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A B O G A D O S

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159

As: 2446/P.

Doctor

GIANCARLO MARCENARO JIMÉNEZ

Superintendente Delegado Para la Propiedad Industrial

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

Rad: 01-053813- -00007-0000

Fec: 2008-09-19 14:27:08 Dep. 2020 NUECREACIONES

Tm. 2 PATENTES

Evo: 1 REGDEPOSITO

Act 603 IMPULSOPROCESAL Folios: 1

EXPEDIENTE: 01-053.813

**ASUNTO: Solicitud de patente a nombre de
Ciba Specialty Holding, Inc.**

Estimado Doctor:

En mi calidad de apoderada de la sociedad solicitante de la patente de la referencia manifiesto a usted lo siguiente:

1. Mediante memorial radicado en ese despacho el 20 de junio de 2003, el cual no ha sido resuelto aún, solicité que se realizara el examen de patentabilidad.
2. En vista de que han transcurrido 3 años y 2 meses, sin que se haya atendido dicha solicitud, ruego a usted se sirva dar las instrucciones del caso para que se proceda de inmediato a resolver este asunto.

Cordialmente,



JIMENA ESCOBAR URIBE
CC 39.779.452 de Usaquén.
T.P. 68228

DIVISION DE NUEVAS CREACIONES

RADICACIÓN EXPEDIENTE No. 01- 53813

EL EXTRACTO DE LA PRESENTE SOLICITUD DE PATENTE DE INVENCION

FUE PUBLICADO EN LA GACETA DE PROPIEDAD INDUSTRIAL No 523, DE

FECHA 27 DE DICIEMBRE DE 2002, EL TERMINO HABIL SEÑALADO POR LA

LEY EXPIRA EL 26 DE MARZO DE 2003.

NOTA: Dentro del plazo de los seis (6) meses siguientes a partir de la fecha de publicación en la gaceta de Propiedad Industrial, deberá solicitar y cancelar el examen de patentabilidad so pena de que la solicitud caiga en abandono, de acuerdo con lo establecido en el Artículo 44 de la Decisión 486/2000.

SE PRESENTARON OPOSICIONES POR PARTE DE TERCEROS.

SI

NO **X**

**SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
DIVISIÓN DE NUEVAS CREACIONES**

2020

Bogotá D.C., 2007-04-16

Doctora

JIMENA ESCOBAR URIBE

Apoderada **CIBA SPECIALTY CHEMICALS HOLDING INC.**

ASUNTO	Radicación	01-53813
	Trámite	002
	Evento	001
	Actuación	430
	Oficio	4583
	Folios	52

Como resultado del examen de fondo, realizado con fundamento en el artículo 45 de la Decisión 486 de la Comisión de la Comunidad Andina, se le comunica:

1. Documentos estudiados:

- A. Para el presente estudio se tuvo en cuenta el capítulo descriptivo, comprendido en los folios 6 a 75 del expediente correspondiente a la solicitud en estudio, tal como fue radicado al inicio del trámite.
- B. El capítulo reivindicatorio tomado en cuenta para el presente estudio comprende 16 reivindicaciones y se encuentra en los folios 76 a 85, tal cual se presentó al inicio del trámite. No es procedente aceptar el capítulo reivindicatorio presentado junto con el oficio de 2003-06-20 porque en la descripción no se encontró la condición de que el artículo polimérico deba ser una fibra para que esté presente una amina estéricamente bloqueada como estabilizador adicional. Por el contrario, "de preferencia, el artículo de poliolefina, poliéster o de poliamida transparente de la invención, contiene también una amina estéricamente bloqueada como estabilizador adicional con el fin de obtener estabilidad óptima a la luz del sustrato". No se menciona la fibra y sí se menciona que se prefiere la adición de la amina estéricamente bloqueada.
- C. Conforme lo establecen los artículos 9, 10 y 11 de la Decisión 486 de la Comisión de la Comunidad Andina, la presenta solicitud en estudio fue presentada el 05 de julio de 2001 y en el momento de la radicación se reclamó prioridad de la solicitud EP00810866.8 de 2000-07-26, cuya copia certificada y traducción del capítulo reivindicatorio se encuentran en los folios 89 a 130.

2. Objeto de la Invención:

- A. Las reivindicaciones 1 a 16 de la solicitud en estudio se refieren a: un artículo de poliolefina, poliéster o poliamida transparente que tiene un espesor comprendido entre 1 y 500 μm el cual es estabilizado contra los efectos de la luz, oxígeno, calor y/o compuestos químicos agresivos mediante adición de 0,005 – 0.030 % en peso, con relación a la poliolefina, poliéster o poliamida de un absorbedor de radiación UV de hidroxifenil triacina.
- B. El objeto de la solicitud se puede clasificar según la clasificación internacional como

C 07 D 251/00.

3. Claridad de la Solicitud:

- A. En el artículo 30 de la decisión 486 de la Comisión de la Comunidad Andina se establece: "Las reivindicaciones definirán la materia que se desea proteger mediante la patente. Deben ser claras y concisas y estar enteramente sustentadas por la descripción. Las reivindicaciones podrán ser independientes o dependientes. Una reivindicación será independiente cuando defina la materia que se desea proteger sin referencia a otra reivindicación anterior. Una reivindicación será dependiente cuando defina la materia que se desea proteger refiriéndose a una reivindicación anterior. Una reivindicación que se refiera a dos o más reivindicaciones anteriores se considerará una reivindicación dependiente múltiple." En el artículo 51 se establece además: "El alcance de la protección conferida por la patente estará determinado por el tenor de las reivindicaciones."
- i. El artículo transparente de la reivindicación 1 es diferente del artículo transparente de la reivindicación 3 y siguientes porque el primero no contiene la amina estéricamente bloqueada, luego pueden constituir dos invenciones diferentes. De la misma manera, el artículo transparente de la reivindicación 11 puede constituir una invención diferente al contener adicionalmente estabilizadores de luz y otros aditivos.
 - ii. El capítulo reivindicatorio carece de concisión en lo que respecta a la definición de las hidroxifenil triazinas puesto que la cantidad de sustituciones posibles en las mismas sustituciones de los sustituyentes es muy grande y ni siquiera está debidamente soportada en la descripción cada una de las innumerables posibilidades en términos de efectividad en la solución del problema planteado. El objeto de la solicitud está reivindicado de manera tan amplia y poco concisa que se encontró una gran cantidad de documentos en el estado de la técnica que afectan su patentabilidad.
 - iii. En las reivindicaciones 12 a 15 tan solo se está indicando la utilidad o campo de aplicación del objeto de la solicitud, más no se está aportando una característica técnica que lo distinga.

De acuerdo con lo anterior, el capítulo reivindicatorio no cumple con el requisito de claridad según lo establecido en el artículo 30 de la Decisión 486. El solicitante deberá anexar un nuevo capítulo reivindicatorio con todas las correcciones aquí requeridas.

4. Evaluación de la unidad de Invención

El artículo 25 de la decisión 486 de la Comisión de la Comunidad Andina establece: "La solicitud de patente sólo podrá comprender una invención o un grupo de invenciones relacionadas entre sí, de manera que conformen un único concepto inventivo."

La presente solicitud carece de unidad de invención porque no hay un concepto común inventivo entre el objeto de las primeras 11 reivindicaciones (el artículo polimérico transparente) y el objeto de la reivindicación 16, puesto que ambos objetos ya eran conocidos antes de la fecha de prioridad de la solicitud en estudio.

Por otra parte, los compuestos que constituyen el objeto de la reivindicación 16 tampoco guardan unidad de invención entre sí porque representan compuestos demasiado disímiles entre sí y la estructura de triazina en algunos (compuestos f, g y k) incluso es doble o, como en el caso del compuesto h, carece de difenilo en la sustitución de dos anillos benzolcos.

De acuerdo con lo anterior, la presente solicitud no cumple con el requisito de unidad de invención según el artículo 25 de la Decisión 486.

5. Reivindicaciones de uso

El artículo 14 de la Decisión 486 de la Comisión de la Comunidad Andina establece: "Los Países Miembros otorgarán patentes para las invenciones, sean de producto o procedimiento, en todos los campos de la tecnología, siempre que sean nuevas, tengan nivel inventivo y sean susceptibles de aplicación industrial"

El uso no se protege, puesto que no está contemplado en la legislación por no corresponder ni a un producto ni a un procedimiento. El objeto de las reivindicaciones 12 a 15 corresponde al uso o campo de aplicación que se pretende dar a la película polimérica transparente.

Por lo tanto en dichas reivindicaciones no se cumple con lo establecido en el artículo 14 de la decisión 486.

6. Determinación del estado de la técnica:

El artículo 16 de la Decisión 486 de la Comisión establece que: "El estado de la técnica comprenderá todo lo que haya sido accesible al público por una descripción escrita u oral, utilización, comercialización o cualquier otro medio antes de la fecha de presentación de la solicitud de patente o, en su caso, de la prioridad reconocida."

"Solo para el efecto de la determinación de la novedad, también se considerará dentro del estado de la técnica el contenido de una solicitud de patente en trámite ante la oficina nacional competente, cuya fecha de presentación o de prioridad fuese anterior a la fecha de presentación o de prioridad de la solicitud de patente que se estuviese examinando, siempre que dicho contenido esté incluido en la solicitud de fecha anterior cuando ella se publique o hubiese transcurrido el plazo previsto en el artículo 40"

La fecha para determinar el estado de la técnica es el 26 de julio de 2000, tomando en cuenta la prioridad reivindicada.

Consultadas las bases de datos y los archivos con que cuenta la entidad, especialmente bajo las clasificaciones C07D251/00, se encontró que antes del 26 de julio de 2000 habían sido publicados los documentos enumerados en la siguiente tabla.

No.	Documento	Título	Fecha de publicación
D1	WO 99/57189	Methods and compositions for protecting polymers from UV light	1999-11-11
D2	WO 98/06575	Polymeric film	1998-02-19

No.	Documento	Título	Fecha de publicación
D3	US 5,998,116	Color-photographic recording material	1999-12-07
D4	US 5,688,995	O-hidroxifenil-S-triazinas	1997-11-18
D5	US 5,288,778	Stabilized polymers having hetero atoms in the main chain	1994-02-22
D6	WO 98/54174	Block oligomers etc.	1998-12-03
D7	GB 1,011,575	Improvements relating to o-Hidroxifenil-s-triazines and their use	1965-12-01
D8	EP 0704560	Stabilization of pigmented fiber with a synergistic mixture etc.	1996-04-03
D9	EP 0 704 437	Red-shifted tris-aryl-s-triazines etc.	1996-04-03
D10	EP 0 483 488	Synergistic ultraviolet absorber compositions containing hydroxy aryl triazines and tetraalkyl piperidines	1992-05-06
D11	DE 199 06 745	Filme und folien auf polypropyleneharzbasis	1999-08-26
D12	GB 2 317 893	Stabilizer combination for organic materials	1998-04-08

7. Evaluación de los requisitos de patentabilidad:

El artículo 14 de la Decisión 486 de la Comunidad Andina establece que: *"Los Países Miembros otorgarán patentes para las invenciones, sean de producto o de procedimiento en todos los campos de la tecnología, siempre que sean nuevas, tengan nivel inventivo y sean susceptibles de aplicación industrial"*.

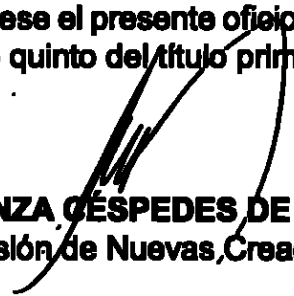
Como ya se expresó en los numerales de claridad y unidad de invención del presente oficio, las deficiencias encontradas en la solicitud estudiada con relación a la falta de concisión hacen que todos los documentos citados afecten su novedad, su nivel inventivo o ambos. Por lo tanto, esta oficina esperará hasta que la solicitante modifique el texto del capítulo reivindicatorio para efectuar un examen de patentabilidad de fondo. Se recuerda que no se deberá ampliar el alcance de la protección solicitada originalmente y que se requiere, preferiblemente, que la solicitante indique en qué parte del texto correspondiente al capítulo descriptivo se encuentra el soporte de las modificaciones que se hicieron al capítulo reivindicatorio. Esto en razón a que, como ya se indicó en el presente oficio, no se encontró el soporte para el texto del capítulo reivindicatorio que había alegado la solicitante mediante oficio del 2003-06-20.

Se anexa copia de las anterioridades mencionadas.

8. Notificación

En cumplimiento del artículo 45 de la decisión 486 de la Comisión de la comunidad Andina, se le indica que debe dar respuesta dentro del término de sesenta días contados a partir de la fecha de la notificación de la presente comunicación. En caso de no dar respuesta al presente requerimiento, o si a pesar de la respuesta subsistieran los impedimentos para la concesión, se denegará la patente.

Notifíquese el presente oficio conforme a lo dispuesto en el numeral 5.2, literal e) del capítulo quinto del título primero de la circular única No. 10 de 2001.


ALIX CARMENZA CÉSPEDES DE VERGEL
Jefe de la División de Nuevas Creaciones

El anterior requerimiento fue notificado por fijación en lista, de fecha 19 ABR 2007

CONCEPTO TÉCNICO Número: 617	EXAMINADOR TÉCNICO Código: 202043
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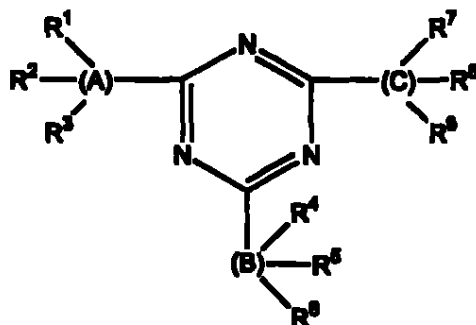


INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

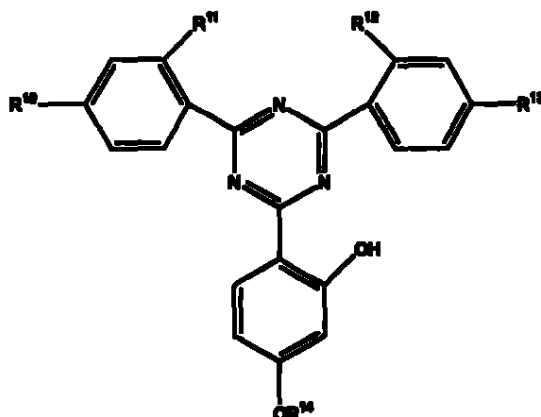
(51) International Patent Classification 6 : C08K 5/00 // (C08K 5/00, 5:3492, 5:3435)		A1	(11) International Publication Number: WO 99/57189
			(43) International Publication Date: 11 November 1999 (11.11.99)
(21) International Application Number: PCT/US99/06862		(81) Designated States: AL, AM, AU, AZ, BA, BB, BG, BR, BY, CA, CN, CU, CZ, DE, DK, DM, DZ, EE, EG, ES, FI, FR, GB, GR, GU, HK, HU, ID, IL, IN, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, RO, RU, SD, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), European patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published With international search report.	
(22) International Filing Date: 30 March 1999 (30.03.99)			
(30) Priority Data: 09/070,627 30 April 1998 (30.04.98) US			
(71) Applicant: CYTEC TECHNOLOGY CORP. [US/US]; 1105 North Market Street, Wilmington, DE 19801 (US).			
(72) Inventor: SAMUELS, Sari-Boh; 27 Romopock Court, Mahwah, NJ 07430 (US).			
(74) Agent: SHERWOOD, Michelle, A. et al.; Cytac Industries Inc., 1937 West Main Street, Stamford, CT 06904-0060 (US).			
(54) Title: METHODS AND COMPOSITIONS FOR PROTECTING POLYMERS FROM UV LIGHT			
(57) Abstract			
A polymeric article, such as an extruded or molded article or a biaxially oriented tape of film, and a method of stabilizing such a polymeric article to protect the article from degradation due to exposure to UV light. The article is formed by blending a polymeric material with from about 50 to about 5,000 ppm of at least one ortho hydroxy tri-aryl triazine light absorber and from about 500 ppm to about 1.25 percent of at least one oligomeric, polymeric, or high molecular weight HALS having a molecular weight of at least about 500, wherein the weight ratio of HALS to triazine light absorber is from about 3:1 to about 20:1, to form a stabilized polymeric composition, and forming an extruded or molded article or a biaxially oriented tape or film from the stabilized polymeric composition.			

7. N,N-bis(2,2,6,6-tetramethyl-4-piperidyl)-1,6-hexane diamine polymer with 2,4,6-trichloro-1,3,5-triazine and 2,4,4-trimethyl-1,2-pentamine
8. Poly-methylpropyl-3-oxy-(4(2,2,6,6-tetramethyl) piperidyl) siloxane
9. Poly-methylpropyl-3-oxy-(4(1,2,2,6,6-pentamethyl) piperidyl)siloxane
10. Polyalkyl-1-oxa-diazaspirodecane products of a reaction of tetramethyl-7-oxa-3,20-diaza-21-oxo-dispiro (5.1.11.12)heneicosane with epichlorohydrin
11. 1,3-propanediamine,N,N=1,2-ethanedilybis-,polymer with 2,4,6-trichloro-1,3,5-triazine, reaction products with N-butyl-2,2,6,6-tetramethyl-4-piperidinamine.

Typically, the triazine light absorber is of formula (III)



wherein A, B and C are each aromatic, at least one of A, B and C is substituted by a hydroxy group ortho of the point of attachment to the triazine ring, and each of R¹ through R⁸ is selected from the group consisting of hydrogen, hydroxy, alkyl, alkoxy, sulfonic, carboxy, halo, haloalkyl and acylamino. Preferably, the triazine light absorber is of formula (IV)



where R¹⁰, R¹¹, R¹² and R¹³ are the same or different, and are individually selected from the group consisting of hydrogen, hydroxy, alkyl, alkoxy, sulfonic, carboxy, halo, haloalkyl and acylamino, and R¹⁴ is hydrogen or C₁ to C₁₈ alkyl. Most preferably, R¹⁰, R¹¹, R¹² and R¹³ are H or CH₃, and R¹⁴ is hydrogen, C₆H₁₃, or C₆H₁₇.

Other useful triazine light absorbers include, but are not limited to

2-(4,6-Diphenyl-1,3,5-triazine-2-yl)-5-(hexyl)oxy-phenol,
 2-(4-((2-hydroxy-3-dodecyloxypropyl)-oxyl-2-hydroxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,
 3,5-triazine, 2-(4-((2-hydroxy-3-tridecyloxypropyl)-oxyl-2-hydroxyphenyl)-
 5 4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine,
 2-(4-((2-hydroxy-3-tridecyloxypropyl)-oxyl-2-hydroxyphenyl)-
 4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, and
 2-(4-((2-hydroxy-3-isooctyloxypropyl)-oxyl-2-hydroxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,
 3,5-triazine, and blends thereof.

10 The light stabilized polymeric article may be formed from a polymeric
 material, such as any of a polyolefin, polyester, polyether, polyketone, polyamide, natural
 or synthetic rubber, polyurethane, polystyrene, high-impact polystyrene, polyacrylate,
 polymethacrylate, polyacetal, polyacrylonitrile, polybutadiene, polystyrene, ABS, SAN
 (styrene acrylonitrile), ASA (acrylate styrene acrylonitrile), cellulosic acetate butyrate,
 15 cellulosic polymer, polyimide, polyamidelimide, polyetherimide, polyphenylsulfide, PPO,
 polysulfone, polyethersulfone, polyvinylchloride, polycarbonate, polyketone, aliphatic
 polyketone, thermoplastic TPU, aminoresin crosslinked polyacrylate or polyester,
 polyisocyanate crosslinked polyester or polyacrylate, phenol/formaldehyde,
 urea/formaldehyde or melamine/formaldehyde resin, drying or non-drying alkyd resin, alkyd
 20 resin, polyester resin, acrylate resins cross-linked with melamine resin, urea resin,
 isocyanate, isocyanurate, carbamate, or epoxy resin, cross-linked epoxy resins derived
 from aliphatic, cycloaliphatic, heterocyclic or aromatic glycidyl compound, which are
 cross-linked with an anhydride or amine, polysiloxane, Michael addition polymer, amine,
 blocked amine with activated unsaturated or methylene compound, ketimine with activated
 25 unsaturated or methylene compound, polyketimine in combination with unsaturated acrylic
 polyacetoacetate resin, polyketimine in combination with unsaturated acrylic resin,
 radiation curable composition, epoxymelamine resin, organic dye, cosmetic product,
 cellulose-based paper formulation, photographic film paper, ink, and blends thereof.

30 Preferably, the light stabilized polymeric article is formed from a polyolefin
 homopolymer, copolymer, or terpolymer, and, more preferably, a homopolymer, copolymer,
 or terpolymer of polyethylene or polypropylene, where the polyethylene or polypropylene is
 a product of polymerization in the presence of at least one single site catalyst, at least one
 Ziegler-Natta catalyst, or both a Ziegler-Natta catalyst and at least one single site catalyst.

35 Other useful polymeric material that may be used to form the articles of the
 invention include, but are not limited to, polyamides, polyesters, polyacetals, and
 polyurethanes.

The present invention is also directed to a light stabilization additive composition, comprising at least one ortho hydroxy tri-aryl triazine light absorber and at least one oligomeric, polymeric, or high molecular weight HALS having a molecular weight of at least about 500, wherein the weight ratio of HALS to triazine light absorber is from about 3:1 to about 20:1, as described above, and to a light stabilization additive concentrate, comprising from about 30 to about 98 percent, preferably from about 50 to about 95 percent, by weight of a polymeric resin, at least one ortho hydroxy tri-aryl triazine light absorber and at least one oligomeric, polymeric, or high molecular weight HALS having a molecular weight of at least about 500, wherein the weight ratio of HALS to triazine light absorber is from about 3:1 to about 20:1, where the concentrate may be in the form of pellets, prills, or pastilles. The additive composition may be formed by spraying solutions of the light absorber and HALS, melt blending, extrusion, or by physical compaction.

The present invention is further directed to a method of forming a stabilized polymeric article. The method comprises blending a polymeric material with from about 50 to about 5,000 ppm of at least one ortho hydroxy tri-aryl triazine light absorber and from about 500 ppm to about 1.25 percent of at least one oligomeric, polymeric, or high molecular weight HALS having a molecular weight of at least about 500, wherein the weight ratio of HALS to triazine light absorber is from about 3:1 to about 20:1, to form a stabilized polymeric composition, and forming an extruded or molded article or a biaxially oriented tape or film from the stabilized polymeric composition.

DETAILED DESCRIPTION OF THE INVENTION

The present invention is directed to compositions for stabilizing polymeric materials, such as molded or extruded articles, biaxially oriented tapes and films, and coatings, to prevent degradation from exposure to UV light, especially UV light having a wavelength of from about 290 to about 350 nm. It has been unexpectedly discovered that when from about 50 to about 5,000 ppm (parts per million) of an ortho hydroxy tri-aryl triazine and from about 500 ppm to about 1.25 percent of an oligomeric, polymeric, or high molecular weight HALS is blended with a polymeric material in a weight ratio of HALS to triazine of from about 3:1 to about 20:1, preferably from about 5:1 to about 10:1, and most preferably from about 6:1 to about 7.5:1, the polymeric material is protected from exposure to UV Light for a period of time substantially greater than afforded by any prior art light stabilizer composition containing a HALS, a UV light absorber, or a combination thereof.

Preferably, the oligomeric, polymeric, or high molecular weight HALS has a molecular weight which is greater than about 500, and, preferably, greater than about

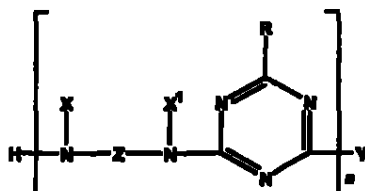
1,000. Suitable HALS are oligomers of the type disclosed in U.S. Patent No. 4,331,586, the contents of which are incorporated herein in their entirety.

HALS useful in the invention include, but are not limited to oligomers of formula (I)

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(I)

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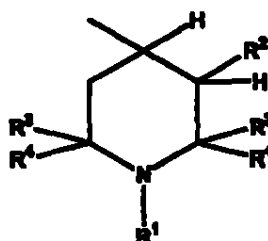


wherein R is morpholino, C₁-C₈ alkylamine, di(C₁-C₈) alkylamine, pyrrolidyl, or cyclohexylamino, and is preferably morpholino or octylamine, X and X', which are the same or different, represent hydrogen, C₁-C₂₀ alkyl, or the radical (II)

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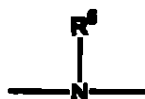
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(II)



25 where R¹ represents hydrogen, C₂-C₃ hydroxyalkyl, C₁-C₈ alkyl, hydroxyl, or oxy; R² represents hydrogen, C₁-C₈ alkyl, or benzyl; R³ and R⁴, which may be the same or different, represent C₁-C₈ alkyl, benzyl, or phenethyl, or together with the carbon to which they are attached form a C₈-C₁₀ cycloalkyl; Z represents C₂-C₂₀ straight chained or branched alkylene, where the alkylene chain may be interrupted by oxy, thio, or

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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : B32B 27/36, 15/06		A1	(11) International Publication Number: WO 98/06575
			(43) International Publication Date: 19 February 1998 (19.02.98)
(31) International Application Number: PCT/GB97/02105		(81) Designated States: AU, BR, CA, CN, JP, KR, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).	
(22) International Filing Date: 7 August 1997 (07.08.97)			
(30) Priority Data: 9617185.5 15 August 1996 (15.08.96) GB		Published With international search report.	
(71) Applicant (for all designated States except US): IMPERIAL CHEMICAL INDUSTRIES PLC (GB/GB); Imperial Chem- ical House, Millbank, London SW1P 3JP (GB).			
(72) Inventors; and (75) Inventors/Applicants (for US only): RUTTER, Philip, Mark (GB/GB); 9 Bessison Street, Gainsborough, Cleveland TS14 6HY (GB). LOVATT, Allan (GB/GB); 11 Brompton Road, Linthorpe, Middlesbrough, Cleveland TS5 6JU (GB).			
(74) Agents: HUMPHRIES, Martyn et al; ICI Group Intellectual Property, P.O. Box 90, Winton, Middlesbrough, Cleveland TS90 3JB (GB).			
(54) Title: POLYMERIC FILM			
(57) Abstract			
A polymeric film has a polyester film substrate (1) containing in the range from 0.1 to 10 % by weight, relative to the weight of the polyester, of at least one UV absorber, and a heat-sealable layer (2) on a surface of the substrate. The film is particularly suitable for use as a protective layer on a metal sheet (6).			

Polymeric Film

This invention relates to a polymeric film, and in particular to a heat-sealable film which comprises an ultra-violet (UV) light absorber, and to a metal sheet comprising said film.

5 Metal sheet, in coil or plate form, needs to be coated with protective layers in order for it to possess adequate corrosion resistance. Generally paint layers, or polymeric films such as polyvinyl chloride (PVC), or a combination of the two have been used to coat metal sheet. Polymeric films have certain advantages over paint layers, such as hardness, weatherability and aesthetic appearance. Unfortunately, polymeric films can
10 be difficult to bond to the primer-coated or painted metal sheet. In addition, for certain applications of coated metal sheet, polymeric films may possess insufficient weatherability, particularly when metal sheet is exposed to sunlight, eg when used as external cladding for buildings.

Polyester films generally exhibit a lack of stability to UV radiation. This lack of
15 stability manifests itself in a yellowing, hazing and cracking of the polyester film on exposure to sunlight, which has limited the potential uses of the film in an outdoor environment.

It is known to increase the stability of polymers, such as polyester to UV light by the incorporation therein of a UV absorbing material. A UV absorber has an extinction
20 coefficient much higher than that of the relevant polymer such that most of the incident UV light is absorbed by the UV absorber instead of by the polymer. The UV absorber generally dissipates the absorbed energy as heat, it does not result in degradation of the polymer chain, with consequent increase in the stability of the polymer to UV light.

Some UV absorbers are actually degraded by UV light which results in a reduction
25 of effect over time. In addition, some UV absorbers have relatively high volatility and/or thermally degrade which can cause problems including reduction in effectiveness, particularly when incorporated into a polymer for making film.

We have now devised a polymeric film and a laminated metal sheet which reduces or overcomes at least one of the aforementioned problems.

30 Accordingly, the present invention provides a polymeric film comprising a polyester film substrate comprising in the range from 0.1% to 10% by weight, relative to the weight of the polyester, of at least one UV absorber, and a heat-sealable layer on a surface of the substrate.

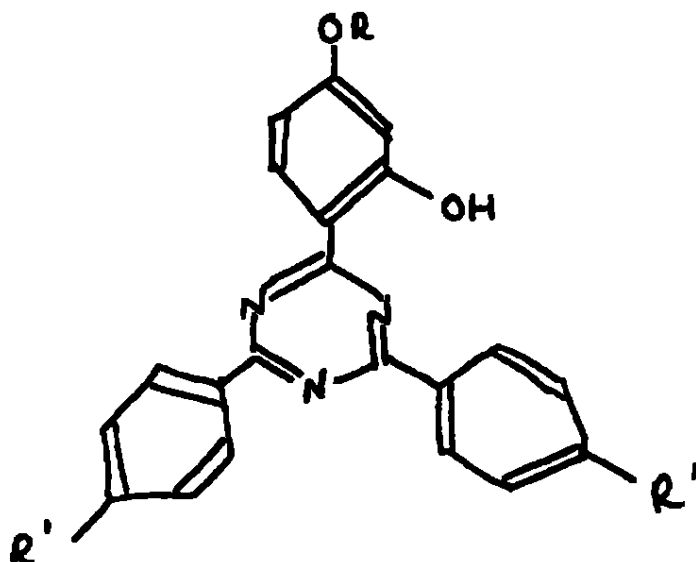
The invention also provides a method of producing a polymeric film which
35 comprises forming a substrate by extruding a layer of molten polyester comprising in the range from 0.1% to 10% by weight, relative to the weight of the polyester, of at

and withdrawn at a rate which will induce longitudinal orientation. Sequential stretching may be effected in a starter process by extruding the thermoplastics material as a flat extrudate which is subsequently stretched first in one direction and then in the other mutually perpendicular direction. Generally, it is preferred to stretch firstly in the longitudinal direction, ie the forward direction through the film stretching machine, and then in the transverse direction. A stretched substrate film may be, and preferably is, dimensionally stabilised by heat-setting under dimensional restraint at a temperature above the glass transition temperature thereof.

In principle, any organic or inorganic UV absorber suitable for use in polyester may be employed in the present invention. Suitable examples include the organic UV absorbers disclosed in *Encyclopaedia of Chemical Technology*, Kirk-Othmer, Third Edition, John Wiley & Sons, Volume 23, Pages 615 to 627. Particular examples of UV absorbers include benzophenones, benzotriazoles (US-A-4684679, US-A-4812488 and US-A-4881805), benzoxazinones (US-A-4446282, US-A-5251084 and US-A-5284539) and triazines (US-A-3244708, US-A-3843371, US-A-4619858, US-A-5288778 and WO 94/05845). The teaching of the aforementioned patent specifications is incorporated herein by reference.

In one embodiment of the invention, the UV absorber may be chemically incorporated in the polyester chain. Preferred UV stable polyesters are produced by incorporating benzophenones in to the polyester, for example as described in EP-A-0008886, EP-A-0031202, EP-A-0031203 and EP-A-0078582, the teaching of which is incorporated herein by reference.

Triazines are preferred UV absorbers, more preferably hydroxyphenyltriazines, and particularly hydroxyphenyltriazine compounds of Formula 1



wherein R is hydrogen, C₁-C₁₂ alkyl, C₂-C₈ alkyl substituted by halogen or by C₁-C₁₂ alkoxy, or is benzyl and R' is hydrogen or methyl. R is preferably C₁-C₁₂ alkyl or benzyl, more preferably C₂-C₈ alkyl, and particularly hexyl. R' is preferably hydrogen. An especially preferred UV absorber is 2-(4,6-diphenyl-1,3,5-triazin-2-yl)-5-(hexyloxy)-phenol, which is commercially available as Tinuvin 1577 FF from Ciba-Additives.

Suitable inorganic UV absorbers include metal oxide particles, such as zinc oxide or titanium dioxide, having a mean crystal size, as determined by electron microscopy, of less than 200 nm, more preferably in the range from 5 to 150 nm, particularly 10 to 100 nm, and especially 15 to 40 nm. Titanium dioxide particles are particularly preferred.

The titanium dioxide particles may be of anatase or rutile crystal form. The titanium dioxide particles preferably comprise a major portion of rutile, more preferably at least 80% by weight, particularly at least 80%, and especially approximately 100% by weight of rutile. The particles can be prepared by standard procedures, such as using the chloride process or preferably by the sulphate process.

In one embodiment of the invention the titanium dioxide particles are coated preferably with inorganic oxides such as aluminium, silicon, zinc, magnesium or mixtures thereof. Preferably the coating additionally comprises an organic compound, such as fatty acids and preferably alcohols, suitably having from 8 to 30, preferably from 12 to 24 carbon atoms. Polydiorganosiloxanes or polyorganohydrogensiloxanes, such as polydimethylsiloxane or polymethylhydrogensiloxane are suitable organic compounds.

The coating is suitably applied to the titanium dioxide particles in aqueous suspension. The inorganic oxides are precipitated in aqueous suspension from water-soluble compounds such as sodium aluminate, aluminium sulphate, aluminium hydroxide, aluminium nitrate, silicic acid or sodium silicate.

Suitable titanium dioxide particles are commercially available, for example "Tiosorb" ultra-fine titanium dioxide particles from Tioxide, UK.

The amount of UV absorber present in the polyester substrate is preferably in the range from 0.2% to 7%, more preferably 0.6% to 4%, particularly 0.8% to 2%, and especially 0.9% to 1.2% by weight, relative to the weight of the polyester.

In one embodiment of the invention, both an organic UV absorber, preferably a triazine, and an inorganic UV absorber, preferably titanium dioxide, are present in the polyester substrate. The ratio, by weight, of inorganic to organic UV absorber is preferably in the range from 0.5 to 10:1, more preferably 1 to 5:1, and particularly 1.5 to 2.5:1.

Particularly improved aesthetic appearance occurs when the external surface of the polyester substrate is matt, preferably exhibiting a 60° gloss value, measured as herein described, of less than 80%, more preferably in the range from 5% to 55%, particularly 20% to 50%, and especially 35% to 45%.

5 The external surface of the polyester substrate suitably exhibits a root mean square surface roughness (Rq), measured as herein described, of greater than 50, preferably in the range from 200 to 1500 nm, more preferably 400 to 1200 nm, and particularly 500 to 1000 nm.

10 The polymeric film is preferably transparent or translucent, preferably having a wide angle haze, being measured according to the standard ASTM D 1003-81, of <75%, more preferably in the range from 30% to 70%, particularly 40% to 65%, and especially 45% to 56%, suitably for a 30 µm thick film. In order to obtain the preferred properties of the polyester film substrate surface it is generally necessary to incorporate relatively small quantities of filler material therein. Suitable fillers include inorganic
15 materials such as silica, china clay, glass, mica, calcium carbonate, and organic materials such as silicone resin particles. Spherical monodisperse fillers may be employed. Silica is a particularly preferred filler.

20 The concentration of filler particles present in the substrate is preferably in the range from 0.001% to 5%, more preferably 0.05% to 3%, particularly 0.5% to 2%, and especially 0.8% to 1.2% by weight, relative to the weight of the polyester.

25 The filler particles preferably have a volume distributed median particle diameter (equivalent spherical diameter corresponding to 50% of the volume of all the particles, read on the cumulative distribution curve relating volume % to the diameter of the particles - often referred to as the "D(v,0.5)" value), as determined by laser diffraction, in the range from 0.3 to 20 µm, more preferably 1 to 10 µm, particularly 3 to 8 µm, and especially 5 to 7 µm.

30 Particle size of the filler particles described herein may be measured by electron microscope, coulter counter, sedimentation analysis and static or dynamic light scattering. Techniques based on laser light diffraction are preferred. The median particle size may be determined by plotting a cumulative distribution curve representing the percentage of particle volume below chosen particle sizes and measuring the 50th percentile. The volume distributed median particle diameter of the filler particles is suitably measured using a Malvern Instruments Mastersizer MS 15 Particle Sizer after dispersing the filler in ethylene glycol in a high shear (eg Chemcoll) mixer.



US005998116A

United States Patent [19]
Hayoz et al.

[11] **Patent Number:** **5,998,116**
 [45] **Date of Patent:** **Dec. 7, 1999**

[54] **COLOR-PHOTOGRAPHIC RECORDING MATERIAL**

[75] **Inventors:** Pascal Hayoz, Marly; Christophe Bulliard, Fribourg; David George Leppard, Marly, all of Switzerland

[73] **Assignee:** Ciba Specialty Chemicals Corporation, Tarrytown, N.Y.

[21] **Appl. No.:** 08/925,017

[22] **Filed:** Sep. 8, 1997

[30] **Foreign Application Priority Data**

Sep. 13, 1996 [CH] Switzerland 2252/96

[51] **Int. Cl.⁶** G03C 1/815

[52] **U.S. Cl.** 430/507; 430/512; 430/551; 430/931

[58] **Field of Search** 430/512, 931, 430/551, 507

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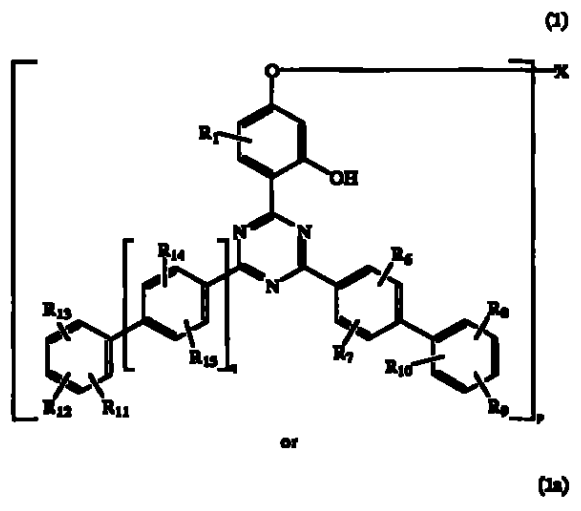
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Primary Examiner—Richard L. Schilling

Attorney, Agent, or Firm—Luther A. R. Hall; Kevin T. Mansfield

[57] **ABSTRACT**

The invention relates to a color-photographic recording material comprising, on a support, a blue-sensitive, a green-sensitive and/or a red-sensitive silver-halide emulsion layer, a protection layer above the sensitive layers, and, if desired, separation layers between the sensitive layers, where at least one of said layers includes a UV absorber of the formula

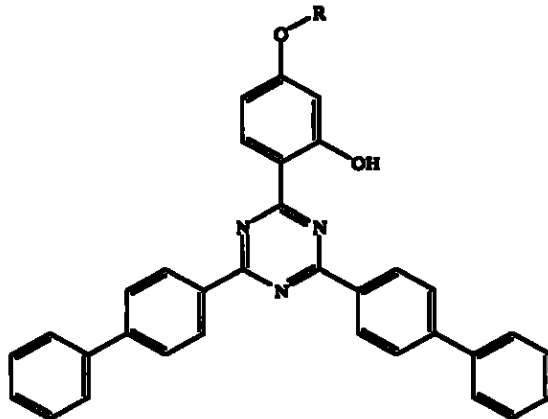


The stabilizers of the formula (1) or (1a) have good inherent stability and high light absorption; the photographic recording material described has excellent stability of the magenta, cyan and yellow layers.

14 Claims, No Drawings

TABLE A4-continued

Compounds of the formula



No.	R	Preparation as in Ex.	m.p.,° C.	Characterization
A6		A2		¹ H-NMR
A7		A2	107-110	¹ H-NMR
A8	CH ₂ CH(C ₂ H ₅)—C ₆ H ₁₃ (n)	A1	63-70	¹ H-NMR
A9	CH ₂ COO—C ₆ H ₁₇ (l)	A3	140-142	¹ H-NMR
A10		A2	156-158	¹ H-NMR
in which x, y and z are each in the range 1-6 and x + y + z = 8				
A11		A2	143-143	¹ H-NMR
A12	CH(n-C ₆ H ₁₃)—COO—C ₂ H ₅	A3	157-159	¹ H-NMR
A13	CH(CH ₃)—COO—C ₂ H ₅	A3	177-178	¹ H-NMR
A14	CH(CH ₃)—COO—C ₆ H ₁₇ (l)	A3	60-70	¹ H-NMR
A15	CH(n-C ₆ H ₁₃)—COO—CH ₃	A3	182-183	¹ H-NMR
A16		A2	105	¹ H-NMR
A17	CH(n-C ₆ H ₁₃)—COO—C ₂ H ₅	A3		¹ H-NMR

EXAMPLE A18

30 g (48 mmol) of compound A17 are stirred at 100° C. for 2 hours together with 3.4 g (60 mmol) of finely powdered KOH in 300 ml of Ethylcellosolve. 100 ml of acetic acid are

then added, causing the product to precipitate. The mixture is filtered, and the product is recrystallized from Ethylcellosolve, giving the free acid (m.p. 196-198° C.) of the formula



US005688995A

United States Patent [19]

Luther et al.

