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(54) Title: PROCESS FOR THE PREPARATION OF OLEFIN POLYMERS

(57) Abstract

The addition of at least one compound of the series of the hydrotalcites, zeolites or metal oxides that does not release water under the reaction conditions to the polymerisation of olefins with solid supported catalysts effects a strong reduction in the corrosive action of the polymers without adversely affecting the polymerisation itself or the properties of the polymers. Further stabilisers may also be added.

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Process for the preparation of olefin polymers

The present invention relates to a process for the preparation of olefin polymers in which hydrotalcites, zeolites or metal oxides and optional stabilisers are added during the polymerisation. The invention also relates to the olefin polymers so obtained.

The low-pressure polymerisation of olefins with organometallic complex catalysts (e.g. Ziegler-Natta catalysts) usually results in a finely powdered polymer which is extruded in an extruder before being shaped by processing. In this granulation, substances such as stabilisers, corrosion inhibitors, colour enhancers, antistatic agents or other processing auxiliaries. However, this granulation is not always desired or possible, inter alia, with polymers of high molecular weight.

Recently, it has proved possible by using solid supported catalysts to prepare spherical, granular-type polymers that no longer have to be granulated by extrusion, but can be processed direct. Suitable supports for these solid catalysts have been found to be in particular spherical magnesium halides of specific particle size as disclosed, inter alia, in DE-A-2 641 960. The anhydrous magnesium halide forms with $TiCl_4$ and electron donors insoluble complexes which are then activated with aluminium alkylene. The stereospecificity and activity are enhanced by using electron donors such as carboxylic acid esters or compounds containing Si-O-C bonds as disclosed, inter alia, in EP-A-45 977.

As the polymers so obtained no longer have to be granulated, it was then desired to add modifiers which are important for processing and long-term stability during polymerisation. The addition of many conventional modifiers (e.g. stabilisers) interferes with the olefin polymerisation and causes discolouration of the polymers.

The machines used in further processing of the polymers, e.g. calanders, are subject to corrosion. The corrosive action of the polymer on metal surfaces is generally attributed to catalyst residues or degradation products of the catalyst system. Up to now it has been necessary to add a corrosion inhibiting compound in a separate processing step.

It is known (EP-A-192 987 or EP-A-0 350 444) that sterically hindered amine stabilisers of the polyalkylpiperidine type do not interfere with the polymerisation and do not substantially discolour the polymer and effect good thermal oxidative stability.

It has further been proposed (EP-A-254 348) to add organic phosphites or phosphonites as antioxidants.

It is also known to add sterically hindered amine stabilisers of the polyalkylpiperidine type in conjunction with organic phosphites or phosphonites during the polymerisation (EP-A-0 351 360).

Surprisingly, it has now been found that the addition of compounds of the series of the hydrotalcites, zeolites or metal oxides which do not release water under the reaction conditions, in conjunction with optional stabilisers, does not interfere with the polymerisation of olefins and substantially prevents corrosion otherwise occurring during polymerisation, and that excellent long-term stability is achieved by adding further stabilisers.

Accordingly, the invention relates to a process for the preparation of olefin polymers by polymerisation using transition metal catalysts, which comprises carrying out the polymerisation by adding at least one compound of the series of the hydrotalcites, zeolites or metal oxides that do not release water under the reaction conditions.

The polymerisation is preferably carried out with a solid supported transition metal catalyst which has been prepared by reacting an aluminium compound carrying at least one alkyl group with a compound of a metal of the IVth subgroup of the Periodic Table.

The olefins polymerisable by this process are ethylene and α-olefins such as propylene, but-1-ene, 4-methylpent-1-ene or 5-methylhex-1-ene, as well as mixtures of olefins, typically ethylene-propylene or propylene in admixture with minor amounts of higher α-olefins. The process for the polymerisation and copolymerisation of propylene is of particular interest.

The polymerisation catalysts are transition metal catalysts. They typically consist of a magnesium dihalide in active form and a titanium compound. Catalysts with the other metals of the IVth subgroup of the Periodic Table (Zr and Hf) are also suitable. By magnesium dihalide in active form is meant one in whose X-ray spectrum the line of strongest reflectivity is broader than the corresponding line in the spectrum of the inactive magnesium halide.

It is preferred to use magnesium dichloride or magnesium dibromide as magnesium dihalide. The titanium compounds preferably contain at least one titanium-halide bond. It is particularly preferred to use titanium tetrachloride.

The titanium compound can be used in conjunction with an electron donor, typically a carboxylic acid ester, as disclosed in EP-A-45 977.

After reaction of the magnesium halide component with the titanium compound and, where appropriate, the electron donor, excess titanium compound and excess electron donor are conveniently washed off with an inert solvent, typically with hexane or heptane.

The catalyst so prepared is activated by reaction with an aluminium compound which carries at least one alkyl group and is used preferably as a solution in an alkane. Exemplary of suitable aluminium alkyls are $Al(C_2H_5)_3$ or $Al(C_4H_9)_3$. It is possible to use an electron donor as co-activator, conveniently an organic silicon compound that contains at least one Si-O-C bond, as disclosed in EP-A-45 977. Typical examples of such silicon compounds are phenyl triethoxysilane, phenyl trimethoxysilane, diphenyl dimethoxysilane, methyl triethoxysilane, dimethyl diethoxysilane or ethyl trimethoxysilane.

Further transition metal catalysts typically consist of a chromium compound on a solid support, e.g. alumina or silica or mixtures thereof. Examples of such catalysts, also called Phillips catalysts, will be found in US-A-2 825 721.

The polymerisation with these catalysts can be carried out by known methods in liquid phase or in the gas phase. The liquid phase may conveniently be an aliphatic hydrocarbon or the liquid monomer itself.

The compounds of the series of the hydrotalcites, zeolites or metal oxides that do not release water under the reaction conditions are added to the polymerisation medium at the start, during, or towards the end of the polymerisation.

Compounds of the series of the hydrotalcites, zeolites or metal oxides are the naturally occurring minerals as well as synthetically prepared compounds.

Compounds of the series of the hydrotalcites may be illustrated by the general formula

$$M^{2+}_{1-x}\cdot M^{3+}_{x}\cdot (OH)_2\cdot (A^{n-})_{x/n}\cdot mH_2O \qquad (I)$$

wherein

M^{2+} = Mg, Ca, Sr, Ba, Zn, Cd, Pb, Sn and/or Ni,

M^{3+} = Al, B or Bi,

A^n is an anion of valency n,

n is a number from 1 to 4,

x is a number from 0 to 0.5,

m is a number from 0 to 2, and

A = OH^-, Cl^-, Br^-, I^-, ClO_4^-, HCO_3^-, CH_3COO^-, $C_6H_5COO^-$, CO_3^{2-}, SO_4^{2-}, $\begin{matrix}COO^- \\ | \\ COO^-\end{matrix}$, $(CHOHCOO)_2^{2-}$, $(CHOH)_4CH_2OHCOO^-$. $C_2H_4(COO)_2^{2-}$, $(CH_2COO)_2^{2-}$, $CH_3CHOHCOO^-$, SiO_3^{2-}, SiO_4^{4-}, $Fe(CN)_6^{3-}$, $Fe(CN)_6^{4-}$ or HPO_4^{2-}.

Other hydrotalcites which may conveniently be used in the process described above are compounds of the general formula Ia

$$M^{2+}_{x}Al_2(OH)_{2x+6nz}(A^{n-})_2\cdot mH_2O \qquad (Ia)$$

wherein M^{2+} is at least one metal of the series of Mg and Zn, Mg being preferred, A^{n-} is an anion of the series of CO_3^{2-}, $\left(\begin{matrix}COO \\ | \\ COO\end{matrix}\right)^{2-}$, OH^- and S^{2-}, and n is the valency of the anions, m is a positive number, preferably from 0.5 to 5, and x and z are positive numbers, and x is preferably 2 to 6 and z is smaller than 2.

Preferred compounds of the series of the hydrotalcites are those of the general formula I

$$M^{2+}_{1-x}\cdot M^{3+}_{x}\cdot (OH)_2\cdot (A^{n-})_{x/n}\cdot mH_2O \qquad (I)$$

wherein M^{2+} is Mg or denotes a solid solution of Mg and Zn, A^{n-} is CO_3^{2-}, x is a number from 0 to 0.5 and m is a number from 0 to 2.

Particularly preferred hydrotalcites are those of formulae

$Al_2O_3 \cdot 6MgO \cdot CO_2 \cdot 12H_2O$,

$Mg_{4,5}Al_2(OH)_{13} \cdot CO_3 \cdot 3,5H_2O$,

$4MgO \cdot Al_2O_3 \cdot CO_2 \cdot 9H_2O$,

$4MgO \cdot Al_2O_3 \cdot CO_2 \cdot 6H_2O$,

$ZnO \cdot 3MgO \cdot Al_2O_3 \cdot CO_2 \cdot 8\text{-}9H_2O$ oder

$ZnO \cdot 3MgO \cdot Al_2O_3 \cdot CO_2 \cdot 5\text{-}6H_2O$.

In the practice of this invention it is also possible to use zeolites of the general formula (X)

$$M_{x/n}[(AlO_2)_x(SiO_2)_y] \cdot wH_2O \qquad (X)$$

wherein n is the charge of the cation M,
M is an element of the first or second main group of the Periodic Table,
y : x is a number from 0.8 to 1.2, and
w is a number from 0.5 to 10.

The preferred per se known zeolites which may be used in the above process have an average pore diameter of 3-5 Å, including those of the NaA type that have an average effective pore diameter of 4 Å, for which reason they are also called 4A zeolites.

Illustrative examples of suitable zeolites are the compounds:

$Na_{12}[(AlO_2)_{12}(SiO_2)_{12}] \cdot 12H_2O$

$Ca_{4,5}Na_3[(AlO_2)_{12}(SiO_2)_{12}] \cdot 30H_2O$

$K_9Na_3[(AlO_2)_{12}(SiO_2)_{12}]\cdot 27H_2O$

Metal oxides can also be used in the process of this invention. Oxides of divalent metals are preferred. Oxides of metals of the second main group or subgroup of the Periodic Table are especially preferred, and zinc or magnesium oxide is most preferred.

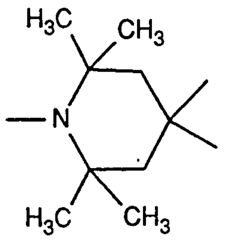
The novel compounds are dried to remove the unbound or only loosely bound water at 50-800°C, preferably 80-400°C, provided they are not already sufficiently dry and have been stored with exclusion of moisture. Drying can be carried out under vacuum or inert gas. The surfaces of the substances can be treated with surface active reagants such as carboxylic acids or linear alcohols of 8 or more carbon atoms, conveniently stearic acid.

The compounds of the series of the hydrotalcites, zeolites or metal oxides or similar synthetically prepared compounds that do not release water under the reaction conditions are normally added in an amount of 0.005 to 5.0 % by weight, preferably from 0.01 to 1 % by weight, based on the polymer.

The process is preferably carried out using additional stabilisers.

A particularly preferred embodiment of the invention comprises carrying out the above process by the further addition of a compound that contains at least one 2,2,6,6-tetramethylpiperidine radical and that has a molecular weight above 500, or by the further addition of a phosphorus(III) compound. The use of such a 2,2,6,6-tetramethylpiperidine compound with a phosphorus(III) compound is particularly preferred.

The sterically hindered amines, preferably piperidines, are known in particular as light stabilisers, but they act here also as antioxidants, i.e. they impart thermal oxidative stability to the polymer. These compounds contain one or more than one group of formula I

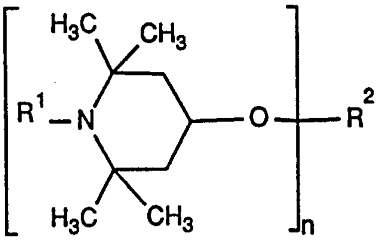


(I),

They may be oligomeric or polymeric compounds.

Particularly important stabilisers are the following classes of tetramethylpiperidines:

a) compounds of formula II



(II),

wherein n is a number from 1 to 4, preferably 1 or 2, R^1 is hydrogen, oxyl, C_1-C_{12}alkyl, C_3-C_8alkenyl, C_3-C_8alkynyl, C_7-C_{12}aralkyl, C_1-C_8alkanoyl, C_3-C_5alkenoyl, glycidyl or a group -$CH_2CH(OH)$-Z, wherein Z is hydrogen, methyl or phenyl, the preferred meaning of R^1 being C_1-C_4alkyl, allyl, benzyl, acetyl or acryloyl, and R^2, if n is 1, is hydrogen, C_1-C_{18}alkyl which may be interrupted by one or more than one oxygen atom, cyanoethyl, benzyl, glycidyl, a monovalent radical of an aliphatic, cycloaliphatic, araliphatic, unsaturated or aromatic carboxylic acid, carbamic acid or or phosphorus containing acid, or is a monovalent silyl radical, preferably a radical of an aliphatic carboxylic acid of 2 to 18 carbon atoms, of a cycloaliphatic carboxylic acid of 7 to 15 carbon atoms, of an α,ß-unsaturated carboxylic acid of 3 to 5 carbon atoms or of an aromatic carboxylic acid of 7 to 15 carbon atoms, and, if n is 2, is C_1-C_{12}alkylene, C_4-C_{12}alkenylene, xylylene, a divalent radical of an aliphatic, cycloaliphatic, araliphatic or aromatic dicarboxylic acid, dicarbamic acid or phosphorus containing acid, or is a divalent silyl radical, preferably a radical of an aliphatic dicarboxylic acid of 2 to 36 carbon atoms, of a cycloaliphatic or aromatic dicarboxylic acid of 8 to 14 carbon atoms, or of an aliphatic, cycloaliphatic or aromatic dicarbamic acid of 8 to 14 carbon atoms, and, if n is 3, is a trivalent radical of an aliphatic, cycloaliphatic or aromatic tricarboxylic acid, of an aromatic tricarbamic acid or of a phosphorus containing acid, or is a trivalent silyl radical, and, if n is 4, is a tetravalent radical of an aliphatic, cycloaliphatic or aromatic tetracarboxylic acid.

Substituents defined as C_1-C_{12}alkyl may typically be methyl, ethyl, n-propyl, n-butyl, sec-butyl, tert-butyl, n-hexyl, n-octyl, 2-ethylhexyl, n-nonyl, n-decyl, n-undecyl or n-dodecyl dar.

R^2 as C_1-C_{18}alkyl may be the groups listed above and may additionally be n-tridecyl, n-tetradecyl, n-hexadecyl or n-octadecyl.

R^1 as C_3-C_8alkenyl may typically be 1-propenyl, allyl, methallyl, 2-butenyl, 2-pentenyl, 2-hexenyl, 2-octenyl, 4-tert-butyl-2-butenyl.

R^1 as C_3-C_8alkynyl is preferably propargyl.

R^1 as C_7-C_{12}aralkyl is preferably phenethyl and, most preferably, benzyl.

R^1 as C_1-C_8alkanoyl is typically formyl, propionyl, butyryl, octanoyl, but is preferably acetyl and, as C_3-C_5alkenoyl, is preferably acryloyl.

R^2 defined as a monovalent radical of a carboxylic acid is typically the radical of acetic acid, capronic acid, stearic acid, acrylic acid, methacrylic acid, benzoic acid or ß-(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid.

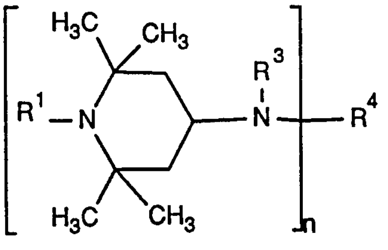
R^2 defined as a divalent radical of a dicarboxylic acid is typically the radical of malonic acid, succinic acid, glutaric acid, adipic acid, suberic acid, sebacic acid, maleic acid, phthalic acid, dibutylmalonic acid, dibenzylmalonic acid, butyl-(3,5-di-tert-butyl-4-hydroxybenzyl)malonic acid or bicycloheptendicarboxylic acid.

R^2 defined as a trivalent radical of a tricarboxylic acid is typically the radical of trimellitic acid or of nitrilotriacetic acid.

R^2 defined as a tetravalent radical of a tetracarboxylic acid is typically the tetravalent radical of butane-1,2,3,4-tetracarbooxylic acid or of pyromellitic acid.

R^2 defined as a divalent radical of a dicarbamic acid is typically the radical of hexamethylenedicarbamic acid or of 2,4-toluylenedicarbamic acid.

b) Compounds of formula (III)



(III),

wherein n is 1 or 2, R^1 is as defined under a), R^3 is hydrogen, C_1-C_{12}alkyl, C_2-C_5hydroxyalkyl, C_5-C_7cycloalkyl, C_7-C_8aralkyl, C_2-C_{18}alkanoyl, C_3-C_5alkenoyl or benzoyl and, R^4, if n is 1, is hydrogen, C_1-C_{18}alkyl, C_3-C_8alkenyl, C_5-C_7cycloalkyl, C_1-C_4alkyl which is substituted by a hydroxyl, cyano, alkoxycarbonyl or carbamido group, glycidyl, a group of formula -CH_2-CH(OH)-Z or of formula -CONH-Z, wherein Z is hydrogen, methyl or phenyl; or, if n is 2, R^4 is C_2-C_{12}alkylene, C_6-C_{12}arylene, xylylene, a -CH_2-CH(OH)-CH_2 group or a -CH_2-CH(OH)-CH_2-O-D-O- group, wherein D is C_2-C_{10}alkylene, C_6-C_{15}arylene, C_6-C_{12}cycloalkylene, or, with the proviso that R^3 is not alkanoyl, alkenoyl or benzoyl, R^4 is also a divalent radical of an aliphatic, cycloaliphatic or aromatic dicarboxylic acid or dicarbamic acid or may also be the -CO- group, or R^3 and R^4, when taken together, if n is 1, may be the divalent radical of an aliphatic, cycloaliphatic or aromatic 1,2- or 1,3-dicarboxylic acid.

Substituents defined as C_1-C_{12}alkyl or C_1-C_{18}alkyl have the meanings already given under a).

Substituents defined as C_5-C_7cycloalkyl are preferably cyclohexyl.

R^3 as C_7-C_8aralkyl is preferably phenylethyl or, most preferably, benzyl. R^3 as C_2-C_5hydroxyalkyl is preferably 2-hydroxyethyl or 2-hydroxypropyl.

R^3 as C_2-C_{18}alkanoyl is typically propionyl, butyryl, octanoyl, dodecanoyl, hexadecanoyl, octadecanoyl, but is preferably acetyl and, as C_3-C_5alkenoyl, is preferably acryloyl.

R^4 as C_2-C_8alkenyl is typically allyl, methallyl, 2-butenyl, 2-pentenyl, 2-hexenyl or 2-octenyl.

R^4 as C_1-C_4alkyl which is substituted by a hydroxyl, cyano, alkoxycarbonyl or carbamido group typically includes 2-hydroxyethyl, 2-hydroxypropyl, 2-cyanoethyl, methoxycarbonylmethyl, 2-ethoxycarbonylethyl, 2-aminocarbonylpropyl or

2-(dimethylcarbamoyl)ethyl.

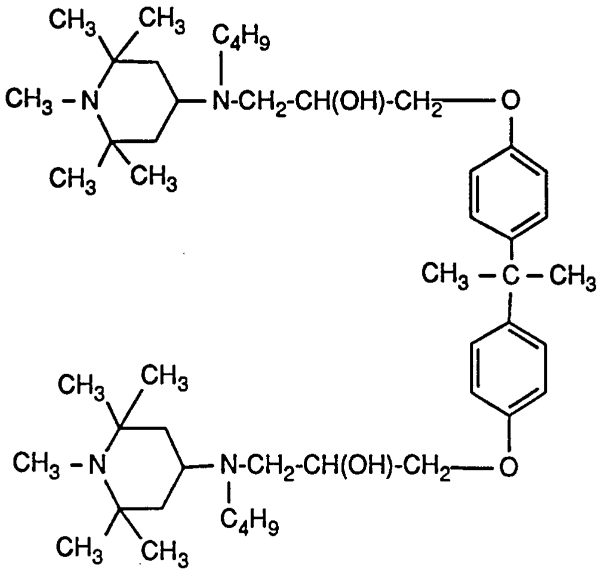
Substituents defined as C_2-C_{12}alkylene may typically be ethylene, propylene, 2,2-dimethylpropylene, tetramethylene, hexamethylene, octamethylene, decamethylene or dodecamethylene.

Substituents defined as C_6-C_{15}arylene may typically be o-, m- or p-phenylene, 1,4-naphthylene or 4,4'-diphenylene.

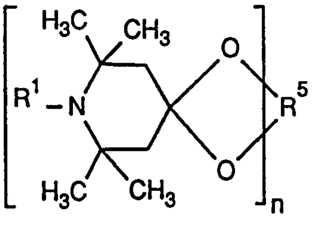
D as C_6-C_{12}cycloalkylene is preferably cyclohexylene.

Illustrative examples of polyalkylpiperidine compounds of this class are the following compounds:

N,N'-bis(2,2,6,6-tetramethylpiperidin-4-yl)-N,N'-dibutyladipamide
N,N'-bis(2,2,6,6-tetramethylpiperidin-4-yl)-N,N'-dicyclohexyl-2-hydroxypropylene-1,3-diamine
the compound of formula



c) Compounds of formula (IV)



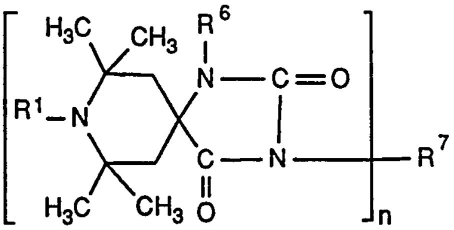
(IV),

wherein n is 1 or 2, R^1 is as defined under a) and R^5, if n is 1, is C_2-C_8alkylene or C_2-C_8hydroxyalkylene or C_4-C_{22}acyloxyalkylene, and, if n is 2, is the $(-CH_2)_2C(CH_2-)_2$ group.

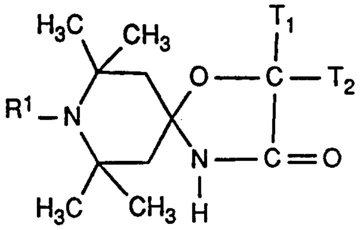
R^5 as C_2-C_8alkylene or C_2-C_8hydroxyalkylene may be ethylene, 1-methylethylene, propylene, 2-ethylpropylene or 2-ethyl-2-hydroxymethylpropylene.

R^5 as C_4-C_{22}acyloxyalkylene may be 2-ethyl-2-acetoxymethylpropylene.

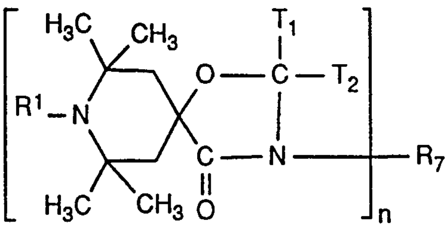
d) Compounds of formulae VA, VB and VC



(VA)



(VB)



(VC)

wherein n is 1 or 2, R^1 is as defined under a), R^6 is hydrogen, C_1-C_{12}alkyl, allyl, benzyl, glycidyl or C_2-C_6alkoxyalkyl, and R^7, if n is 1, is hydrogen, C_1-C_{12}alkyl, C_3-C_5alkenyl, C_7-C_9aralkyl, C_5-C_7cycloalkyl, C_2-C_4hydroxyalkyl, C_2-C_6alkoxyalkyl, C_6-C_{10}aryl, glycidyl or a group of formula -(CH_2)p-COO-Q or of formula -(CH_2)p-O-CO-Q, wherein p is 1 or 2 and Q is C_1-C_4alkyl or phenyl, or if n is 2, is C_2-C_{12}alkylene, C_4-C_{12}alkenylene, C_6-C_{12}arylene, a -CH_2-CH(OH)-CH_2-O-D-O-CH_2-CH(OH)-CH_2- group, wherein D is C_2-C_{10}alkylene, C_6-C_{15}arylene, C_6-C_{12}cycloalkylene, or is a -$CH_2CH(OZ')CH_2$-$(OCH_2$-$CH(OZ')CH_2)_2$- group, wherein Z' is hydrogen, C_1-C_{18}alkyl, allyl, benzyl, C_2-C_{12}alkanoyl or benzoyl, T_1 and T_2 are each independently of the other hydrogen or C_6-C_{10}aryl or C_7-C_9aralkyl which may be substituted by halogen or C_1-C_4alkyl, or T_1 and T_2, together with the linking carbon atom, form a C_5-C_{12}cycloalkane ring.

Substituents defined as C_1-C_{12}alkyl may typically be methyl, ethyl, n-propyl, n-butyl, sec-butyl, tert-butyl, n-hexyl, n-octyl, 2-ethylhexyl, n-nonyl, n-decyl, n-undecyl or n-dodecyl.

Substituents defined as C_1-C_{18}alkyl may be the groups cited above and may additionally be n-tridecyl, n-tetradecyl, n-hexadecyl or n-octadecyl.

Substituents defined as C_2-C_6alkoxyalkyl may typically be methoxymethyl, ethoxymethyl, propoxymethyl, tert-butoxymethyl, ethoxyethyl, ethoxypropyl, n-butoxyethyl, tert-butoxyethyl, isopropoxyethyl or propoxypropyl.

R^7 as C_3-C_5alkenyl may be 1-propenyl, allyl, methallyl, 2-butenyl or 2-pentenyl.

R^7, T_1 and T_2 as C_7-C_9aralkyl are preferably phenethyl or, most preferably, benzyl. A cycloalkane ring formed by T_1 and T_2 together with the linking carbon atom may be a cyclopentane, cyclohexane, cyclooctane or cyclododecane ring.

R^7 as C_2-C_4hydroxyalkyl may be 2-hydroxyethyl, 2-hydroxypropyl, 2-hydroxybutyl or 4-hydroxybutyl.

R^7, T_1 and T_2 as C_6-C_{10}aryl are preferably phenyl, α- or ß-naphthyl, which may be substituted by halogen or C_1-C_4alkyl.

R^7 as C_2-C_{12}alkylene may typically be ethylene, propylene, 2,2-dimethylpropylene, tetramethylene, hexamethylene, octamethylene, decamethylene or dodecamethylene.

R^7 as C_4-C_{12}alkenylene is preferably 2-butenylene, 2-pentenylene or 3-hexenylene.

R^7 as C_6-C_{12}arylene is typically o-, m- or p-phenylene, 1,4-naphthylene or 4,4'-diphenylene.

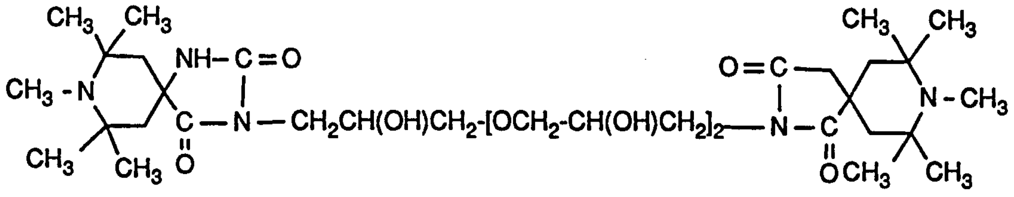
Z' as C_2-C_{12}alkanoyl may be propionyl, butyryl, octanoyl, dodecanoyl, but is preferably acetyl.

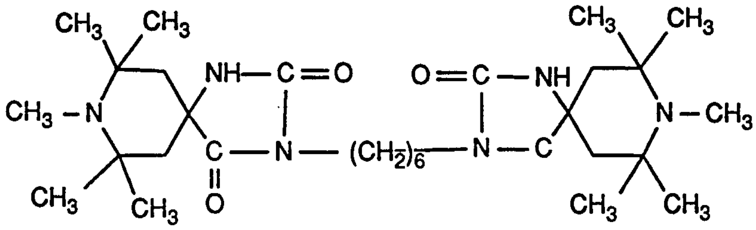
D as C_2-C_{10}alkylen, C_6-C_{15}arylene or C_6-C_{12}cycloalkylene is as defined under b).

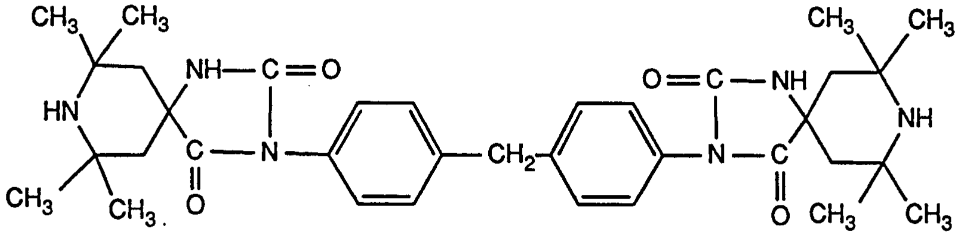
Illustrative examples of polyalkylpiperidines of this class are the following compounds:

2,2,4,4-tetramethyl-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

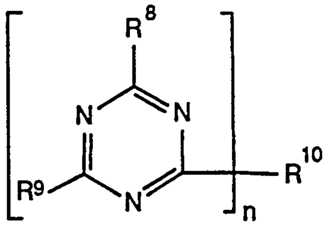
or the compounds of the following formulae:





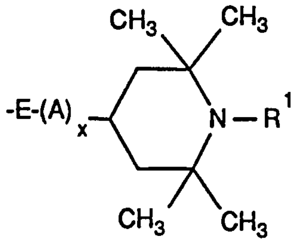


e) Compounds of formula VI

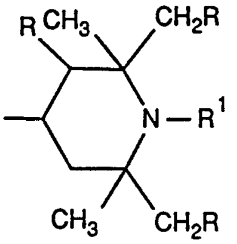


(VI),

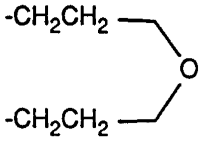
wherein n is 1 or 2 and R^8 is a group of formula



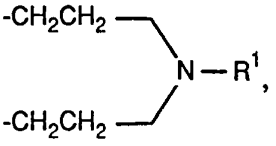
wherein R^1 is as defined under a), E is -O- or $-NR^{11}-$, A is C_2-C_6alkylene or $-(CH_2)_3-O-$ and x is 0 or 1, R^9 has the meaning of R^8 or is a group $-NR^{11}R^{12}$, $-OR^{13}$, $-NHCH_2OR^{13}$ or $-N(CH_2OR^{13})_2$, R^{10}, if n = 1, has the meaning of R^8 or R^9, and, if n = 2, is a group -E-B-E-, wherein B is C_2-C_6alkylene which may be interrupted by $-N(R^{11})-$, R^{11} is C_1-C_{12}alkyl, cyclohexyl, benzyl or C_1-C_4hydroxyalkyl or a group of formula



R^{12} is C_1-C_{12}alkyl, cyclohexyl, benzyl, C_1-C_4hydroxyalkyl, and R^{13} is hydrogen, C_1-C_{12}alkyl or phenyl, or R^{11} and R^{12}, when taken together, are C_4-C_5alkylene or C_4-C_5oxaalkylene, typically

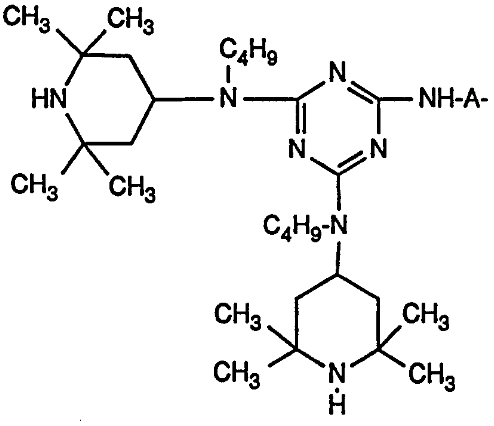


, or are a group of formula



,

or R^{11} and R^{12} are also each a group of formula



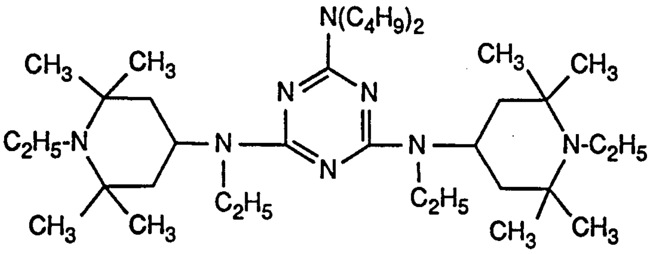
Substituents defined as C_1-C_{12}alkyl may typically be methyl, ethyl, n-propyl, n-butyl, sec-butyl, tert-butyl, n-hexyl, n-octyl, 2-ethylhexyl, n-nonyl, n-decyl, n-undecyl or n-dodecyl dar.

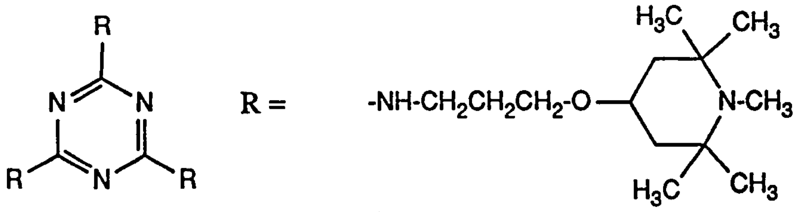
Substituents defined as C_1-C_4hydroxyalkyl may typically be 2-hydroxyethyl, 2-hydroxypropyl, 3-hydroxypropyl, 2-hydroxybutyl or 4-hydroxybutyl.

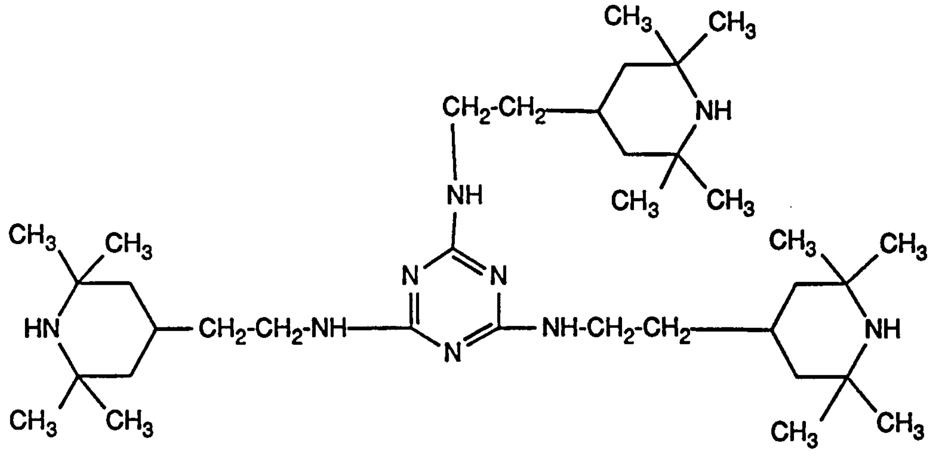
A as C_2-C_6alkylene may be ethylene, propylene, 2,2-dimethylpropylene, tetramethylene or hexamethylene.

R^{11} and R^{12} together as C_4-C_5alkylene or oxaalkylene may be tetramethylene, pentamethylene or 3-oxapentamethylene.

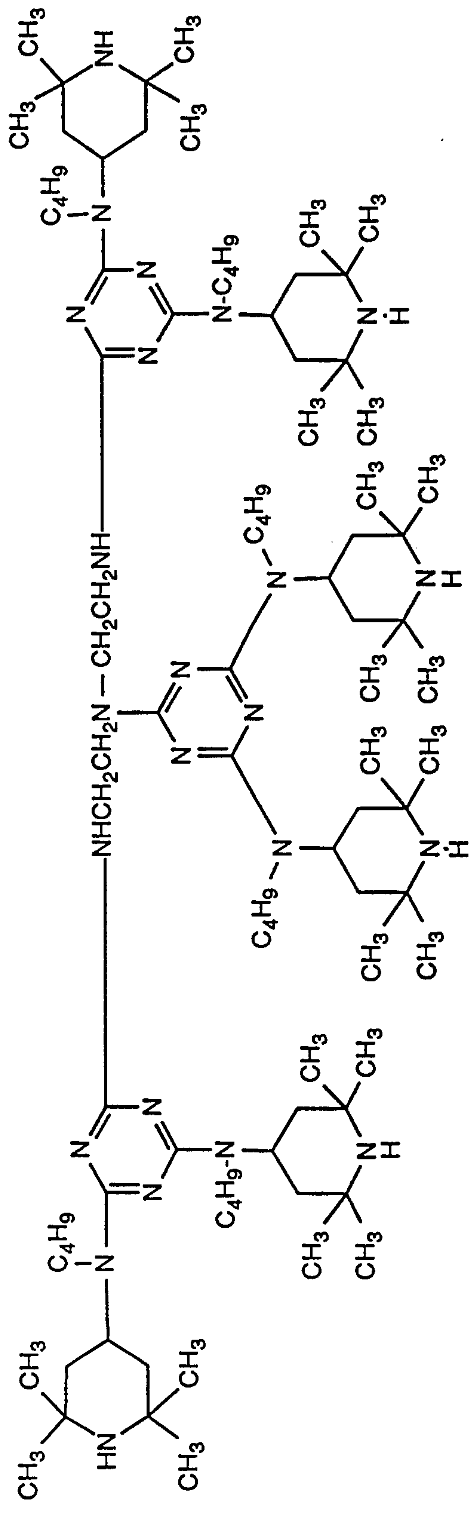
Illustrative examples of polyalkylpiperidines of this class are the compounds of the following formulae:



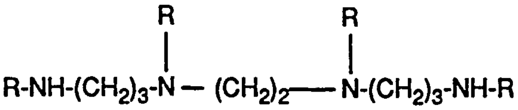




74)

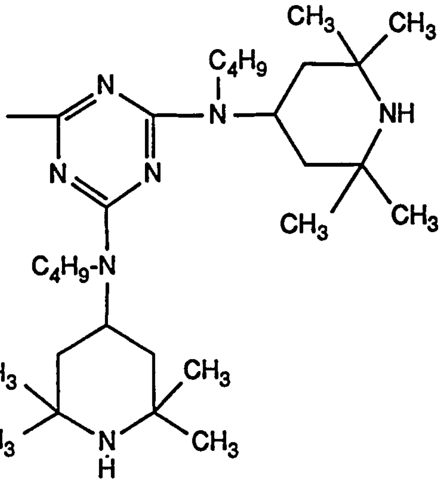


75)

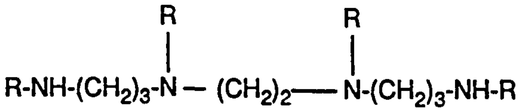


$$R\text{-}NH\text{-}(CH_2)_3\text{-}\overset{R}{\overset{|}{N}}-(CH_2)_2-\overset{R}{\overset{|}{N}}\text{-}(CH_2)_3\text{-}NH\text{-}R$$

R =

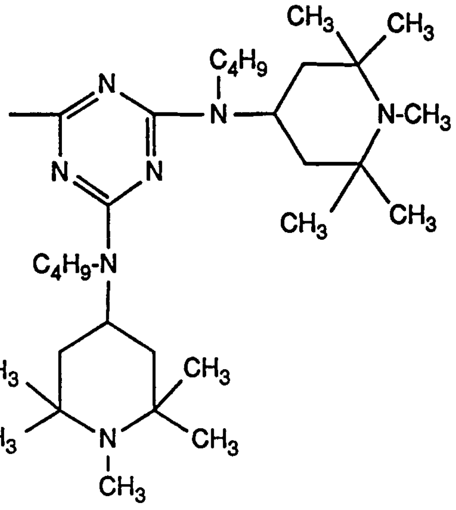


76)

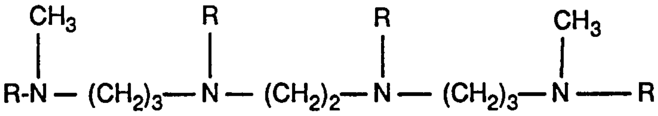


$$R\text{-}NH\text{-}(CH_2)_3\text{-}\overset{R}{\overset{|}{N}}-(CH_2)_2-\overset{R}{\overset{|}{N}}\text{-}(CH_2)_3\text{-}NH\text{-}R$$

R =

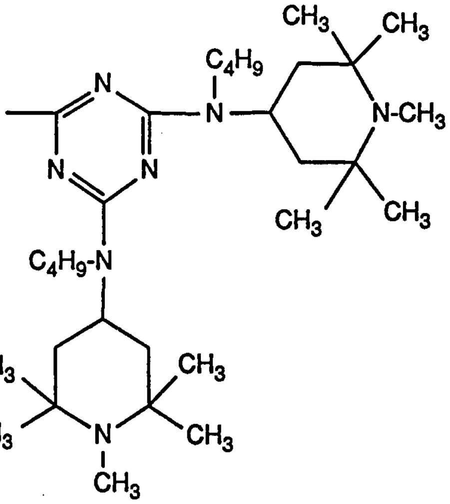


77)

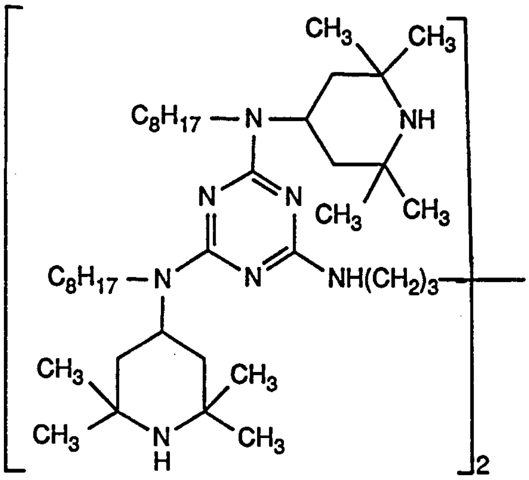


$$R\text{-}\overset{CH_3}{\overset{|}{N}}-(CH_2)_3-\overset{R}{\overset{|}{N}}-(CH_2)_2-\overset{R}{\overset{|}{N}}-(CH_2)_3-\overset{CH_3}{\overset{|}{N}}-R$$

R =



78)



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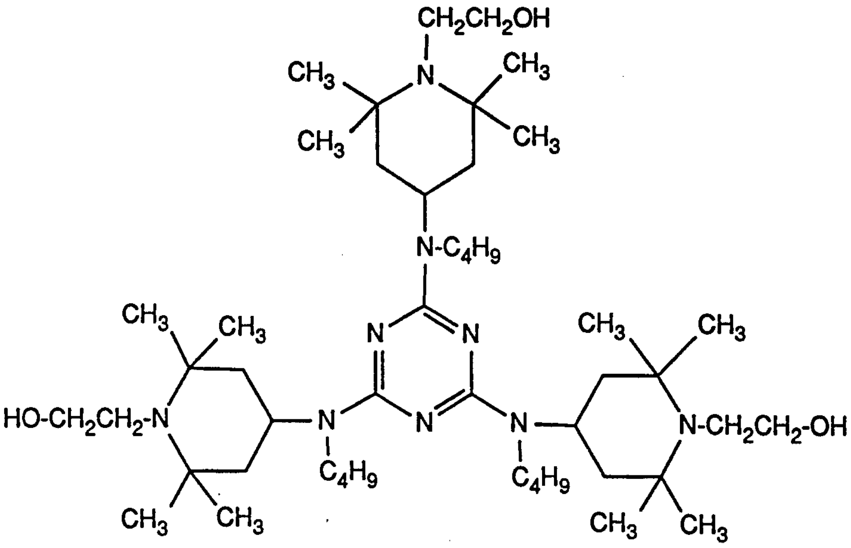

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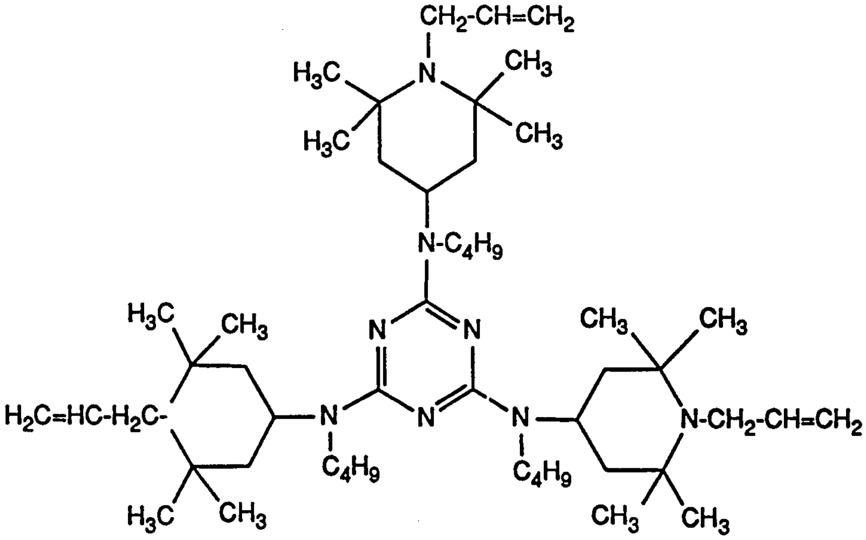
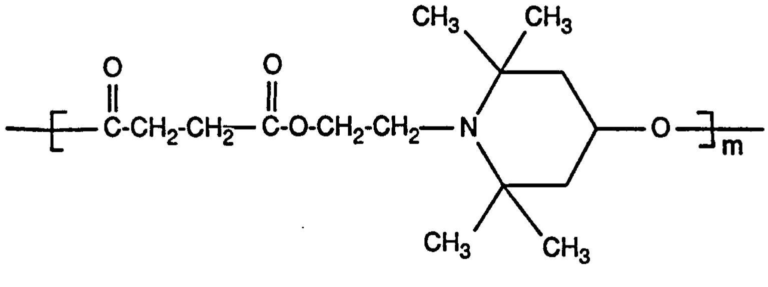


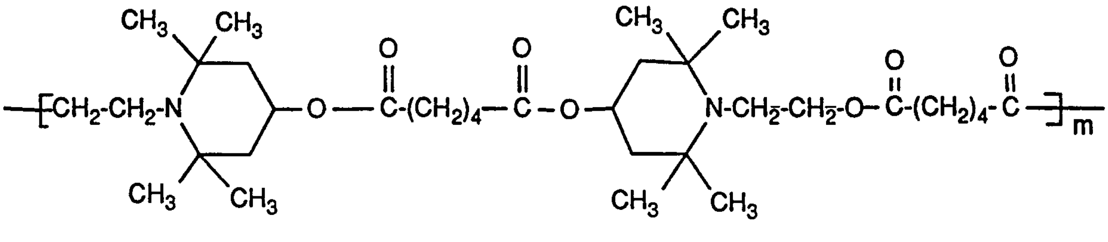
f) Oligomeric or polymeric compounds whose structural repeating unit contains one or more than one 2,2,6,6-tetraalkylpiperidine radical of formula (I), preferably polyesters, polyethers, polyamides, polyamines, polyurethanes, polyureas, polyaminotriazines, poly(meth)acrylates, polysiloxanes, poly(meth)acrylamides and their copolymers which contain such radicals.

Illustrative examples of 2,2,6,6-polyalkylpiperidine light stabilisers of this class are the compounds of the following formulae, wherein m is a number from 2 to about 200.

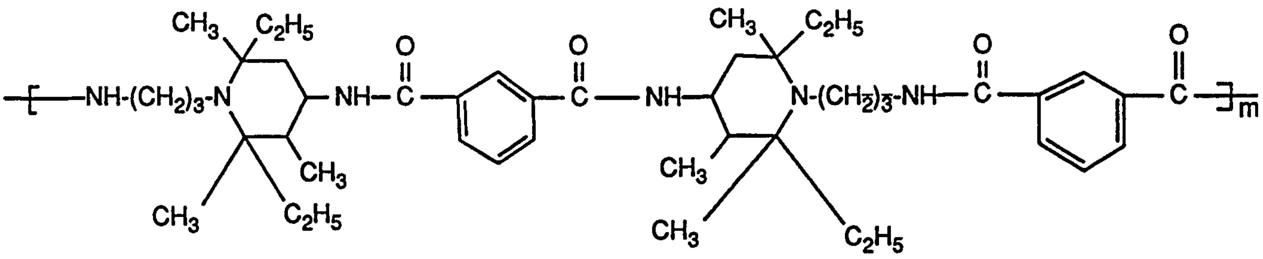
81)



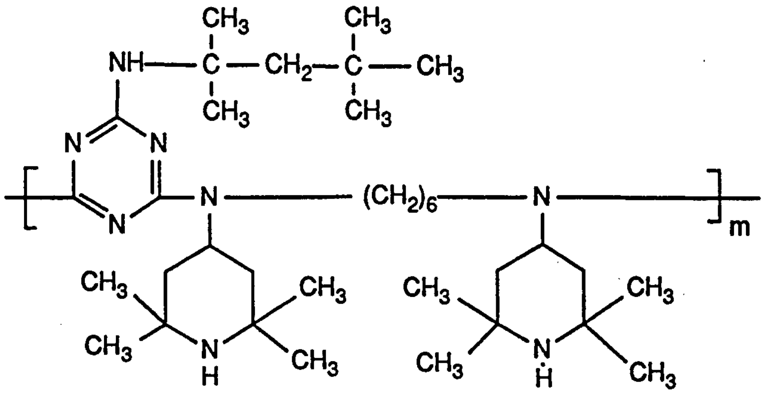
82)



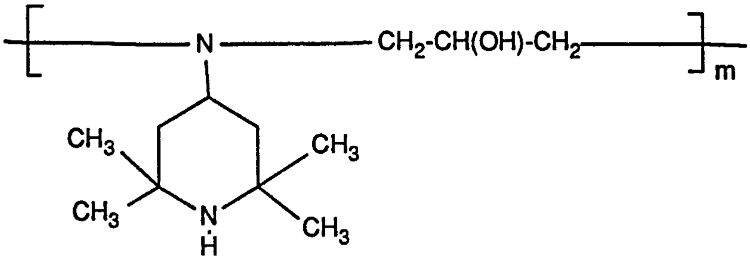
83)



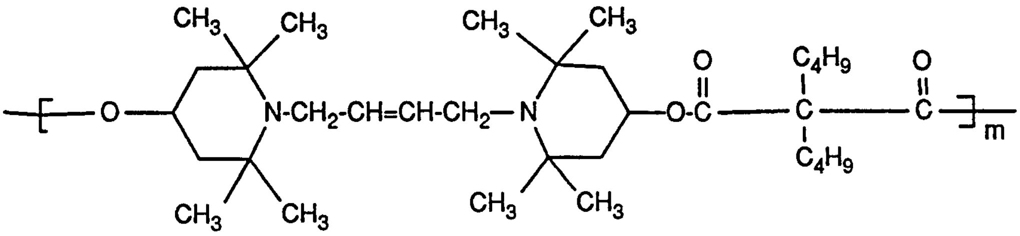
84)



85)



86)



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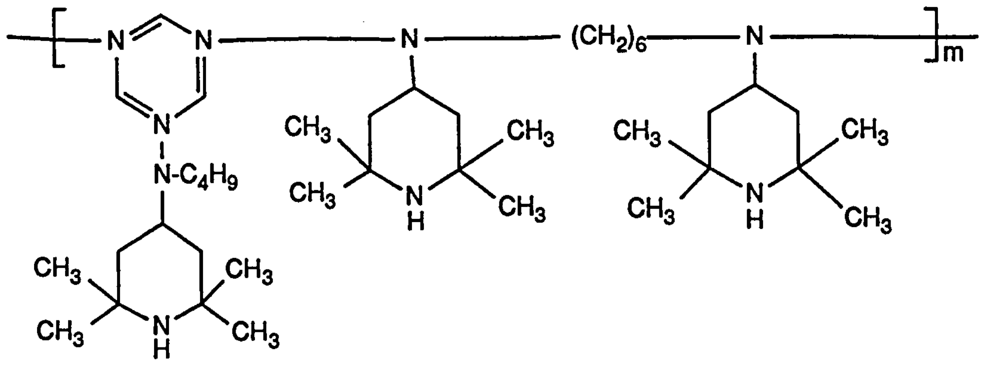

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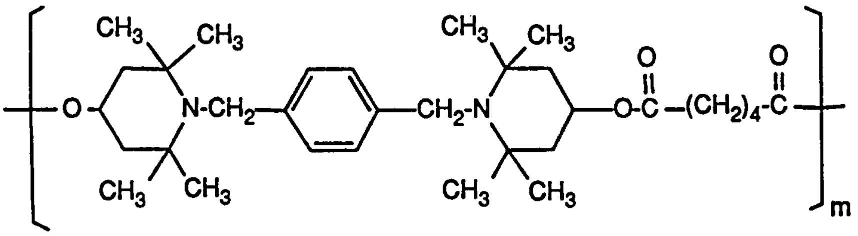
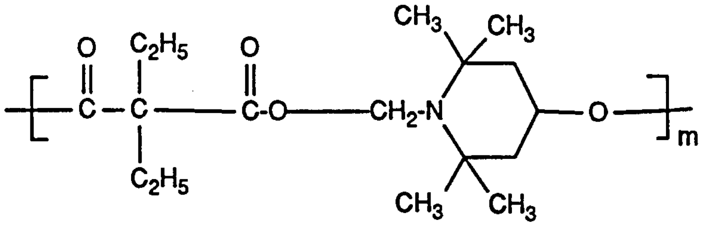
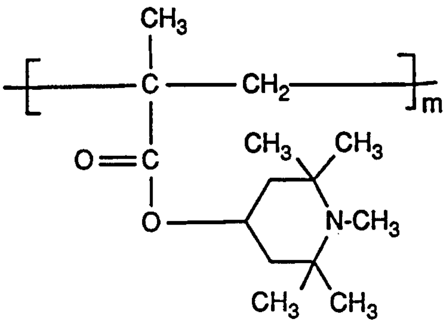


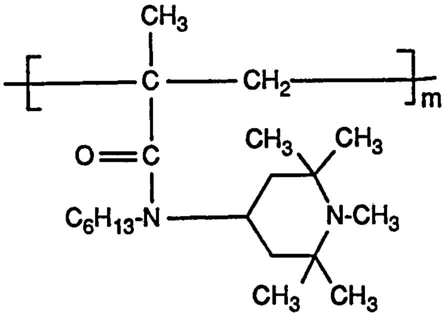
89)



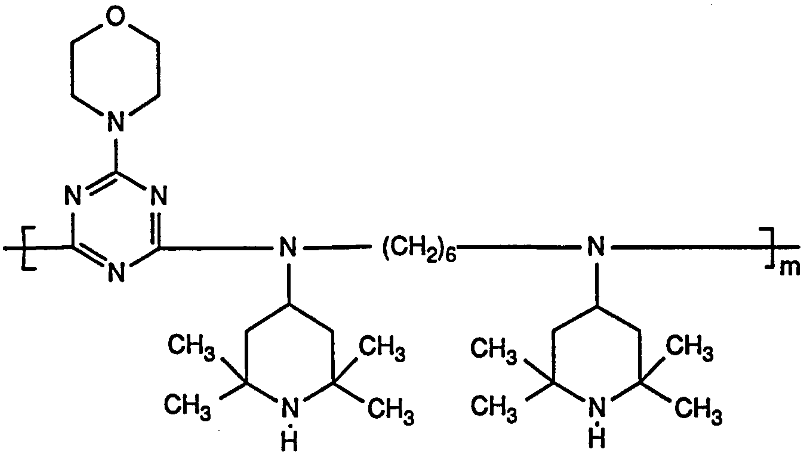
90)



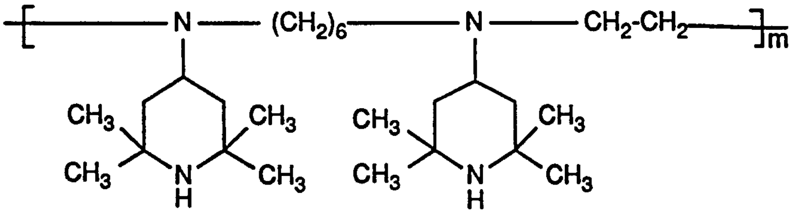
91)


CH3
C
CH2
m
O
C
CH3
CH3
C6H13-N
N-CH3
CH3
CH3

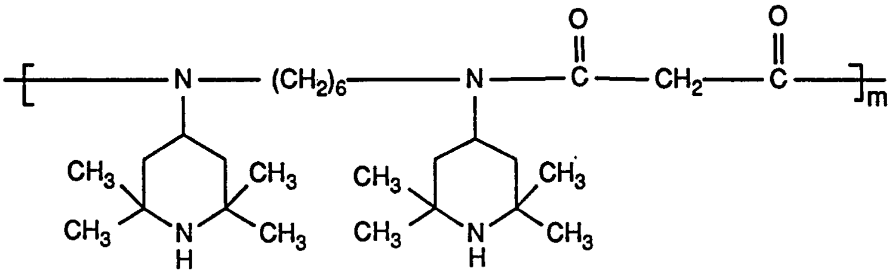
92)


O
N
N
N
N
N
(CH2)6
N
m
CH3
CH3
CH3
CH3
N
H
CH3
CH3
CH3
CH3
N
H

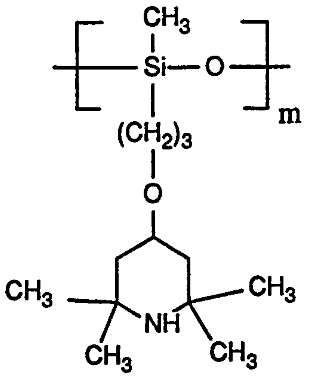
93)


N
(CH2)6
N
CH2-CH2
m
CH3
CH3
CH3
CH3
N
H
CH3
CH3
CH3
CH3
N
H

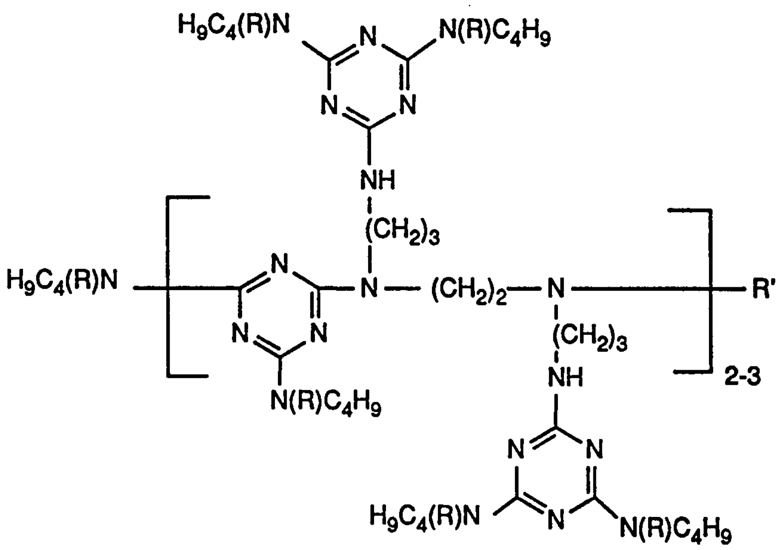
94)


O
O
N
(CH2)6
N
C
CH2
C
m
CH3
CH3
CH3
CH3
N
H
CH3
CH3
CH3
CH3
N
H

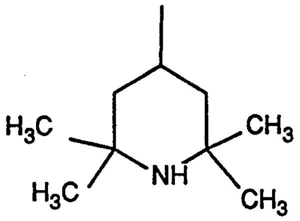
95)



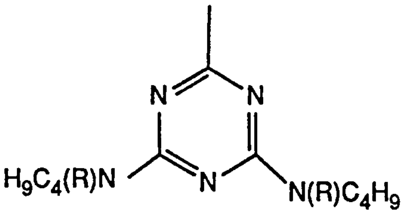
96)



wherein R=



and R'=

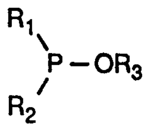


or H

Among these classes of light stabilisers, classes e) and f) are especially suitable, in particular those tetraalkylpiperidines which contain s-triazine groups. Other particularly suitable compounds are compounds 74, 76, 84, 87, 92 und 95.

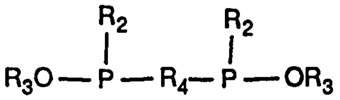
The amount of tetramethylpiperidine added will depend on the desired degree of stabilisation. Normally 0.01 to 5 % by weight, preferably 0.05 to 1 % by weight, based on the polymer, will be added. It is preferred that the molar ratio of tetramethylpiperidine and aluminium alkyl should not be substantially greater then 1.

The phosphorus(III) compounds added as optional additional stabilisers to the polymerisation may be phosphites, phosphonites or phosphinites. They may contain one or more than one phosphoric ester group. It is preferred to use a phosphorus(III) compound of formula A, B, C or D



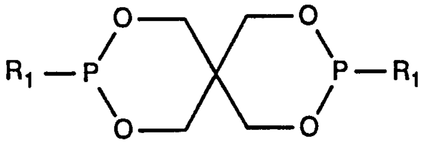
$$(R_1)(R_2)P{-}OR_3$$

A

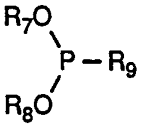


$$R_3O{-}\underset{}{\overset{R_2}{\overset{|}{P}}}{-}R_4{-}\overset{R_2}{\overset{|}{P}}{-}OR_3$$

B



C



$$(R_7O)(R_8O)P{-}R_9$$

D

wherein R_1 and R_2 are each independently of the other C_1-C_{12}alkyl, C_5-C_8cycloalkyl, phenyl, phenyl which is substituted by one to three C_1-C_{12}alkyl groups, or are a radical $-OR_3$,
R_3 is C_6-C_{20}alkyl, C_5-C_8cycloalkyl, phenyl or phenyl which is substituted by one to three C_1-C_{12}alkyl groups, and
R_4 is unsubstituted phenylene or naphthylene or phenylene or naphthylene which are substituted by C_1-C_{12}alkyl, or is a radical-O-R_5-O-, wherein
R_5 is unsubstituted phenylene or naphthylene or phenylene or naphthylene which are substituted by C_1-C_{12}alkyl, or is a radical -Phen-R_6-Phen-, wherein Phen is phenylene,
R_6 is -O-, -S-, $-SO_2-$, $-CH_2-$, or $-C(CH_3)_2-$,
R_7 and R_8 are each independently of the other phenyl or phenyl which is substituted by one to three C_1-C_{12}alkyl groups, and the two substituents R_7 and R_8 may also be linked

by a C_1-C_{12}alkylene group, and
R_9 is F, Cl, Br or I, preferably F.

Among the compounds of formula A it is preferred to use those compounds wherein R_1 and R_2 are a radical -OR_3 and R_3 is C_6-C_{20}alkyl, phenyl or phenyl which is substituted by one to three C_1-C_{12}alkyl groups.

Among the compounds of formula B it is preferred to use those compounds wherein R_2 is a radical -OR_3, R_3 is phenyl or phenyl which is substituted by one to three C_1-C_{12}alkyl groups, and R_4 is a diphenylene radical.

Among the compounds of formula C it is preferred to use those compounds wherein R_1 is a radical -OR_3, R_3 is phenyl or phenyl which is substituted by one to three C_1-C_{12}alkyl groups.

It is preferred to use a phosphorus(III) compound which contains at least one P-O-Ar group, and Ar is a mono-, di- or trialkylphenyl radical.

Illustrative examples of eligible phosphorus(III) compounds are:

triphenyl phosphite, decyl diphenyl phosphite, phenyl didecyl phosphite, tris(nonylphenyl) phosphite, trilauryl phosphite, trioctadecyl phosphite, distearyl pentaerythritol diphosphite, tris(2,4-di-tert-butylphenyl) phosphite, diisodecyl pentaerythritol diphosphite, bis(2,4-di-tert-butylphenyl) pentaerythritol diphosphite, tristearyl sorbitol triphosphite, tetrakis(2,4-di-tert-butylphenyl)-4,4'-biphenylene diphosphonite, bis(2,6-di-tert-butyl-4-methylphenyl) pentaerythritol diphosphite.

The amount of phosphorus(III) compound will depend on the amount of piperidine compound added. Normally 0.01 to 1 % by weight, preferably 0.05 to 0.5 % by weight, is added, based on the polymer.

Besides the phosphorus(III) compound, it is possible to add further co-stabilisers and modifiers that do not interfere with the polymerisation. It is preferred at add antioxidants of the sterically hindered phenol type to the polymerisation. These phenols are standard antioxidants for organic materials and are frequently used for stabilising polymers. Illustrative examples of such phenolic antioxidants are:

1. Alkylated monophenols, for example 2,6-di-tert-butyl-4-methylphenol, 2-tert-butyl-4,6-dimethylphenol, 2,6-di-tert-butyl-4-ethylphenol, 2,6-di-tert-butyl-4-n-butylphenol, 2,6-di-tert-butyl-4-isobutylphenol, 2,6-dicyclopentyl-4-methylphenol, 2-(α-methylcyclohexyl)-4,6-dimethylphenol, 2,6-dioctadecyl-4-methylphenol, 2,4,6-tricyclohexylphenol, 2,6-di-tert-butyl-4-methoxymethylphenol, 2,6-dinonyl-4-methylphenol, 2,4-dimethyl-6-(1'-methylundec-1'-yl)phenol, 2,4-dimethyl-6-(1'-methylheptadec-1'-yl)phenol, 2,4-dimethyl-6-(1'-methyltridec-1'-yl)phenol and mixtures thereof.

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

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

4. 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) and 4,4'-bis-(2,6-dimethyl-4-hydroxyphenyl) disulfide.

5. 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'-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, 1,1-bis(3,5-dimethyl-2-hydroxyphenyl)butane, 2,2-bis(3,5-di-tert-butyl-4hydroxyphenyl)propane, 2,2-bis(5-tert-butyl-4-hydroxy-2-methylphenyl)-4-n-dodecylmercaptobutane and 1,1,5,5-tetra(5-tert-butyl-4-hydroxy-2-methylphenyl)pentane.

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

7. 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 and bis[4-(1,1,3,3-tetramethylbutyl)phenyl] 2,2-bis(3,5-di-tert-butyl-4-hydroxybenzyl)malonate.

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

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

10. 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 and the calcium salt of monoethyl 3,5-di-tert-butyl-4-hydroxybenzylphosphonate.

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

12. Esters of β-(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid with mono- or polyhydric alcohols, for example with methanol, ethanol, 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)oxamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane and 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane.

13. Esters of β-(5-tert-butyl-4-hydroxy-3-methylphenyl)propionic acid with mono- or polyhydric alcohols, for example with methanol, ethanol, 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)oxamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane and 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo-[2.2.2]octane.

14. Esters of β-(3,5-dicyclohexyl-4-hydroxyphenyl)propionic acid with mono- or polyhydric alcohols, for example with methanol, ethanol, 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)oxamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane and 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo-[2.2.2]-octane.

15. Esters of 3,5-di-tert-butyl-4-hydroxyphenylacetic acid with mono- or polyhydric alcohols, for example with methanol, ethanol, 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)oxamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane and 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane.

16. Amides of β-(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid, for example N,N'-bis-(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)hexamethylenediamine, N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)trimethylenediamine and N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)hydrazine.

Preferred antioxidants are those listed in 6, 8, 9, 12, 13, 14 and 16, especially 6, 8, 9 and

12. Particularly suitable antioxidants are octadecyl ß-(3,5-di-tert-butyl-4-hydroxyphenyl)-propionate and 1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl)-2,4,6-trimethylbenzene.

The amount of antioxidant added will depend on the amount of phosphorus(III) compound. Normally 0.005 to 0.5 % by weight, preferably 0.01 to 0.2 % by weight, based on the polymer, is added.

The invention is illustrated in more detail by the following non-limitative Examples in which, and also in the description and claims, parts and percentages are by weight, unless otherwise stated.

Example 1: Preparation of the catalyst
25 g of anhydrous magnesium chloride and 5 g of titanium tetrachloride-ethyl benzoate complex are milled in in a ball mill with stainless steel balls for 24 hours at room temperature (c. 22°C) under argon. The solid catalyst component so obtained contains 2 % titanium.

Polymerisation of propylene
The polymerisation is carried out in a 3 litre stirred and thermostatically controlled stainless steel autoclave which is evacuated before the start of the polymerisation for 30 minutes at 110°C (13 Pa) and is afterwards flushed for 30 minutes with propylene gas at 110°C. The autoclave is cooled to 20°C and 300 mg of S-1, 300 mg of H-1 and 300 mg of P-1 are added to the autoclave as solid or as 5-10 % solution in hexane. Then 25 mg of the solid catalyst component are activated for 10 minutes with half of a solution of 4 mmol of triethyl aluminium and 1.6 mmol of triethoxyphenylsilane in 25 ml of hexane and suspended in the autoclave under argon. The autoclave is flushed with the second half of the hexane solution. The autoclave is closed and charged with hydrogen (6 kPa) and 600 g of liquid propylene. With stirring, the contents of the autoclave are heated to 70°C and kept at this temperature for 4 hours. Excess propylene is then discharged and the resultant polymer is treated with 10 ml of isopropanol at 70°C to deactivate the catalyst and then dried under vaccum for 1 hour at 70°C.

The following tests are carried out on the polymer:

For the corrosion test, the polymer is compression moulded on a hot press for 30 minutes at 280°C between carefully cleaned iron plates. The iron plates are then stored for

24 hours at 100 % humidity at room temperature (c. 22°C). Corrosion is assessed visually.

The colour of the polymer is characterised by the Yellowness Index (YI) according to ASTM D 1925-70.

The polymer corrodes the iron plates only insignificantly. It has a YI of 2.3.

Comparative Example 2:

The procedure of Example 1 is repeated, but without using 300 mg of S-1, to give a polymer which, with the same catalyst yield, severely corrodes the iron plates and has a YI of 2.5.

Examples 3 and 4:

The procedure of Example 1 is repeated, replacing S-1 with 300 mg of S-2/300 mg of S-5, to give a polymer that corrodes the iron plates insignificantly/slightly and has a YI of 2.3/ 2.2.

Example 5:

Polypropylene powder, prepared as in Example 3, is processed in a Brabender plastograph for 10 minutes at 230°C. The melt is taken from the kneader and compressed to a c. 5 mm board. In the corrosion test, the iron plates exhibit no corrosion after the melt processing.

Comparative Example 6:

The polymer prepared according to comparative Example 2 is processed as described in Example 5. The iron plates are severely corroded after the melt processing.

Examples 7 and 8:

The stability to oxidative degradation is measured by the time taken until marked embrittlement of the polymer occurs in oven ageing at elevated temperature. This test is carried out with boards which are obtained by compression moulding polypropylene powder obtained as described in Example 1 by adding 300 mg of S-1, 300 mg of H-1 and 300 mg of P-1 and 300 mg of S-5, 300 mg of H-1 and 300 mg of P-1 at 230°C. The time taken until embrittlement is 11 days for both polymers at an oven temperature of 135°C.

Comparative Example 9:

A polymer prepared and tested in accordance with the particulars of Examples 7 and 8, but without the addition of S-1 and S-5, also becomes brittle after 11 days. This finding means that the addition of S-1 and S-5 does not affect the stability of the polymer to oxidative degradation.

Comparative Example 10:

A polymer prepared and tested in accordance with the particulars of Examples 7 and 8, but without the addition of S-1 and S-5 as well as H-1 and P-1, becomes brittle after 1 day.

Examples 11-14:

Polymerisation is carried out as described in Example 1, but using 44 mg of solid catalyst component, 6.4 mmol of triethyl aluminium and 2.4 mmol of triethoxyphenylsilane. The following compounds are used instead of compounds S-1 and H-1:

Example	Additive	Corrosion	YI
11	H-1 + S-3	slight	2.3
12	H-1 + S-4	slight	2.5
13	H-2 + S-3	slight	2.5
14	H-3 + S-3	slight	2.8

The following additives are used in the Examples:

S-1: $[Mg_{4,5}Al_2(OH)_{13}CO_3 \cdot 3,5H_2O]$ (this compound is sold by by Kyowa Chemicals, Japan, under the tradename DHT-4A). The compound is vacuum dried over phosphorus pentoxide at 95°C for 24 hours.

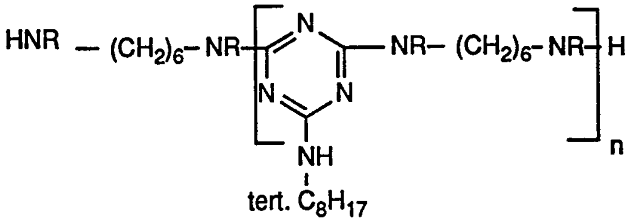
S-2: $[Mg_{4,5}Al_2(OH)_{13}CO_3 \cdot 3,5H_2O]$ calcined (this compound is sold by by Kyowa Chemicals, Japan, under the tradename DHT-4C).

S-3: zink oxide (dried)

S-4: molecular sieve 4A (dried)

S-5: magnesium oxide (dried)

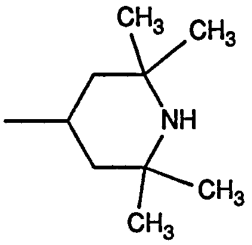
H-1



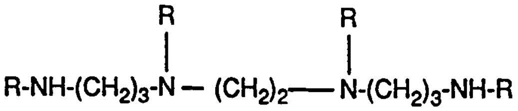
, where

$\overline{M}_n > 2500$

R is

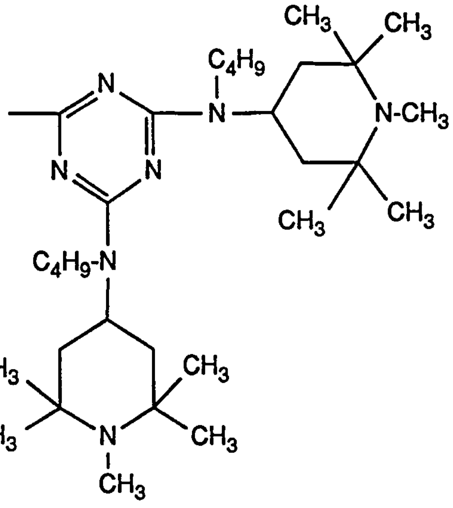


H-2:

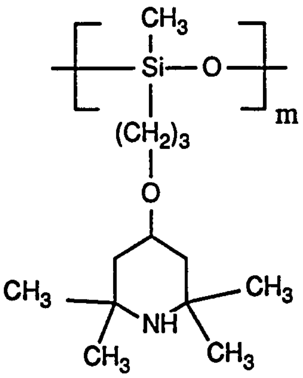


$$R\text{-}NH\text{-}(CH_2)_3\text{-}\underset{}{\overset{R}{N}}-(CH_2)_2-\overset{R}{N}\text{-}(CH_2)_3\text{-}NH\text{-}R$$

R =

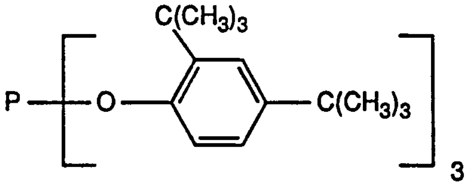


H-3:



M_n>1500

P-1



What is claimed is:

1. A process for the preparation of an olefin polymer by polymerisation with a transition metal catalyst, which comprises carrying out the polymerisation by adding at least one compound of the series of the hydrotalcites, zeolites or metal oxides that does not release water under the reaction conditions.

2. A process according to claim 1, which comprises preparing an olefin polymer by using a solid supported catalyst which has been prepared by reacting an aluminium compound carrying at least one alkyl group with a compound of a metal of the IVth subgroup of the Periodic Table.

3. A process according to claim 1, wherein the catalyst is a chromium compound which is on a support.

4. A process according to claim 1, wherein the compound of the series of the hydrotalcites, zeolites, metal oxides or a similarly synthetically prepared compound that does not release water under the reaction conditions is used after drying at 50-800°C, preferably from 80-400°C.

5. A process according to claim 1, which comprises the use of a synthetically prepared hydrocalcite or zeolite.

6. A process according to claim 1, wherein the hydrotalcite conforms to the general formulae

$$M^{2+}{}_{1-x} \cdot M^{3+}{}_{x} \cdot (OH)_2 \cdot (A^{n-})_{x/n} \cdot mH_2O \qquad \text{(I)}$$

wherein

M^{2+} = Mg, Ca, Sr, Ba, Zn, