AU9474915

(12) PATENT ABRIDGMENT (11) Document No. AU-B-74915/94
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 698316

(54) Title
PROCESS FOR STABILISING STYRENE-CONTAINING RECYCLED PLASTIC MATERIALS AND STABI LISER MIXTURES THEREFOR

International Patent Classification(s)
(51)[6] **C08L 025/04** **C08J 011/04** **C08K 013/02**

(21) Application No. : **74915/94** (22) Application Date : **07.07.94**

(87) PCT Publication Number : **WO95/02639**

(30) Priority Data

(31) Number	(32) Date	(33) Country
2135/93	**15.07.93**	**CH SWITZERLAND**
404/94	**10.02.94**	**CH SWITZERLAND**

(43) Publication Date : **13.02.95**

(44) Publication Date of Accepted Application : **29.10.98**

(71) Applicant(s)
CIBA SPECIALTY CHEMICALS HOLDING INC.

(72) Inventor(s)
KURT HOFFMANN; HEINZ HERBST; RUDOLF PFAENDNER; FRANCISZEK SITEK

(74) Attorney or Agent
DAVIES COLLISON CAVE , GPO Box 3876, SYDNEY NSW 2001

(57) Claim

1. A process for stabilising recycled styrene-containing plastic materials, recovered from domestic, commercial and industrial waste or from useful material collections, against thermo-oxidative degradation, which process comprises incorporating in said plastic materials 0.01 to 10% by weight of a mixture of a) at least one sterically hindered phenol and b) at least one inorganic compound selected from metal oxides, metal hydroxides or metal carbonates, with the proviso that no organic phosphite or phosphonite is present.

26. A mixture for stabilising recycled styrene-containing plastic materials recovered from domestic, commerical or industrial waste or from useful material collections against thermo-oxidative degradation, which mixture comprises a) at least one sterically hindered phenol, b) at least one inorganic compound selected from metal oxides, metal hydroxides or metal carbonates and, as optional component c), a metal salt of a fatty acid with the proviso that no organic phosphite or phosphonite is present.

27. A stabiliser mixture according to claim 26, comprising in 100 parts

(A) as component a) 5-90 parts of triethylene glycol bis[3(3-tert-butyl-4-hydroxy-5-methylphenyl)]propionate, as component b) 10-95 parts of calcium oxide;

(B) as component a) 5-90 parts of the octadecyl ester of β-(3,5-di-tert-butyl-4-hydroxy-phenyl)propionic acid, as component b) 10-95 parts of calcium oxide; or

../2

(C) as component a) 5-90 parts of triethylene glycol bis[3(3-tert.butyl-4-hydroxy-5-methylphenyl)]propionate, as component b) 5-90 parts of calcium oxide, and as component c) 5-90 parts of calcium stearate.

28. A recycled styrene-containing plastic material recovered from domestic, commerical or industrial waste or from useful material collections and stabilized against thermo-oxidative degradation, which plastic material comprises a) at least one sterically hindered phenol, b) at least one inorganic compound selected from metal oxides, metal hydroxides or metal carbonates and, as optional component c), at least one metal salt of a fatty acid with the proviso that no organic phosphite or phosphonite is present.

OPI DATE 13/02/95 APPLN. ID 74915/94
AOJP DATE 23/03/95 PCT NUMBER PCT/EP94/02234

AU9474915

(PCT)

(51) International Patent Classification 6 : C08L 25/04, C08K 13/02

A1

(11) International Publication Number: WO 95/02639

(43) International Publication Date: 26 January 1995 (26.01.95)

(21) International Application Number: PCT/EP94/02234

(22) International Filing Date: 7 July 1994 (07.07.94)

(30) Priority Data:

2135/93-6	15 July 1993 (15.07.93)	CH
404/94-4	10 February 1994 (10.02.94)	CH

(81) Designated States: AM, AU, BB, BG, BR, BY, CA, CN, CZ, FI, GE, HU, JP, KE, KG, KP, KR, KZ, LK, LT, LV, MD, MG, MN, MW, NO, NZ, PL, RO, RU, SD, 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).

Published

With international search report.

Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(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)*: HOFFMANN, Kurt [DE/DE]; Am Kochengraben 30, D-64686 Lautertal 1 (DE). HERBST, Heinz [DE/DE]; Hohensteiner Strasse 40, D-64686 Lautertal-Reichenbach (DE). PFAENDNER, Rudolf [DE/DE]; Sackgasse 3, D-64658 Rimbach/Odenwald 1 (DE). SITEK, Franciszek [CH/CH]; Grossmattweg 11, CH-4106 Therwil (CH).

(74) Common Representative: CIBA-GEIGY AG; Patentabteilung, Klybeckstrasse 141, CH-4002 Basel (CH).

(71) Ciba Specialty Chemicals Holding Inc.
Klybeckstrasse 141, CH-4057
Basel Switzerland

AUSTRALIAN PATENT OFFICE SEC 104

(54) Title: PROCESS FOR STABILISING STYRENE-CONTAINING RECYCLED PLASTIC MATERIALS AND STABILISER MIXTURES THEREFOR

(57) Abstract

Recycled styrene-containing plastic materials occurring in the domestic, commercial or industrial sectors and in useful material collections, can be stabilised against thermo-oxidative degradation by addition of a combination of a sterically hindered phenol with an inorganic compound selected from the series of the metal oxides, metal hydroxides or metal carbonates and, as optional component, a metal salt of a fatty acid.

Process for stabilising styrene-containing recycled plastic materials and stabiliser mixtures therefor

The present invention relates to a process for stabilising recycled plastic materials containing styrene or α-methylstyrene occurring mainly in the domestic, commercial or industrial sectors and in useful material collections, and to the stabiliser mixtures useful therefor.

The recycling of waste materials is a problem of increasing importance for ecological reasons. The recycling of paper, textiles, glass and metals is already being carried out on a large scale, whether through separate collection or by sorting waste. The reuse of waste plastics is basically also possible, provided the waste consists mainly of thermoplastic polymers. The styrene-containing waste plastics occurring in the domestic, commercial or industrial sector, or waste plastics or scrap material originating from collections or from obligatory returnables in specific sectors of industry, as for example in the automotive, electrical and packaging industries, may be styrene homopolymers such as PS, CPS or EPS, as well as copolymers such as IPS, HIPS, SBS, SB, SEBS, SIS, ABS, ASA, SAN and MBS or mixtures thereof.

Hitherto it has been possible to use plastic recyclates only for purposes for which relatively low demands are made of the material properties, typically for use as fillers or for utilities in which thick-walled parts can be used, for example sound-insulating walls.

Uniform recycled waste plastics may occur as production waste (punch waste, shavings) or in separately recovered waste materials (e.g. EPS collections). The difficulty of finding suitable stabilisers resides here especially in the nature of the degradation that has occurred over an extended period of time or also that may be caused by brief mechanical stress as during processing (agglomeration, compacting).

It has now been found that recycled styrene-containing plastics can be stabilised against thermo-oxidative degradation in simple and economic manner with a mixture of per se known stabilisers and hence reprocessed to useful products.

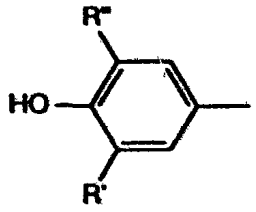
Specifically, the invention relates to a process for stabilising recycled styrene-containing plastic materials, recovered from domestic, commercial and industrial waste or from useful material collections, against thermo-oxidative degradation, which process comprises incorporating in said plastic materials 0.01 to 10% by weight of a mixture of a) at least one sterically hindered phenol and b) at least one inorganic compound selected from metal oxides, metal hydroxides or metal carbonates, with the proviso that no organic phosphite or phosphonite is present.

A preferred weight ratio of a:b is from 20:1 to 1:20, more particularly from 10:1 to 1:10 and, most preferably, from 1:1 to 1:5.

The styrene-containing plastics to be stabilised are conveniently punch wastes from foamed PS (packing material) or ABS waste from casings (electrical/electronic) and automotive utilities, flame-proofed polystyrenes, blends and mixtures with virgin material. Illustrative examples of suitable polystyrene-containing blends are PC/ABS, PBT/ABS or PBT/ASA. Suitable plastics to be stabilized have a styrene content of more than 5 % by weight, preferably more than 10 % by weight.

It is preferred to incorporate 0.01 to 5 % by weight, most preferably 0.02 to 2 % by weight, of the mixture of a and b in the recyclate.

The sterically hindered phenols used as component a) are known stabilisers for protecting plastics, especially polyolefins, against thermo-oxidative ageing. These compounds preferably contain at least one group of formula



(I)

wherein R' is hydrogen, methyl or tert-butyl, and R'' is unsubstituted or substituted alkyl or substituted alkylthioalkyl.

Representative examples of such sterically hindered phenols are:

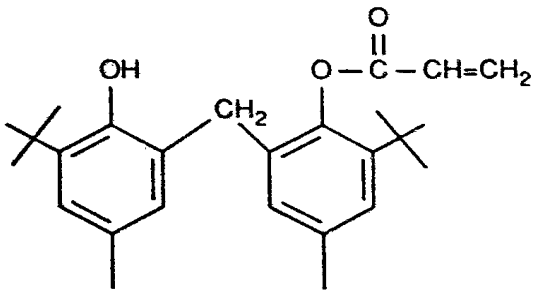
AUSTRALIAN PATENT OFFICE

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, 2,6-dinonyl-4-methylphenol, 2,6-di-tert-butyl-4-methoxyphenol, 2,5-di-tert-butylhydroquinone, 2,5-di-tert-amyl-hydroquinone, 2,6-diphenyl-4-octadecyloxyphenol, 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), 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'-methylenebis(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, 1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl)-2,4,6-trimethylbenzene, bis(3,5-di-tert-butyl-4-hydroxybenzyl)sulfide, isooctyl 3,5-di-tert-butyl-4-hydroxybenzylmercaptoacetate, bis(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl)dithiolterephthalate, 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, dioctadecyl 3,5-di-tert-butyl-4-hydroxybenzylphosphonate, and the calcium salt of monoethyl 3,5-di-tert-butyl-4-hydroxybenzylphosphonate, as well as compounds derived from tocopherol.

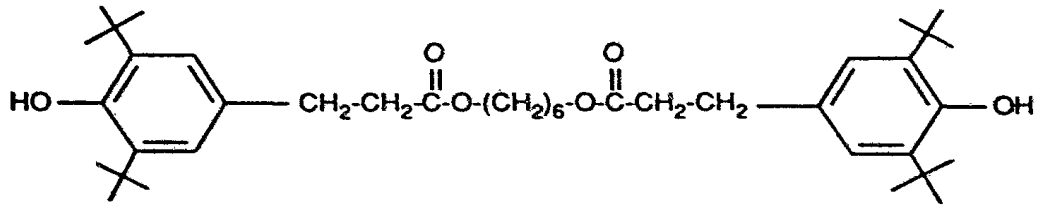
Especially preferred sterically hindered phenols suitable for use as component a) are the esters of β-(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid and of β-(5-tert-butyl-4-hydroxy-3-methylphenyl)propionic acid with monohydric or polyhydric alcohols, as with methanol, octanol, octadecanol, 1,6-hexanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl) isocyanurate, N,N'-bis(hydroxyethyl)oxamide, and the amides of these acids, for example N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)-

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

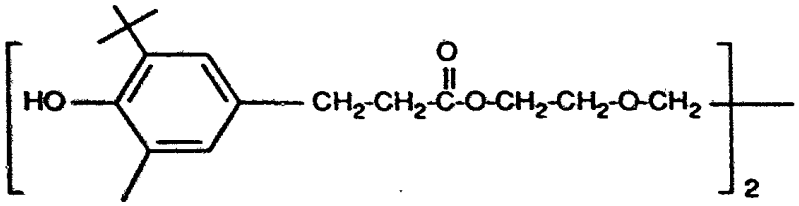
Further particularly preferred compounds are:
2-(1-(2-hydroxy-3,5-di-tert-pentylphenyl)ethyl-4,6-di-tert-pentylphenylacrylate



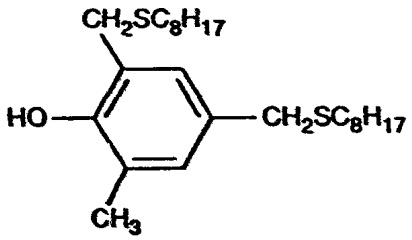
{2-(1,1-dimethylethyl)-6-[[3-(1,1-dimethylethyl)-2-hydroxy-5-methylphenyl]-methyl]-4-methylphenyl 2-propenoate};



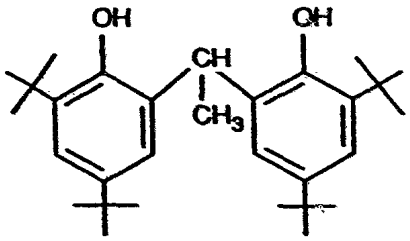
{1,6-hexanediyl 3,5-bis(1,1-dimethylethyl)-4-hydroxyphenylpropanoate};



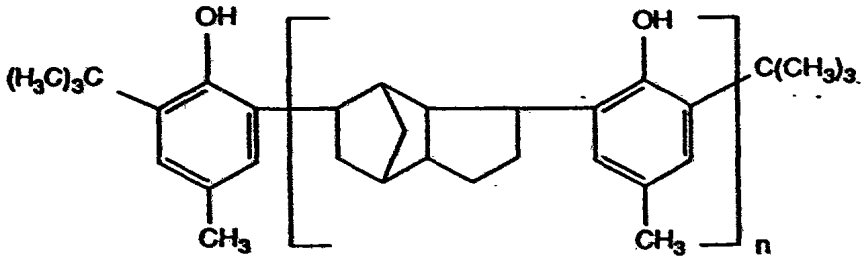
{1,2-ethanediylbis(oxy-2,1-ethanediyl) 3-(1,1-dimethylethyl)-4-hydroxy-5-methylphenyl-propanoate};



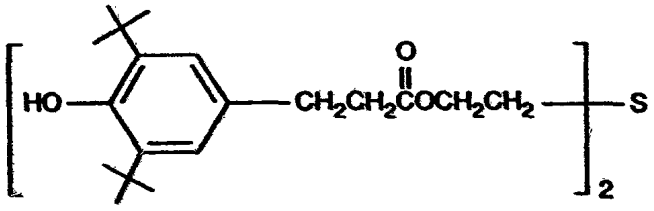
{2-methyl-4,6-bis[(octylthio)methyl]phenol};



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

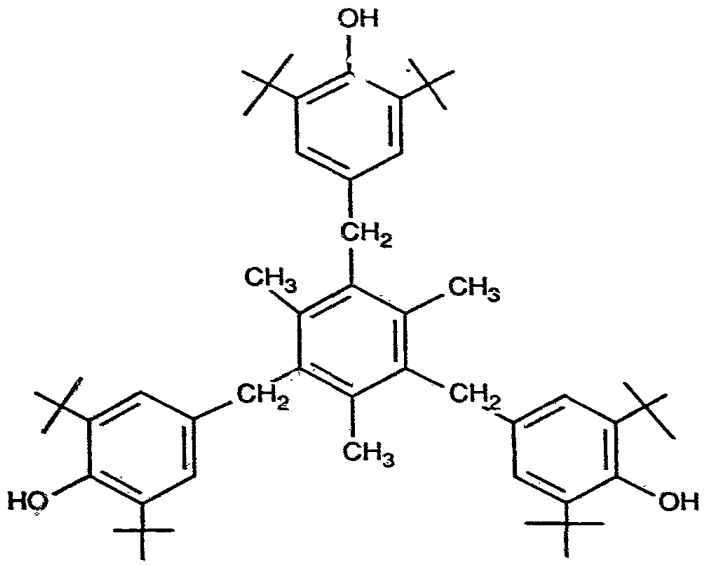


{butylated reaction product of para-cresol and dicyclopentadien (average molecular weight: 600-700, n=2)}

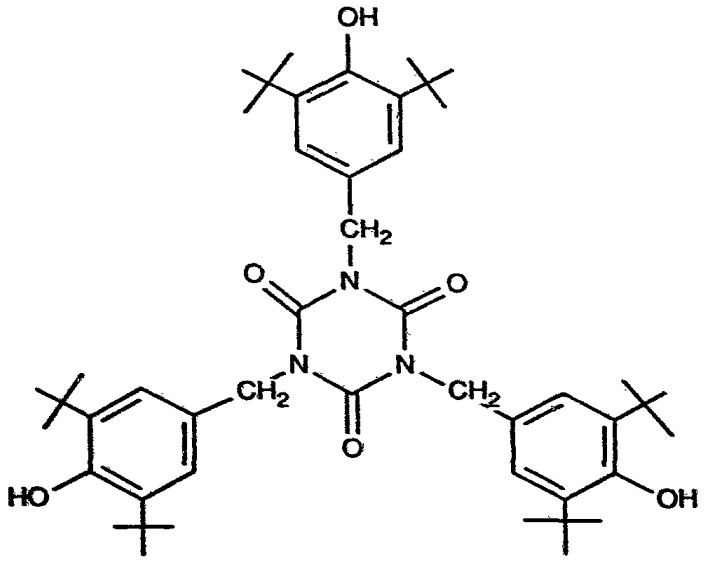


{thiodi-2,1-ethanediyl 3,5-bis(1,1-dimethylethyl)-4-hydroxyphenylpropanoate};

AUSTRALIAN PATENT OFFICE



{4,4',4"-[(2,4,6-trimethyl-1,3,5-benzenetriyl)tris-(methylene)]tris[2,6-bis(1,1-dimethyleth-yl)phenol};



{1,3,5-tris[[3,5-bis(1,1-dimethylethyl)-4-hydroxyphenyl]methyl]-1,3,5-triazine-2,4,6-(1H,3H,5H)trione}.

Component a is most preferably the octadecyl ester of β-(3,5-di-tert-butyl-4-hydroxyphen-yl)propionic acid, triethylene glycol bis[3(3-tert-butyl-4-hydroxy-5-methylphenyl)]-propionate, 1,6-hexanediol bis[3(3,5-di-tert-butyl-4-hydroxyphenyl)]propionate and 2,2'-methylenebis(4-methyl-6-tert-butylphenol)monoacrylate.

Component b) is an inorganic compound selected from the series of the metal oxides, metal hydroxides or metal carbonates.

Preferably component b) is selected from the metal oxides, metal hydroxides or metal carbonates of the elements of main group II and subsidiary groups IV and VII, the oxides being particularly preferred, typically MgO, MnO_2, ZnO and, most preferably, CaO.

A mixture of different components b) may also be used. For example, component b) may be a mixture of calcium oxide and calcium carbonate.

A metal hydroxide is typically magnesium hydroxide and a metal carbonate is typically calcium carbonate. Salts with different anions may also be used, for example magnesium aluminium hydroxycarbonates, so-called hydrotalcites.

It is further useful to add a metal salt of a fatty acid, the metal being preferably an element of main or subsidiary group II or tin.

These metal salts are preferably zinc, magnesium, tin or, more particularly, calcium salts selected from the series of the aliphatic saturated C_2-C_{22}carboxylates, of the aliphatic olefinic C_3-C_{22}carboxylates, of the aliphatic C_2-C_{22}carboxylates which are substituted by at least one OH group, of the cyclic or bicyclic C_5-C_{22}carboxylates, of the aromatic C_7-C_{22}carboxylates, of the aromatic C_7-C_{22}carboxylates which are substituted by at least one OH group, of the C_1-C_{16}alkyl-substituted phenylcarboxylates and of the phenyl-C_1-C_{16}alkylcarboxylates, of which the stearates and laurates, lactates, 2-ethylhexanoates and behenates are preferred.