[11] Patent Number: 5,688,995

[45] Date of Patent: Nov. 18, 1997

[34] O-HYDROXYPHENYL-S-TRIAZINES

[75] Inventors: Helmut Luther, Grenzach-Wyhlen;
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[73] Assignee: Ciba-Geigy Corporation, Tarrytown,
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[21] Appl. No.: 649,949

[22] Filed: May 15, 1996

[30] Foreign Application Priority Data

May 18, 1995 [CH] Switzerland 147995

[31] Int. Cl.⁶ C07C 229/00

[32] U.S. Cl. 562/30; 544/180; 544/216

[38] Field of Search 544/180, 216;
562/30

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Primary Examiner—Terresa M. Mosley
Attorney, Agent, or Firm—Kevin T. Mansfield

[57] ABSTRACT

A description is given of o-hydroxyphenyl-s-triazines containing at least two alkoxyphenyl-substituents. They have the formula (1).

The compounds according to the invention are particularly suitable as sunscreen agents in cosmetic preparations.

8 Claims, No Drawings

- sponding lactones, such as polyethylene terephthalate, polybutylene terephthalate, poly-1,4-dimethylolcyclohexane terephthalate, polyhydroxybenzoates, as well as block polyether esters derived from hydroxyl-terminated polyethers; and also polyesters modified with polycarbonates or MBS.
19. Polycarbonates and polyester carbonates.
 20. Polysulfones, polyether sulfones and polyether ketones.
 21. Crosslinked polymers derived from aldehydes on the one hand and phenols, urea or melamine on the other hand, such as phenol/formaldehyde resins, urea/formaldehyde resins and melamine/formaldehyde resins.
 22. Drying and non-drying alkyd resins.
 23. Unsaturated polyester resins derived from copolyesters of saturated and unsaturated dicarboxylic acids with polyhydric alcohols and vinyl compounds as crosslinking agents, and also halogen-containing modifications thereof of low flammability.
 24. Crosslinkable acrylic resins derived from substituted acrylates, for example from epoxy acrylates, urethane acrylates or polyester acrylates.
 25. Alkyd resins, polyester resins and acrylate resins crosslinked with melamine resins, urea resins, polyisocyanates or epoxy resins.
 26. Crosslinked epoxy resins derived from polyepoxides, for example from bisglycidyl ethers, or cycloaliphatic dicarboxides.
 27. Natural polymers such as cellulose, natural rubber, gelatin and derivatives thereof which have been chemically modified in a polymer-homologous manner, for example cellulose acetates, cellulose propionates and cellulose butyrates, or the cellulose ethers such as methyl cellulose; as well as resins and derivatives.
 28. Blends (polyblends) of the aforementioned polymers, for example PP/EPDM, polyamide/EPDM or ABS, PVC/EVA, PVC/ABS, PVC/MBS, PC/ABS PBTP/ABS, PC/ASA, PC/PBT, PVC/CPE, PVC/acrylates, POM/thermoplastic PUR, PC/thermoplastic PUR, POM/acrylate, POM/MBS, PPO/HIPS, PPO/PA 6.6 and copolymers, PA/HDPE, PA/PP or PA/PPO.
- Particular preference is given to the use of compounds according to the invention as stabilizers in coating materials of any type. This also means a process in accordance with the above description, in which the organic polymer is a binder for a coating material. The coating materials may be pigmented or unpigmented coatings or metallic effect paints. They may contain an organic solvent or may be solvent-free, or may be aqueous coating materials.
- The coatings can contain as binder at least one of the polymers listed above. Examples of coatings containing specific binders are as follows:
1. coatings based on cold- or hot-crosslinkable alkyd, acrylate, polyester, epoxy or melamine resins or mixtures of such resins, where appropriate with the addition of an acidic curing catalyst;
 2. two-component polyurethane coatings based on hydroxyl-containing acrylate, polyester or polyether resins and aliphatic or aromatic polyisocyanates;
 3. one-component polyurethane coatings based on blocked polyisocyanates which are unblocked during stoving;
 4. two-component coatings based on (poly)ketimines and aliphatic or aromatic polyisocyanates;
 5. two-component coatings based on (poly)ketimines and an unsaturated acrylate resin or a polyacetoacetate resin or a methyl methacrylamidoglycolate;
 6. two-component coatings based on carboxyl- or amino-containing polyacrylates and polyepoxides;

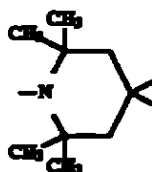
7. two-component coatings based on acrylate resins containing anhydride groups and on a polyhydroxyl or polyamino component;
 8. two-component coatings based on (poly)oxazolidines and on acrylate resins containing anhydride groups, or on unsaturated acrylate resins or aliphatic or aromatic polyisocyanates;
 9. two-component coatings based on unsaturated polyacrylates and polymalonates;
 10. thermoplastic polyacrylate coatings based on thermoplastic acrylate resins or externally crosslinking acrylate resins in combination with etherified melamine resins; and
 11. coating systems based on siloxane-modified or fluorine-modified acrylate resins.
- The coatings can also be radiation-curable materials. In this case, the binder comprises monomeric or oligomeric compounds which contain ethylenic double bonds and are converted into a crosslinked, high molecular weight form by irradiation with actinic light or with electron beams. In such cases the binder is usually a mixture of such compounds.
- The coatings can be applied in a single coat or in two coats, the stabilizers according to the invention preferably being added to the unpigmented uppermost coat.
- The coatings can be applied to the substrates (metal, plastic, wood, etc.) by the customary method, for example by brushing, spraying, flowcoating, dipping or electrophoresis.
- The quantity of the stabilizer of the formula (1) added depends on the respective substrate and on its intended use. In general, quantities of from 0.01 to 5% by weight are sufficient, with preference being given to the use of from 0.05 to 3% by weight based on the polymer to be stabilized. According to the invention, polymers containing from 0.01 to 5% by weight, especially from 0.05 to 3% by weight, of at least one compound of the formula (1) are therefore particularly suitable.
- In certain cases it may be advantageous to use two or more compounds of the formula (1). In addition, one or more other stabilizers and/or other additives may be included, for example the following types of compounds:
1. Antioxidants
 - 1.1. Alkylated monophenols, for example 2,6-di-tert-butyl-4-methylphenol, 2-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-isobutylphenol, 2,6-dicyclopentyl-4-methylphenol, 2-(α -methylcyclohexyl)-4,6-dimethylphenol, 2,6-dioctadecyl-4-methylphenol, 2,4,6-tricyclohexylphenol, 2,6-di-tert-butyl-4-methoxymethylphenol, 2,6-di-nonyl-4-methylphenol, 2,4-dimethyl-6-(1-methylundec-1'-yl)-phenol, 2,4-dimethyl-6-(1'-methylheptadec-1'-yl)-phenol, 2,4-dimethyl-6-(1'-methyl tridec-1'-yl)phenol and mixtures thereof.
 - 1.2. Alkylthiomethylphenols, for example 2,4-di-octylthiomethyl-6-tert-butylphenol, 2,4-di-octylthiomethyl-6-methylphenol, 2,4-di-octylthiomethyl-6-ethylphenol, 2,6-didodecylthiomethyl-4-nonylphenol.
 - 1.3. Hydroquinones and alkylated hydroquinones, for example 2,6-di-tert-butyl-4-methoxyphenol, 2,5-di-tert-butylhydroquinone, 2,5-di-tert-amylhydroquinone, 2,6-diphenyl-4-octadecyloxyphenol, 2,6-di-tert-butylhydroquinone, 2,5-di-tert-butyl-4-hydroxyanisole, 3,5-di-tert-butyl-4-hydroxyanisole, bis(3,5-di-tert-butyl-4-hydroxyphenyl)adipate.
 - 1.4. Hydroxylated thiodiphenyl ethers, for example 2,2'-thiobis(6-tert-butyl-4-methylphenol), 2,2'-thiobis(4-

5,688,995

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- polyamides, polyurethanes, alkali metal salts and alkaline earth metal salts of higher fatty acids, for example calcium stearate, zinc stearate, magnesium behenate, magnesium stearate, sodium ricinoleate, potassium palmitate, antimony pyrocatecholate or tin pyrocatecholate.
8. Nucleating agents, for example 4-tert-butylbenzoic acid, adipic acid, diphenylacetic acid.
9. Fillers and reinforcing agents, for example calcium carbonate, silicates, glass fibres, asbestos, talc, kaolin, mica, barium sulfate, metal oxides and hydroxides, carbon black, graphite.
10. Other additives, for example plasticizers, lubricants, emulsifiers, pigments, optical brighteners, flameproofing agents, antistatic agents, blowing agents.
11. Benzofuranones and indolizones, for example those disclosed in U.S. Pat. No. 4,325,863 or U.S. Pat. No. 4,338,244.

Of particular importance are stabilized polymers which contain an additional quantity of a light stabilizer from the class of the sterically hindered amines and/or from the class of the 2-(2'-hydroxyphenyl)benzotriazoles. Sterically hindered amines are understood as meaning in particular those compounds containing one or more groups of the formula



in the molecule, it being possible for these compounds to be monomeric, oligomeric or polymeric. Examples of such compounds can be found in Section 2.6 above of the list of possible additional stabilizers.

The addition of the compounds of formula (1) and, if desired, of further additives to the polymers can take place before or during shaping of the polymers, for example by mixing in powder form or by addition to the melt or solution of the polymer or to a suitable coating formulation containing a polymeric binder.

Accordingly the invention also provides the polymers stabilized by the addition of at least one compound of the formula (1), which polymers can, if desired, also contain other additives. The polymers thus stabilized can be used in various forms, for example as fibres, films, fibrous tapes, profiles, hollow articles, sheets, double-walled sheets or as binders for coatings, paints, adhesives and cements. Their use in coatings is of particular interest.

The novel UV absorbers are additionally suitable as light stabilizers in cosmetic preparations, for example for hair- or skin-dressing.

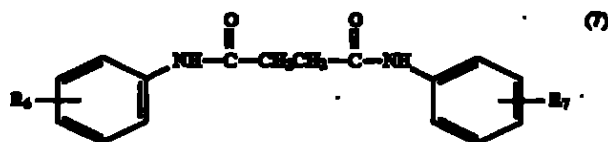
The invention, consequently, additionally provides a cosmetic preparation comprising at least one compound of the general formula (1) and cosmetically acceptable excipients or auxiliaries.

For cosmetic use the light stabilizers according to the invention usually have a mean particle size in the range from 0.02 to 2 μ , preferably from 0.05 to 1.5 μ and very particularly from 0.1 to 1.0 μ . The insoluble UV absorbers according to the invention can be brought to the desired particle size by customary methods, for example milling using a jet, ball, vibration or hammer mill, for example. Milling is preferably carried out in the presence of from 0.1 to 30% by weight, preferably from 0.5 to 15% by weight, based on the UV absorber, of a milling aid such as, for example, an alkylated vinylpyrrolidone polymer, a vinylpyrrolidone-vinyl acetate copolymer, an acyl glutamate or, in particular, a phospholipid.

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In addition to the UV absorbers according to the invention, the cosmetic preparations may also contain one or more further UV absorbers, examples being oxanilides, triazoles, vinyl-containing amides or cinnamides.

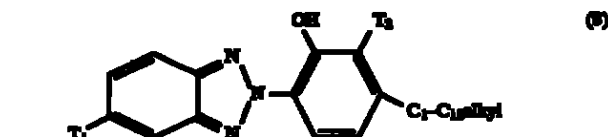
Examples of suitable oxanilides are compounds of the formula



in which

R₆ and R₇, independently of one another are C₁-C₁₈alkyl or C₁-C₁₈alkoxy.

Preferred triazole compounds are of the formula

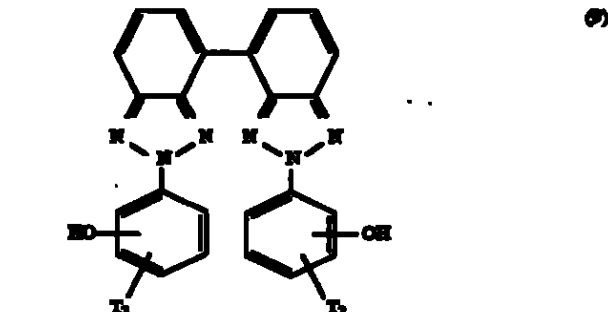


in which

T₁ is C₁-C₁₈alkyl or, preferably, hydrogen; and

T₂ is unsubstituted or phenyl-substituted C₁-C₁₈alkyl.

A further class of triazole compounds is of the formula



in which

T₃ is as defined for formula (8).

Preferred vinyl-containing amides are of the formula



in which

R₉ is C₁-C₁₈alkyl, preferably C₁-C₈alkyl or phenyl, phenyl being substituted by two or three substituents selected from hydroxyl, C₁-C₁₈alkyl or C₁-C₁₈alkoxy or a -C(=O) in which

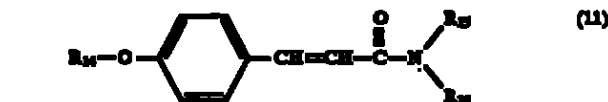
R₁₀ is C₁-C₁₈alkyl;

R₁₀, R₁₁, R₁₂ and R₁₃, independently of one another are hydrogen or C₁-C₁₈alkyl;

Y is N or O; and

n is 0 or 1.

Preferred cinnamic acid derivatives are of the formula



in which

R₁₄ is hydroxyl or C₁-C₈alkoxy, preferably methoxy or ethoxy;

United States Patent [19]
Schmitter et al.

US005288778A
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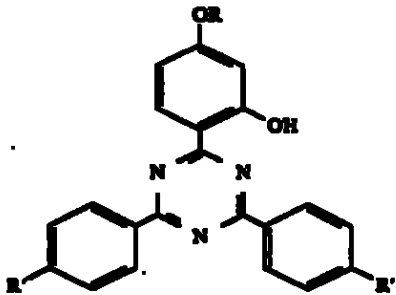
- [54] **STABILIZED POLYMERS HAVING
HETERO ATOMS IN THE MAIN CHAIN**
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- [58] **Field of Search** 524/100

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- [57] **ABSTRACT**
Hydroxyphenyltriazines of formula I



wherein R is hydrogen, C₁–C₁₂alkyl, C₂–C₆alkyl substituted by halogen or by C₁–C₁₂alkoxy, or is benzyl and R' is hydrogen or methyl, are especially suitable as stabilisers for thermoplastic polymers that comprise hetero atoms in the main chain.

11 Claims, No Drawings

2,4-di-p-tolyl-6-(2-hydroxy-4-benzyloxyphenyl)-1,3,5-triazine

2,4-di-p-tolyl-6-(2-hydroxy-4-(2-hexyloxyethoxy)-phenyl)-1,3,5-triazine.

The compounds of formula I are known compounds or can be prepared analogously to known compounds. They can be prepared in principle by etherifying the corresponding 2,4-diaryl-6-(2,4-dihydroxyphenyl)-1,3,5-triazines. The etherification takes place selectively in the 4-position, because the OH group in the 2-position is sterically hindered by a hydrogen bridge bond. The preparation and etherification of the 2,4-dihydroxyphenyltriazines are described, for example, in *Helv. Chim. Acta* 55 (1972), 1566-95; EP-A-395 938; U.S. Pat. No. 3,118,887; U.S. Pat. No. 3,242,175 or U.S. Pat. No. 3,244,708.

The amount of stabilizer to be used depends on the polymer to be stabilized and on the intended use of the stabilized polymer. In general, the polymer composition according to the invention comprises from 0.1 to 15, especially from 0.1 to 5, parts by weight of stabilizer (component b) to 100 parts by weight of polymer (component a).

The stabilizer (component b) may also be a mixture of two or more compounds of formula I. Apart from the stabilizer of formula I, the polymer composition may also comprise other known stabilizers, for example antioxidants, light-stabilizers, metal deactivators or processing stabilizers. The following compounds are examples thereof.

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-isobutylphenol, 2,6-di-cyclopentyl-4-methylphenol, 2-(α -methylcyclohexyl)-4,6-dimethylphenol, 2,6-dimethylphenol, 2,6-di-octadecyl-4-methylphenol, 2,4,6-tri-cyclohexylphenol, 2,6-di-tert-butyl-4-methoxymethylphenol, 2,6-di-nonyl-4-methylphenol, 2,4-dimethyl-6-(1'-methyl-undec-1'-yl)-phenol, 2,4-dimethyl-6-(1'-methyl-heptadec-1'-yl)-phenol, 2,4-dimethyl-6-(1'-methyl-tridec-1'-yl)-phenol and mixtures thereof.

1.2. Alkylthiomethylphenols, for example 2,4-di-octylthiomethyl-6-tert-butylphenol, 2,4-di-octylthiomethyl-6-methylphenol, 2,4-di-octylthiomethyl-6-ethylphenol, 2,6-di-dodecylthiomethyl-4-nonylphenol.

1.3. Hydroquinones and alkylated hydroquinones, for example 2,6-tert-butyl-4-methoxyphenol, 2,5-di-tert-butyl-hydroquinone, 2,5-di-tert-amyl-hydroquinone, 2,6-diphenyl-4-octadecyloxyphenol, 2,6-di-tert-butyl-hydroquinone, 2,5-di-tert-butyl-4-hydroxyanisole, 3,5-di-tert-butyl-4-hydroxyanisole, 3,5-di-tert-butyl-4-hydroxyphenyl stearate, bis(3,5-di-tert-butyl-4-hydroxyphenyl)adipate.

1.4. 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), 4,4'-thio-bis(3,6-di-sec-amylphenol), 4,4'-bis(2,6-dimethyl-4-hydroxyphenyl)disulfide.

1.5. 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(4,6-di-

tert-butylphenol), 2,2'-ethylidene-bis(4,6-di-tert-butylphenol), 2,2'-ethylidene-bis(6-tert-butyl-4-isobutylphenol), 2,2'-methylene-bis[6-(α -methylbenzyl)-4-nonylphenol], 2,2'-methylene-bis[6-(α , α -di-methylbenzyl)-4-nonylphenol], 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-bis(3-tert-butyl-3-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, ethylene glycol bis[3,3-bis(3'-tert-butyl-4'-hydroxyphenyl)butyrate], bis(3-tert-butyl-4-hydroxy-5-methylphenyl)dicyclopentadiene, bis[2-(3'-tert-butyl-2'-hydroxy-5'-methyl-benzyl)-6-tert-butyl-4-methylphenyl]terephthalate, 1,1-bis(3,5-dimethyl-2-hydroxyphenyl)butane, 2,2-bis(3,5-di-tert-butyl-4-hydroxyphenyl)propane, 2,2-bis(5-tert-butyl-4-hydroxy-2-methylphenyl)-4-n-dodecylmercaptobutane, 1,1,5,5-tetra(5-tert-butyl-4-hydroxy-2-methylphenyl)pentane.

1.6. O-, N- and S-benzyl compounds, for example 3,5,3',5'-tetra-tert-butyl-4,4'-dihydroxydibenzyl ether, octadecyl-4-hydroxy-3,5-dimethylbenzyl mercaptoacetate, tris(3,5-di-tert-butyl-4-hydroxybenzyl)amine, bis(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl)dithioterephthalate, bis(3,5-di-tert-butyl-4-hydroxybenzyl)sulfide, lauroyl-3,5-di-tert-butyl-4-hydroxybenzyl mercaptoacetate.

1.7. Hydroxybenzylated malonates, for example dioctadecyl-2,2-bis(3,5-di-tert-butyl-2-hydroxybenzyl)malonate, di-octadecyl-2-(3-tert-butyl-4-hydroxy-5-methylbenzyl)-malonate, di-dodecylmercaptoethyl-2,2-bis(3,5-di-tert-butyl-4-hydroxybenzyl)malonate, di-[4-(1,1,3,3-tetramethylbutyl)-phenyl]-2,2-bis(3,5-di-tert-butyl-4-hydroxybenzyl)malonate.

1.8. Hydroxybenzyl aromatic compounds, for example 1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl)-2,4,6-trimethylbenzene, 1,4-bis(3,5-di-tert-butyl-4-hydroxybenzyl)-2,3,5,6-tetramethylbenzene, 2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl)phenol.

1.9. Triazine compounds, for example 2,4-bis-octylmercapto-6-(3,5-di-tert-butyl-4-hydroxyanilino)-1,3,5-triazine, 2-octylmercapto-4,6-bis(3,5-di-tert-butyl-4-hydroxyanilino)-1,3,5-triazine, 2-octylmercapto-4,6-bis(3,5-di-tert-butyl-4-hydroxyphenoxy)-1,3,5-triazine, 2,4,6-tris(3,5-di-tert-butyl-4-hydroxyphenoxy)-1,2,3-triazine, 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, 2,4,6-tris(3,5-di-tert-butyl-4-hydroxyphenylethyl)-1,3,5-triazine, 1,3,5-tris(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)hexahydro-1,3,5-triazine, 1,3,5-tris(3,5-dicyclohexyl-4-hydroxybenzyl)isocyanurate.

1.10. Benzyl phosphonates, for example dimethyl-2,5-di-tert-butyl-4-hydroxybenzyl phosphonate, diethyl-3,5-di-tert-butyl-4-hydroxybenzyl phosphonate, dioctadecyl-3,5-di-tert-butyl-4-hydroxybenzyl phosphonate, dioctadecyl-5-tert-butyl-4-hydroxy-3-methylbenzyl phosphonate, calcium salt of 3,5-di-tert-butyl-4-hydroxybenzylphosphonic acid monoethyl ester.

