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(21) International Application Number: PCT/EP94/04105 (22) International Filing Date: 9 December 1994 (09.12.94) (30) Priority Data: 3818/93-6 22 December 1993 (22.12.93) CH (71) Applicant (for all designated States except US): CIBA-GEIGY AG [CH/CH]; Klybeckstrasse 141, CH-4002 Basle (CH). (72) Inventors; and (75) Inventors/Applicants (for US only): PFAENDNER, Rudolf [DE/DE]; Sackgasse 3, D-64668 Rimbach/Odenwald 1 (DE). HERBST, Heinz [DE/DE]; Hohensteiner Strasse 40, D-64686 Lautertal-Reichenbach (DE). HOFFMANN, Kurt [DE/DE]; Am Kochengraben 30, D-64686 Lautertal 1 (DE). (74) Common Representative: CIBA-GEIGY AG; Patentabteilung, Klybeckstrasse 141, CH-4002 Basle (CH).		(81) Designated States: AM, AU, BB, BG, BR, BY, CA, CN, CZ, EE, FI, GE, HU, JP, KG, KP, KR, KZ, LK, LR, LT, LV, MD, MG, MN, NO, NZ, PL, RO, RU, SI, SK, TJ, TT, UA, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD, SZ). Published <i>With international search report.</i>
(54) Title: PROCESS FOR THE STABILIZATION OF AND STABILIZER MIXTURES FOR PVDC-CONTAINING POLYOLEFIN MIXTURES (57) Abstract Plastic mixtures, in particular recycled plastic mixtures, comprising predominantly polyolefins and 0.05-20 % by weight of PVDC can be stabilized against thermo-oxidative degradation by addition of a combination of an organic phosphite or phosphonite and a metal salt of a fatty acid.		

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Process for the stabilization of and stabilizer mixtures for PVDC-containing polyolefin mixtures

The invention relates to a process for the stabilization of PVDC-containing polyolefin mixtures, in particular recyclates, and to the stabilizer mixtures which can be used for this purpose.

Copolymers based on vinylidene chloride (PVDC), for example with vinyl chloride, acrylonitrile, acrylates or ethylene as comonomers, are used as coating materials and films as a barrier layer in the packaging of foods, pharmaceuticals and other products in order to achieve impermeability, for example to water and oxygen, fats, gases and flavours. Further information on PVDC is given in H. Domininghaus "Die Kunststoffe und ihre Eigenschaften", VDI-Verlag, Düsseldorf, 4th Edn., 1992, pages 219ff.

The recycling of such materials, which are generally in the form of laminates (multilayer films), usually in combination with polyolefins, such as LDPE (high-pressure polyethylene), HDPE and PP (polypropylene), and their conversion into new products, for example by extrusion and injection moulding, causes problems, even at very low PVDC concentrations, due to decomposition and discoloration and thus unsatisfactory mechanical properties. A corresponding situation applies to the processing of film mixtures from collected valuable materials, which can contain PVDC, for example as a coating on a film, which in general cannot be separated out by physical methods.

US 5,075,355 describes a process for the stabilization of recycled PVDC-containing films. In addition to the use of a supported polymer and a pyrophosphate, the process requires a metal hydroxide complex of the hydrotalcite type.

Other ways of stabilizing PVDC-containing polymers are described in EP-A 0 510 800, US 5,286,424 and EP-A 0 604 136.

Thus, there continues to be a demand, and this is the object of the present invention, for the provision of a process which enables the processing of PVDC-containing plastic mixtures, predominantly comprising polyolefins, without significant discoloration and/or with retention of the mechanical properties in an economical and technically feasible manner.

It has now been found that PVDC-containing plastic mixtures, in particular recyclates, can

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be stabilized in a simple and economical manner against thermo-oxidative degradation during processing and subsequent use by a mixture of an organic phosphite or phosphonite and a metal salt of a fatty acid.

The invention relates to a process for the stabilization of a plastic mixture predominantly comprising polyolefins and 0.05-20 % by weight PVDC, which comprises adding (a) at least one organic phosphite or phosphonite and (b) at least one metal salt of a fatty acid to this mixture.

The plastic mixtures to be stabilized are, for example, film offcuts generated in the production of multilayer films, films coated with an aqueous PVDC dispersion or film mixtures from collected valuable materials. However, fresh plastic mixtures can also be employed in the process.

These plastic mixtures comprise predominantly polyolefins. Preferred plastic mixtures comprise 80-99.95 % by weight, in particular 95-99.9 % by weight, of polyolefins and 0.05-20 % by weight, in particular 0.1-5 % by weight, of PVDC, it also being possible for the polyolefins to be in the form of mixtures. Small amounts of polymers such as polystyrene, PET, PVC or polyamide can also be present. Furthermore, the term polyolefins also includes copolymers such as EVA. It may furthermore be expedient, in particular in the case of polyolefin mixtures, to add compatibility improvers (compatibilizers).

In particular, the invention relates to the stabilization of recycled plastic mixtures of said composition. Recycled plastic mixtures may also contain small amounts of foreign materials, for example paper, pigments and adhesives, which are frequently difficult to remove. These foreign materials can also originate from contact with diverse substances during use or treatment, for example fuel residues, paint residues, traces of metal, initiator residues or traces of water.

In the plastic mixtures, the dominant polyolefins are usually polyethylene (PE) and polypropylene (PP), in particular low-density polyethylene (LDPE), linear low-density polyethylene (LLDPE) and high-density polyethylene (HDPE), furthermore copolymers such as ethylene-propylene (EPM) and ethylene-propylene-diene (EPDM) copolymers, and ULDPE and MDPE. Particular preference is given to the stabilization of PVDC-containing polyolefin recyclates containing polypropylene, HD polyethylene or LD polyethylene.

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The novel process preferably uses from 0.05 to 10 % by weight, particularly preferably from 0.05 to 5 % by weight, very particularly preferably from 0.1 to 2 % by weight, based on the plastic mixture, of the mixture of (a) and (b).

