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(54) Stabilizing composition for polymers

- (57) A stabilizing composition useful as a processing and light stabilizer for polymers such as polyurethane and polyolefins comprises
- a mono- or di- phosphite or mono- or diphosphonite
- a chroman derivative (especially α -tocopherol or derivatives thereof); and b)
- a light stabilizer (component c) selected from (i) a polymer containing at least one hindered amine light stabilizer group, preferably a polysiloxane containing a hindered amine light stabilizer group and/or ii) the combination of an oxanilide and a hindered amine light stabilizer (HALS) compound.

COMPOSITIONS FOR STABILIZING POLYMERS

The invention relates to new compositions for stabilizing polymers, for example, polyurethane.

According to the invention, there is provided a stabilizing composition, useful as a processing and light stabilizer for polymers such as polyurethane comprising:

- a) a mono- or di- phosphite or mono- or diphosphonite (component a)
- b) a chroman derivative (especially α -tocopherol or derivatives thereof) (component b); and
- c) a light stabilizer (component c) selected from
 - i) a polymer containing at least one hindered amine light stabilizer group, preferably polysiloxane containing a hindered amine light stabilizer group (component i) and/or
 - ii) the combination of an oxanilide and a hindered amine light stabilizer (HALS) compound (component ii).

Preferred mono- and di- phosphites for use in a composition according to the invention are those of formula I or II

$$\begin{array}{c} O-R_{1} & (I) \\ R_{1}-O-P & \\ O-R_{1} & \\ \\ R_{1}-O-P & C-CH_{2} & CH_{2}-O \\ O-CH_{2} & CH_{2}-O \end{array} \qquad (II)$$

$$\begin{array}{c} O-CH_2 CH_2 - O \\ R_1-O-P CC \\ O-CH_2 CH_2 - O \end{array} P-O-R_1 \tag{II}$$

in which each R_1 independently is a group derived from an aliphatic, alicyclic or aromatic alcohol containing one or two OH groups.

Aromatic alcohol, in the Specification, include phenols.

Preferred mono- or diphosphonites are selected from compounds of formula III

in which m is 0 or 1;

n is 0 or 1;

p is 0 or 1;

each R_9 , independently, is a group derived from an aliphatic, alicyclic or aromatic alcohol containing one or two OH groups; whereby the two -OH groups are not positioned to be able to form a P-containing ring; (hereinafter defined as the monovalent significances of R_9);

or both groups R_9 form a group derived from an aliphatic, alicyclic or aromatic alcohol containing two OH groups in such a position that they can form a cyclic group with a single phosphorus atom (hereinafter defined as the divalent significances of R_9):

 R_{10} is a monovalent or divalent significance of R_{9} ;

Y is -O-, -S-, -CH(R_3)- or - C_6H_4 -;

where R_3 is hydrogen, C_{1-8} alkyl or $COOR_4$ and R_4 is C_{1-8} alkyl. More preferably the mono-

and diphosphonites are diphosphonites, most preferably tetrakis (2,4-tert.butyl phenyl) biphenylene diphosphonite (commercially available as SANDOSTAB P-EPQ from SANDOZ Chemicals Ltd.).

Preferably R_1 is R_1 ' where R_1 ' is a linear or branched C_{1-22} alkyl or phenyl, unsubstituted or substituted by 1 to 3 linear or branched C_{1-12} alkyl groups (such substitution when present, preferably being C_{1-4} alkyl).

Preferably R_3 is R_3 ' where R_3 ' is hydrogen or methyl.

Preferably R_4 is R_4 ' where R_4 ' is C_{1-4} alkyl.

Preferred phosphites of component a) are selected from tris(2,4-di-t.butylphenyl)-phosphite, tris(nonylphenyl)phosphite, di-isodecylphenyl phosphite, trilaurylphosphite, bis (2,6-di-t.butyl-4-methylphenyl)pentaerythrityl diphosphite, bis (2,4-di-t.butyl phenyl)pentaerythrityl diphosphite.