1.11. Acylaminophenols, for example 4-hydroxybenzoic acid anilide, 4-hydroxystearic acid anilide, N-(3,5-di-tert-butyl-4-hydroxyphenyl)-carbamic acid octyl ester.

1.12. Esters of β -(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid with mono- or polyhydric alcohols, for example methanol, ethanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol,

di-*tert*-butyl oxanilide, mixtures of *o*- and *p*-methoxy-disubstituted and of *o*- and *p*-ethoxy-disubstituted oxanilides.

2.8. Further 2-(2-hydroxyphenyl)-1,3,5-triazines, for example 2,4,6-tris(2-hydroxy-4-octyloxyphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-octyloxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2,4-dihydroxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2,4-bis(2-hydroxy-4-propoxyphenyl)-6-(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-octyloxyphenyl)-4,6-bis(4-methylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-dodecyloxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2,8-bis(2-hydroxy-4-(2-hydroxy-3-butoxy-propoxy)phenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-(2-hydroxy-3-octyloxy-propoxy)phenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine.

3. Metal deactivators, for example *N,N'*-diphenyloxalic acid diamide, *N*-salicylal-*N'*-salicyloylhydrazine, *N,N'*-bis(salicyloyl)hydrazine, *N,N'*-bis(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionylhydrazine, 3-salicyloylaminio-1,2,4-triazole, bis(benzylidene)oxalic acid dihydrazide, oxanilide, isophthalic acid dihydrazide, sebacic acid bisphenylhydrazide, *N,N'*-diacetal-adipic acid dihydrazide, *N,N'*-bis-salicyloyl-oxalic acid dihydrazide, *N,N'*-bis-salicyloyl-thiopropionic acid dihydrazide.

4. Phosphites and phosphonites, for example triphenyl phosphite, diphenylalkyl phosphites, phenyldialkyl phosphites, tris(alkenylphenyl)phosphite, trialkaryl phosphite, trioctadecyl phosphite, distearyl-pentaerythritol diphosphite, tris(2,4-di-*tert*-butylphenyl)phosphite, diisododecyl-pentaerythritol diphosphite, bis(2,4-di-*tert*-butylphenyl)pentaeerythritol diphosphite, bis(2,6-di-*tert*-butyl-4-methylphenyl)pentaeerythritol diphosphite, bisdodecyl-oxy-pentaerythritol diphosphite, bis(2,4-di-*tert*-butyl-6-methylphenyl)pentaeerythritol diphosphite, bis(2,4,6-*tert*-butylphenyl)pentaeerythritol diphosphite, tristearylsorbitol triphosphite, tetrakis(2,4-di-*tert*-butylphenyl)-4,4'-biphenylene diphosphonite, 6-isooctyloxy-2,4,8,10-tetra-*tert*-butyl-12H-dibenz[d,g]-1,3,2-dioxaphosphocine, 6-fluoro-2,4,8,10-tetra-*tert*-butyl-12-methyl-dibenz[d,g]-1,3,2-dioxaphosphocine.

5. Peroxide-destroying compounds, for example esters of β -thio-dipropionic acid, for example the lauryl, stearyl, myristyl or tridecyl ester, mercaptobenzimidazole, the zinc salt of 2-mercaptobenzimidazole, zinc dibutyl dithiocarbamate, dioctadecyl disulfide, pentaerythritol tetrakis(β -dodecylmercapto)propionate.

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

7. Basic co-stabilisers, for example melamine, polyvinylpyrrolidone, dicyandiamide, triallyl cyanurate, urea derivatives, hydrazine derivatives, amines, polyamides, polyurethanes, alkali metal and alkaline earth metal salts of higher fatty acids, for example calcium stearate, zinc stearate, magnesium behenate, magnesium stearate, sodium ricinoleate, potassium palmitate, antimony pyrocatecholate or stannic pyrocatecholate.

8. Nucleation agents, for example 4-*tert*-butylbenzoic acid, adipic acid, diphenylacetic acid.

9. Fillers and thickeners, for example calcium carbonate, silicates, glass fibres, asbestos, talcum, kaolin, mica, barium sulfate, metal oxides and hydroxides, carbon black, graphite.

10. Other additives, for example plasticisers, lubricants, emulsifiers, pigments, optical brighteners, flame-retardants, antistatic agents, blowing agents.

The addition of the stabiliser and, where appropriate, further additives to the polymer is advantageously effected before the shaping, for example by mixing the pulverulent components or by adding the stabiliser to the melt or solution of the polymer.

The invention therefore relates also to a method for stabilising thermoplastic polymers that comprise hetero atoms in the main chain against damage by light, oxygen and heat, which method comprises adding to the polymers as stabiliser at least one compound of formula I, and to the use of compounds of formula I for stabilising thermoplastic polymers that comprise hetero atoms in the main chain against damage by light, oxygen and heat.

The resulting stabilised polymer compositions can be converted in accordance with customary methods, for example hot compression moulding, spinning, extruding or injection moulding, into shaped articles, for example fibres, films, small strips, sheets, profiled sheets, vessels, pipes and other profiles.

The invention therefore relates also to the use of the polymer composition according to the invention for the preparation of a shaped article.

Also of interest is the use of the polymer composition according to the invention is multilayer systems. In that case a polymer composition according to the invention having a relatively high content of stabiliser of formula I, for example 5-15% by weight, is applied in a thin layer (10-100 μ m) to a shaped article made from a polymer that comprises little or no stabiliser of formula I. The layer can be applied simultaneously with the shaping of the basic article, for example by means of so-called co-extrusion. The layer can, however, also be applied to the ready-shaped basic article, for example by means of lamination with a film or coating with a solution. The outer layer or layers of the finished article act as a UV filter which protects the interior of the article against UV light. The outer layer preferably comprises 5-15% by weight, especially 5-10% by weight, of at least one stabiliser of formula I.

The invention therefore relates further to the use of the polymer composition according to the invention for the preparation of multi-layer systems, wherein the outer layer(s) is(are) a polymer composition according to the invention in a thickness of 10-100 μ m, while the inner layer consists of a polymer that may comprise little or no stabiliser of formula I.

Of especial interest is the use of a polymer composition according to the invention wherein component (a) is a polycarbonate for the preparation of multi-layer systems.

The polymers stabilised in that manner are distinguished by good fastness to weathering, and especially by a high degree of resistance to UV light. For that reason they retain their mechanical properties and their colour and lustre over a long period of time, even when used outside.

The Examples that follow serve to illustrate the invention in detail, without limiting it thereto. In the Examples parts and percentages are by weight; room temperature denotes a temperature from 20° to 25° C. The following UV absorbers are used:

Ph-1: 2,4-diphenyl-6-(2-hydroxy-4-propoxyphenyl)-1,3,5-triazine;

PCT

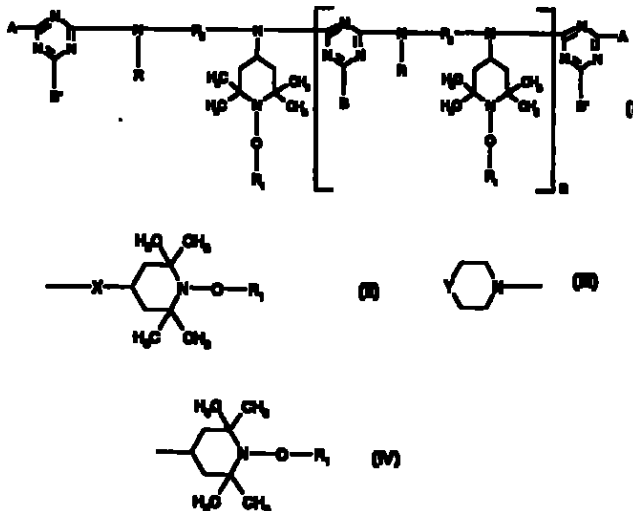
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(21) International Application Number: PCT/IB98/00714 (22) International Filing Date: 14 May 1998 (14.05.98) (30) Priority Data: 97810326.5 27 May 1997 (27.05.97) HP (34) Countries for which the regional or international application was filed: DE et al. (71) Applicant (for all designated States except US): CIBA SPECIALTY CHEMICALS HOLDING INC. [CH/CH]; Klybeckstrasse 141, CH-4057 Basel (CH). (72) Inventors; and (75) Inventors/Applicants (for US only): GALBO, James, Peter [US/US]; 28 White Farm Road, Wingdale, NY 12594 (US). LELLI, Nicola [IT/CH]; Hohe Winde-Strasse 62, CH-4059 Basel (CH). BORZATTA, Valerio [IT/IT]; Via Novelli, 2, I-40127 Bologna (IT). WOLF, Jean-Pierre [CH/CH]; Motiastasse 130, CH-1791 Courtemar (CH). ACKERMAN, Michael [US/US]; 12 Primrose Lane, New City, NY 10956 (US). PICCINELLI, Piero [IT/IT]; Via del Lavoro, 2, I-40037 Sasso Marconi (IT).	(74) Agent: HALL, Luther, A., R.; Ciba Specialty Chemicals Corporation, Patent Dept., 540 White Plains Road, P.O. Box 2005, Tarrytown, NY 10591-9005 (US). (81) Designated States: AT, AU, BG, BR, CA, CH, CN, CZ, DE, DK, ES, FI, GB, HU, ID, IL, JP, KP, KR, LU, MX, NO, NZ, PL, PT, RO, SE, SG, SI, SK, TR, UA, US, Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM). Published With international search report.	

(54) Title: BLOCK OLIGOMERS CONTAINING 1-HYDROCARBYLOXY-2,2,6,6-TETRAMETHYL-4-PIPERIDYL GROUPS AS STABILIZERS FOR ORGANIC MATERIALS



(57) Abstract

Compounds of formula (I), in which the polydispersity M_w/M_n is for example 1; n is 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13 or 14; the radicals R_1 are for example C_1-C_{18} alkyl or C_3-C_{12} cycloalkyl; R_2 is for example C_2-C_{12} alkylene; the radicals A and B^* are independently of one another $-OR_3$, $-N(R_4)(R_5)$ or a group of formula (II); R_3 , R_4 and R_5 , which are identical or different, are for example hydrogen or C_1-C_{18} alkyl, or $-N(R_4)(R_5)$ is additionally a group of formula (III) with Y being $-O-$, $-CH_2-$, $-CH_2CH_2-$ or $>N-CH_2$; X is $-O-$ or $>N-R_6$; R_6 is for example hydrogen or C_1-C_{18} alkyl; R is preferably a group of formula (IV); and B has one of the meanings given for A ; with the proviso that in the individual recurrent units of formula (I), each of the radicals B , R , R_1 and R_2 has the same or a different meaning. The indicated compounds are useful as light stabilizers, heat stabilizers and oxidation stabilizers for organic materials, in particular synthetic polymers.

the formula (I) being present in the composition has preferably a polydispersity $\overline{M}_w/\overline{M}_n$ of 1 to 1.7, in particular 1 to 1.6.

The compounds of the formula (I) or a mixture thereof can be used in various proportions depending on the nature of the material to be stabilized, on the end use and on the presence of other additives.

In general, it is appropriate to use, for example, 0.01 to 5 % by weight of the compounds of the formula (I) or the mixture thereof, relative to the weight of the material to be stabilized, preferably 0.05 to 2 %, in particular 0.05 to 1 %.

The compounds of the formula (I) or the mixture thereof can be added, for example, to the polymeric materials before, during or after the polymerization or crosslinking of the said materials. Furthermore, they can be incorporated in the polymeric materials in the pure form or encapsulated in waxes, oils or polymers.

In general, the compounds of the formula (I) or the mixture thereof can be incorporated in the polymeric materials by various processes, such as dry mixing in the form of powder, or wet mixing in the form of solutions or suspensions or also in the form of a masterbatch which contains the compounds of the formula (I) or the mixture thereof in a concentration of 2.5 to 25 % by weight; in such operations, the polymer can be used in the form of powder, granules, solutions, suspensions or in the form of latices.

The materials stabilized with the compounds of the formula (I) or the mixture thereof can be used for the production of mouldings, films, tapes, monofilaments, fibres, surface coatings and the like.

If desired, other conventional additives for synthetic polymers, such as antioxidants, UV absorbers, nickel stabilizers, pigments, fillers, plasticizers, corrosion inhibitors and metal deactivators, can be added to the organic materials containing the compounds of the formula (I) or mixtures thereof.

Particular examples of said conventional additives are:

zyl)-4-nonylphenol], 2,2'-methylenebis[6-(α,α -dimethylbenzyl)-4-nonylphenol], 4,4'-methylenebis(2,6-di-tert-butylphenol), 4,4'-methylenebis(6-tert-butyl-2-methylphenol), 1,1-bis(5-tert-butyl-4-hydroxy-2-methylphenyl)butane, 2,6-bis(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, ethylene glycol bis[3,3-bis(3'-tert-butyl-4'-hydroxyphenyl)butyrate], bis(3-tert-butyl-4-hydroxy-5-methylphenyl)dicyclopentadiene, bis[2-(3'-tert-butyl-2'-hydroxy-5'-methylbenzyl)-6-tert-butyl-4-methylphenyl]terephthalate, 1,1-bis-(3,5-dimethyl-2-hydroxyphenyl)butane, 2,2-bis-(3,5-di-tert-butyl-4-hydroxyphenyl)propane, 2,2-bis-(5-tert-butyl-4-hydroxy-2-methylphenyl)-4-n-dodecylmercaptobutane, 1,1,5,5-tetra-(5-tert-butyl-4-hydroxy-2-methylphenyl)pentane.

1.7. O-, N- and S-benzyl compounds, for example 3,5,3',5'-tetra-tert-butyl-4,4'-dihydroxydibenzyl ether, octadecyl-4-hydroxy-3,5-dimethylbenzylmercaptoacetate, tridecyl-4-hydroxy-3,5-di-tert-butylbenzylmercaptoacetate, tris(3,5-di-tert-butyl-4-hydroxybenzyl)amine, bis(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl)dithioterephthalate, bis(3,5-di-tert-butyl-4-hydroxybenzyl)sulfide, isooctyl-3,5-di-tert-butyl-4-hydroxybenzylmercaptoacetate.

1.8. Hydroxybenzylated malonates, for example dioctadecyl-2,2-bis-(3,5-di-tert-butyl-2-hydroxybenzyl)-malonate, di-octadecyl-2-(3-tert-butyl-4-hydroxy-5-methylbenzyl)-malonate, di-dodecylmercaptoethyl-2,2-bis-(3,5-di-tert-butyl-4-hydroxybenzyl)malonate, bis[4-(1,1,3,3-tetramethylbutyl)phenyl]-2,2-bis(3,5-di-tert-butyl-4-hydroxybenzyl)malonate.

1.9. Aromatic hydroxybenzyl compounds, for example 1,3,5-tris-(3,5-di-tert-butyl-4-hydroxybenzyl)-2,4,6-trimethylbenzene, 1,4-bis(3,5-di-tert-butyl-4-hydroxybenzyl)-2,3,5,6-tetramethylbenzene, 2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl)phenol.

1.10. Triazine Compounds, for example 2,4-bis(octylmercapto)-6-(3,5-di-tert-butyl-4-hydroxyanilino)-1,3,5-triazine, 2-octylmercapto-4,6-bis(3,5-di-tert-butyl-4-hydroxyanilino)-1,3,5-triazine, 2-octylmercapto-4,6-bis(3,5-di-tert-butyl-4-hydroxyphenoxy)-1,3,5-triazine, 2,4,6-tris(3,5-di-tert-butyl-4-hydroxyphenoxy)-1,2,3-triazine, 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, 2,4,6-tris(3,5-di-tert-butyl-4-hydroxyphenylethyl)-1,3,5-triazine, 1,3,5-tris(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)-hexahydro-1,3,5-triazine, 1,3,5-tris(3,5-dicyclohexyl-4-hydroxybenzyl)isocyanurate.

ate, hexadecyl 3,5-di-tert-butyl-4-hydroxybenzoate, octadecyl 3,5-di-tert-butyl-4-hydroxybenzoate, 2-methyl-4,6-di-tert-butylphenyl 3,5-di-tert-butyl-4-hydroxybenzoate.

2.4. Acrylates, for example ethyl α -cyano- β,β -diphenylacrylate, isooctyl α -cyano- β,β -diphenylacrylate, methyl α -carbomethoxycinnamate, methyl α -cyano- β -methyl-p-methoxy-cinnamate, butyl α -cyano- β -methyl-p-methoxy-cinnamate, methyl α -carbomethoxy-p-methoxycinnamate and N-(β -carbomethoxy- β -cyanovinyl)-2-methylindoline.

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, with or without additional ligands such as n-butylamine, triethanolamine or N-cyclohexyldiethanolamine, nickel dibutyldithiocarbamate, nickel salts of the monoalkyl esters, e.g. the methyl or ethyl ester, of 4-hydroxy-3,5-di-tert-butylbenzylphosphonic acid, nickel complexes of ketoximes, e.g. of 2-hydroxy-4-methylphenyl undecylketoxime, nickel complexes of 1-phenyl-4-lauroyl-5-hydroxypyrazole, with or without additional ligands.

2.6. Sterically hindered amines, for example bis(2,2,6,6-tetramethyl-4-piperidyl)sebacate, bis(2,2,6,6-tetramethyl-4-piperidyl)succinate, bis(1,2,2,6,6-pentamethyl-4-piperidyl)sebacate, bis(1-octyloxy-2,2,6,6-tetramethyl-4-piperidyl)sebacate, bis(1,2,2,6,6-pentamethyl-4-piperidyl) n-butyl-3,5-di-tert-butyl-4-hydroxybenzylmalonate, the condensate of 1-(2-hydroxyethyl)-2,2,6,6-tetramethyl-4-hydroxypiperidine and succinic acid, linear or cyclic condensates of N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)hexamethylenediamine and 4-tert-octylamino-2,6-dichloro-1,3,5-triazine, tris(2,2,6,6-tetramethyl-4-piperidyl)nitrilotriacetate, tetrakis(2,2,6,6-tetramethyl-4-piperidyl)-1,2,3,4-butane-tetracarboxylate, 1,1'-(1,2-ethanediy)-bis(3,3,5,5-tetramethylpiperazinone), 4-benzoyl-2,2,6,6-tetramethylpiperidine, 4-stearyloxy-2,2,6,6-tetramethylpiperidine, bis(1,2,2,6,6-pentamethylpiperidyl)-2-n-butyl-2-(2-hydroxy-3,5-di-tert-butylbenzyl)malonate, 3-n-octyl-7,7,9,9-tetramethyl-1,3,8-triazaspiro[4.5]decan-2,4-dione, bis(1-octyloxy-2,2,6,6-tetramethylpiperidyl)sebacate, bis(1-octyloxy-2,2,6,6-tetramethylpiperidyl)succinate, linear or cyclic condensates of N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)hexamethylenediamine and 4-morpholino-2,6-dichloro-1,3,5-triazine, the condensate of 2-chloro-4,6-bis(4-n-butylamino-2,2,6,6-tetramethylpiperidyl)-1,3,5-triazine and 1,2-bis(3-aminopropylamino)ethane, the condensate of 2-chloro-4,6-di-(4-n-butylamino-1,2,2,6,6-pentamethylpiperidyl)-1,3,5-triazine and 1,2-bis(3-aminopropylamino)ethane, 8-acetyl-3-dodecyl-7,7,9,9-tetramethyl-1,3,8-triazaspiro[4.5]decane-2,4-dione, 3-dodecyl-1-(2,2,6,6-tetrame-

thyl-4-piperidyl)pyrrolidin-2,5-dione, 3-dodecyl-1-(1,2,2,6,6-pentamethyl-4-piperidyl)pyrrolidine-2,5-dione, a mixture of 4-hexadecyloxy- and 4-stearoyloxy-2,2,6,6-tetramethylpiperidine, a condensation product of N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)hexamethylenediamine and 4-cyclohexylamino-2,6-dichloro-1,3,5-triazine, a condensation product of 1,2-bis(3-aminopropylamino)ethane and 2,4,6-trichloro-1,3,5-triazine as well as 4-butylamino-2,2,6,6-tetramethylpiperidine (CAS Reg. No. [136504-98-6]); N-(2,2,6,6-tetramethyl-4-piperidyl)-n-dodecylsuccinimid, N-(1,2,2,6,6-pentamethyl-4-piperidyl)-n-dodecylsuccinimid, 2-undecyl-7,7,9,9-tetramethyl-1-oxa-3,8-diaza-4-oxo-spiro[4,5]decane, a reaction product of 7,7,9,9-tetramethyl-2-cycloundecyl-1-oxa-3,8-diaza-4-oxospiro [4,5]decane und epichlorohydrin, 1,1-bis(1,2,2,6,6-pentamethyl-4-piperidyl)oxycarbonyl-2-(4-methoxyphenyl)ethene, N,N'-bisformyl-N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)hexamethylenediamine, diester of 4-methoxymethylene-malonic acid with 1,2,2,6,6-pentamethyl-4-hydroxypiperidine, poly(methylpropyl-3-oxy-4-(2,2,6,6-tetramethyl-4-piperidyl))siloxane, reaction product of maleic acid anhydride- α -olefin-copolymer with 2,2,6,6-tetramethyl-4-aminopiperidine or 1,2,2,6,6-pentamethyl-4-aminopiperidine.

