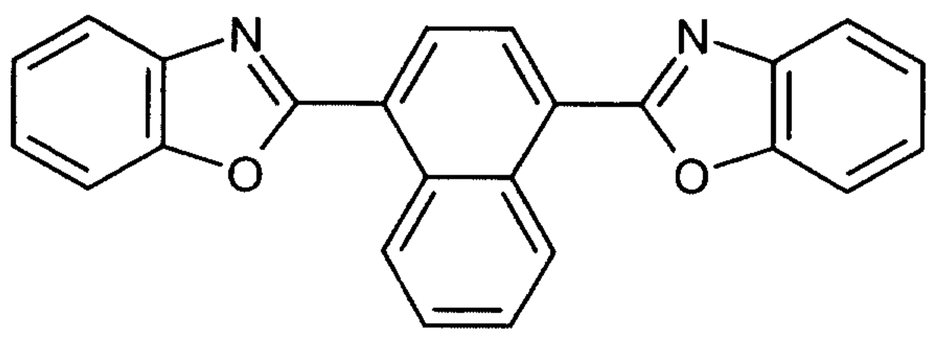
Uvitex® OB is 2,2'-(2,5-thiophenediyl)bis[5-(1,1-dimethylethyl) benzoxazole; it is available from Ciba Spezialchemie, Lampertheim, Germany.

Leukopur® EGM is 7-(2H-naphtho[1,2-d]triazol-2-yl)-3-phenyl-2H-1-benzopyran-2-one; it is available from Clariant GmbH, Frankfurt am Main, Germany.

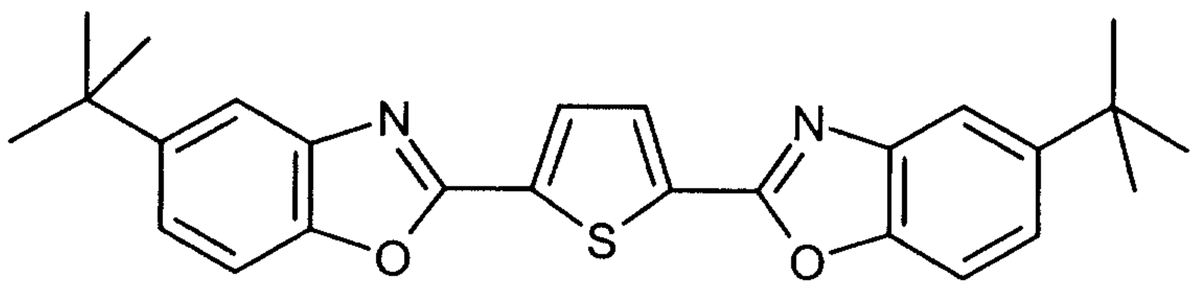
Hostalux® KS-N is 2-[4-[2-[4-(2-benzoxazolyl)phenyl]ethenyl]phenyl]-5-methyl benzoxazole; it is available from Clariant GmbH, Frankfurt am Main, Germany.

Hostalux® KCB is 1,4-bis(2-benzoxazolyl) naphthaline; it is available from Clariant GmbH, Frankfurt am Main, Germany.

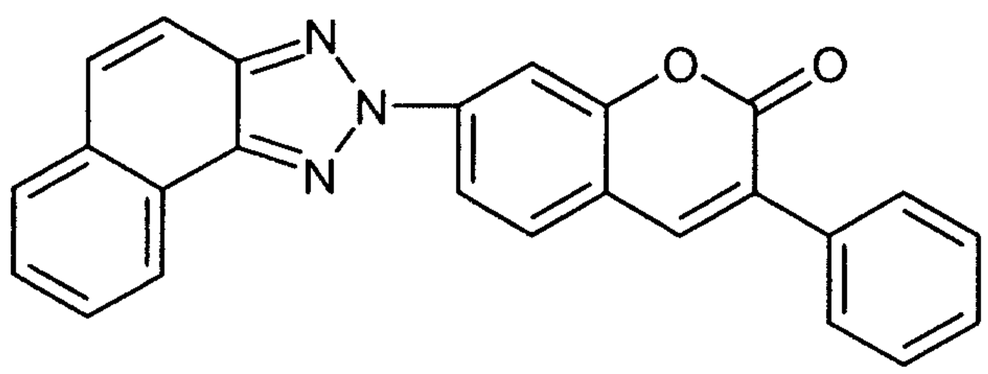
These are the structural formulae for the cited optical brighteners:



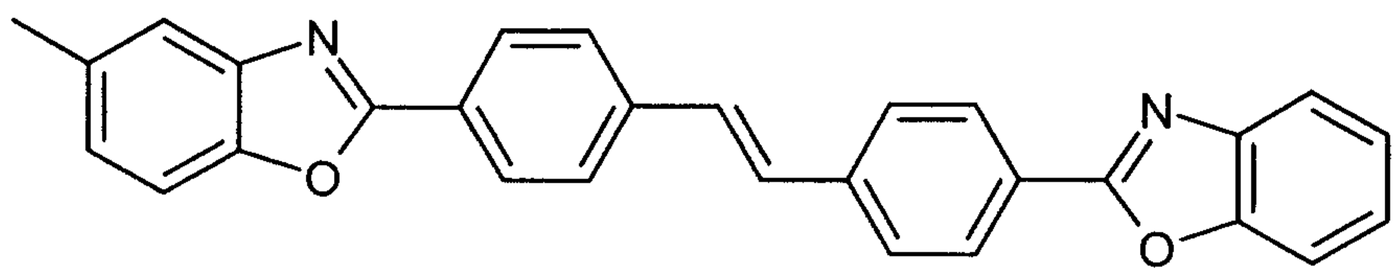
Hostalux® KCB



Uvitex® OB



Leukopur® EGM



Hostalux® KS-N

2. Production of specimens and weathering

The aforementioned compounds were used to produce specimens (4 mm thick sheets, known as "4 mm coloured specimens") by injection moulding. These were subjected to artificial weathering and their weathering resistance was tested.

Weathering was performed in accordance with ISO 4892-2 using a CI 65A Weather-O-meter supplied by Atlas, USA, with a 6.5 kW xenon burner and a borosilicate/borosilicate filter at a radiation intensity of 0.5 W/m^2 at 340 nm. The weathering cycle was: 102 min exposure to light and 18 min exposure to light and spraying with demineralised water. The maximum black standard temperature was 60°C (+/- 5°C).

Table 2 shows the results of the weathering:

	Transmission (%) / Yellowness index		
Compound no.	After 0 hours weathering	After 3500 hours weathering	After 6300 hours weathering
1	86.8 / 3.4	70.8 / 14.1	64.6 / 16.6
2	87.0 / 4.4	71.8 / 14.3	65.0 / 16.1
3	86.9 / 4.6	71.1 / 18.6	64.4 / 21.1
4	86.2 / 3.5	73.6 / 11.7	65.2 / 13.7

The transmission was measured in accordance with the standards ASTM E 308 and ASTM D 1003. A Pye-Unicam device was used. The measurement geometry 0° / diffuse, calculated according to light type C, was used.

The yellowness index YI was determined in accordance with the standard ASTM E 313.

The fluorescence of the coloured specimens was evaluated by placing them under a UV lamp and visually assessing the intensity of the blue fluorescent light.

Table 3 summarises the results:

Key:

+ = intense blue fluorescence

0 = slight blue fluorescence

Compound no.	After 0 hours weathering	After 3500 hours weathering	After 6300 hours weathering
1	+	+	O
2	+	+	+
3	+	+	O
4	+	+	+

The examples show that the fluorescence of the coloured specimens according to the invention is visible even after long weathering periods. The coloured specimens according to the invention therefore appear more attractive to the eye.