Preferred chroman derivatives are of those of formula IV

$$\begin{array}{c} \text{CH}_3 \\ \text{HO} \\ \text{CH}_3 \\ \text{CH}_3 \end{array} \qquad \text{(IV)}$$

or -CH $_2$ -CH $_2$ -O-CO-R $_6$ where R $_6$ is selected from C $_{7\text{-}30}$ alkyl, -CH $_2$ CH $_2$ -S-(C $_{1\text{-}30}$ alkyl) or

Preferred polysiloxanes are compounds of formula V

$$\begin{array}{c} C_{1-6}alkyl \\ -(-Si-O-)n_a \\ (CH_2)_2-6 \\ O \\ H \\ CH_3 \\ CH_3 \\ R \end{array} \qquad (V)$$

in which $n_a = 1$ to 100, preferably 5 to 30.

R is selected from hydrogen, C_{1-8} alkyl, oxygen, OR_8 or $-CO-R_5$ where R_5 is $-C(R_8)=CH_2$, C_{1-6} alkyl, phenyl, $-COC_6H_5$, $-CH_2C_6H_5$, $-COOC_{1-12}$ alkyl, COOH, or NR_7R_8 , where R_7 is hydrogen, C_{1-12} alkyl, C_{5-6} cycloalkyl, phenyl, phenyl C_{1-4} alkyl or C_{1-12} alkylphenyl and R_8 is C_{1-12} alkyl or hydrogen.

Preferred oxanilides are those of formula VII

$$\begin{array}{c|c} (R_{12})_2 & (R_{12})_2 \\ \hline A & N & \infty \\ R_{11} & R_{13} & R_{13} \end{array} \qquad (VII)$$

in which each R_{11} independently is selected from hydrogen, C_{1-18} alkyl, C_{1-18} alkoxy, halogen, hydroxy, phenyl and phenoxy; and

each R_{12} , independently, is selected from hydrogen, halogen, hydroxy, C_{1-8} alkyl and C_{1-8} alkoxy; and

each R₁₃, independently, is hydrogen or methyl.

Preferably R_{11} is R_{11} where R_{11} is selected from hydrogen, hydroxy, C_{1-4} alkyl and C_{1-4} alkoxy, more preferably R_{11} is hydrogen.

Preferably R_{12} is R_{12} ' where R_{12} ' is selected from hydrogen, hydroxy, C_{1-4} alkyl and C_{1-4} alkoxy, more preferably on phenyl group A and B, one R_{12} is hydrogen and the other R_{12} is R_{12} " where R_{12} " is C_{1-4} alkyl or C_{1-4} alkoxy. Preferably R_{12} " on ring A is a C_{1-4} alkyl and on ring B R_{12} " is a C_{1-4} alkoxy.

Preferably R₁₃ is hydrogen.

Preferably both R₁₂ groups are ortho to one another.

Preferred HALS compounds are 2,2,6,6-tetramethylpiperidine compounds. More preferred HALS compounds are those of formula VI

in which R is selected from hydrogen, C_{1-8} alkyl, oxygen or -COR $_5$; where R $_5$ is $C(R_8)=CH_2$, C_{1-6} alkyl, phenyl, -NR $_7$ R $_8$, -CO- C_6 H $_5$, -CH $_2$ C $_6$ H $_5$, -COOC $_{1-12}$ alkyl or -COOH;

where R_7 is hydrogen, C_{1-12} alkyl, C_{5-6} cycloalkyl (preferably cyclohexyl), phenyl, phenyl C_{1-4} alkyl or C_{1-12} alkylphenyl and

R₈ is hydrogen or C₁₋₁₂alkyl;

 R_{15} is hydrogen, C_{1-22} alkyl, C_{1-22} alkoxy, $-N(R_3)$ -CO-CO- R_{20} ; or -NH-C(R_3)=N- R_{21} ; R_3 is hydrogen, C_{1-18} alkyl or COOR $_4$ where R_4 is C_{1-8} alkyl

 R_{20} is an amide forming group and R_{21} is C_{1-18} alkyl, phenyl, unsubstituted or substituted by 1 to 3 groups selected from C_{1-18} alkyl, C_{1-4} alkoxy and halogen; or R_{15} is