2.7. Oxamides, for example 4,4'-dioctyloxyoxanilide, 2,2'-diethoxyoxanilide, 2,2'-dioctyloxy-5,5'-di-tert-butoxanilide, 2,2'-didodecyloxy-5,5'-di-tert-butoxanilide, 2-ethoxy-2'-ethyloxanilide, N,N'-bis(3-dimethylaminopropyl)oxamide, 2-ethoxy-5-tert-butyl-2'-ethoxanilide and its mixture with 2-ethoxy-2'-ethyl-5,4'-di-tert-butoxanilide, mixtures of o- and p-methoxy-disubstituted oxanilides and mixtures of o- and p-ethoxy-disubstituted oxanilides.

2.8. 2-(2-Hydroxyphenyl)-1,3,5-triazines, for example 2,4,6-tris(2-hydroxy-4-octyloxyphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-octyloxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2,4-dihydroxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2,4-bis(2-hydroxy-4-propyloxyphenyl)-6-(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-octyloxyphenyl)-4,6-bis(4-methylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-dodecyloxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-tridecyloxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-[2-hydroxy-4-(2-hydroxy-3-butyloxy-propoxy)phenyl]-4,6-bis(2,4-dimethyl)-1,3,5-triazine, 2-[2-hydroxy-4-(2-hydroxy-3-octyloxy-propyloxy)phenyl]-4,6-bis(2,4-dimethyl)-1,3,5-triazine, 2-[4-(dodecyloxy/tridecyloxy-2-hydroxypropoxy)-2-hydroxy-phenyl]-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-[2-hydroxy-4-(2-hydroxy-3-dodecyloxy-propoxy)phenyl]-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-hexyloxy)phenyl-4,6-diphenyl-1,3,5-triazine, 2-(2-hydroxy-4-methoxyphenyl)-4,6-diphenyl-1,3,5-triazine, 2,4,6-tris[2-hydroxy-4-(3-

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PATENT SPECIFICATION

NO DRAWINGS

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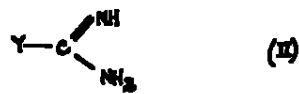
COMPLETE SPECIFICATION

Improvements relating to *o*-Hydroxyphenyl-*s*-Triazines and their use

We, J. R. GIGY A.G., a body corporate organised according to the laws of Switzerland, of 215 Schwarzwaldallee, Basle, Switzerland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
The present invention concerns new *o*-hydroxyphenyl-*s*-triazines, a process for the production thereof, their use for the stabilising of light-sensitive organic material and for the production of light filters and, as industrial product, the organic material stabilised with the aid of these triazines as well as light filters containing the new *o*-hydroxyphenyl-*s*-triazines.
It has been found that valuable UV absorbers are obtained if 1 mol of an amidine of the formula I

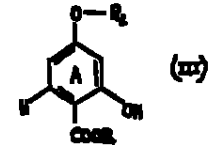


and 1 mol of an amidine of formula II

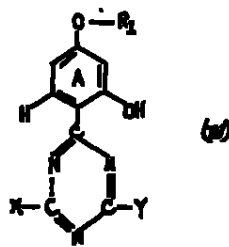


in which formulae
X and Y independently of each other each
ii ———— .j

represent hydrogen or an alkyl, alkenyl, cycloalkyl or aralkyl group which may be substituted,
are reacted with 1 mol of an *o*-hydroxy- benzene carboxylic acid ester of formula III



wherein R₁ represents hydrogen or an alkyl, alkenyl or aralkyl group which may be substituted, and
R represents a hydrocarbon radical which may be substituted, and the benzene ring A is possibly further substituted in the positions 3' and 5' by alkyl or alkenyl groups each having 1 to 10 carbon atoms
to form a compound of formula IV



wherein X and Y have the meanings given in formulae I or II and R₁ and A have the meanings given in formula III.

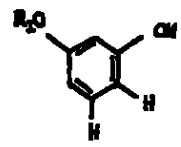
In the formulae I, II and IV, the alkyl groups symbolised by X and Y have, for example, 1 to 18 carbon atoms. Examples are the methyl, ethyl, propyl, isopropyl, butyl, tert. butyl, amyl, hexyl, octyl, decyl, dodecyl, tetradecyl, hexadecyl or octadecyl group; of these, alkyl groups having 1 to 10 carbon atoms are preferred. The alkyl groups may be further substituted in which case, for example, they may have, among others, the formula -alkylene-E-D₁. In this formula, "alkylene" represents a divalent aliphatic radical having in particular 1 to 12, preferably 1 to 4 carbon atoms, and E represents either -O- or -S- or -N(D₂)-. Each of D₁ and D₂ independently represents an alkyl radical preferably containing 1 to 8 carbon atoms and each represents hydrogen if E is oxygen or nitrogen. Suitable groups of the formula -alkylene-E-D₁ are, for example, the ω -hydroxyalkyl, ω -alkoxyalkyl, ω -alkylmercaptoalkyl, ω -aminoalkyl groups such as the hydroxymethyl, 2-hydroxyethyl, 2-methoxyethyl, 2-ethoxyethyl, 2-butoxyethyl, 2-methylmercaptoethyl, 2-butylmercaptoethyl, 2-dodecylmercaptoethyl, 2-N,N-dimethylaminoethyl, 2-N,N-diethylaminoethyl or the ω -aminodecyl group.

Each of X and Y can also be a halogeno-alkyl group preferably containing 1 to 4 carbon atoms such as the chloromethyl, bromomethyl, 2-chloroethyl or 4-chlorobutyl group. As alkaryl group X or Y represent, e.g. the vinyl group, the Δ^1 or Δ^2 -propyl or the Δ^8 -heptadecenyl group, of which the low alkenyl groups having 2 to 6 carbon atoms are preferred. It is possible for the alkenyl groups to be substituted by aryl groups then they represent e.g. the β -phenylvinyl (=styryl group) or the 2-phenyl-propen-(1)-yl-(1) group. As cycloalkyl groups, X or Y have 5 to 10, preferably however, 6 to 7 carbon atoms. Examples are the cyclohexyl, methylcyclohexyl or ethylcyclohexyl group. If X or Y is an aralkyl group, then this contains 7 to 12, preferably 7 to 9 carbon atoms; examples are the benzyl, phenylethyl, p-butylbenzyl, p-chlorobenzyl or p-methoxyphenyl group. Compounds in which X is the same as Y are particularly easily produced.

Alkyl groups symbolised by R₁ in formulae III and IV preferably have 1 to 12 carbon atoms; thus R₁ is, for example, the methyl, ethyl, propyl, butyl, amyl, hexyl, octyl, decyl or dodecyl group. The alkyl groups may be substituted if desired. Examples of alkyl substituents are halogens such as chlorine or bromine, free or etherified hydroxyl or cyano groups as well as free or modified carboxyl groups. By "modified carboxyl groups" mainly carboxylic acid ester, but also carboxylic acid amide groups are to be under-

stood; in the latter case, carboxylic acid alkylamide groups, in particular those having a tertiary amide nitrogen atom, are preferred. Cyano and free or modified carboxyl groups can be at any C atom of the alkyl group whilst the halogens and the free or etherified hydroxyl groups are bound to a carbon atom of the alkyl group which is different from the α -carbon atom. Examples of further substituted alkyl groups R₁ are the 2-chloro- or 2-bromo-ethyl group, 2-hydroxyethyl, 4-hydroxybutyl, 2-methoxyethyl, 2-ethoxyethyl, 2-cyclohexyloxyethyl, 2-cyanoethyl, carbomethoxymethyl, carbomethoxymethyl, carbododecyloxymethyl or the N,N-dimethylcarbamoxymethyl group. As alkenyl group, R₁ is in particular the Δ^2 -propenyl group which can be substituted by low alkyl groups. If R₁ is an aralkyl group then it contains 7 to 12, preferably 7 to 9, carbon atoms; examples are the benzyl or a methylbenzyl group. R in formula III is an alkyl radical, which may be substituted, having 1 to 18, preferably 1 to 6, carbon atoms, e.g. the methyl, ethyl, methoxyethyl, ethoxyethyl, cyanomethyl or a carbalkoxyalkyl radical, particularly the carbomethoxy, carbethoxy and carbopropoxy ethyl radical. Also, R represents a cycloalkyl radical having 5 to 10, preferably 6 to 7, carbon atoms, particularly the cyclohexyl radical, or an aralkyl radical having 7 to 12 carbon atoms, mainly the benzyl radical. It is advantageous, however, if R is a monocyclic aryl radical having 6 to 12, preferably 6 to 10 carbon atoms, such as the phenyl, a methylphenyl or a halogenophenyl radical.

Some of the starting materials of formulae I, II and III are known and can be produced by methods known per se. Amidines of the formula I or II are obtained, for example, from nitriles of the formulae X-CN or Y-CN by conversion into corresponding iminoethers and reaction of the latter with ammonia; the *o*-hydroxy-benzene carboxylic acid esters of formula III are obtained, for example, from the corresponding salicylic acids by esterification. The salicylic acids are advantageously obtained by reacting the phenols of the formula



with carbon dioxide according to Kolbe whilst groups R₁ which are not hydrogen can be introduced before or after performing the Kolbe synthesis.

The reaction to form the *o*-hydroxyphenyl triazines is performed by heating the starting materials I, II and III, in equimolar ratios. Advantageously, the reaction is performed in

boiling organic solvents, particularly when amidines having a high melting point are used. Suitable solvents are mainly alcohols such as methanol, ethanol, ethylene glycol monomethyl or monoethyl ether, or also dioxane.

If desired, any reactive substituents present in the new *o*-hydroxyphenyl-*s*-triazines can subsequently be altered. If X or Y is an alkoxyalkyl group then this can be converted with hydrobromic acid into the corresponding bromoalkyl group. *o*-Hydroxyphenyl-*s*-triazines having halogenoalkyl side groups are produced advantageously by this method. Exchangeable halogen can also be replaced by reaction with aqueous sodium hydroxide solution, with alkali alcoholates or alkali phenolates, with ammonia, primary or secondary amines, by the hydroxyl group or by an ether group or by an amino group; if the *o*-hydroxyphenyl-*s*-triazines contain alcoholic or phenolic hydroxyl groups, these can be esterified or etherified.

In particular, the *o*-hydroxyphenyl-*s*-triazines in which R₄ is an alkyl, alkenyl or aralkyl group which may be substituted are obtained by etherifying the corresponding triazines having a free hydroxyl group. Suitable etherification agents are esters of strong acids such as hydrochloric, hydrobromic, hydroiodic acid, sulphuric acid or *p*-toluene sulphonic acid, with the corresponding alkyl, alkenyl or aralkyl alcohols. Compounds of formula IV, in which X or Y is an alkenyl radical are produced advantageously from corresponding compounds in which X or Y is a halogenoalkyl, hydroxyalkyl, alkoxyalkyl or aminoalkyl radical by removal of halogen hydride or splitting off of water or alcohol or amine, optionally after modification into quaternary ammonium salts, by the methods usual in organic chemistry. Such triazines having unsaturated side chains can also be produced by reacting simple alkyl triazines, particularly methyl triazines, with aldehydes while splitting off water.

The new *o*-hydroxyphenyl-*s*-triazines are distinguished by excellent fastness to light in polymeric carriers and have high molar extinction in the region of 290–350 mμ which has a favourable influence on the protective action. Compounds which contain double bonds in the side chains which are in conjugation with the triazine ring, i.e. those in which X and/or Y is/are a Δ²-alkenyl or Δ²-aralkenyl group, particularly a β-phenyl-vinyl group, are distinguished by particularly high absorption power. In general, however, they are somewhat less fast to light than compounds which do not contain such conjugated double bonds in the side chains. Compared with previously known compounds of similar constitution, with comparable solubility and light fastness the new triazines are distinguished by less yellow colouration and, with comparable yellow colouration they are distinguished by better solubility in organic solvents and in polymers. This is important in two respects: the use of UV absorbers is to hinder, among other things, the photochemical discolouration, particularly of colourless substrata such as, e.g. polystyrene or polymethyl methacrylate. However, if the UV absorber has a yellow colour of its own, the substratum to be protected is already discoloured from the beginning so that in this connection the action of the UV absorber is illusory; in addition, better solubility with, at the same time, comparable self-colour of the UV absorber is of great importance in their application and in the production of very thin light filters.

Those compounds of formula IV are particularly advantageous in which the sum of the carbon atoms in X, Y, R₁ and the substituents of the ring A is greater than three but smaller than 25.

The new *o*-hydroxyphenyl-*s*-triazines of formula IV are incorporated into the light-sensitive carriers or polymeric carriers for light filters in amounts of 0.01 to 30%. The amount of triazine to be used depends, among other things, on the thickness of the light filter to be produced. For very thin layers such as, e.g. for lacquer coatings, amounts of 1 to 20% are preferred, for thick layers such as, e.g. in polymethacrylate sheets on the other hand, amounts of 0.01 to 1% are preferred.

Organic polymers, both thermoplastic polymers and thermosetting polymers are the main carriers for the new *o*-hydroxyphenyl-*s*-triazines. This includes completely synthetic polymers as well as natural polymers as well as their polymeric homologous chemical modification products. Of the completely synthetic polymers mainly pure addition and pure condensation polymers, also however, condensation polymers cross-linked by addition polymerization, are used. The addition polymers which are employed as carriers for the new UV absorbers can be arranged in the following main types:

1. Homopolymers and copolymers of vinyl and vinylidene monomers which are converted into the corresponding polymers by radical, ionic or metal-organic polymerization initiators. Examples of such monomers, the polymers of which are suitable carriers, are:
Polymerisable ethylenic unsaturated halogen-hydrocarbon compounds, in particular vinyl chloride, vinyl fluoride and vinylidene chloride.
- Polymerisable hydrocarbons having a double bond capable of addition, particularly styrene, isobutylene, ethylene and propylene. Both the atactic and the isotactic forms of polymers can be used.
- α,β-unsaturated polymerisable carboxylic acids and functional derivatives thereof such as acrylic acid, methacrylic acid, acrylonitrile, alkyl esters (—particularly low alkyl esters—)

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(54) **Stabilization of pigmented fiber with a synergistic mixture of hindered amine and UV absorber**

(57) Pigmented thermoplastic fiber, especially pigmented polypropylene fiber, are stabilized against the deleterious effects of actinic radiation by a synergistic

combination of a hindered amine light stabilizer plus a UV absorber such as an o-hydroxyphenylbenzotriazole or an o-hydroxyphenyl-s-triazine.

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2-[2-hydroxy-3,5-di(α , α -dimethylbenzyl)phenyl]-2H-benzotriazole;
 2,4-diphenyl-6-(2-hydroxy-4-hexyloxyphenyl)-s-triazine;
 2,4-bis(2,4-dimethylphenyl)-6-(2-hydroxy-4-octyloxyphenyl)-s-triazine;
 2-(2-hydroxy-3- α -cumyl-5-tert-octylphenyl)-2H-benzotriazole;
 5-benzenesulfonyl-2-(2-hydroxy-3,5-di-tert-butylphenyl)-2H-benzotriazole;
 2-hydroxy-4-dodecyloxybenzophenone; and
 2-hydroxy-4-octyloxy-benzophenone.

Most preferably, the hindered amines are

the polycondensation product of 1-(2-hydroxyethyl)-2,2,6,6-tetramethyl-4-hydroxypiperidine and succinic acid;
 the polycondensation product of 4,4'-hexamethylene-bis(amino-2,2,6,6-tetramethylpiperidine) and 2,4-dichloro-6-tert-octylamino-s-triazine;
 the polycondensation product of 4,4'-hexamethylene-bis(amino-2,2,6,6-tetramethylpiperidine) and 2,4-dichloro-6-morpholino-s-triazine;
 poly[methyl 3-(2,2,6,6-tetramethylpiperidin-4-yloxy)propylsiloxane;
 bis(2,2,6,6-tetramethylpiperidin-4-yl) cyclohexylenedioxymethylmalonate;
 1,3,5-tris[N-cyclohexyl-N-[2-(2,2,6,6-tetramethylpiperazin-3-on-4-yl)ethyl]amino-s-triazine;
 N,N',N'',N'''-tetrakis[4,6-bis(butyl-(2,2,6,6-tetramethylpiperidin-4-yl)amino)-s-triazin-2-yl]-1,10-diamino-4,7-diaza-decane; and
 2,2,6,6-tetramethylpiperidin-4-yl C₁₆-C₂₀alkanoate.

Most especially, the UV absorber is

2-[2-hydroxy-3-tert-butyl-5-[2-(methoxycarbonyl)ethyl]phenyl]-2H-benzotriazole;
 2-[2-hydroxy-3,5-di(α , α -dimethylbenzyl)phenyl]-2H-benzotriazole;
 2,4-diphenyl-6-(2-hydroxy-4-hexyloxyphenyl)-s-triazine;
 2,4-bis(2,4-dimethylphenyl)-6-(2-hydroxy-4-octyloxyphenyl)-s-triazine; or
 2-(2-hydroxy-3- α -cumyl-5-tert-octylphenyl)-2H-benzotriazole; and
 the hindered amine is
 the polycondensation product of 1-(2-hydroxyethyl)-2,2,6,6-tetramethyl-4-hydroxypiperidine and succinic acid;
 the polycondensation product of 4,4'-hexamethylene-bis(amino-2,2,6,6-tetramethylpiperidine) and 2,4-dichloro-6-tert-octylamino-s-triazine;
 the polycondensation product of 4,4'-hexamethylene-bis(amino-2,2,6,6-tetramethylpiperidine) and 2,4-dichloro-6-morpholino-s-triazine; or
 N,N',N'',N'''-tetrakis[4,6-bis(butyl-(2,2,6,6-tetramethylpiperidin-4-yl)amino)-s-triazin-2-yl]-1,10-diamino-4,7-diazadecane.

The fibers of the instant invention are made from the thermoplastic polymer in a standard or conventional manner, for example, using melt spinning, solution (dry) spinning or fibrillation of thin films. The individual filaments are typically about 50 microns or less. These can be joined into multifilament yarns of higher denier. The ultimate article prepared can have individual yarns of different polymers if desired.

Additionally, the instant invention also pertains to a stabilized pigment composition which comprises

- (a) an organic or inorganic pigment, and
- (b) an effective stabilizing amount of a mixture of

- (i) a hindered amine, and
- (ii) a UV absorber.

Preferred components (a), (bi) and (bii) are basically as described above for the pigmented and stabilized fibers of this invention.

The UV absorber is selected from the group consisting of the 2-hydroxyphenylbenzotriazoles, o-hydroxyphenyl-s-triazines, 2-hydroxybenzophenones, benzoxazinones, α -cyanoacrylates, oxanilides, nickel complexes and benzoates.

Preferably, the UV absorber is a benzotriazole or an s-triazine.

The hindered amine is preferably derived from a 2,2,6,6-tetramethylpiperidine.

The stabilized pigment composition is where the effective amount of a combination of stabilizers of this invention is 10 to 50% by weight, based on the pigment; where the effective amount of hindered amine is 1 to 40% by weight, based on the pigment; and where the effective amount of the UV absorber is 1 to 40% by weight, based on the pigment.

(19)



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C07D 403/14, C07D 403/10,
C09D 139/04

(21) Application number: 95810471.3

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(84) Designated Contracting States: AT BE CH DE ES FR GB IT LI NL (30) Priority: 27.07.1994 US 281381 (71) Applicant: CIBA-GEIGY AG CH-4002 Basel (CH) (72) Inventors: Stevenson, Tyler Arthur Teaneck, NJ 07960 (US)	- Ravichandran, Ramanathan Nanuet, NY 10954 (US) - Holt, Mark Stephen West Nyack, NY 10990 (US) - Phan, Thuy Ngoc North Tarrytown, NY 10591 (US) - Birbaum, Jean-Luc, Dr. Higashinada-ku, Kobe 656 (JP) - Toan, Vien Van, Dr. CH-1745 Lentigny (CH)
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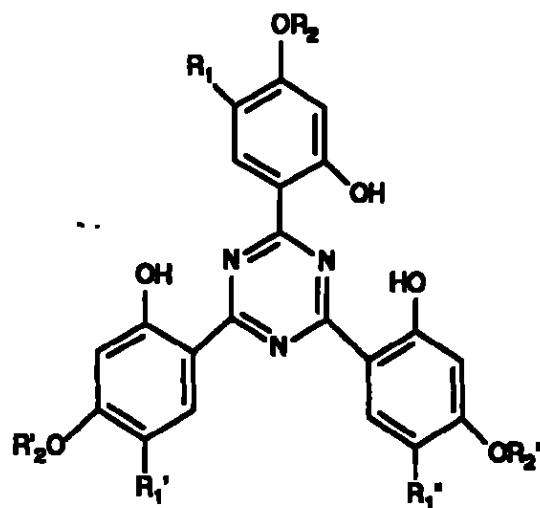
(54) Red-shifted tri-aryl-s-triazines and compositions stabilized therewith

(57) Tri-aryl-s-triazines which contain from one to three resorcinol derived moieties with at least one of said moieties substituted at the 5-position with an alkyl, phenylalkyl, halogen, thio or sulfonyl group have UV spectra

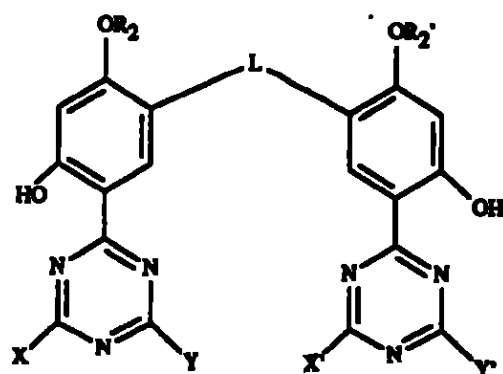
which are red-shifted to the near UV range and provide excellent stabilization to polymeric substrates against the deleterious effects of actinic light.

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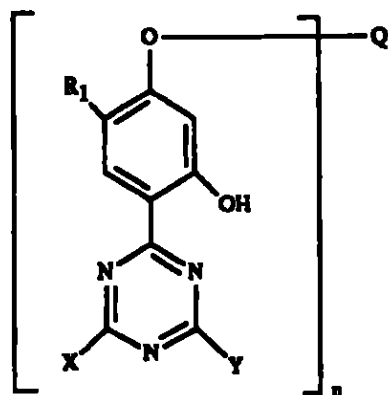
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III



IV



V

where in the compounds of formula I

X and Y are the same or different and are phenyl or phenyl substituted with one to three lower alkyl, halogen, hydroxy or alkoxy;

R₁ is 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, halogen, -SR₃, -SOR₃, or -SO₂R₃; said alkyl or cycloalkyl substituted by one to eight halogen, -R₄, -OR₅, -N(R₆)₂, =NR₅=O, -CON(R₆)₂, -COR₅, -COOR₅, -OCOR₅, -CN, -NO₂, -SR₆, -SOR₆, -SO₂R₆, -P(O)(OR₆)₂, morpholinyl, piperidinyl, 2,2,6,6-tetramethylpiperidinyl, piperazinyl or N-methylpiperazinyl groups

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and the hard polyorganosiloxanes described, for example, in U.S. Patent No. 4,355,147.

31. Polyketimines in combination with unsaturated acrylic polyacetoacetate resins or with unsaturated acrylic resins. The unsaturated acrylic resins include the urethane acrylates, polyether acrylates, vinyl or acryl copolymers with pendant unsaturated groups and the acrylated melamines. The polyketimines are prepared from polyamines and ketones in the presence of an acid catalyst.

32. Radiation curable compositions containing ethylenically unsaturated monomers or oligomers and a polyunsaturated aliphatic oligomer.

33. Epoxymelamine resins such as light-stable epoxy resins crosslinked by an epoxy functional coetherified high solids melamine resin such as LSE-4103 (Monsanto).

In general, the compounds of the present invention are employed from about 0.01 to about 20% by weight of the stabilized composition, although this will vary with the particular substrate and application. An advantageous range is from 0.1 to 10%, e.g. 1 to 5%; preferably 1.5 to 2.5%.

Other compositions of special interest include those which additionally contain a UV absorber selected from the group consisting of the benzophenones, benzotriazoles, cyanoacrylic acid derivatives, hydroxyaryl-s-triazines, organic nickel compounds and oxanilides.

Preferred UV absorbers are selected from the group consisting of 2-[2-hydroxy-3,5-di-(α,α -dimethylbenzyl)phenyl]-2H-benzotriazole, 2-[2-hydroxy-3-(α,α -dimethylbenzyl)-5octylphenyl]-2H-benzotriazole, 2-(2-hydroxy-3,5-di-tert-amyphenyl)-2H-benzotriazole, 2-[2-hydroxy-3-tert-butyl-5-(ω -hydroxy-octa(ethyleneoxy)carbonyl)ethylphenyl]-2H-benzotriazole, 2-[2-hydroxy-3-tert-butyl-5-(2-octyloxycarbonylethyl)phenyl]-2H-benzotriazole, 4,4'-dioctyloxycanilide, 2,2'-dioctyloxy-5,5'-di-tert-butylcanilide, 2,2'-didodecyloxy-5,5'-di-tert-butylcanilide, 2-ethoxy-2'ethyloxanilide, 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, 2,6-bis(2,4-dimethylphenyl)-4-[2-hydroxy-4-(2-hydroxy-3-dodecyloxypropoxy)phenyl]-s-triazine and 2,2'-dihydroxy-4,4'-dimethoxybenzophenone.

Additional compositions of interest include those which additionally contain an effective stabilizing amount of a phenolic antioxidant; those which additionally contain a hindered amine derivative; or which additionally contain a phosphite or phosphonite stabilizer.

Compositions of special interest also include those wherein the organic material is an enamel of high solids content used for an industrial finish; is used as a coil coating; is used as a penetrating wood finish or is used as a film-forming wood finish.

When the instant compounds also contain a reactive functional group, said compounds can be chemically bonded by either condensation or free radical addition reaction to the polymer substrate. This provides for a non-migrating, non-sublimable UV absorber stabilizer. Such reactive functional groups include hydroxy, amino, amido, carboxyl and ethylenically unsaturated moieties.

The various organic materials useful in the instant invention are described in detail later in this application as well as are the various coadditives whose concomitant use with the instant compounds is often found to be highly beneficial.

The resulting stabilized polymer compositions of the invention may optionally also contain from about 0.01 to about 5%, preferably from about 0.025 to about 2%, and especially from about 0.1 to about 1% by weight of various conventional additives, such as the materials listed below, or mixtures thereof.

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-isobutylphenol, 2,6-dicyclopentyl-4-methylphenol, 2-(α -methylcyclohexyl)-4,6-dimethylphenol, 2,6-dioctadecyl-4-methylphenol, 2,4,6-tricyclohexylphenol, 2,6-di-tert-butyl-4-methoxymethylphenol, nonylphenols which are linear or branched in the side chains, for example, 2,6-di-nonyl-4-methylphenol, 2,4-dimethyl-6-(1'-methylundec-1'-yl)phenol, 2,4-dimethyl-6-(1'-methylheptadec-1'-yl)phenol, 2,4-dimethyl-6-(1'-methyltridec-1'-yl)phenol and mixtures thereof.

1.2. Alkylthiomethylphenols, for example 2,4-dioctylthiomethyl-6-tert-butylphenol, 2,4-dioctylthiomethyl-6-methylphenol, 2,4-dioctylthiomethyl-6-ethylphenol, 2,6-di-dodecylthiomethyl-4-nonylphenol.

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⑪ Publication number: **0 483 488 A1**

⑫ **EUROPEAN PATENT APPLICATION**

⑪ Application number: 91114903.7

⑪ Int. Cl.⁴: **C08K 5/34, //(C08K5/3435, 5:3492)**

⑫ Date of filing: 04.09.91

⑫ Priority: 29.10.90 US 605199

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⑫ Date of publication of application:
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⑫ Designated Contracting States:
AT BE CH DE DK ES FR GB GR IT LI LU NL SE

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⑫ **Synergistic ultraviolet absorber compositions containing hydroxy aryl triazines and tetraalkyl piperidines.**

⑫ **A synergistic stabilizer composition for polymers is described containing (i) a hydroxy-group containing triazine, and (ii) a 2,2,6,6-tetraalkyl piperidine compound. Also, described is a method of stabilizing polymers.**

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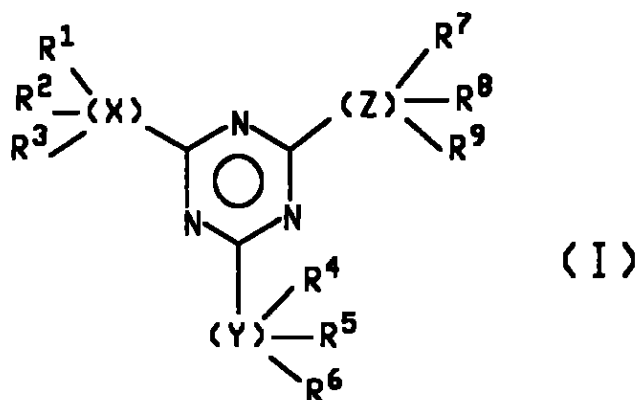
wherein X,Y,Z are each the same or different aromatic carbocyclic radicals, and at least one of the X, Y, and Z has a hydroxy group substituted ortho to the point of attachment to the triazine ring, and an OR group substituted at a point para to the attachment of the triazine ring and, wherein the R moiety of the OR group is, independently, a linear, branched aliphatic or cycloaliphatic alkyl moiety containing 1 to 12 carbon atoms and is:

- (1) interrupted by one or more oxygen atoms; or
- (2) substituted by one or more hydroxy groups or alkoxy groups of 1 to 12 carbon atoms; or
- (3) both interrupted and substituted by the above groups of (1) and (2); and

wherein R¹ to R⁹ are selected from the group consisting of hydrogen, hydroxy, alkyl of 1 to 12 carbon atoms, alkoxy of 1 to 12 carbon atoms, sulfonic, halo, carboxy, haloalkyl, and acrylamino; and (B) a 2,2,6,6-tetraalkyl piperidine compound.

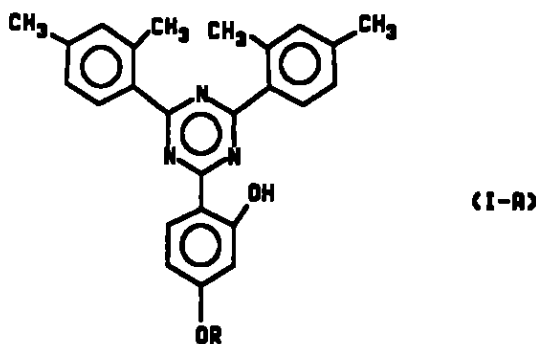
2. TRIAZINES OF THE INVENTION

The hydroxy group-containing triazines of this invention are represented by Formula I:



as described in the preceding section.

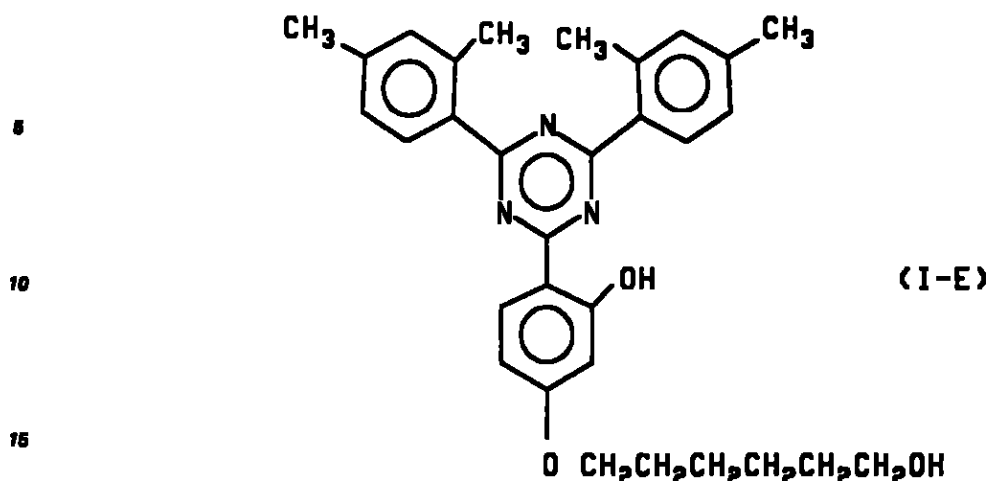
An example of the preferred embodiment of this invention is a class of triazines represented by Formula I-A:



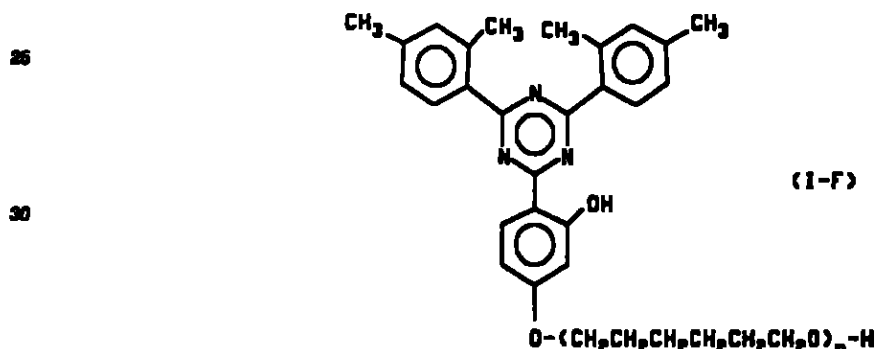
wherein the R moiety is, independently, a linear, branched aliphatic, or cycloaliphatic alkyl moiety of 1 to 12 carbon atoms, and is:

- (1) both interrupted by one or more oxygen atoms; or
- (2) substituted by one or more hydroxy groups or alkoxy groups of 1 to 12 carbon atoms; or
- (3) both interrupted and substituted by the above groups of (1) and (2).

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20 In the preparation of triazine I-E, it is of course possible to obtain, in addition to triazine I-E, small amounts of another triazine compound containing repeating units of $-(CH_2CH_2CH_2CH_2CH_2CH_2O)-$ as represented by the Formula I-F:

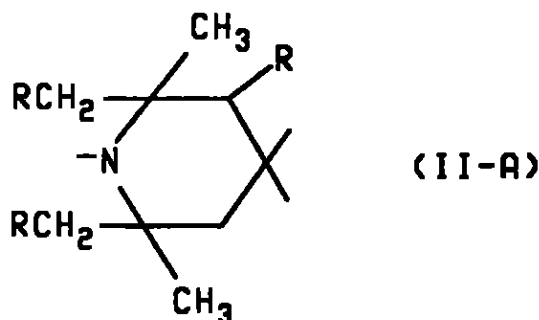


The presence of small amounts of triazine I-F in triazine I-E is permissible and sometimes even beneficial since presence of oligomers may improve the compatibility of the triazine ultraviolet absorber in coatings compositions.

4. THE 2,2,6,6-TETRAALKYL PIPERIDINE COMPOUNDS USED IN THE COMPOSITION OF THE INVENTION

The HALS useful in the method of this invention are 2,2,6,6-tetraalkylpiperidines, their acid addition salts or complexes with metal compounds. These HALS are well known in the art and include compounds which contain a group represented by Formula II:

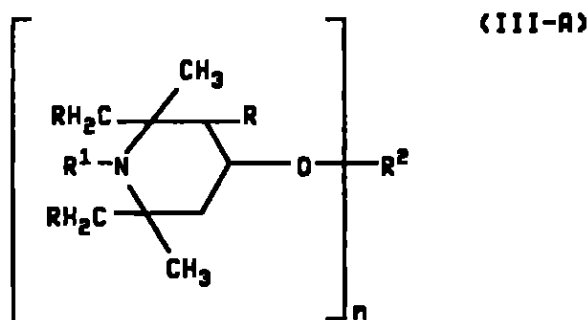
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wherein R is hydrogen or methyl.

HALS utilizable in this invention also include, but are not limited to, compounds represented by the following:

1. Formula III-A



wherein:

n is a number from 1-4 inclusive, preferably 1 to 2;

R is as defined in Formula II-A;

R¹ is hydrogen, oxyl, hydroxy, C₁ to C₁₈ alkoxy, alkyl, C₂-C₁₈ alkenyl or alkynyl, C₇-C₁₂ aralkyl, C₁-C₆ alkanoyl, C₂-C₆ alkenoyl, glycidyl, a group -CH₂CH(OH)-Z wherein Z is hydrogen, methyl or phenyl, with R¹ preferably being hydrogen, C₁-C₁₂ alkyl, allyl, benzyl, acetyl or acryloyl;

R², when n is 1, is hydrogen, C₁-C₁₈ alkyl optionally interrupted by one or more oxygen atoms, cyanoethyl, benzyl, glycidyl, a monovalent radical of an aliphatic, cycloaliphatic, araliphatic or aromatic carboxylic acid, or of carbamic acid, or of a phosphorous-containing acid, or a monovalent silyl radical, preferably a radical of an aliphatic carboxylic acid having 2-18 carbon atoms, of a cycloaliphatic carboxylic acid having 5-12 carbon atoms or of an aromatic carboxylic acid having 7-15 carbon atoms;

R², when n is 2, is C₁-C₁₂ alkylene, C₂-C₁₂ alkenylene, xylylene, a bivalent radical of an aliphatic, cycloaliphatic, araliphatic or aromatic dicarboxylic acid, of a dicarbamic acid or of a phosphorous-containing acid, or a bivalent silyl radical, preferably a radical of an aliphatic dicarboxylic acid having 2-36 carbon atoms, of a cycloaliphatic or aromatic dicarboxylic acid having 8-14 carbon atoms, or of an aliphatic, cycloaliphatic or aromatic dicarbamic acid having 8-14 carbon atoms;

R², when n is 3, is a trivalent radical of an aliphatic, cycloaliphatic or aromatic tricarboxylic acid, of an aromatic tricarbamic acid or of a phosphorous-containing acid, or a trivalent silyl radical; and

R², when n is 4, is a tetravalent radical of an aliphatic, cycloaliphatic or aromatic tetracarboxylic acid;

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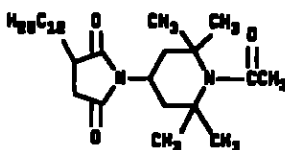
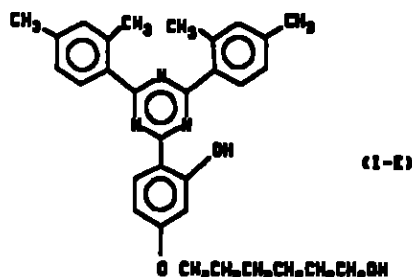
1. Antioxidants which are alkylated phenols, alkylated hydroquinones, hydroxylated thiophenyl ethers, alkylidene-bisphenols, benzyl compounds, acylaminophenols, esters of β -(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid with monohydric or polyhydric alcohols, and amides of β -(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid;
2. Other ultraviolet light stabilizers;
3. Metal deactivators;
4. Phosphites, phosphonites, and phosphines;
5. Compounds which decompose peroxides such as phosphites, phosphonites, and thioesters;
6. Nucleating agents;
7. Filters; and
8. Other additives, for example, plasticizers, lubricants, emulsifiers, pigments, fluorescent whitening agents, flameproofing agents, antistatic agents and blowing agents.

Proportions of Stabilizers :

The HALS are generally used in amounts within the range of from about 0.01 to about 5 wt % based on the weight of total resin solids. The UVA of this invention are used in amounts within the range of from about 0.01 to about 5 wt % based on the weight of total resin solids. The weight ratio of HALS to UVA is from about 500:1 to about 1:500 with ratios of from 5:1 to 1:5 being preferred.

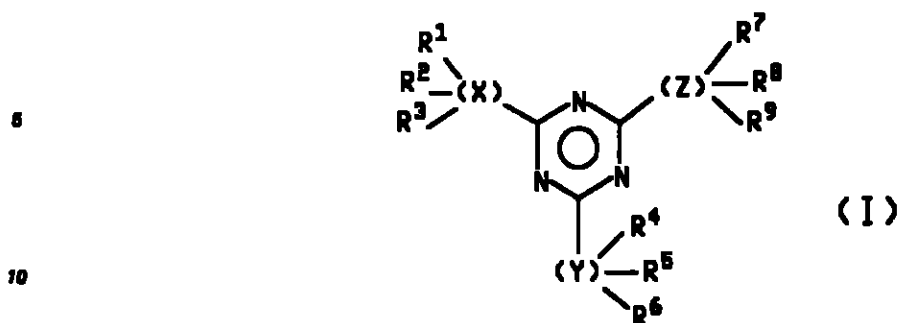
Synergistic Combinations :

The UVA of this invention represented by Formula (I-A) are synergistically combined with the HALS represented by Formula (X) to produce synergistically stabilized coatings. For example, the preferred synergistic combination is:



5. LIGHT STABILIZED POLYMERS OF THE INVENTION

The light stable compositions of the invention comprises:
(A) a hydroxy group-containing triazine represented by Formula I



As previously described in section (1) of DETAILED DESCRIPTION OF THE INVENTION.