Metal salts of fatty acids such as calcium stearate, zinc stearate and magnesium stearate, are very particularly preferred.

It is also possible to use a mixture of different above mentioned components. For example, a mixture of calcium laurate and calcium stearate or of zinc stearate and calcium stearate may be used.

A metal salt of a fatty acid is usually added in a ratio of 10:1 to 1:10, based on the ratio of (a+b):metal salt.

The invention further relates to a mixture for stabilising recycled styrene-containing plastic materials recovered from domestic, commerical or industrial waste or from useful material collections against thermo-oxidative degradation, which mixture comprises a) at least one sterically hindered phenol, b) at least one inorganic compound selected from metal oxides, metal hydroxides or metal carbonates and, as optional component c), a metal salt of a fatty acid with the proviso that no organic phosphite or phosphonite is present.

Very particularly preferred stabiliser mixtures comprise, in 100 parts,

(A) as component a) 5-90 parts of triethylene glycol bis[3(3-tert-butyl-4-hydroxy-5-methylphenyl)]propionate, as component b) 10-95 parts of calcium oxide;

(B) as component a) 5-90 parts of the octadecyl ester of β-(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid, as component b) 10-95 parts of calcium oxide; or

(C) as component a) 5-90 parts of triethylene glycol bis[3(3-tert.butyl-4-hydroxy-5-methylphenyl)]propionate, as component b) 5-90 parts of calcium oxide, and as component c) 5-90 parts of calcium stearate.

The invention further relates to a recycled styrene-containing plastic material recovered from domestic, commerical or industrial waste or from useful material collections and stabilized against thermo-oxidative degradation, which plastic material comprises a) at least one sterically hindered phenol, b) at least one inorganic compound selected from metal oxides, metal hydroxides or metal carbonates and, as optional component c), at least one metal salt of a fatty acid with the proviso that no organic phosphite or phosphonite is present.

Preferred recycled styrene-containing thermoplastic materials, preferred stabiliser mixtures and the use thereof correspond in their components and mixture ratios to the preferred embodiments discussed in detail in connection with the process.

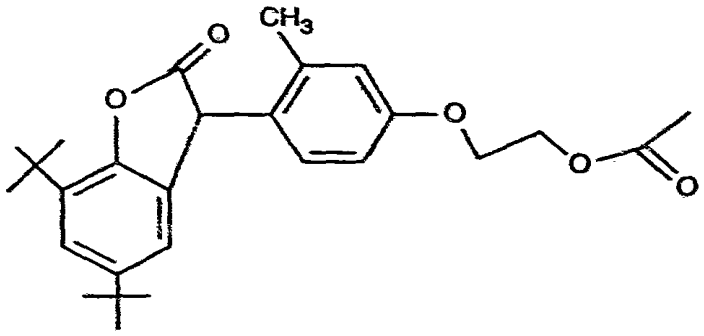
The addition of these combinations to the recyclate makes it possible to carry out the thermoplastic processing with reduced degradation and/or prolongs the life of the materials fabricated from the recyclate.

The stabilising action of the mixture of components a) and b), especially the processing stability and long-term stability, may be synergistically enhanced by the addition of so-called thiosynergists. These are thioethers, preferably thioesters, of thiodipropionic acid. Typical examples are the lauryl, stearyl, myristyl or tridecyl esters of thiodipropionic acid or distearyl disulfide. These thiosynergists are preferably added in an amount of 0.1

AUSTRALIAN PATENT OFFICE

to 1 % by weight, based on the recyclate.

Further suitable stabilisers of the series of the lactates, e.g. calcium lactate, calcium stearoyl-2-lactate, or lactones such as



can likewise be used.

If the object fabricated from the recycled plastics material is also required to have superior light stability, then it is advisable to add one or more light stabilisers, most suitably those of the series of the benzophenones, benzotriazoles, oxalanilides and the sterically hindered amines. Representative examples of such compounds are:

2-Hydroxybenzophenones, for example the 4-hydroxy, 4-methoxy, 4-octyloxy, 4-decyloxy, 4-dodecyloxy, 4-benzyloxy, 4,2',4'-trihydroxy, 2'-hydroxy-4,4'-dimethoxy derivative.

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'-octyloxy, 3',5'-di-tert-amyl, 3',5'-bis(α,α-dimethylbenzyl) derivative.

Oxamides, for example 4,4'-dioctyloxyoxanilide, 2,2'-dioctyloxy-5,5'-di-tert-butoxanilide, 2,2'-didodecyloxy-5,5'-di-tert-butoxanilide, 2-ethoxy-2'-ethyl-oxanilide, 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-substituted oxanilides as well as 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, the bis(1,2,2,6,6-pentamethylpiperidyl) ester of n-butyl-3,5-di-tert-butyl-4-hydroxybenzylmalonic acid, the condensate of 1-hydroxyethyl-2,2,6,6-tetra-

methyl-4-hydroxypiperidine and succinic acid, the condensate 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-oxopiperazino)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 as well as polysiloxanes which contain 2,2,6,6-tetramethyl-4-piperidinyl groups.

The light stabilisers are preferably incorporated in an amount of 0.01 to 2 % by weight, more particularly 0.05 to 1 % by weight, based on the plastic material. The preferred light stabiliser is a benzotriazole or a sterically hindered amine or a combination thereof.

If necessary, further customary additives for plastics can be incorporated in the recycled styrene-containing plastic material, conveniently fillers such as wood flour or mica, reinforcing agents such as glass fibres, glass beads or mineral fibres, pigments, plasticisers, lubricants, flame retardants, antistatic agents or blowing agents. Such additives will depend on the envisaged use of the recyclate.

The stabilised recyclates can be used for a wide variety of purposes, typically for profiles, sheets, films, structural components, vehicle components and machine parts, and containers of all kinds, typically bottles, foamed materials such as sound-insulating boards or packaging material.

The recyclate can also be used in admixture with type-specific virgin plastics or together with type-specific virgin plastics, for example in a co-extrusion process.

The following Examples illustrate the inventive process and the stabiliser mixture in more detail. Unless otherwise indicated, parts and percentages are by weight.