R₁₆ is hydrogen or C₁₋₈alkyl; or

 $R_{\rm 15}$ and $R_{\rm 16}$ together with the C-atom to which they are attached, form a group of formula a)

$$\begin{array}{c|c} O-C & (CH_2)_{11} \\ \hline C & \\ C & \\ \hline C & \\ C & \\ C & \\ \hline C & \\ C & \\ \hline C & \\ C & \\$$

Preferably R is R' where R' is hydrogen, C_{1-4} alkyl or -COR $_5$ ' where R $_5$ ' is C_{1-4} alkyl or -COCC $_{1-4}$ alkyl, more preferably R" where R" is hydrogen, methyl or -COCH $_3$.

More preferred 2,2,6,6-tetramethylpiperidinyl compounds are of formula VI'

where R' is hydrogen, C₁₋₄alkyl or -CO-R₅' where R₅' is C₁₋₄alkyl or -CO-OC₁₋₄alkyl.

Preferably the ratio of components a) and b) to c) is 3:1 to 1:3, more preferably 1:1.

Preferably the ratio of component a) to component b) is 10:1 to 1:2, more preferably 6:1 to 1:2, more preferably 4:1.

Preferably in compositions according to the invention the amounts of components a) to c) are as follows:

30-50% (preferably 40%) component a)
5-20% (preferably 10%) component b) and
30-65% (preferably 50%) component c).

If more than one light stabilizer is present in component c) they are preferably an oxanilide and a HALS compound. Preferably the ratio of oxanilide to HALS compound is 3:1 to 1:3, preferably 2:1.

Preferably the compositions according to the invention are in the form of liquid preparations, preferably without plasticizer or solvent.

According to the invention there is further provided a polymeric composition comprising a polymeric material and a stabilizing amount (preferably 0.2-8% based on the weight of polymeric material) of a stabilizing composition defined above.

Polymeric materials that can be stabilized by a stabilizing composition according to the invention include homopolymers, copolymers and polymer blends of:

Cellulose acetate; Cellulose acetobutyrate; Cellulose acetopropionate; Cresolformaldehyde resin; Carboxymethylcellulose; Cellulose nitrate; Cellulose propionate; Casein plastics; Casein-formaldehyde; Cellulose triacetate; Ethyl cellulose; Epoxy resins; Methyl cellulose: Melamine-formaldehyde resins; Polyamide; Polyamideimide; Polyacrylonitrile; Polybutene-1 and -2; Polybutylacrylate; Poly-(butyleneterephthalate); Polycarbonate; Poly(chlorotrifluoroethylene); Poly(diallylphthalate); chlorinated Polyethylene; Poly(etherketone); Poly- etherimide; Polyethyleneoxide; Polyethersulphone; Poly(ethylene-terephthalate); Polytetrafluoroethylene; Phenolformaldehyde resins; Polyimide; Polyisobutylene; Polyisocyanurate; Polymethacrylimide; Polymethylmethacrylate; Poly(4-methylpentene-1); Poly(α -methyl styrene); Polyoxymethylene; Polyformaldehyde; Polyacetal; Poly- propylene; Polyphenylene ether; Polyphenylenesulphide; Polyphenylene-sulphone; Polystyrene; Polysulphone; Polyurethane; Polyvinyl acetate; Polyvinyl alcohol; Polyvinylbutyral; chlorinated Polyvinyl chloride; Polyvinylidene chloride; Polyvinylidene fluoride; Polyvinylfluoride; Polyvinylformaldehyde; Polyvinylformaldehyde; Polyvinylcarbazol; Polyvinylpyrrolidone; Silicon saturated polyester; urea-formaldehyde resins; unsaturated polyester; polyacrylate; polymethacrylate; polyacrylamide; maleinate resins; phenolic resins; aniline resins; furane resins; carbamide resins; epoxide resins and silicon resins.