- (B) a polymer to be stabilized, and
(C) a 2,2,6,6-tetraalkylpiperidine compound.

The polymer material to be stabilized is a synthetic resin or polymer such as an acrylic or a polyester film or coating, a polyolefin such as polyethylene or polypropylene usually in the form of a fibers, film, or thick sections, an engineering grade polyester, polycarbonate, polyamide, polystyrene, or polyurethane. Curable or polymerizable mixtures leading to cured or polymerized materials are also included in the definition of polymer materials usable in the composition of the invention.

For example, a curable composition comprises hexamethoxymethyl melamine, a polyhydroxy functional material, an acid cure catalyst, and the two part stabilizer composition of this invention.

The improved method of the invention of stabilizing a polymer utilizes the above compositions. The method, proportion of ingredients, and synergistic combinations are described in greater detail below.

8. IMPROVED METHOD OF STABILIZING POLYMERS

The improved method of the invention of stabilizing a polymer comprises incorporating into said polymer a stabilizingly and synergistically effective amount of the novel synergistic ultraviolet absorber compositions of the invention previously described in section (1) of the DETAILED DESCRIPTION OF THE INVENTION.

The synthetic resins and the polymers to be stabilized by the improved method of the invention are the polymers described in the preceding section and include curable or polymerizable compositions leading to crosslinked or polymeric materials.

If it is preferred to incorporate the stabilizer in the form of a liquid, rather than a solid, the use of saturated or nearly saturated solutions of concentrated stabilizing composition (comprising solvent and novel triazine) is preferred since less solvent (and consequently lower level of volatile organic components) will be introduced into a polymer, coating or film to be stabilized.

The following examples are provided for the purpose of illustration only. The examples should not be construed as limiting the invention in any way as variations of the invention are possible which do not depart from the spirit and scope of the invention.

EXAMPLE 1

A mixture of 2,4-di-(2,4-dimethylphenyl)-6-(2,4-dihydroxyphenyl)-1,3,5-triazine (20g, 0.048 mole), 6-chloro-1-hexanol (7.04g, 0.05 mole), available from Aldrich Chemicals, Milwaukee, WI, potassium iodide (0.37g, 0.0022 mole), PEG 400 (1.9g, 0.005 mole), available from Aldrich Chemicals, Milwaukee, WI, sodium hydroxide (2.0g, 0.05 mole) in methyl isobutyl ketone was reflux (120-122°C) for 18 hrs. After cooling to 85°C, water (50 ml) was added and the reaction mixture was acidified with 37% hydrochloric acid to pH 1, and the resulting aqueous layer was removed. The organic layer was washed twice with warm water (75 ml per each washing) and the volatiles were removed under reduced pressure. The oily residue was dissolved in acetone and decolorized with activated charcoal and filtered. Cooling to 22°C gave 2,4-di-(2,4-dimethylphenyl)-6-[2-hydroxy-4-(6-hydroxy-1-hexyloxy)phenyl]-1,3,5-triazine (I-E) as a pale yellow solid (10g), m.p. 117-118°C. The filtrate was concentrated under a reduced pressure to give a second crop of triazine I-E bringing the total weight of product to 21g (87% yield). It was characterized to be 2,4-di-(2,4-dimethylphenyl)-6-[2-hydroxy-4-(6-hydroxy-1-hexyloxy)phenyl]-1,3,5-triazine (I-E).

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① **BUNDESREPUBLIK
DEUTSCHLAND**



**DEUTSCHES
PATENT- UND
MARKENAMT**

② **Offenlegungsschrift**
③ **DE 199 06 745 A 1**

④ Int. Cl.⁸
C 08 L 23/10
C 08 K 5/3475
C 08 K 5/3492

⑤ Aktenzeichen: 199 06 745.7
⑥ Anmeldetag: 18. 2. 99
⑦ Offenlegungstag: 28. 8. 99

DE 199 06 745 A 1

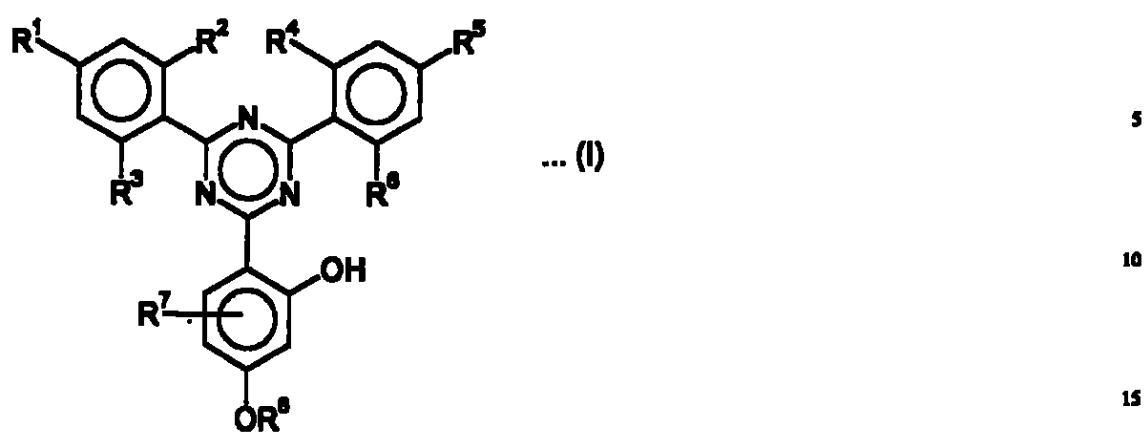
Unionspriorität: 10-037221 19. 02. 98 JP ⑧ Anmelder: Idemitsu Petrochemical Co., Ltd., Tokio/Tokyo, JP ⑨ Vertreter: Türk, Gille, Hrebal, 40593 Düsseldorf	⑩ Erfinder: Itageki, Hiroshi, Ichihara, Chiba, JP; Tamura, Satoshi, Ichihara, Chiba, JP; Setou, Kouji, Ichihara, Chiba, JP
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Die folgenden Angaben sind den vom Anmelder eingereichten Unterlagen entnommen

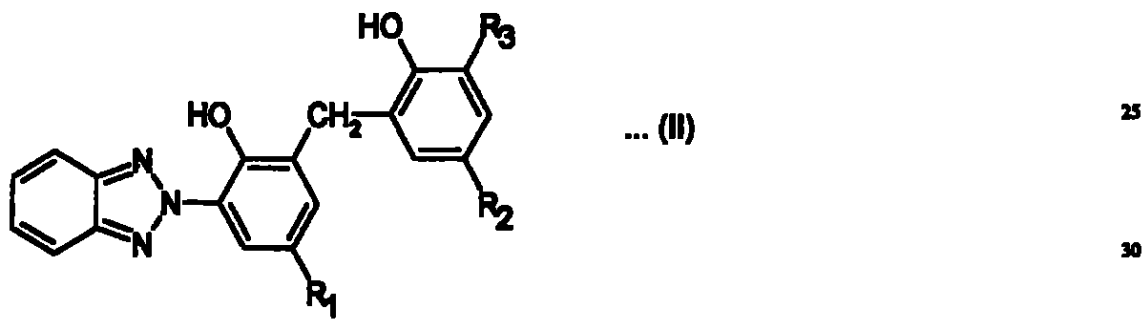
⑪ **Filme und Folien auf Polypropylenharzbasis**
Die Erfindung beschreibt Filme, Folien oder Schichten, die aus einer Zusammensetzung gebildet werden, die 100 Gewichtsteile eines Harzes auf Polypropylenbasis und von 0,01 bis 5 Gewichtsteile eines oder mehrerer spezifischer Ultraviolett-Absorptionsmittel enthält.

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worin R¹ bis R⁸ jeweils ein Wasserstoffatom oder eine Alkyl-, eine Aryl- oder eine Alkoxygruppe mit 1 bis 10 Kohlenstoffatomen sind, und
(D) eine Verbindung der Formel (II):



worin R₁ bis R₃ jeweils ein Wasserstoffatom, eine Alkyl-, Aryl- oder Alkoxygruppe mit 1 bis 10 Kohlenstoffatomen darstellen.

Unter diesen Ultraviolett-Absorptionsmitteln sind die Verbindungen (A) und (B) Benzotriazole. Unter den verschiedenen Benzotriazolverbindungen ist die Auswahl der spezifischen Benzotriazole (A) und (B) von besonderer Bedeutung, und diese sind besonders für die Erreichung der Wirkung der Erfindung bevorzugt.
Die Kombination der folgenden Benzotriazolverbindungen (E) und (F) ist ebenfalls in der Erfindung wirksam.

- (E) 2,2'-Methylenbis[4-(1,1,3,3-tetramethylbutyl)-6-[(2H-benzotriazol-2-yl)phenol]] und
(F) 2-[2-Hydroxy-3,5-bis(α,α'-dimethylbenzyl)phenyl]-2H-benzotriazol.
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In dieser Kombination beträgt das Gewichtsverhältnis der Verbindung (E) zur Verbindung (F) bevorzugt zwischen 1 : 9 und 9 : 1.

Als Verbindung (C) der Formel (I) sind besonders bevorzugt: 2,4-Bis(2,4-dimethylphenyl)-6-(2-hydroxy-4-n-octyloxyphenyl)-1,3,5-triazin und 2-[4,6-Di(2,4-xylyl)-1,3,5-triazin-2-yl]-5-octyloxyphenol; und als Verbindung (D) der Formel (II) ist besonders 6-(2-Benzotriazolyl)-4-t-octyl-6'-t-butyl-4'-methyl-2,2'-methylenbisphenol bevorzugt.

100 Gewichtsteile des Harzes auf Polypropylenbasis werden zusammen mit 0,01 bis 5 Gewichtsteilen, bevorzugt 0,05 bis 2,5 Gewichtsteilen, noch bevorzugter 0,25 bis 2,0 Gewichtsteilen einer oder mehrerer Verbindungen, ausgewählt aus den Verbindungen (A) bis (D), die oben erwähnt sind, oder beiden Komponenten (E) und (F) vermischt. Dafür ist 2,4-Bis(2,4-dimethylphenyl)-6-(2-hydroxy-4-n-octyloxyphenyl)-1,3,5-triazin besonders als Verbindung (C) der Formel (I) bevorzugt, und 6-(2-Benzotriazolyl)-4-t-octyl-6'-t-butyl-4'-methyl-2,2'-methylenbisphenol ist besonders bevorzugt als Verbindung (D) der Formel (II). Wenn die Menge des Ultraviolett-Absorptionsmittels, das dem Harz zugesetzt wird, weniger als 0,01 Gewichtsteile beträgt, ist es schwierig, die Filme, Folien und ihre verschiedenen bearbeiteten Sekundärprodukte des Harzes am Altern zu hindern. Auf der anderen Seite führt, selbst wenn die Menge größer als 5 Gewichtsteile ist, die Zugabe einer solch großen Menge des Ultraviolett-Absorptionsmittels nur zu einem geringen Anstieg in der Wirkung und führt im Gegenteil zum Ausbluten bzw. Auslaufen.

Falls gewünscht, können beliebige andere Ultraviolett-Absorptionsmittel auf Benzotriazolbasis, Ultraviolett-Absorptionsmittel auf Benzophenonbasis und Lichtstabilisatoren auf der Basis gehinderter Amine zu der Harzzusammensetzung für die Verwendung der Harzprodukte gegeben werden, ohne daß die Aufgabe der Erfindung beeinträchtigt wird.

Die anderen Ultraviolett-Absorptionsmittel auf Benzotriazolbasis schließen z. B. ein: 2-(3,5-Di-t-butyl-2-hydroxyphenyl)-5-chlorbenzotriazol, 2-(3-t-Butyl-5-methyl-2-hydroxyphenyl)-5-chlorbenzotriazol, 2-(3,5-Di-t-amyl-2-hydroxyphenyl)benzotriazol, 2-(3,5-Di-t-butyl-2-hydroxyphenyl)benzotriazol, 2-(5-t-Butyl-2-hydroxyphenyl)benzotriazol, 2-[2-Hydroxy-3-(3,4,5,6-tetrahydrophthalimidomethyl)-5-methylphenyl]benzotriazol, 2-(2-Hydroxy-4-octyloxyphenyl)benzotriazol, Reaktionsprodukte von 3-[3-(2H-Benzotriazol-2-yl)-5-t-butyl-4-hydroxyphenyl]propionsäuremethylether/Polyethylenglycol 300, 2-(3,5-Di-t-pentyl-2-hydroxyphenyl)-2H-benzotriazol, 2-(2H-benzotriazol-2-yl)-4-me-

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thyl-6-(3,4,5,6-tetrahydrophthalimidyImethyl)phenol, etc.

Die Absorptionsmittel auf Benzophenonbasis schließen z. B. 2,4-Dihydroxybenzophenon, 2-Hydroxy-4-n-dodecyl-oxybenzophenon, 1,4-Bis(4-benzoyl-3-hydroxyphenoxy)butan, etc. ein.

Die Lichtstabilisatoren auf Basis gehinderter Amine schließen z. B. ein: Bis (2,2,6,6-tetramethyl-4-piperidyl)-sebacat, 5 Tetrakis(2,2,6,6-tetramethyl-4-piperidyl)-1,2,3,4-butanetetracarboxylat, 2,2,6,6-tetramethyl-4-piperidylbenzoat, Bis-
(1,2,2,6,6-pentamethyl-4-piperidyl)-2-(3,5-di-t-butyl-4-hydroxybenzyl)-2-n-butylmalonat, Bis(N-methyl-2,2,6,6-tetra-
methyl-4-piperidyl)sebacat, 1,1'-(1,2-EthandiyI)bis(3,3,5,5-tetramethylpiperadion), (gemischtes 2,2,6,6-Tetramethyl-
4-piperidyl/Tridecyl)-1,2,3,4-butanetetracarboxylat, (gemischtes 1,2,2,6,6-Pentamethyl-4-piperidyl/Tridecyl)-1,2,3,4-bu-
10 tantetracarboxylat, Tetrakis(1,2,2,6,6-pentamethyl-4-piperidyl)-1,2,3,4-butanetetracarboxylat, 1-[2-[3-(3,5-Di-t-butyl-4-
hydroxyphenyl)propionyloxy]ethyl]-4-[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionyloxy]-2,2,6,6-tetramethylpiperidin,
8-Benzyl-7,7,9,9-tetramethyl-3-octyl-1,3,8-triazaspiro[4,5]-undecan-2,4-dion, 8-Acetyl-3-dodecyl-7,7,9,9-tetramethyl-
1,3,8-triazaspiro[4,5]decan-2,4-dion, Bis(1-octyloxy-2,2,6,6-tetramethyl-4-piperidyl)sebacat, etc.

[3] Formulierung und Formen

15 In der Erfindung kann das Harz auf Polypropylenbasis mit dem oben erwähnten Ultraviolett-Absorptionsmittel und
wahlweise mit beliebigen anderen verschiedenen Additiven z. B. anderen Ultraviolett-Absorptionsmitteln, Stabilisato-
ren auf Phenolbasis, organische Stabilisatoren auf Phosphitbasis, Stabilisatoren auf Thioetherbasis, ebenso wie anorga-
nischen oder organischen Füllstoffen, antistatischen Mitteln, Chlor-abfangenden Mitteln, Antiblockmitteln, Antir-
20 übungsmitteln, organischen Flammenschutzmitteln, Flammretardierungspromotoren, Farbstoffen, Pigmenten, natürlichen
Ölen, synthetischen Ölen, Wachsen, etc. vermischt werden. Um diese Bestandteile zu vermischen können gewöhnliche
bekannte Verfahren angewendet werden. Zum Beispiel können sie mit einem Taumel-Mischer, einem Henschel-Mischer
oder ähnlichem vermischt werden, oder nachdem sie gemischt worden sind, kann die resultierende Mischung in der
Schmelze geknetet und granuliert werden durch einen Einschnellen- oder Mehrschneckenextruder oder durch einen
25 Knetter, einen Banbury-Mischer oder ähnliches. Falls erforderlich, kann ein Hochkonzentrations-Ultraviolett-Absorpti-
onsmittel wie das oben erwähnte mit dem Harz auf Polypropylenbasis verknetet werden, um einen Masterbatch herzu-
stellen, und der resultierende Masterbatch kann mit dem zusätzlichen Harz auf Polypropylenbasis vermischt werden, um
die beabsichtigte Harzzusammensetzung auf Polypropylenbasis herzustellen.

Wenn das Polymer in der Form eines pulverförmigen Polymers durch Polymerisation hergestellt wurde, kann das Fo-
30 liesharz auf Polypropylenbasis zur Verwendung in der Erfindung mit einem Peroxid in einem Extruder abgebaut werden,
um sein Molekulargewicht zu verringern. Die Harzzusammensetzung, die das so abgebaute Harz enthält, ist leicht beim
Formen zu handhaben. Das zum Erreichen eines niedrigen Molekulargewichtes mit dem Peroxid abgebaute Harz kann
einen erhöhten Grad des Fließvermögens aufweisen, aber seine Pentadenfraktion, seine Peakschmelztemperatur und
seine Schmelzenthalpie verändert sich nur wenig. Das für diese Zwecke verwendete Peroxid schließt z. B. ein: 2,5-Di-
35 methyl-2,5-di-(t-butylperoxy)hexan, 1,3-Bis(t-butylperoxyisopropyl)benzol, 2,5-Dimethyl-2,5-di-(t-butylperoxy)hexin-
3, etc. Wenn das Harz mit dem Peroxid, dem Antioxidationsmittel, einem Stabilisator und einem Chlorabfangmittel ver-
mischt wird, kann es wahlweise bevorzugt hier zugegeben werden.

In der Erfindung kann das Formmaterial auf Basis des Polypropylenharzes, zu dem die oben erwähnten Additive ge-
40 geben worden sind, in Folien und Filme durch bekannte Formverfahren, z. B. durch Aufblasformen, Gießformen, Kalen-
drierformen oder ähnliches hergestellt werden.

Die Folien und Filme können weiter einer Sekundärbearbeitung z. B. Aufkleben von bedruckten Substraten oder For-
men im Vakuum unterworfen werden, um verschiedene geformte Endprodukte wie dekorative Filme, Schutzfilme, etc.
herzustellen.

In den Filmen und Folien der Erfindung sind die Additive wirksam vor Ausbluten, das zu einer Beeinträchtigung der
45 Oberflächenerscheinung der Filme und Folien führen würde, geschützt, selbst wenn die Filme und Folien unter gewöhn-
lichen Raumtemperaturbedingungen auf Abruf für die nachfolgende Sekundärbearbeitung, z. B. für die Laminierung mit
Substraten oder für das Bedrucken gelagert werden.

Die Erfindung wird nun im Hinblick auf die folgenden Beispiele genauer beschrieben.

50 Beispiel 1

1. Herstellung des Propylenfolienharzes

1-1. Herstellung der Magnesiumverbindung

55 Ein Glasreaktor mit einem Volumen von ungefähr 6 Litern, ausgerüstet mit einem Rührer, wurde vollständig mit Stick-
stoffgas gespült, und 2430 g Ethanol, 16 g Iod und 160 g metallisches Magnesium wurden hinzugegeben. Diese wurden
erhitzt und unter Rückfluß reagieren gelassen, bis sich kein Wasserstoffgas mehr im Reaktionssystem bildete, um ein fe-
stes Reaktionsprodukt herzustellen. Die so hergestellte Reaktionsmischung, die das feste Produkt enthielt, wurde unter
60 vermindertem Druck getrocknet, um eine Magnesiumverbindung zu erhalten.

1-2. Herstellung einer festen Katalysatorkomponente (W)

65 In einen 5 Liter Glasreaktor, der vollständig mit Stickstoffgas gespült worden war, wurden 160 g der Magnesiumver-
bindung (nicht gemahlen), erhalten in Schritt 1-1, 800 ml reines Heptan, 24 ml Siliciumtetrachlorid und 23 ml Die-
thylphthalat gegeben. Dann wurde das Reaktionssystem bei 80°C gehalten, und 770 ml Titantetrachlorid wurden unter
Rühren hinzugegeben und bei 110°C für 2 Stunden umgesetzt. Die resultierende feste Komponente wurde entnommen
und mit reinem Heptan bei 90°C gewaschen. Dazu wurden 1220 ml Titantetrachlorid gegeben und bei 110°C für 2 Stun-

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den umgesetzt. Dies wurde dann vollständig mit reinem Heptan gewaschen, um die feste Katalysatorkomponente (W) zu erhalten.

1-3. Gasphasenpolymerisation

In einem 200 Liter Polymerisationsreaktor wurde die feste Katalysatorkomponente (W), erhalten in 1-2 mit einer Geschwindigkeit von 6,0 g/hr, Triisobutylaluminium (TIBA) mit einer Geschwindigkeit von 0,2 Mol/hr, 1-Allyl-3,4-dimethoxybenzol (ADMB) mit einer Geschwindigkeit von 0,006 Mol/hr, Cyclohexylmethyldimethoxysilan (CHMDMS) mit einer Geschwindigkeit von 0,003 Mol/hr und Propylen mit einer Geschwindigkeit von 43 kg/hr gefördert. Darin wurde das Monomer bei 70°C und 28 kg/cm² G polymerisiert. Die Menge des gebildeten Polymers betrug 30 kg/hr.

Das Polymer besaß eine Grenzviskosität $[\eta]$ (135°C in Decalin) von 5,04 dl/g.

Der unlösliche Gehalt in siedendem n-Heptan des Polymers betrug 88,2 Gew.-%. Die in siedendem n-Heptan unlösliche Komponente im Polymer besaß $[\eta]$ von 5,42 dl/g, und die in siedendem n-Heptan lösliche Komponente davon besaß $[\eta]$ von 2,07 dl/g.

Auf der anderen Seite war die Pentadenfraktion, $\text{mm}(1-\text{mmm}) \times 10$ des Homopolymers, berechnet aus dem ¹³C-NMR-Spektralmuster, 24,3%; die Peakschmelztemperatur (T_m), gemessen durch DSC betrug 158,7°C, und die Schmelzenthalpie (ΔH) betrug 80,7 J/g. Es wurde keine invertierte Bindung gegenüber der Kopf-Schwanz-Bindung der Propylenheiten im Polymer gefunden.

Das hier erhaltene pulverförmige Polymer wurde mit 2,5-Dimethyl-2,5-di-(t-butylperoxy)hexan vermischt, wozu ein Antioxidationsmittel, ein Stabilisator und ein Chlorabfangmittel hinzugegeben wurde. Die resultierende Mischung wurde durch eine 40 mmφ Düse extrudiert, um Pellets mit einer Schmelzflußrate (MFR, 230°C, 2,16 kgf) von 2,5 g/10 min zu erhalten. Auf der anderen Seite wurde das Polymer mit dem Peroxid abgebaut, um sein Molekulargewicht zu verringern. Es wurde keine Veränderung in der Pentadenfraktion, der Peakschmelztemperatur und der Schmelzenthalpie zwischen dem ursprünglichen Polymer und dem abgebauten niedermolekularen Polymer gefunden. Das erhaltene Harz besaß ein Zugelastizitätsmodul von 500 MPa.

2. Filmbildung und Bewertung der Filmproben

100 kg der Propylenfolienharzpellets, die hier hergestellt worden waren, wurden mit 1,1 kg eines Ultraviolett-Absorptionsmittels 2-(2-Hydroxy-5-t-octylphenyl)benzotriazol (Cyasorb UV5411 von Cytec Industries Co.) vermischt, und durch einen 40 mmφ T-Düsenextruder (Formtemperatur: 270°C) extrudiert, um einen Film mit einer Dicke von 100 µm zu ergeben. Die Ultraviolett-Durchlässigkeit des einfachen Films wurde gemessen unter Verwendung eines automatischen Shimadzu-Spektrophotometers UV2400 und sie betrug nicht mehr als 3% bei 300 nm im UV-Wellenlängenbereich.

Die Ausblut-Beständigkeit der Folie wurde bewertet mit den Temperaturbedingungen von Lagerhäusern im Sommer oder unter Berücksichtigung der Bedingungen im Schritt der Härtung von Klebstoffen auf Urethanbasis für die Folienlaminiierung. Genauer wurde die Folie in einem Geer-Ofen bei 40°C für 240 Stunden gehalten, und die äußere Erscheinung und die Trübung untersucht.

Der Trübungsgrad der Folie wurde entsprechend JIS-K7105 gemessen, wofür das Gerät Nippon Denaboku Kogyo 1001DP verwendet wurde. "A-Trübung" bezeichnet den Unterschied der Trübung der Folie vor dem Test und nach dem Test.

Für die äußere Erscheinung wurde die Folie visuell untersucht. "O" bedeutet, daß keine Veränderung bei dem untersuchten Film verglichen mit dem frisch hergestellten Film.

"X" bezeichnet, daß die Oberfläche des untersuchten Films infolge von Ausbluten des Additivs geweißt war.

Die Testdaten sind in Tabelle 1 gezeigt.

Beispiel 2

Filmproben wurden hergestellt und bewertet in der gleichen Weise wie in Beispiel 1, ausgenommen, daß 2-(2H-Benzotriazol-2-yl)-6-dodecyl-4-methylphenol (Tinurvin 571 von Ciba Specialty Chemicals Co.) als Ultraviolett-Absorptionsmittel verwendet wurde. Die Testergebnisse sind in Tabelle 1 gezeigt.

Beispiel 3

Filmproben wurden hergestellt und bewertet in der gleichen Weise wie in Beispiel 1, ausgenommen daß 2,4-Bis(2,4-dimethylphenyl)-6-(2-hydroxy-4-n-octyloxyphenyl)-1,3,5-triazin (Cyasorb UV1164 von Cytec Industries Co.) als Ultraviolett-Absorptionsmittel verwendet wurde. Die Testdaten sind in Tabelle 1 gezeigt.

Beispiel 4

Filmproben wurden hergestellt und bewertet in der gleichen Weise wie in Beispiel 1, ausgenommen daß 6-(2-Benzotriazolyl)-4-t-octyl-6'-t-butyl-4'-methyl-2,2'-methylenbisphenol (JAST-500 von Joboku Chemical Industry Co.) als Ultraviolett-Absorptionsmittel verwendet wurde. Die Testdaten sind in Tabelle 1 gezeigt.

Beispiel 5

Filmproben wurden hergestellt und bewertet in der gleichen Weise wie in Beispiel 1, ausgenommen daß eine Kombination von 0,7 kg 2,2'-Methylen-bis[4-(1,1,3,3-tetramethylbutyl)-6-[(2H-benzotriazol-2-yl)phenol]] (Adekstab LA31

(12) UK Patent Application (19) GB (11) 2 317 893 (13) A

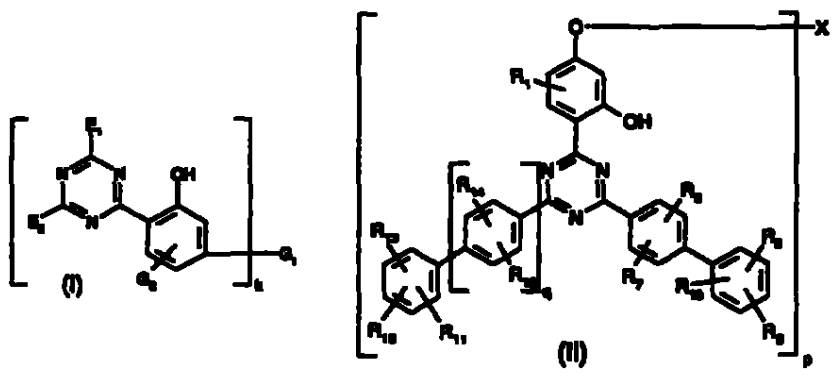
(43) Date of A Publication 08.04.1998

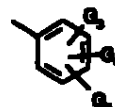
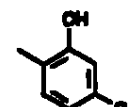
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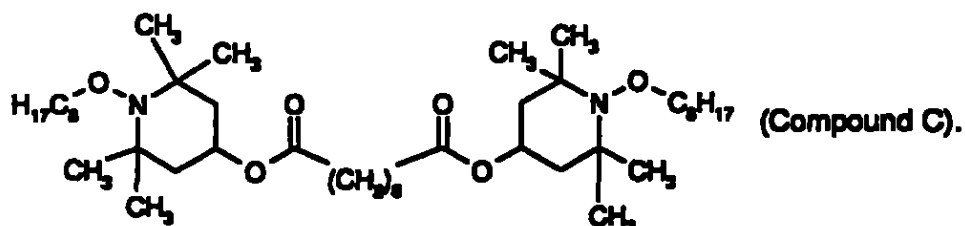
(51) INT CL⁸
C08K 5/3482 5/38 5/534 , C08D 133/06 281/00 //
(C08K 5/3482 5/3435)
(52) UK CL (Edition P)
C3K KCZ K211 K220 K221 K240 K261 K274 K277 K282
K283 K290 K291 K292 K293 K294 K296 K297 K298
C3W W100 W111 W216 W217 W218 W225 W230
W304 W305 W306 W314 W315 W316 W325 W328
W329
U16 S1389 S1391 S1392 S1582 S1620 S2230
(56) Documents Cited
GB 2297081 A WO 88/28431 A1
(58) Field of Search
UK CL (Edition P) C3K KCZ KCZ
INT CL⁸ C08K 5/00 5/34 5/3477 5/3482 , G03C 1/018
ONLINE: CHASS, CLAIMS, JAPRO, RAPRA, WPI

(54) Stabilizer combination for organic materials
(57) Mixtures comprising a compound of the formula I and a compound of the formula II



In which E₁ and E₂ are  or  , q is 0 or 1, p and k are each 1 or 2, and the remaining symbols are as defined in claim 1, or claim 2 are used for stabilizing organic material, especially coating materials, e.g. paints containing a resin binder.

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The comparison used is a clearcoat containing no light stabilizer and a clearcoat stabilized using the individual components; the corresponding results are marked in the tables below with an asterisk (*).

The clearcoat is diluted to spray viscosity with Solvesso®100 and applied to a prepared aluminium panel (coil coat, filler, silver metallic or blue metallic base-coat) and the painted panel is baked at 130°C for 30 minutes. This gives a clearcoat dry-film thickness of 40-50 µm.

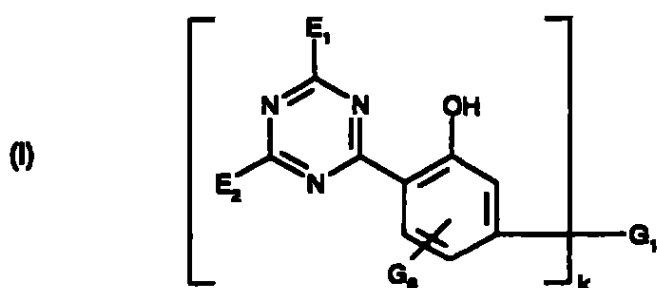
The samples are then subjected to weathering in an UVCON® weathering device from Atlas Corp. (UVB-313 lamps) with a cycle of 8 h of UV irradiation at 70°C and 4 h of condensation at 50°C. Further samples are subjected to natural weathering (Florida, 5° south, SAE J-1975).

The surface gloss (20° gloss in accordance with DIN 67530) and the colour change (ΔE in accordance with DIN 6174) of the samples are measured at regular intervals.

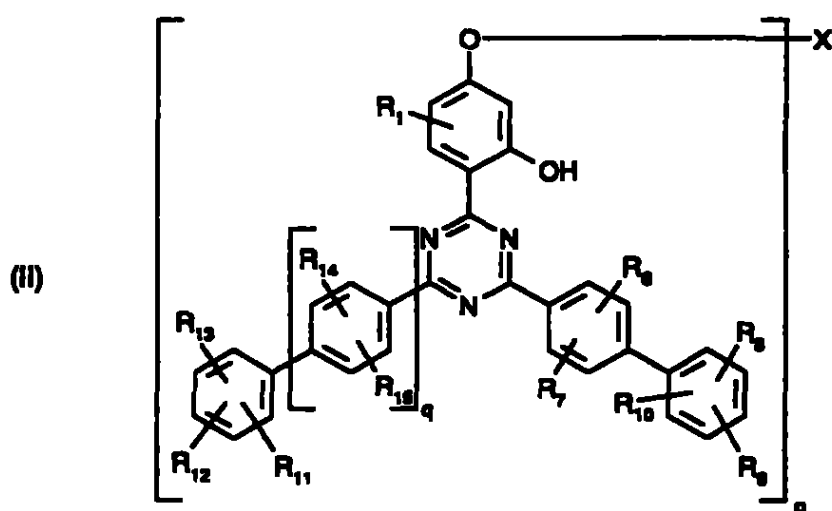
The results are compiled in Tables C1 and C2 below. All amounts are based on the solids content of the clearcoat.

WHAT IS CLAIMED IS:

1. A mixture comprising a compound of the formula I



and a compound of the formula II



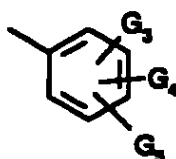
in which, in formula I

G_1 is hydrogen or $-OG$;

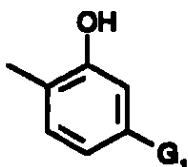
k is 1 or 2 ; and, if $k = 1$,

E_1 and E_2 , independently of one another are a group of the formula Ia or Ib

(Ia)



(Ib)



and

G is hydrogen or C₁-C₁₈alkyl; or is C₁-C₁₈alkyl which is substituted by OH, C₁-C₁₈alkoxy, C₅-C₁₂cycloalkoxy, allyloxy, halogen, =O, -COOH, -COOG₉, -CONH₂, -CONHG₉, -CON(G₉)(G₁₀), -NH₂, -NHG₉, =NG₉, -N(G₉)(G₁₀), -NHCOG₁₁, -CN, -OCO G₁₁, phenoxy and/or C₁-C₁₈alkyl-, C₁-C₁₈alkoxy- or halo-substituted phenoxy; or G is C₃-C₃₀alkyl which is interrupted by -O- and can be substituted by OH; or G is C₃-C₆alkenyl; glycidyl; C₅-C₁₂cycloalkyl; C₅-C₁₂cycloalkyl substituted by OH, C₁-C₄alkyl or -OCO G₁₁; C₇-C₁₁phenylalkyl which is unsubstituted or substituted by OH, Cl, C₁-C₁₈alkoxy or C₁-C₁₈alkyl; -CO-G₁₂ or -SO₂-G₁₃;

G₃, G₄ and G₆, independently of one another are H, C₁-C₁₂alkyl; C₂-C₆alkenyl; C₁-C₁₈alkoxy; C₅-C₁₂cycloalkoxy; C₂-C₁₈alkenoxy; halogen; -C=N; C₁-C₄haloalkyl; C₇-C₁₁phenylalkyl; COOG₉; CONH₂; CONHG₉; CONG₉G₁₀; sulfo; C₂-C₁₈acylamino; OCO G₁₁; phenoxy; or phenoxy, C₁-C₁₂alkyl or C₁-C₁₈alkoxy each of which is substituted by C₁-C₁₈alkyl, C₁-C₁₈alkoxy or halogen; and one radical G₃ in formula I additionally embraces the meaning -NG₁₆G₁₇;

G₈ embraces the meanings set out below for R₁ in formula II;

G₈ is C₁-C₁₈alkyl; C₃-C₁₈alkenyl; C₃-C₃₀alkyl which is interrupted by O, NH, NG₉ or S and/or is substituted by OH; C₁-C₄alkyl which is substituted by -P(O)(OG₁₄)₂, -N(G₉)(G₁₀) or -OCO G₁₁, and/or OH; glycidyl; C₅-C₁₂cycloalkyl; C₁-C₄alkylcyclohexyl; phenyl; C₇-C₁₄alkylphenyl; C₈-C₁₈bicycloalkyl; C₈-C₁₅bicycloalkenyl; C₈-C₁₅tricycloalkyl; C₈-C₁₈bicycloalkylalkyl; or C₇-C₁₁phenylalkyl;

G₉ and G₁₀ independently of one another are C₁-C₁₂alkyl; C₃-C₁₂alkoxyalkyl; C₂-C₁₈alkanoyl; C₄-C₁₈dialkylaminoalkyl or C₅-C₁₂cycloalkyl; or

G₉ and G₁₀ together are C₃-C₆alkylene or -oxaalkylene or -azaalkylene ;

G₁₁ is C₁-C₁₈alkyl; C₁-C₁₂alkoxy; C₂-C₁₈alkenyl; C₇-C₁₁phenylalkyl;

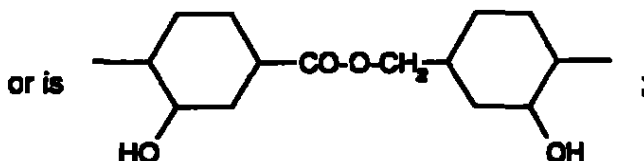
C₇-C₁₁phenylalkoxy; C₅-C₁₂cycloalkyl; C₅-C₁₂cycloalkoxy; phenoxy or phenyl; or is C₃-C₃₀alkyl which is interrupted by -O- and can be substituted by OH;

G_{12} is C_1 - C_{18} alkyl; C_2 - C_{18} alkenyl; phenyl; C_1 - C_{18} alkoxy; C_2 - C_{18} alkenyloxy;
 C_2 - C_{20} alkoxy which is interrupted by O, NH, NG_9 or S and/or is substituted by OH;
 cyclohexyloxy; phenoxy; C_7 - C_{14} alkylphenoxy; C_7 - C_{11} phenylalkoxy;
 C_1 - C_{12} alkylamino; phenylamino; tolylamino or naphthylamino;
 G_{13} is C_1 - C_{12} alkyl; phenyl; naphthyl or C_7 - C_{14} alkylphenyl;
 G_{14} is C_1 - C_{12} alkyl, methylphenyl or phenyl;
 G_{15} is hydrogen or C_1 - C_{20} alkyl;
 G_{17} is hydrogen, C_1 - C_{20} alkyl, C_7 - C_{13} phenylalkyl, $-C(=O)-G_{18}$, $-C(=O)-NH-G_{16}$;
 and
 G_{18} is C_1 - C_{20} alkyl; C_2 - C_{20} alkyl which is interrupted by 1 to 6 oxygen atoms and/or
 is substituted by OH, halogen, NH_2 , NHG_9 or NG_9G_{10} ; C_1 - C_{20} alkoxy; phenyl;
 C_7 - C_{13} phenylalkyl or C_2 - C_{20} alkenyl;

and, if $k = 2$,

E_1 and E_2 are a group of the formula Ia;

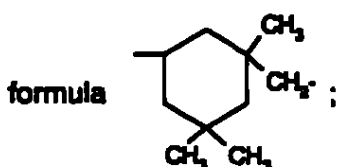
G is C_2 - C_{18} alkylene, C_4 - C_{12} alkenylene, xylylene, C_2 - C_{20} alkylene which is
 interrupted by O and/or substituted by OH, or a group of the formula
 $-CH_2CH(OH)CH_2O-G_{20}-OCH_2CH(OH)CH_2-$, $-CO-G_{21}-CO-$, $-CO-NH-G_{22}-NH-CO-$,
 $-(CH_2)_j-COO-G_{22}-OOC-(CH_2)_j-$, in which j is a number from the range from 1 to 3,



G_{20} is C_2 - C_{10} alkylene; C_4 - C_{20} alkylene which is interrupted by O, phenylene, or a
 group -phenylene-E-phenylene-, in which E is -O-, -S-, $-SO_2$ -, $-CH_2$ -, $-CO$ -, or
 $-C(CH_3)_2$ -;

G_{21} is C_2 - C_{10} alkylene, C_2 - C_{10} oxaalkylene, C_2 - C_{10} thiaalkylene, C_6 - C_{12} arylene or
 C_2 - C_6 alkenylene;

G_{22} is C_2 - C_{10} alkylene, phenylene, tolylene, diphenylmethane or a group of the



G_8 is hydrogen;

G is C_1 - C_{18} -alkyl or benzyl; or is C_2 - C_8 -alkyl substituted by OH, C_1 - C_{18} -alkoxy, phenoxy and/or $-OCO G_{11}$; or is C_1 - C_8 -alkyl substituted by $-COO G_8$

G_9 is C_1 - C_8 -alkyl or C_2 - C_8 -alkenyl; and

G_{11} is C_1 - C_4 -alkyl or C_2 - C_3 -alkenyl;

and in which in the compound of the formula II

R_6 to R_{15} are H;

q is 1;

p is 1;

X and Y , independently of one another, are R_7 ; C_2 - C_{12} -alkyl which is substituted by R_8 ;

C_3 - C_{20} -alkyl which is interrupted by one or more oxygen atoms and substituted by one or more groups R_8

R_8 is hydroxy; C_1 - C_{20} -alkoxy; cyclohexyloxy; $-OR_8$; R_8 ; allyl;

R_7 is hydrogen; C_1 - C_{20} -alkyl; cyclohexyl;

R_2 is $-COR'$; $-COOR'$;

R' is hydrogen; C_1 - C_{20} -alkyl; C_4 - C_{20} -alkyl which is interrupted by oxygen; cyclohexyl or C_1 - C_4 -alkyl/cyclohexyl.

7. A composition comprising

A) an organic material sensitive to damage by light, oxygen and/or heat, and

B) as stabilizer, a mixture comprising a compound of the formula I and a compound of the formula II.

8. A composition according to claim 7, comprising from 0.01 to 15 parts by weight of component B per 100 parts by weight of component A.

9. A composition according to claim 7, comprising in addition to components A and B one or more other stabilizers or any other additives.

10. A composition according to claim 7, comprising as component A a synthetic organic polymer.

11. A composition according to claim 7, comprising as component A a thermoplastic polymer, a binder for coatings or a photographic material.