Furthermore, the novel process preferably uses from 0.01 to 2 % by weight of (a) and from 0.05 to 5 % by weight of (b), particularly preferably from 0.02 to 0.1 % by weight of (a) and from 0.1 to 2 % by weight of (b), in each case based on the plastic mixture.

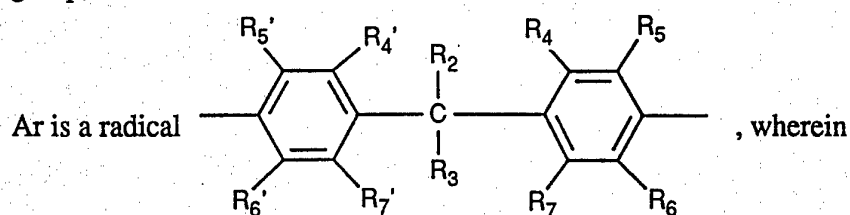
The organic phosphites or phosphonites which can be used as component (a) are known as stabilizers for plastics, in particular as processing stabilizers for polyolefins.

They are predominantly aromatic phosphites and phosphonites, for example triphenyl phosphite, diphenyl alkyl phosphites, phenyl dialkyl phosphites, tris(diphenyl alkyl phosphite)amines, tris(nonylphenyl) phosphite, trilauryl phosphite, trioctadecyl phosphite, distearyl pentaerythrityl diphosphite, tris(2,4-di-tert-butylphenyl) phosphite, distearyl pentaerythrityl diphosphite, bis(2,4-di-tert-butylphenyl) pentaerythrityl diphosphite, tristearyl sorbitol triphosphite, tetrakis(2,4-di-tert-butylphenyl)-4,4'-biphenylene diphosphonite, 3,9-bis(2,4-di-tert-butyl-4-methylphenoxy)-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane, 3,9-tris(2,4,6-tris-tert-butylphenoxy)-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane, 2,2'-ethyldienebis(4,6-di-tert-butylphenyl) fluorophosphite and phosphites of the formula

$(R_1O)_2P-O-[-Ar-O-P(OR_1)-O]_n-Ar-O-P(OR_1)_2$, wherein

R_1 is C_1 - C_{18} alkyl, C_6 - C_{15} aryl, C_5 - C_6 cycloalkyl, C_7 - C_9 aralkyl, or a

C_1 - C_{18} monoalcoholresidue containing at least one oxetane group, under the condition that at least one of R_1 is such a C_1 - C_{18} monoalcoholresidue containing at least one oxetane group; and

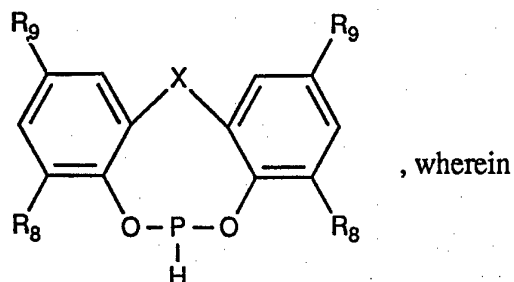


R_2 and R_3 , independently of one another, are H, C_1 - C_{18} alkyl or C_6 - C_{18} -aryl; and

R_4 , R_4' , R_5 , R_5' , R_6 , R_6' , R_7 , and R_7' , independently of one another, are H, C_1 - C_{18} alkyl, C_5 - C_6 cycloalkyl, C_6 - C_{18} aryl, C_1 - C_{18} alkoxy, C_1 - C_{18} aryloxy or halogen;

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as well as phosphorous acid esters of the formula



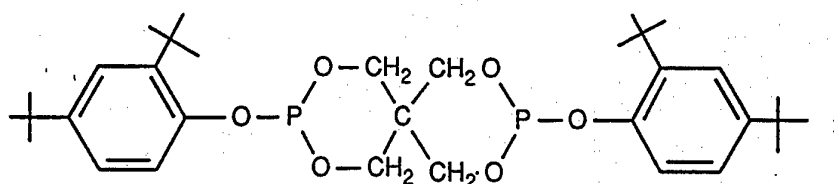
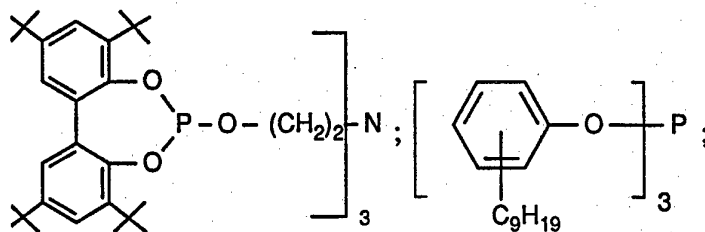
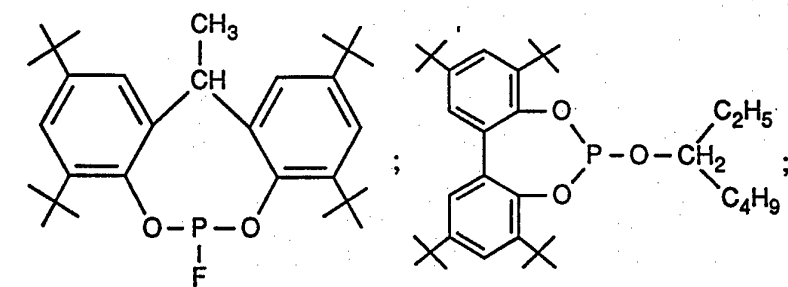
R_8 and R_9 , independently of one another, are C_1 - C_9 alkyl, C_5 - C_6 cycloalkyl, C_7 - C_9 aralkyl or C_6 - C_{19} aryl; and

X is -S- or -CH- R_{10} , in which R_{10} is H, C_1 - C_6 alkyl or C_5 - C_6 cycloalkyl.