Examples of suitable copolymers include:

Acrylonitrile/butadiene/acrylate; Acrylonitrile/butadiene/styrene; Acrylonitrile/methylmeth-acrylate; Acrylonitrile/styrene/acrylic ester; Acrylonitrile/ethylene-propylenediene/styrene; Acrylonitrile/ chlorinated polyethylene/styrene; Ethylene/ethylacrylate; Ethylenemeth-acrylic acid ester; Ethylene/propylene; Ethylene/propylene-diene; Ethylene/vinyl acetate; Ethylene/vinyl alcohol; Ethylene/tetrafluoro-ethylene; Tetrafluoroethylene/ hexafluoro-propylene; Methacrylate /butadiene/styrene; Melamine/phenol-formaldehyde; Polyester blockamide; Perfluoro-alkoxy-alkane; Styrene/acrylonitrile; Styrene/butadiene; Styrene/maleic acid anhydride; Styrene/α-methylstyrene; Vinylchloride/ethylene; Vinylchloride/ethylene; Vinylchloride/ methyl-methacrylate; Vinylchloride/ethylene/vinyl acetate; Vinylchloride/ methyl-methacrylate; Vinylchloride/octylacrylate; Vinylchloride/vinyl acetate; and Vinylchloride/vinylidene chloride.

Preferred polymeric materials that can be stabilized are polyolefins such as polypropylene, polyethylene (e.g. high density polyethylene, low density polyethylene, linear low density polyethylene or medium density polyethylene), polybutylene, poly-4-methylpentene and copolymers thereof and polyurethane.

Preferred polyurethanes are those prepared from isocyanate resins and polyols. Preferred isocyanates are those commercially available as Desmodur, Elastan, Lupranat, Tedimon, Scuranat, Suprasec, Systanat, Hylene, Isonate (-Papi), Multrathane, Nacconate and Sumidur.

Preferred Polyols are those commericially available as Desmophen, Lupranol, Lupraphen, Glendion, Napiol, Scuranol, Caradol, Daltolac, Daltorez, Diorez, Estolan, Propylan, Armol, Bermodol, Isonol, Metpol, Multron, Multranol, Niax Polyol, Pluracol, Quadrol, Thanol, Voranol and Sumiphen.

Such polyurethanes are as describes in Saechtling: Kunststoff Taschenbuch 23 Ausgabe - published by Carl Hansen Verlag 1986 (esp. p. 339-410). The contents of this book are incorporated herein by reference.

Further additives that can be added to a stabilizing or a polymeric composition according to the invention include antioxidants, such as sterically hindered phenols, secondary aromatic amines or thioethers, such as described in "Kunststoff-Additive" - Gächter /Müller, Ed. 3, 1990 p.42-50, the contents of which are incorporated herein by reference; U.V. stabilizers such as sterically hindered amines (for example N-unsubstituted, N-alkyl or N-acyl substituted 2,2,6,6-tetra-methylpiperidine compounds) [also known as hindered amine light stabilizers - HALS] and U.V. absorbers (e.g. 2-(2'-hydroxyphenyl) -benztriazoles, 2-hydroxybenzophenones, 1,3-bis-(2'-hydroxybenzoyl-) benzene salicylates, cinnamates and oxalic acid diamides;), U.V. quenchers such as benzoates and substituted benzoates, antistatic agents, flameproofing agents, softeners, nucleating agents, metal deactivators, biocides, impact modifiers, fillers, pigments and fungicides.

Stabilizing compositions according to the invention may be added to the polymeric material before, during or after the polymerization step and may be added in solid or molten form, in solution preferably as a liquid concentrate containing from 10 to 80 % by weight of the composition and 90 to 20 % by weight of solvent or as a solid masterbatch composition containing 10 to 80 % (more preferably 40 to 70 %) by weight of the composition and 90 to 20 % (more preferably 60 to 30 %) by weight of a solid polymeric material which is identical with or compatible with the material to be stabilized.