Examples 1 to 17 (Tables 1-3)

Stabilisation of flame-proofed, foamed waste polystyrene

For ease of processing, the foamed material was compacted by heating under vacuum for 1 h to 100°C. The compacted material was milled. The flame-proofed waste polystyrene has a bromine content of c. 0.5 %. Sample 1 and sample 2 are two different batches.

46 g of the EPS recyclate are kneaded for 10 minutes in a Brabender W 50 mixing chamber heated to 220°C (40 rpm). The additives (Tables 1-3) are added to the mixing chamber right at the start together with the plastics mixture. Mixing is stopped after 10 min, the polymer blend is removed from the mixing chamber and premoulded at 30°C/c. 50 KN for 1 min.

2 mm thick pressed sheets are fabricated from this moulding at 200°C/50 KN and the melt volume index (DIN 53 735; ISO 1133/12; 200°C/5 kg) is determined after comminution.

An analogous procedure is followed in the comparison Examples.

Table 1:

Brabender experiment (20 min, 220°C, 40 rpm)
with flame-proofed EPS (compacted, sample 1)

	%	Additive	MVI	YI
comparison	-	none	98.1	83.9
comparison	0.20	AO-1	64.0	80.5
Example 1	0.15 / 0.5	AO-1 / M-1	47.4	31.1
Example 2	0.05 / 0.15	AO-1 / M-1	48.3	27.8

YI: according to ASTM D 1925-70 (DIN 5033)

Table 2:

Brabender experiment (20 min, 220°C, 40 rpm)
with flame-proofed EPS (compacted, sample1)

	%	Additive	MVI	YI
comparison	-	none	98.1	83.9
comparison	0.20	AO-3	60.6	70.6
Example 3	0.15 / 0.5	AO-3 / M-1	39.5	32.8
Example 4	0.10 / 0.10	AO-3 / M-1	52.7	26.1
Example 5	0.05 / 0.15	AO-3 / M-1	51.2	28.8
Example 6	0.15 / 0.15	AO-3 / M-1	43.4	34.3
Example 7	0.10 / 0.075 / 0.025	AO-3 / M-1 / F-1	47.4	30.7
Example 8	0.10 / 0.5 / 0.5	AO-3 / M-1 / F-1	46.1	30.9
Example 9	0.10 / 0.025 / 0.075	AO-3 / M-1 / F-1	47.6	34.1

YI: according to ASTM D 1925-70 (DIN 5033)

Table 3:

Brabender experiment (20 min, 220°C, 40 rpm)
with flame-proofed EPS (compacted, sample 2)

	%	Additive	MVI
comparison	-	none	146.2
comparison	0.20	AO-2	103.1
comparison	0.30	AO-2	106.8
Example 10	0.150 / 0.050	AO-2 / M-1	87.0
Example 11	0.125 / 0.075	AO-2 / M-1	80.5
Example 12	0.10 / 0.10	AO-2 / M-1	82.1
Example 13	0.20 / 0.10	AO-2 / M-1	76.4
Example 14	0.25 / 0.10	AO-2 / M-1	63.0
Example 15	0.30 / 0.10	AO-2 / M-1	60.0
Example 16	0.20 / 0.05 / 0.05	AO-2 / M-1 / F-1	60.9
Example 17	0.30 / 0.05 / 0.05	AO-2 / M-1 / F-1	55.0

The stabilised samples exhibit a lower MVI value and a diminished discolouration expressed by the YI value than in the comparison Examples.

Examples 18-20 (Table 4)
Stabilisation of polystyrene recyclate (EPS recyclate) from packaging materials

45 g of the compacted EPS are kneaded for 10 minutes in a Brabender W 50 mixing chamber heated to 220°C (46 rpm). The additives (Table 4) are added to the mixing chamber right at the start together with the plastics mixture. Mixing is stopped after 10 min, the polymer blend is removed from the mixing chamber and premoulded at 30°C/c. 50 KN for 1 min.

2 mm thick pressed sheets are fabricated from this moulding at 200°C/50 KN and the melt volume index (DIN 53 735; ISO 1133/12; 200°C/5 kg) is determined after comminution.

An analogous procedure is followed in the comparison Examples.

Table 4:

Mixing chamber (20 min, 220°C, 46 rpm)
with recyclate from EPS packing material (granulate)

	%	Additive	MVI
comparison	-	none	44.9
comparison	0.1	AO-3	32.1
comparison	0.1	M-1	33.8
Example 18	0.05 / 0.05	AO-3 / M-1	30.4
Example 19	0.025 / 0.075	AO-3 / M-1	31.9
Example 20	0.05 / 0.04 / 0.01	AO-3 / M-1 / F-1	31.8

The stabilised samples exhibit a lower MVI value than in the comparison Examples.

Example 21 (Table 5)
Stabilisation of waste polystyrene (impact-modified)

48 g of the IPS recyclate from packaging material (yoghurt beakers) are kneaded for 10 minutes in a Brabender W 50 mixing chamber heated to 220°C (46 rpm). The additives (Table 5) are added to the mixing chamber right at the start together with the plastics mixture. Mixing is stopped after 10 min, the polymer blend is removed from the mixing chamber and premoulded at 30°C/c. 50 KN for 1 min.

2 mm thick pressed sheets are fabricated from this moulding at 200°C/50 KN and from these sheets dumbbells are punched. These dumbbells are aged at 80°C in a circulating air oven. Samples are taken from the oven at defined intervals of time and investigated for the degree of yellowing (Table 5).

An analogous procedure is followed in the comparison Examples.

Table 5

Oven ageing of samples of waste IPS (yoghurt beakers) at 80°C

10 min in the mixing chamber at 220°C, 46 rpm, 2 mm pressed sheet

Additive	Comparison 1 no additive	Comparison 2 0.05% AO-3	Example 21 0.05% AO-3 / 0.05% M-1
Oven ageing [h]	YI	YI	YI
0	-0.5	-0.5	-0.6
197	0.6	---	---
408	5.7	---	-0.5
504	---	0.9	---
601	9.7	---	0.3
720	---	2.6	---
800	13.7	---	1.5
935	---	4.0	---
1007	16.1		1.7

The stabilised samples exhibit a substantially diminished increase in yellowing than the samples in the comparison Examples.

Examples 22-26:

In a mixer, granular foamed polystyrene recyclate (EPS recyclate) from packaging material is homogenised with the stabilisers (Table 6) and then extruded three times in succession on a twin-screw kneader (220°C). Before extrusion and after each extrusion, the melt volume index is determined (MVI; 200°C; 5 kg) according to DIN 53 735 (ISO 1133/12).