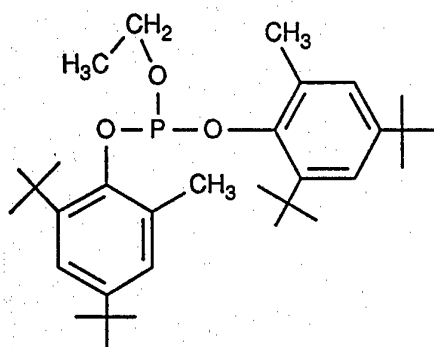
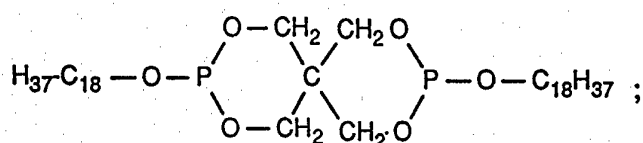
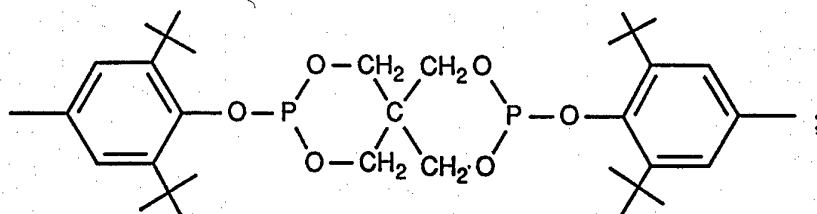
Particular preference is given to the following phosphites and phosphonites:

tris(2,4-di-tert-butylphenyl) phosphite;

tetrakis(2,4-di-tert-butyl)-4,4'-biphenylene diphosphonite;



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Component (a) is very particularly preferably tris(2,4-di-tert-butylphenyl) phosphite.

Component (b) is a metal salt of a fatty acid, where the metal may be, in particular, an element of main or sub-group II or aluminium or tin.

These are, in particular, tin or preferably calcium, zinc, magnesium or aluminium salts from the series consisting of aliphatic saturated C₂-C₂₂carboxylates, aliphatic olefinic C₃-C₂₂carboxylates, aliphatic C₂-C₂₂carboxylates which are substituted by at least one OH group, cyclic or bicyclic C₅-C₂₂carboxylates, aromatic C₇-C₂₂carboxylates, aromatic C₇-C₂₂carboxylates which are substituted by at least one OH group, C₁-C₁₆alkyl-substituted phenylcarboxylates and phenyl C₁-C₁₆alkylcarboxylates, preference being given to behenates, in particular stearates, laurates and oleates.

Component (b) is very particularly preferably calcium stearate, zinc stearate, magnesium stearate or aluminium stearate.

It is also possible to use a mixture of various components (a) and (b). For example, component (b) may be a mixture of calcium laurate and calcium stearate or of zinc

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stearate and calcium stearate, calcium stearate and zinc oleate or calcium stearate and zinc laurate.

The addition of the stabilizer mixtures to the plastic mixture allows thermoplastic processing with reduced degradation and/or extends the service life or preserves the mechanical properties of the materials produced from the recycle.

It is also possible to use further conventional plastic additives which improve the processing or the material properties of the plastic mixture, for example polyols and/or compatibilizers.

Examples of suitable polyols are: pentaerythritol, dipentaerythritol, tripentaerythritol, bistrimethylolpropane, bistrimethylolethane, trismethylolpropane, sorbitol, maltitol, isomaltitol, lactitol, isomaltitol, lycasine, mannitol, lactose, leucrose, tris(hydroxyethyl) isocyanurate, palatinitol, tetramethylolcyclohexanol, tetramethylolcyclopentanol, tetramethylolcyclopyranol, glycerol, diglycerol, polyglycerol and 1-0- α -D-glycopyranosyl-D-mannitol dihydrate.

The polyols can be used in an amount of, for example, from 0.01 to 20 parts by weight, expediently from 0.1 to 20 parts by weight, in particular from 0.1 to 10 parts by weight, based on 100 parts by weight of PVDC-containing plastic mixture.

The compatibilizers can be, for example, copolymers, in particular block copolymers, of styrene with butadiene and, if desired, acrylonitrile. They can be copolymers of ethylene and propylene, and may contain a third monomer component, for example butadiene. Chlorinated polyethylene or ethylene-vinyl acetate copolymers are also suitable as compatibilizers. Further suitable compatibilizers contain, in particular, polar groups, e.g. maleic anhydride-styrene copolymers or graft polymers containing acrylic acid groups.

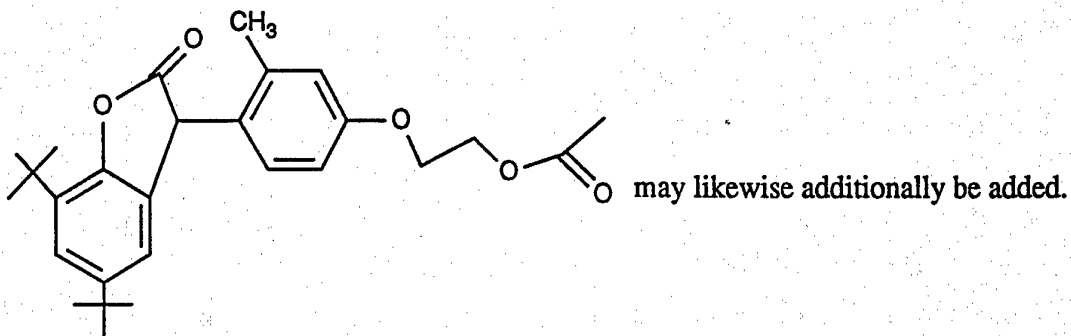
The polymeric compatibilizers are generally used in amounts of 1-20 % by weight, based on the plastic mixture to be stabilized.

The stabilizing action of the mixture of (a) and (b), in particular the long-term stability, may be synergistically increased by the addition of so-called thiosynergists. These are aliphatic thioethers, in particular esters of thiodipropionic acid. Examples are the lauryl, stearyl, myristyl and tridecyl esters of thiodipropionic acid or distearyl disulfide. These thiosynergists are preferably used in an amount of from 0.1 to 1 % by weight, based on the

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plastic mixture.

Further suitable stabilizers from the series consisting of the lactates, e.g. calcium lactate and calcium stearyl-2-lactate, or lactones, e.g.



If high light stability is also required of the article produced from the plastic mixture, the addition of one or more light stabilizers is advisable. Suitable light stabilizers are, in particular, those from the series consisting of the benzophenones, benzotriazoles, oxanilides and sterically hindered amines. Examples of such compounds are:

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

2-(2'-Hydroxyphenyl)benzotriazoles, for example the 5'-methyl, 3',5'-di-tert-butyl, 5'-tert-butyl, 5'-(1,1,3,3-tetramethylbutyl), 5-chloro-3',5'-di-tert-butyl, 5-chloro-3'-tert-butyl-5'-methyl, 3'-sec-butyl-5'-tert-butyl, 4'-octoxy, 3',5'-di-tert-amyl and 3',5'-bis(α,α -dimethylbenzyl) derivatives.

Oxalamides, for example 4,4'-dioctyloxyoxanilide, 2,2'-dioctyloxy-5,5'-di-tert-butyloxanilide, 2,2'-didodecyloxy-5,5'-di-tert-butyloxanilide, 2-ethoxy-2'-ethyloxanilide, N,N'-bis(3-dimethylaminopropyl)oxalamide, 2-ethoxy-5-tert-butyl-2'-ethyloxanilide and mixtures thereof with 2-ethoxy-2'-ethyl-5,4'-di-tert-butyloxanilide, and mixtures of o- and p-methoxy- and of o- and p-ethoxy-disubstituted oxanilides.

Sterically hindered amines, for example bis(2,2,6,6-tetramethylpiperidyl) sebacate, bis(1,2,2,6,6-pentamethylpiperidyl) sebacate, bis(1-octyloxy-2,2,6,6-tetramethyl-4-piperidyl) sebacate, bis(1,2,2,6,6-pentamethylpiperidyl) n-butyl-3,5-di-tert-butyl-4-hydroxybenzylmalonate, the product of the condensation of

1-hydroxyethyl-2,2,6,6-tetramethyl-4-hydroxypiperidine and succinic acid, the product of the condensation of N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)hexamethylenediamine and 4-tert-octylamino-2,6-dichloro-1,3,5-s-triazine or 4-morpholino-2,6-dichloro-1,3,5-triazine, tetrakis(2,2,6,6-tetramethyl-4-piperidyl) 1,2,3,4-butanetetraoate, bis(2,2,6,6-tetramethylpiperidyl) succinate, N-(1,2,2,6,6-pentamethyl-4-piperidyl)- α -dodecylsuccinimide, N-(2,2,6,6-tetramethyl-4-piperidyl)- α -dodecylsuccinimide, 2,4,6-tris[N-pentyl-2-(3,3,5,5-tetramethyl-2-oxo-piperazino)ethylamino]-1,3,5-triazine, 2,2,4,4-tetramethyl-7-oxa-3,20-diaza-21-oxo-dispiro[5,1,11,2]heneicosane, 2,2,4,4-tetramethyl-20-(2-dodecyloxycarbonylethyl)-7-oxa-3,20-diaza-21-oxo-dispiro[5,1,11,2]heneicosane, 8-acetyl-3-dodecyl-1,3,8-triaza-7,7,9,9-tetramethylspiro[4,5]decane-2,4-dione, 1,5,8,12-tetrakis[2,4-bis(N-butyl-1,2,2,6,6-pentamethyl-4-piperidylamino)-1,3,5-triazin-6-yl]-1,5,8,12-tetraazadodecane, and polysiloxanes containing 2,2,6,6-tetramethyl-4-piperidinyl groups.

The light stabilizers are preferably added in an amount of from 0.01 to 2 % by weight, in particular from 0.05 to 0.5 % by weight, based on the plastic mixture. The light stabilizer used is preferably a combination of a benzotriazole with a sterically hindered amine.

The addition of antioxidants, in particular phenolic antioxidants, does not prevent any damage during processing of the plastic mixture. If low demands are made of the colour stability and in particular long-term applications, the addition of a phenolic antioxidant may be advantageous.

Phenolic antioxidants which may be mentioned are:

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-dinonyl-4-methylphenol, 2,4-dimethyl-6-(1'-methyl-undec-1'-yl)-phenol, 2,4-dimethyl-6-(1'-methylheptadec-1'-yl)phenol, 2,4-dimethyl-6-(1'-methyltridec-1'-yl)phenol and mixtures thereof.

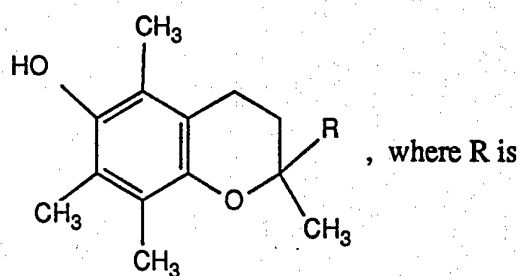
1.2. Alkylthiomethylphenols, for example 2,4-dioctylthiomethyl-6-tert-butylphenol, 2,4-dioctylthiomethyl-6-methylphenol, 2,4-dioctylthiomethyl-6-ethylphenol, 2,6-didodecylthiomethyl-4-nonylphenol.

1.3. Hydroquinones and alkylated hydroquinones, for example 2,6-di-tert-butyl-4-

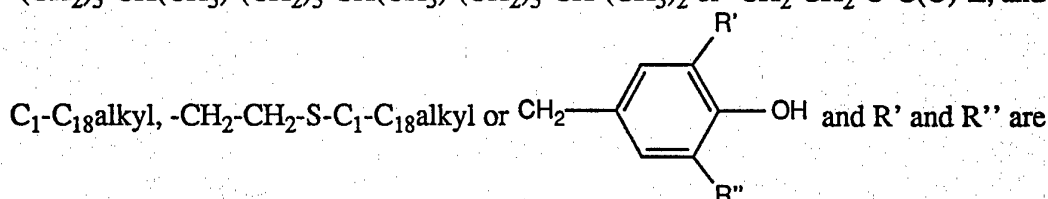
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methoxyphenol, 2,5-di-tert-butylhydroquinone, 2,5-di-tert-amylhydroquinone, 2,6-diphenyl-4-octadecyloxyphenol, 2,6-di-tert-butylhydroquinone, 2,5-di-tert-butyl-4-hydroxyanisole, 3,5-di-tert-butyl-4-hydroxyanisole, 3,5-di-tert-butyl-4-hydroxyphenyl stearate, bis(3,5-di-tert-butyl-4-hydroxyphenyl) adipate.