The stabilizing compositions according to the invention may be incorporated by known methods into the polymeric material to be stabilized. Of particular importance is dry-blending of the compositions according to the invention with the polymer or coating

shaped polymer particles, e.g. polymer spheres, with the present compositions in the form of a liquid, a solution or a suspension/dispersion. Of particular importance is blending of the compounds with thermoplastic polymers in the melt, for example in a melt blender or during the formation of shaped articles, including films, tubes, fibres and foams by extrusion, injection moulding, blow moulding, spinning or wire coating. The compositions according to the invention are particularly useful for polypropylene and polyethylene articles of every type and polyurethane.

Further, in this specification, where a range is given, the figures defining the range are included therein. Any group capable of being linear or branched is linear or branched unless indicated to the contrary.

For the avoidance of doubt, in this specification t-butyl means tertiary butyl, $(-C(CH_3)_3)$.

The new stabilizer compositions are especially suitable for use in polyolefins and especially α - polyolefins prepared using processing catalysts known as Generation II to Generation V catalysts and which have not been subjected to a catalyst removal step. By the term "catalyst removal step" used herein is meant a step for the purpose of positively removing the catalyst residues contained in the polymerized polyolefins or treating the polyolefins with the compound which can react with the catalyst residue and inactivate or solubilize the residue, such as alcohols or water, and then removing the inactivated or solubilized catalyst residue by physical means such as filtration, washing and centrifuging. Thus, in the case of suspension polymerization, the step of separating the resulting polymer from a dispersion medium, such as a solvent or a liquefied monomer, does not fall under the above-mentioned definition of the catalyst residue removal step, although the catalyst dissolved in the dispersion medium may be removed by a separation step. The step of adding a small amount of catalyst poisons such as ethers, alcohols, ketones, esters and water to the resulting polymer, to inactivate the catalyst remaining after the

completion of polymerization, or the step of treating the resulting polymer suspension with gas such as steam or nitrogen to remove the dispersion medium also does not fall under the above-mentioned definition of the "catalyst residue-removal" step.

What we mean by Generation I catalysts are titanium halide catalysts and an organo aluminium compound or an organo aluminium halide.

What we mean by Generation II catalysts are Generation I catalysts supported on an organo magnesium compound or based on an organo chromium compound supported on SiO₂.

What we mean by a Generation III catalyst is a Ziegler type complex catalyst supported on a halogen containing magnesium compound.

What we mean by a Generation IV catalyst is a Generation III catalyst with a silane donor.

What we mean by Generation V catalysts is a bis-indenyl organo titanium compound supported on alumoxane or bis cyclopentadienyl titanium halides activated by aluminium alkyl compound.

Further generations of highly specific catalysts, especially useful for manufacturing highly stereoregular poly- α -olefins, which are presently under development, belong in the sense of the present invention also to the aforementioned generations of supported catalyst systems. Examples for the microstructure of such highly stereoregular polyolefins are given by syndiotactic polypropylene, isotactic stereoblock polymers, isotactic polypropylene containing stearic defects randomly distributed along the polymer chain (so called anisotactic polypropylene) or stereoirregular steroblock polymers. Due to the

rapid progress in the development of newer generation catalyst systems the commercial significance of these polymers with novel, highly interesting properties increases more and more. However, residues of such further catalyst generations, as long as they contain metals of the 3d, 4d and 5d series of the periodic system supported analogously to the earlier catalyst generations, can also cause disadvantageous properties in the polymer, as long as such residues are still present in the polymer even if in a deactivated form. Due to this, it can therefore be expected that the new compositions according to the invention are also suitable for overcoming such disadvantageous properties of the polymer. This means that any disadvantageous interaction between processing stabilizers and the aforementioned residues of catalysts of further generations, particularly the hydrolysis of phosphites and phosphonites, is most effectively inhibited.