Table 6:

	Stabiliser mixture	MVI after 0	1	2	3 extrusions
--	without stabiliser	23.2	25.8	26.3	26.9
Ex. 22	0.15 % AO-2 + 0.1 % M-1	23.0	23.7	23.9	24.1
Ex. 23	0.2 % AO-2 + 0.1 % M-1	23.0	24.2	23.3	24.2
Ex. 24	0.1 % AO-3 + 0.1 % M-1	23.0	23.5	22.1	23.6
Ex. 25	0.1 % AO-3 + 0.2 % M-1	23.0	23.0	23.1	23.3
Ex. 26	0.2 % AO-3 + 0.1 % M-1	23.0	23.6	23.6	24.1

The stabilised samples exhibit only an insignificant increase in the MVI value after repeated extrusion, thus indicating very good stabilisation.

Examples 27 to 29:

A granular EPS recyclate from production waste (Examples 27-30) or from packaging material (Examples 31-39) is kneaded with the stabilisers (Tables 7 and 8) for 10 minutes in a Brabender W 50 mixing chamber heated to 220°C (40 rpm). The polymer blends are removed from the mixing chamber and premoulded at 30°C/c. 20 KN for 1 min and then sheets are fabricated (thickness: 2 mm) at 200°C/50 KN on a press. The melt volume index is determined from the comminuted sheets (MVI; 200°C; 5 kg) according to DIN 53 735 (ISO 1133/12).

Table 7:

	Stabiliser mixture	MVI (200/5)
--	without stabiliser	44.4
Ex. 27	0.2 % AO-2 + 0.1 % M-1	18.8
Ex. 28	0.1 % AO-3 + 0.1 % M-1	17.6
Ex. 29	0.1 % AO-3 + 0.2 % M-1	17.0
Ex. 30	0.2 % AO-3 + 0.1 % M-1	16.0

Table 8:

	Stabiliser mixture	MVI (200/5)
--	without stabiliser	56.8
Ex. 31	0.1 % AO-2 + 0.05 % M-1	32.3
Ex. 32	0.1 % AO-2 + 0.1 % M-1	32.9
Ex. 33	0.3 % AO-2 + 0.2 % M-1	27.5
Ex. 34	0.05 % AO-3 + 0.05 % M-1	32.7
Ex. 35	0.05 % AO-3 + 0.1 % M-1	32.3
Ex. 36	0.05 % AO-3 + 0.2 % M-1	31.9
Ex. 37	0.15 % AO-3 + 0.05 % M-1	28.2
Ex. 38	0.15 % AO-3 + 0.1 % M-1	27.6
Ex. 39	0.15 % AO-3 + 0.2 % M-1	27.4

The stabilised samples exhibit a lower MVI value, thus indicating very good stabilisation.

The following stabilisers are used in the foregoing Examples:

AO-1 2,2'-methylenebis(4-methyl-6-tert-butylphenol)monoacrylate

AO-2 octadecyl ester of β-(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid

AO-3 bis(triethylene glycol) ester of β-(3-tert-butyl-4-hydroxy-5-methylphenyl)propionic acid

M-1 calcium oxide

F-1 calcium stearate

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A process for stabilising recycled styrene-containing plastic materials, recovered from domestic, commercial and industrial waste or from useful material collections, against thermo-oxidative degradation, which process comprises incorporating in said plastic materials 0.01 to 10% by weight of a mixture of a) at least one sterically hindered phenol and b) at least one inorganic compound selected from metal oxides, metal hydroxides or metal carbonates, with the proviso that no organic phosphite or phosphonite is present.

2. A process according to claim 1, wherein the weight ratio of a:b is from 20:1 to 1:20.

3. A process according to claim 1, wherein the weight ratio of a:b is from 10:1 to 1:10.

4. A process according to claim 1, wherein the weight ratio of a:b is from 1:1 to 1:5.

5. A process according to claim 1, wherein a metal salt of a fatty acid is used as further additive.

6. A process according to claim 5, wherein the weight ratio of (a+b):metal salt is from 10:1 to 1:10.

7. A process according to claim 1, wherein the recycled plastic material is a polymer containing styrene or α-methylstyrene.

8. A process according to claim 7, wherein the recycled plastic material is a styrene homopolymer.

9. A process according to claim 7, wherein the recycled plastic material is a styrene copolymer.

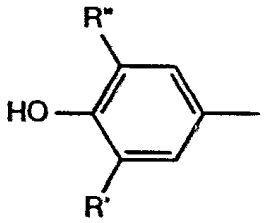
10. A process according to claim 7, wherein the recycled plastic is a polystyrene-containing blend.

11. A process according to claim 1, wherein 0.01 to 5 % by weight of the mixture of a and b is incorporated in the recycled plastic.

AUSTRALIAN PATENT OFFICE

12. A process according to claim 1, wherein 0.02 to 2 % by weight of the mixture of a and b is incorporated in the recycled plastic.

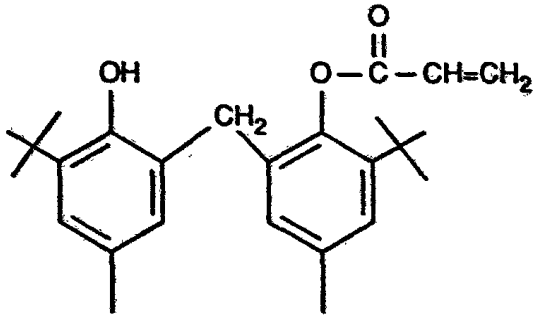
13. A process according to claim 1, wherein component a is a compound that contains at least one group of formula (I)



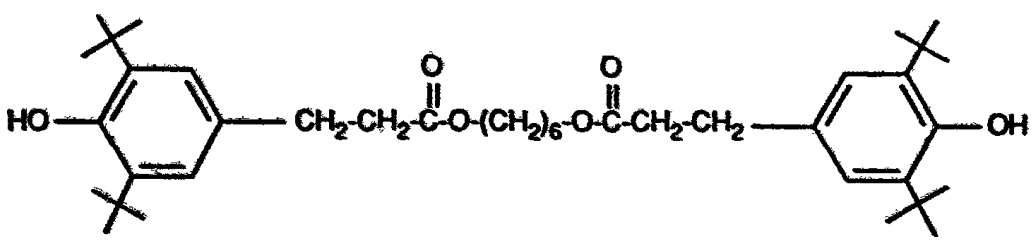
(I)

wherein R' is hydrogen, methyl or tert-butyl, and R'' is unsubstituted or substituted alkyl or substituted alkylthioalkyl.

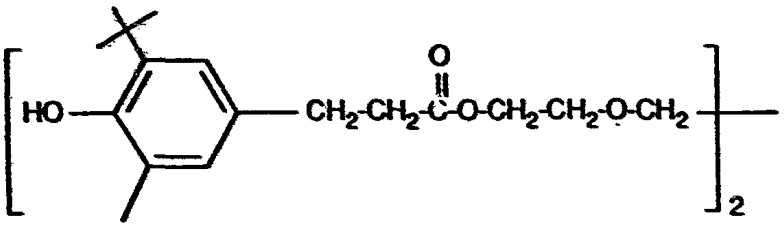
14. A process according to claim 1, wherein component a is a compound selected from 2-(1-(2-hydroxy-3,5-di-tert-pentylphenyl)ethyl-4,6-di-tert-pentylphenylacrylate



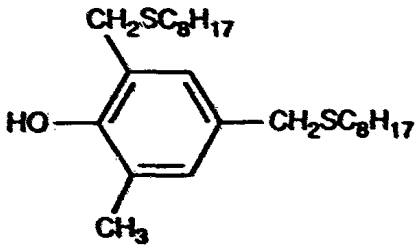
{2-(1,1-dimethylethyl)-6-[[3-(1,1-dimethylethyl)-2-hydroxy-5-methylphenyl]-methyl]-4-methylphenyl 2-propenoate};



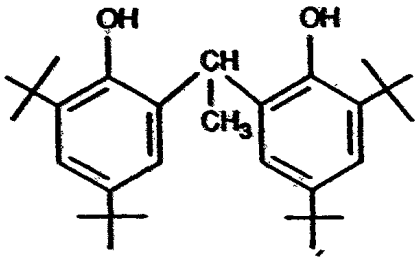
{1,6-hexanediyl 3,5-bis(1,1-dimethyl-ethyl)-4-hydroxyphenylpropanoate};



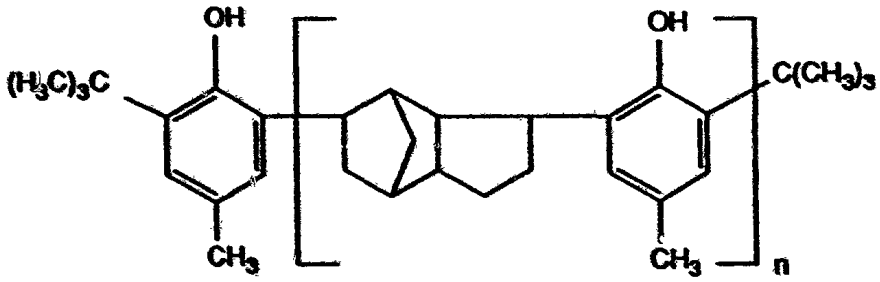
{1,2-ethanediylbis(oxy-2,1-ethanediyl) 3-(1,1-dimethylethyl)-4-hydroxy-5-methylphenyl-propanoate};



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

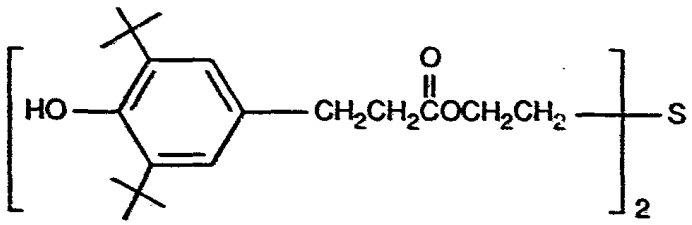


{2,2'-ethylidenebis(4,6-di-tert-butylphenol)};

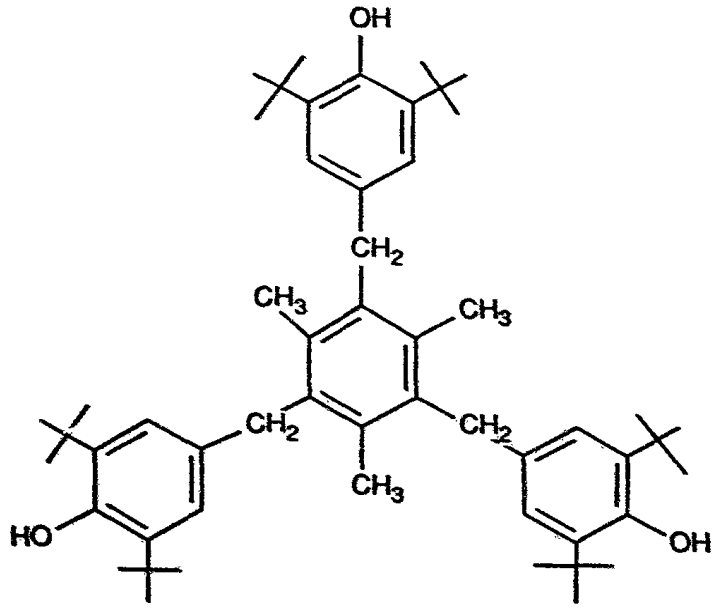


{butylated reaction product of para-cresol and dicyclopentadien (average molecular weight: 600-700, n=2)}

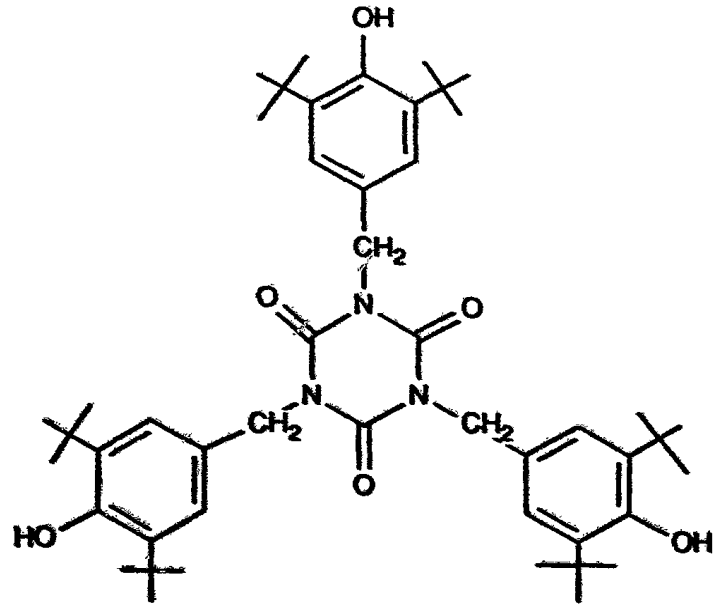
AUSTRALIAN PATENT OFFICE



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



{4,4',4"-[(2,4,6-trimethyl-1,3,5-benzenetriyl)tris-(methylene)]tris[2,6-bis(1,1-dimethyleth-yl)phenol};



{1,3,5-tris[[3,5-bis(1,1-dimethylethyl)-4-hydroxyphenyl]methyl]-1,3,5-triazine-2,4,6(1H,3H,5H)-trione};
the octadecyl ester of β-(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid, triethylene glycol bis[3(3-tert-butyl-4-hydroxy-5-methylphenyl)]propionate, 1,6-hexanediol bis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)]propionate and 2,2'-methylenebis(4-methyl-6-tert-butylphenol)monoacrylate.