1.4. Chroman derivatives of the formula



$-(\text{CH}_2)_3-\text{CH}(\text{CH}_3)-(\text{CH}_2)_3-\text{CH}(\text{CH}_3)-(\text{CH}_2)_3-\text{CH}-(\text{CH}_3)_2$ or $-\text{CH}_2-\text{CH}_2-\text{O}-\text{C}(\text{O})-\text{Z}$, and Z is



hydrogen, methyl or tert-butyl, for example α -tocopherol, β -tocopherol, γ -tocopherol, δ -tocopherol and mixtures thereof (vitamin E).

1.5. Hydroxylated thiodiphenyl ethers, for example

2,2'-thiobis(6-tert-butyl-4-methylphenol), 2,2'-thiobis(4-octylphenol), 4,4'-thiobis(6-tert-butyl-3-methylphenol), 4,4'-thiobis(6-tert-butyl-2-methylphenol), 4,4'-thiobis(3,6-di-sec-amylphenol), 4,4'-bis(2,6-dimethyl-4-hydroxyphenyl) disulfide.

1.6. Alkylidene bisphenols, for example 2,2'-methylenebis(6-tert-butyl-4-methylphenol),

2,2'-methylenebis(6-tert-butyl-4-ethylphenol), 2,2'-methylenebis[4-methyl-6-(α -methylcyclohexyl)phenol], 2,2'-methylenebis(4-methyl-6-cyclohexylphenol), 2,2'-methylene-bis(6-nonyl-4-methylphenol), 2,2'-methylenebis(4,6-di-tert-butylphenol), 2,2'-ethylidenebis(4,6-di-tert-butylphenol), 2,2'-ethylidenebis(6-tert-butyl-4-isobutylphenol), 2,2'-methylenebis[6-(α -methylbenzyl)-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, 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, dioctadecyl 2-(3-tert-butyl-4-hydroxy-5-methylbenzyl)malonate, didodecylmercaptoethyl 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.

1.9. 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.

1.10. 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.

1.11. Benzylphosphonates, for example dimethyl 2,5-di-tert-butyl-4-hydroxybenzylphosphonate, diethyl 3,5-di-tert-butyl-4-hydroxybenzylphosphonate, dioctadecyl 3,5-di-tert-butyl-4-hydroxybenzylphosphonate, dioctadecyl 5-tert-butyl-4-hydroxy-3-methylbenzylphosphonate, calcium salt of monoethyl 3,5-di-tert-butyl-4-hydroxybenzyl phosphonate.

1.12. Acylaminophenols, for example 4-hydroxylauranilide, 4-hydroxystearanilide, octyl N-(3,5-di-tert-butyl-4-hydroxyphenyl)carbamate.

1.13. Esters of β -(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid with monohydric or polyhydric alcohols, for example with methanol, ethanol, octanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl) isocyanurate, N,N'-bis(hydroxyethyl)oxalamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo-[2.2.2]octane.

1.14. Esters of β -(5-tert-butyl-4-hydroxy-3-methylphenyl)propionic acid, with monohydric or polyhydric alcohols, for example methanol, ethanol, octanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl) isocyanurate, N,N'-bis(hydroxyethyl)oxalamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo-[2.2.2]octane.

1.15. Esters of β -(3,5-dicyclohexyl-4-hydroxyphenyl)propionic acid, with monohydric or polyhydric alcohols, for example methanol, ethanol, octanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl) isocyanurate, N,N'-bis(hydroxyethyl)oxalamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo-[2.2.2]-octane.

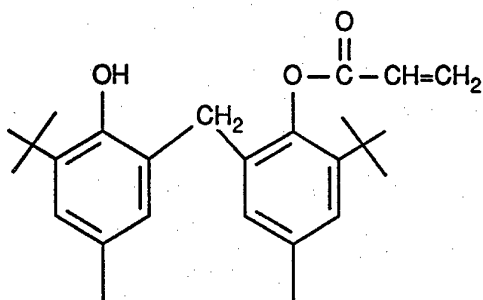
1.16. Esters of 3,5-di-tert-butyl-4-hydroxyphenylacetic acid, with monohydric or polyhydric alcohols, for example methanol, ethanol, octanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl) isocyanurate, N,N'-bis(hydroxyethyl)oxalamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo-[2.2.2]-octane.

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

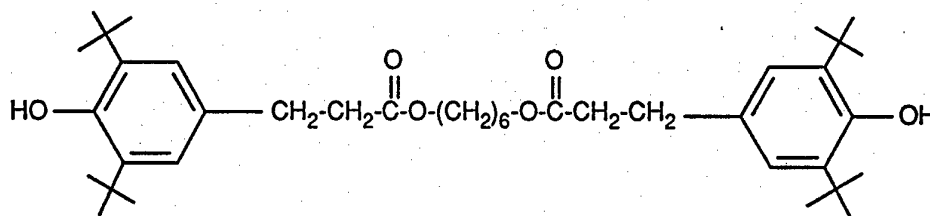
- 12 -

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

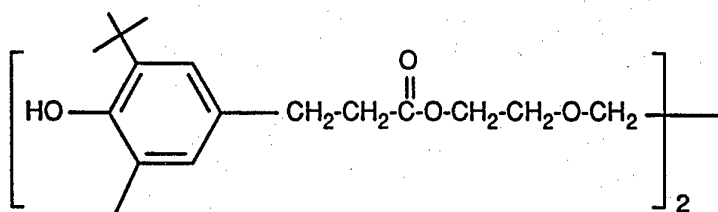
Preference is given to antioxidants such as:



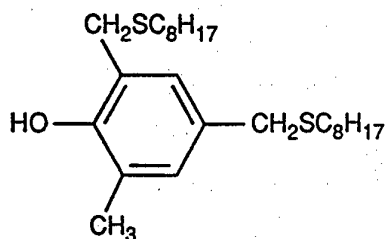
{2-(1,1-dimethylethyl)-6-[[3-(1,1-dimethylethyl)-2-hydroxy-5-methylphenyl]methyl]-4-methylphenyl 2-propenoate};



{1,6-hexanediyl 3,5-bis(1,1-dimethylethyl)-4-hydroxyphenylpropanoate};

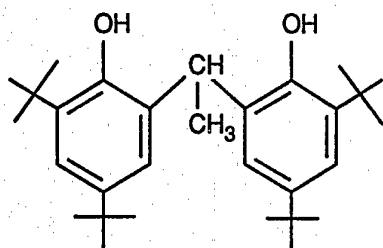


{1,2-ethanediylbis(oxy-2,1-ethanediyl) 3-(1,1-dimethylethyl)-4-hydroxy-5-methylphenylpropanoate};

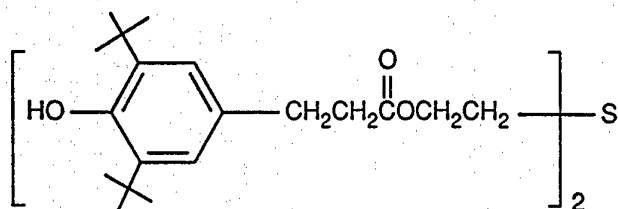


{2-methyl-4,6-di[(octylthio)methyl]phenol};

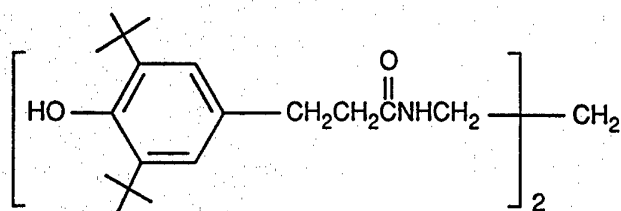
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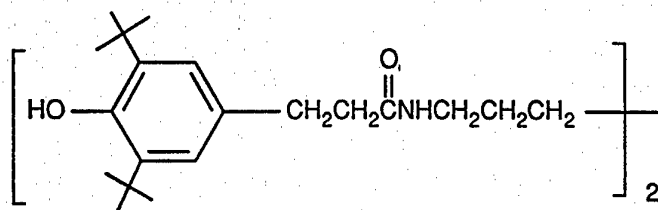
{2,2'-ethyldenebis(4,6-di-tert-butylphenol)};



{thiodi-2,1-ethanediyl bis-3,5-di(1,1-dimethylethyl)-4-hydroxyphenylpropanoate};

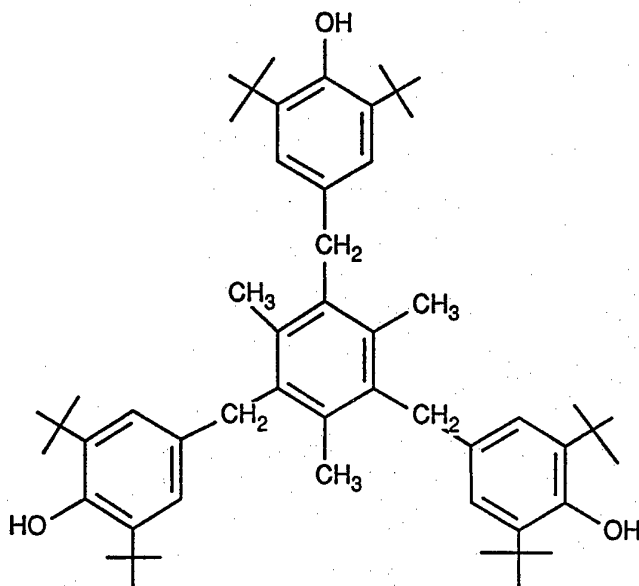


{1,3-propanediylbis(3,5-di(1,1-dimethylethyl)-4-hydroxyphenylpropanamide)};



{di-1,3-propanediylbis(3,5-di(1,1-dimethylethyl)-4-hydroxyphenylpropanamide)};

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{4,4',4''-[(2,4,6-trimethyl-1,3,5-phenyltriyl)tris(methylene)]tris[2,6-bis(1,1-dimethylethyl)phenol]};

and the pentaerythrityl, octyl and octadecyl esters of β -(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid.

The present invention furthermore relates to a stabilizer mixture comprising (a) at least one organic phosphite or phosphonite and (b) at least one metal salt of a fatty acid, and to the use thereof for the stabilization of a plastic mixture, in particular a recycled plastic mixture, comprising predominantly polyolefins and 0.05-20 % by weight of PVDC.

The present invention furthermore relates to a plastic mixture, in particular a recycled plastic mixture, comprising predominantly polyolefins and 0.05-20 % by weight of PVDC which furthermore comprises (a) at least one organic phosphite or phosphonite and (b) at least one metal salt of a fatty acid.

Preferred (recycled) plastic mixtures, preferred stabilizer mixtures and their use conform in their components and mixing ratios to the preferences mentioned in greater detail under the process.

Specific and preferred stabilizer mixtures are those comprising 2-30 % by weight of aromatic phosphite, 10-70 % by weight of metal salt of a fatty acid and 5-60 % by weight of polyol, and very particularly those comprising 2-30 % of tris(2,4-di-tert-butylphenyl) phosphite, 5-35 % of calcium stearate or laurate, 5-35 % of zinc stearate or laurate and 5-60 % of pentaerythritol.

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The novel stabilizer mixtures and, if desired, the additives mentioned can be employed in compacted, extruded form or on a support material, or can be added directly to the plastic mixture as individual substances, a mixture or in the form of powders. They are distinguished by very good dispersibility.