These generations of catalysts are described in the Twelfth Annual International Conference on Advances in the stabilization and Controlled Degradation of Polymers held in Luzern, Switzerland, 21-23 May 1990 in an article on pages 181 to 196 inclusive by Rolf Mülhaupt entitled "New Trends in Polyolefin Catalysts and Influence on Polymer Stability". The contents of this article is incorporated herein by reference and especially Table I on page 184 describing the Generation of Catalysts:

TABLE I Polyolefin Catalyst Evolution

Generation Example		Cat.Act. % Act.Ti (gPP/gTi h atm)		(%hept.ins.)	Process Technology
I.	TiCl₄/AIR₃	40	0.01	45%	removal of cat.residues and atactic PP
	TiCl ₃ /AIEt ₂ Cl	30	0.1	92%	removal of catalyst residues
11	Mg(OEt ₂)/TiCl ₄ /AIR ₃	40000		50%	no removal of cat.residues
	SiO ₂ /Cp ₂ Cr	40000	HDPE		(mainly HDPE/LLDPE)
Ш	Mod.TiCl ₃ cat. MgCl ₂ /TiCl ₄ /AIR ₃ + ester donor	5000 20000	1 10	95% 92%	no purification
IV	MgCl ₂ /TiCl ₄ /AIR ₃ + silane donor	40000	18	99%	no purification no extrusion
V	Bis-indenyl-TiR ₂ on	40000	100	99%	novel PPs, narrow MWD
	(AICH ₃ O) ₂				

in which R is an organo group; HDPE is high density polyethylene, LLDPE is linear low density polyethyene, Cp is cyclopentadienyl, Et is ethyl, PP is polypropylene, MWD is

molecular weight distribution and x is an integer above 2.

Polymeric compositions according to the invention have both good stabilizing properties and good light fastness properties.

The invention will be illustrated by the following Example.

Example

Samples preparation

Ground formulation:

90 parts by weight

thermoplastic polyurethane (TPU) granules ("Pellethane

2355-65D" from Dow Chemical, USA)

10 parts by weight

Additive and "Carrier"

10 parts of Additive being light stabilizing compounds I or II or non-light stabilizing additives A and B being liquid, are previously incorporated in a solid and opaque system (the so-called "Carrier") consisting of:

37.0 parts by weight SBS granules ("Cariflex TR1102" from Shell Chemical, U.K.)

19.5 parts by weight LDPE powder MFI:70 from Verplast, Italy

24.7 parts by weight PE WAX 520 from BASF, Germany and

8.8 parts by weight an antiblocking agent Silica compound ("Syloblock 44" from

Grace, USA)

100.0 parts by weight

Note: The "Carrier" enables TPU to be used to mould opaque sporting shoe soles.

Preparation:

100 g of the above blend (of the carrier and additive) are homogeneously processed on a two-roll laboratory open mill (Meccaniche Moderne, Italy) at 110°-115°C for about 5-7

minutes.

The resulting rough crepe (2-3 mm thick) is hand-cut by scissors in very small irregular pieces and added to 900 g of TPU granules in a laboratory tumbler and tumbled for about 5 minutes.

This mixture is then fed to the hopper of a "Negri & Bossi V5-8FA" (Italy) laboratory injection moulding machine. Operating at a temperature of 200°-220°C (cold mould) 1.5 mm thick specimens are moulded for the subsequent accelerated light degradation exposure.

Light exposure

The above specimens are exposed in an Atlas Weather-O-Meter WRCi 65, cam 7 (USA) (Black panel 63°C; 50% R.H., according to ASTM D 2565), for 20-70-162 hours and visually examined for comparative yellowing discoloration and classified by the "Wool Blue Scale" (ranking from 8, the best (no discoloration) to 1, the worst (total discoloration)):

Carrier + Additive	After 20 h	After 70 h	After 162 h
	6	4	4
II	6	5	4
Α	5	3	2
В	5	3	2

Additive used:

Additive I is

a) 50% of a composition comprising

57% of the compound

29% of

where R is $nC_{12}H_{25}$ and $n-C_{14}H_{29}$ (Composition A); and 14% xylene and

b) 50% of a composition comprising 80% trilaurylphosphite and 20% α -tocopherol (Composition B).

Additive II is a composition comprising

- a) 50% of Composition B and
- b) 50% of polymethylpropyl 3-oxy [4(2,2,6,6-tetramethyl)piperidinyl] siloxane, a compound of the formula

where n_a is a number from 1 to 30.