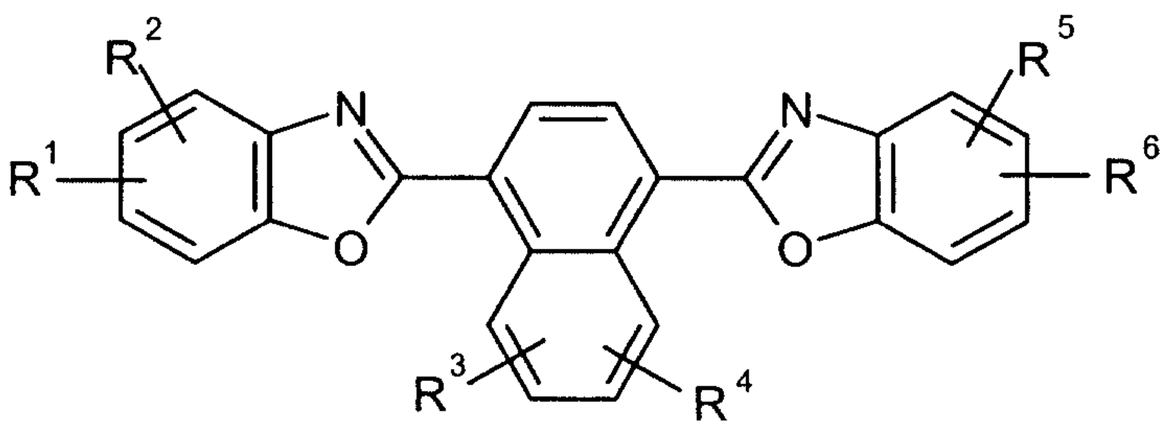
The examples also show that the yellowing of the coloured specimens according to the invention is less than that of the comparative experiments. The coloured specimens according to the invention therefore appear more attractive to the eye.

Claims

1. A composition containing

a) a polymer selected from the group consisting of polycarbonate and polyester carbonate and

b) an OB compound selected from the group consisting of a compound according to formula I,



(1)

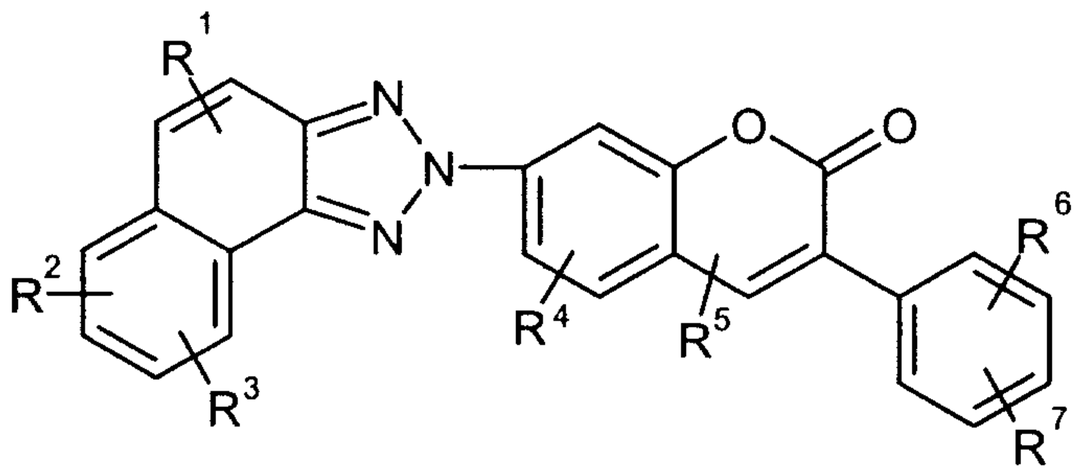
wherein

R^1, R^2, R^5 and R^6 mutually independently stand for H, alkyl, aryl, heteroaryl or halogen,

and wherein

R^3 and R^4 mutually independently stand for H, alkyl, aryl, heteroaryl or halogen,

and a compound according to formula 2,



(2)

wherein

R^1, R^2, R^3, R^4, R^5, R^6 and R^7 mutually independently stand for H, alkyl, aryl, heteroaryl, halogen or cyano.

2. Composition according to claim 1, wherein the polymer is selected from the group consisting of bisphenol A homopolycarbonate, bisphenol TMC homopolycarbonate, 4,4'-dihydroxydiphenyl homopolycarbonate and a copolycarbonate that contains more than 50 mol% repeat units, which are derived from a monomer selected from the group consisting of bisphenol A, bisphenol TMC and 4,4'-dihydroxydiphenyl.

3. Composition according to one of claims 1 or 2, wherein the composition additionally contains

c) UV absorber.

4. Product containing the composition according to one of claims 1 to 3.

5. Product according to claim 4, wherein it is multi-layer and wherein it contains the composition according to one of claims 1 to 3 in at least one layer.

6. Product according to one of claims 4 or 5, wherein it is selected from the group consisting of sheet, profile or pipe.