The incorporation of the stabilizers in the plastic mixture is effected by the known and usual methods.

If required, further conventional plastic additives, for example fillers, such as sawdust or mica, reinforcing materials, such as glass fibres, glass beads or mineral fibres, pigments, plasticizers, lubricants, flameproofing agents, antistatics or blowing agents, can be added to the (recycled) plastic mixtures. Such additives depend on the intended use.

The (recycled) plastic mixtures stabilized in this way can be used for a wide variety of purposes, for example again for films, tubes, sheets, profiles, construction parts or containers.

In the case of recyclates, these can also be mixed with fresh plastics or employed together with fresh plastics, for example in a coextrusion process.

The examples below illustrate the novel process and stabilizer mixture in greater detail.

Here, as in the remainder of the description, "  " represents a tert-butyl radical, parts are parts by weight and percentages are per cent by weight, unless stated otherwise.

Examples 1 + 2: A mixture comprising

89 parts of Lupolen 3062 F[®] (LDPE; BASF, DE);

10 parts of Levapren 450[®] (EVA; Bayer, DE); and

1 part of Ixan PV 880[®] (PVDC; Deutsche Solvay Werke, DE);

is homogenized in a Brabender mixer ((Brabender Plasticorder PL 2001/3, W50 mixing compartment) at 190°C with addition of the stabilizers shown in the table below. To this end, first the mixture of LDPE and EVA granules is melted (2 minutes) with addition of the stabilizers, the PVDC is then added, and finally the entire mixture is compounded for 3 minutes.

The mixture is removed from the Brabender mixer and pressed for 2 minutes at 190°C to

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give sheets with a thickness of 2 mm.

After this double temperature treatment, the yellowness index (YI) of the sheets is determined in accordance with ASTM D 1925-70. The values given in the table below show that the best stabilization (lowest YI values) is achieved by the novel process.

Table 1:

	Additives*	TSC*	YI
Example 1	0.225 calcium stearate 0.335 zinc stearate 0.440 pentaerythritol 0.200 P-1	1.2	22
Example 2	0.180 calcium stearate 0.268 zinc stearate 0.352 pentaerythritol 0.200 P-1	1.0	32
Comparative Example 1	no additives	---	80
Comparative Example 2	0.225 calcium stearate 0.335 zinc stearate 0.440 pentaerythritol	1.0	35
Comparative Example 3	0.500 P-1	0.5	82

* Additives: parts per 100 parts of polymer mixture

* TSC: total stabilizer concentration in %

"P-1" represents tris(2,4-di-tert-butylphenyl) phosphite

Examples 3 + 4: A mixture of
86 parts of LDPE (Lupolen[®] 3062 F; BASF)
10 parts of EVA (Levapren[®] 450; Bayer)

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4 parts of PVDC (Ixon[®] PV 880; Solvay)
is compounded at a temperature in the range from 165 to 175°C at 30 rpm in a Haake
TW 100 twin-screw extruder (heating zones: 165/165/165/170/175°C).

The product is subsequently re-extruded under the above conditions without additive
(Comparative Example 4) or with the stated additives, the granules are pressed to give a
sheet, and the yellowness index is determined in accordance with ASTM D 1925-70.

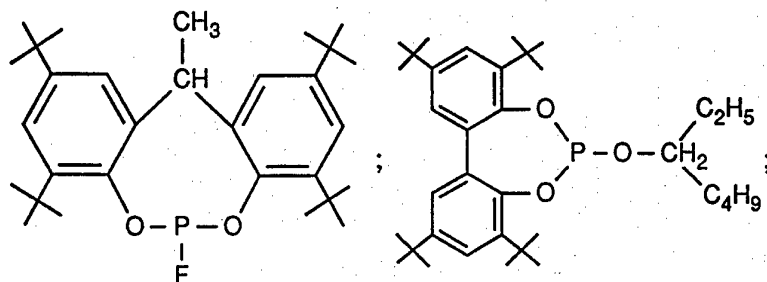
Comparative Example 4	no additive	YI = 67
Example 3	0.112 % calcium stearate 0.168 % zinc stearate 0.220 % pentaerythritol 0.100 % P-2	YI = 48
Example 4	0.112 % calcium stearate 0.168 % zinc stearate 0.220 % pentaerythritol 0.100 % P-2	YI = 53

"P-2" represents tetrakis(2,4-tert-butylphenyl)-4,4'-biphenylene diphosphonite

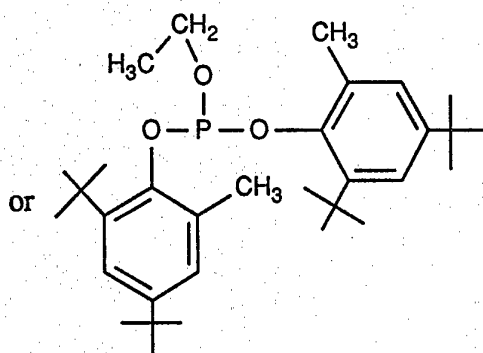
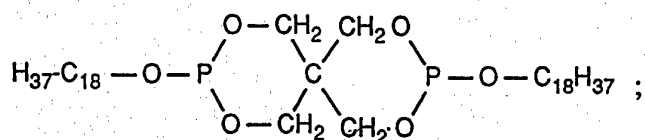
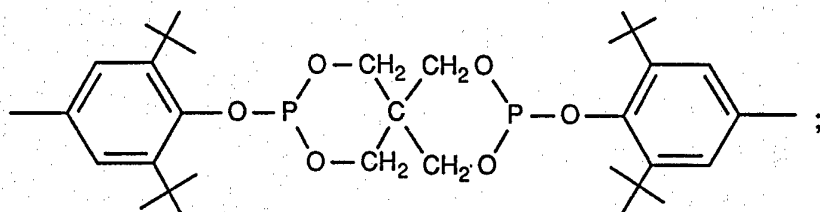
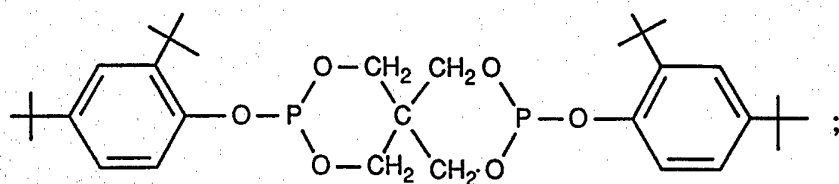
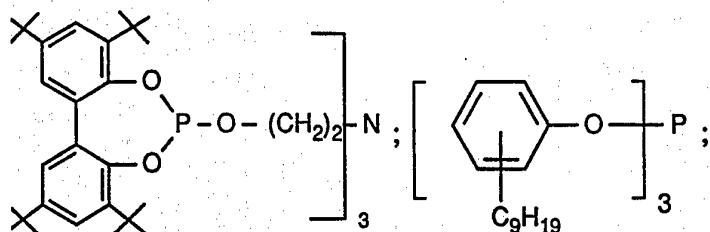
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WHAT IS CLAIMED IS:

1. A process for the stabilization of a plastic mixture predominantly comprising polyolefins and 0.05-20 % by weight of PVDC, which comprises adding (a) at least one organic phosphite or phosphonite and (b) at least one metal salt of a fatty acid to this mixture.
2. A process according to claim 1, wherein the plastic mixture comprises 0.1-5 % by weight of PVDC.
3. A process according to claim 1, wherein the plastic mixture is a recycle.
4. A process according to claim 1, wherein 0.05-10 % by weight, based on the plastic mixture, of a mixture of (a) and (b) is used.
5. A process according to claim 1, wherein 0.05-5 % by weight, based on the plastic mixture, of a mixture of (a) and (b) is used.
6. A process according to claim 1, wherein 0.01-2 % by weight of (a) and 0.05-5 % by weight of (b), in each case based on the plastic mixture, are used.
7. A process according to claim 1, wherein component (a) is an aromatic phosphite.
8. A process according to claim 1, wherein component (a) is one of the compounds
tris(2,4-di-tert-butylphenyl) phosphite;
tetrakis(2,4-di-tert-butyl)-4,4'-biphenylene diphosponite;



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9. A process according to claim 1, wherein component (a) is tris(2,4-di-tert-butylphenyl) phosphite.

10. A process according to claim 1, wherein component (b) is a metal salt of a fatty acid, where the metal is an element from main group or sub-group II, aluminium or tin.

11. A process according to claim 1, wherein component (b) is magnesium stearate,

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magnesium laurate, tin stearate, tin laurate, zinc stearate, zinc laurate, aluminium stearate, aluminium laurate, calcium stearate or calcium laurate.

12. A process according to claim 1, wherein component (b) is calcium stearate or zinc stearate.

13. A process according to claim 1, wherein component (b) is a mixture of various metal salts of fatty acids, where the metal is an element from main group or sub-group II, aluminium or tin.

14. A process according to claim 1, wherein, in addition to components (a) and (b), a polyol and/or a compatibilizer is used.

15. A stabilizer mixture comprising (a) at least one organic phosphite or phosphonite and (b) at least one metal salt of a fatty acid.

16. A stabilizer mixture according to claim 15, comprising 2-30 % of aromatic phosphite, 10-70 % of metal salt of a fatty acid and 5-60 % of polyol.

17. A stabilizer mixture according to claim 15, comprising 2-30 % of tris-(2,4-di-tert-butylphenyl) phosphite, 5-35 % of calcium stearate or laurate, 5-35 % of zinc stearate or laurate and 5-60 % of pentaerythritol.

18. The use of a stabilizer mixture comprising (a) at least one organic phosphite or phosphonite and (b) at least one metal salt of a fatty acid for the stabilization of a plastic mixture predominantly comprising polyolefins and 0.05-20 % by weight of PVDC.

19. The use of a stabilizer mixture according to claim 18, where the plastic mixture to be stabilized is a recycle.

20. A plastic mixture predominantly comprising polyolefins and 0.05-20 % by weight of PVDC, and furthermore comprising (a) at least one organic phosphite or phosphonite and (b) at least one metal salt of a fatty acid.

21. A plastic mixture according to claim 20, wherein the plastic mixture is a recycle.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/EP 94/04105

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C08K 13/00, C08K 5/52, C08K 5/098, C08L 23/02
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C08K, C08L

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

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

CA SEARCH, EDOC, WPI

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US, A, 4348308 (M.MINAGAWA ET AL.), 7 Sept 1982 (07.09.82), claim 1 --	1,7,10,12, 13,15
X	GB, A, 1481281 (TENNECO CHEMICALS, INC.), 27 July 1977 (27.07.77), claims 1,11 --	1,7,10,15
X	US, A, 4346025 (W.E.LEISTNER ET AL.), 24 August 1982 (24.08.82), claim 1 --	1,7,10,13,15
X	US, A, 3501430 (L.B.WEISFELD), 17 March 1970 (17.03.70), claim 1 -- -----	1,7,15

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
 "B" earlier document but published on or after the international filing date
 "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
 "O" document referring to an oral disclosure, use, exhibition or other means
 "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

Date of mailing of the international search report

14 March 1995

10.04.95

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INGA-KARIN PETERSSON

INTERNATIONAL SEARCH REPORT

Information on patent family members

09/02/95

International application No.

PCT/EP 94/04105

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A- 4348308	07/09/82	JP-C- 1337034 JP-A- 55000747 JP-B- 61000378	11/09/86 07/01/80 08/01/86
GB-A- 1481281	27/07/77	CA-A- 1063791 DE-A- 2515377 FR-A,B- 2274648 JP-C- 1150989 JP-A- 50141644 JP-B- 57043571 SE-B,C- 400781 SE-A- 7504022	09/10/79 23/10/75 09/01/76 14/06/83 14/11/75 16/09/82 10/04/78 13/10/75
US-A- 4346025	24/08/82	JP-C- 1383639 JP-A- 55106255 JP-B- 61050494	09/06/87 14/08/80 05/11/86
US-A- 3501430	17/03/70	NONE	