Additive A is TPU alone ("Pellethane 2355-65D") from Dow Chemical, USA.

Additive B is 90% TPU + 10% Carrier.

CLAIMS:

- 1. A stabilizing composition comprising:
 - a) a mono- or di- phosphite or mono- or diphosphonite (component a)
 - b) a chroman derivative (component b); and
 - c) a light stabilizer (component c) selected from
 - i) a polymer containing at least one hindered amine light stabilizer group (component i) and/or
 - ii) the combination of an oxanilide and a hindered amine light stabilizer (HALS) compound (component ii).
- 2. A stabilizing composition according to Claim 1 in which the mono- or di- phosphites are of formula I or II

$$R_1 - O - P'$$
 $O - R_1$
(I)

in which each R₁ independently is a group derived from an aliphatic, alicyclic or aromatic alcohol containing one or two OH groups.

3. A stabilizing compositions according to Claim 1 in which the mono- or diphosphonites are selected from compounds of formula III

in which m is 0 or 1;

n is 0 or 1;

p is 0 or 1;

each R_9 , independently, is a group derived from an aliphatic, alicyclic or aromatic alcohol containing one or two OH groups; whereby the two -OH groups are not positioned to be able to form a P-containing ring; (hereinafter defined as the monovalent significances of R_9);

or both groups R_9 form a group derived from an aliphatic, alicyclic or aromatic alcohol containing two OH groups in such a position that they can form a cyclic group with a single phosphorus atom (hereinafter defined as the divalent significances of R_9):

 R_{10} is a monovalent or divalent significance of R_{9} ;

Y is -O-, -S-, -CH(
$$R_3$$
)- or C_6H_4 -;

where R_3 is hydrogen or C_{1-8} alkyl or $COOR_4$ and R_4 is C_{1-8} alkyl.

4. A stabilizing composition according to any one of the preceding claims in which the chroman derivatives are selected from compounds of formula IV

$$\begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \end{array} \tag{IV}$$

or $-CH_2-CH_2-O-CO-R_6$ where R_6 is selected from C_{7-30} alkyl, $-CH_2CH_2-S-(C_{1-30}$ alkyl) or

5. A stabilizing composition according to any one of the preceding claims in which the polysiloxanes are selected from compounds of formula V

$$\begin{array}{c} C_{1}\text{-}_{e}\text{alkyl} \\ -(-\text{Si-O-})n_{a} \\ (\text{CH}_{2})_{2}\text{-}_{8} \\ \text{O} \\ \text{H} \\ \text{CH}_{3} \\ \text{CH}_{3} \\ \text{CH}_{3} \\ \text{R} \end{array} \tag{V}$$

in which $n_a = 1$ to 100,

R is selected from hydrogen, $C_{1.8}$ alkyl, oxygen $-CO-R_5$ or OR_8 ; where R_5 is $-C(R_8)=CH_2$, $C_{1.6}$ alkyl, phenyl, $-COC_6H_5$, $-CH_2C_66H_5$ $-COOC_{1.12}$ alkyl, COOH or NR_7R_8 , where R_7 is hydrogen, $C_{1.12}$ alkyl, $C_{5.6}$ cyclo alkyl, phenyl, phenyl $C_{1.4}$ alkyl or $C_{1.12}$ alkylphenyl and R_8 is $C_{1.12}$ alkyl or hydrogen.

 A stabilizing composition according to any one of the preceding claims in which the oxanilides are of formula VII

$$(VII)$$

$$R_{11}$$

$$R_{13}$$

$$R_{13}$$

$$R_{13}$$

$$R_{11}$$

in which each R_{11} independently is selected from hydrogen, C_{1-18} alkyl, C_{1-18} alkoxy, halogen, hydroxy, phenyl and phenoxy; and

each R_{12} , independently, is selected from hydrogen, halogen, hydroxy, C_{1-8} alkyl and C_{1-8} alkoxy; and

each R₁₃, independently, is hydrogen or methyl.

- 7. A stabilizing composition according to Claim 6 in which R_{11} is R_{11} ' where R_{11} ' is selected from hydrogen, hydroxy, C_{1-4} alkyl and C_{1-4} alkoxy; R_{12} is R_{12} ' where R_{12} ' is selected from hydrogen, hydroxy, C_{1-4} alkyl and C_{1-4} alkoxy; and R_{13} is hydrogen.
- 8. A stabilizing composition according to any one of the preceding claims in which the HALS compound is of formula VI

$$R \longrightarrow N$$
 R_{16}
 R_{15}
 R_{15}
 R_{15}
 R_{15}
 R_{15}
 R_{15}
 R_{15}

in which R is selected from hydrogen, C_{1-8} alkyl, oxygen, -COR $_5$ or OR $_8$; where R $_5$ is $C(R_8)=CH_2$, C_{1-6} alkyl, phenyl, -NR $_7$ R $_8$, -CO- C_6 H $_5$, -CH $_2$ C $_6$ H $_5$, -COOC $_{1-12}$ alkyl or -COOH;

where $\rm R_7$ is hydrogen, $\rm C_{1\text{--}12}$ alkyl, $\rm C_{5\text{--}6}$ cycloalkyl phenyl, phenyl $\rm C_{1\text{--}4}$ alkyl or $\rm C_{1\text{--}12}$ alkylphenyl and

R₈ is hydrogen or C₁₋₁₂alkyl;

 R_{15} is hydrogen, C_{1-22} alkyl, C_{1-22} alkoxy, $-N(R)_5$ -CO-CO- R_{20} ; or -NH-C(R)₅=N- R_{21} ;

 R_3 is hydrogen, C_{1-18} alkyl or -COOR₄ where R_4 is C_{1-8} alkyl

 R_{20} is an amide forming group and R_{21} is C_{1-18} alkyl, phenyl, unsubstituted or substituted by 1 to 3 groups selected from C_{1-18} alkyl, C_{1-4} alkoxy and halogen; or R_{15} is

R₁₆ is hydrogen or C₁₋₈alkyl; or

 R_{15} and R_{16} together with the C-atom to which they are attached, form a group of formula a)

- A stabilizing composition substantially as herein described with reference to the Example.
- 10. A polymeric composition comprising a polymeric material and a stabilizing amount of a composition according to any one of the preceding claims.
- 11. A polymeric composition comprising 0.2-8% of a stabilizing composition according to any one of Claims 1 to 9.

12. A polymeric composition substantially as herein described with reference to the Example.

_xaminer's report to the Comptroller under Section 17 (The Search Report)

Application number

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Relevant Technica	ıl fields	Search Examiner
(i) UK CI (Edition	K) C3K (KCA, KCB, KCD, KCE, KCF, KCZ)	
(ii) Int CI (Edition	5) C08K; C08L	B J BALDOCK
Databases (see ov (i) UK Patent Offic	•	Date of Search
(ii) ONLINE DATA	ABASES: WPI	19 NOVEMBER 1992

Documents considered relevant following a search in respect of claims 1–12

Category (see over)	Identity of docume	ent and relevant passages	Relevant to claim(s)
A	EP 0312927 A	(BASF)	At least 1, 10
A	EP 0263524 A2	(BASF)	At least 1, 10
A	US 4806580	(BASF)	At least 1, 10
A	US 4925888	(BASF)	At least 1, 10
A	DE 3725926 A	(BASF)	At least 1, 10
A	JP 630137941 A	(MITSUI TOATSU) See WPI Accession Number:- 88-201284/29	At least 1, 10
A	JP 020225542 A	(CHISSO) See WPI Accession Number:- 90-316731/42	At least 1, 10
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Category	Identity of document and relevant passages	Relevant to claim(s,
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Categories	of documents	
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X: Document indicating lack of novelty or of inventive step.

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P: Document published on or after the declared priority date but before the filing date of the present application.

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Databases: The UK Patent Office database comprises classified collections of GB, EP, WO and US patent specifications as outlined periodically in the Official Journal (Patents). The on-line databases considered for search are also listed periodically in the Official Journal (Patents).