15. A process according to claim 1, wherein component a) is the octadecyl ester of β-(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid, triethylene glycol bis[3(3-tert-butyl-4-hydroxy-5-methylphenyl)]propionate, 1,6-hexanediol bis[3(3,5-di-tert-butyl-4-hydroxyphenyl)]propionate and 2,2'-methylenebis(4-methyl-6-tert-butylphenol)monoacrylate.

16. A process according to claim 1, wherein component b) is an inorganic compound selected from metal oxides.

17. A process according to claim 1, wherein component b) is calcium oxide.

18. A process according to claim 1, wherein a metal salt of a fatty acid is added as additional component, the metal being an element of main or subsidiary group II or tin.

19. A process according to claim 1, wherein a stearate, lactate or laurate of magnesium, tin, zinc or calcium, or a mixture thereof, is used as additional component.

20. A process according to claim 1, wherein calcium stearate or zinc stearate is used as additional component.

21. A process according to claim 1, wherein a thiosynergist selected from the series of the esters of thiodipropionic acid is further added to the plastic recyclate.

22. A process according to claim 1, wherein a thiosynergist selected from the series of the esters thiodipropionic acid is further added to the plastic recyclate in an amount of 0.1 to 1 % by weight, based on said recyclate.

23. A process according to claim 1, wherein at least one light stabiliser selected from the series of the benzophenones, benzotriazoles, oxanilides or sterically hindered amines, or a mixture thereof, is further added to the plastic recyclate.

AUSTRALIAN PATENT OFFICE

24. A process according to claim 1, wherein at least one light stabiliser selected from the series of the benzophenones, benzotriazoles, oxanilides or sterically hindered amines, or a mixture thereof, is further added to the plastic recyclate in an amount of 0.01 to 2 % by weight.

25. A process according to claim 1, wherein a light stabiliser selected from the series of the benzotriazoles, or a light stabiliser selected from the series of the sterically hindered amines, is added to the plastic recyclate.

26. A mixture for stabilising recycled styrene-containing plastic materials recovered from domestic, commerical or industrial waste or from useful material collections against thermo-oxidative degradation, which mixture comprises a) at least one sterically hindered phenol, b) at least one inorganic compound selected from metal oxides, metal hydroxides or metal carbonates and, as optional component c), a metal salt of a fatty acid with the proviso that no organic phosphite or phosphonite is present.

27. A stabiliser mixture according to claim 26, comprising in 100 parts

(A) as component a) 5-90 parts of triethylene glycol bis[3(3-tert-butyl-4-hydroxy-5-methylphenyl)]propionate, as component b) 10-95 parts of calcium oxide;

(B) as component a) 5-90 parts of the octadecyl ester of β-(3,5-di-tert-butyl-4-hydroxy-phenyl)propionic acid, as component b) 10-95 parts of calcium oxide; or

(C) as component a) 5-90 parts of triethylene glycol bis[3(3-tert.butyl-4-hydroxy-5-methylphenyl)]propionate, as component b) 5-90 parts of calcium oxide, and as component c) 5-90 parts of calcium stearate.

28. A recycled styrene-containing plastic material recovered from domestic, commerical or industrial waste or from useful material collections and stabilized against thermo-oxidative degradation, which plastic material comprises a) at least one sterically hindered phenol, b) at least one inorganic compound selected from metal oxides, metal hydroxides or metal carbonates and, as optional component c), at least one metal salt of a fatty acid with the proviso that no organic phosphite or phosphonite is present.

AUSTRALIAN PATENT OFFICE

INTERNATIONAL SEARCH REPORT

Internat Application No PCT/EP 94/02234

A. CLASSIFICATION OF SUBJECT MATTER

C 08 L 25/04, C 08 K 13/02

According to International Patent Classification (IPC) or to both national classification and IPC 6

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C 08 L, C 08 K

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,P	WO, A, 94/07 951 (CIBA-GEIGY AG) 14 April 1994 (14.04.94), page 1, line 9 - page 3, line 14; page 4 - page 10; page 12, line 10 - page 14, last line; claims. --	1-20, 23-25, 29
A	EP, A, 0 064 343 (MOBIL/OIL CORPORATION) 10 November 1982 (10.11.82), the whole document. --	1-14, 18-20, 23-25
A	EP, A, 0 506 614 (CIBA-GEIGY) 30 September 1992 (30.09.92), page 3, line 20 - page 4, line 17; examples; claims. ----	1-29

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

☐ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" 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
08 November 1994	29. 11. 94

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax (+31-70) 340-3016	TENGLER e.h.

ANHANG — ANNEX — ANNEXE

zum internationalen Recherchenbericht über die internationale Patentanmeldung Nr.

to the International Search Report to the International Patent Application No.

au rapport de recherche international relatif á la demande de brevet international n°

PCT/EP 94/02234 SAE 95044

In diesem Anhang sind die Mitglieder der Patentfamilien der in obengenannten internationalen Recherchenbericht angeführten Patentdokumente angegeben. Diese Angaben dienen nur zur Unterrichtung und erfolgen ohne Gewähr.

This Annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The Office is in no way liable for these particulars which are given merely for the purpose of information.

La présente annexe indique les membres de la famille de brevets relatifs aux documents de brevets cités dans le rapport de recherche international visée ci-dessus. Les reseignements fournis sont donnés á titre indicatif et n'engagent pas la responsibilité de l'Office.

In Recherchenbericht angeführtes Patentdokument Patent document cited in search report Document de brevet cité dans le rapport de recherche	Datum der Veröffentlichung Publication date Date de publication	Mitglied(er) der Patentfamilie Patent family member(s) Membre(s) de la famille de brevets	Datum der Veröffentlichung Publication date Date de publication
WO A1 9407951	14-04-94	keine - none - rien	
EP A1 64343	10-11-82	AU A1 82246/82	04-11-82
		JP A2 57185305	15-11-82
EP A2 506614	30-09-92	CA AA 2063970	28-09-92
		EP A3 506614	11-08-93
		JP A2 5132577	28-05-93
		US A 5298540	29-03-94


END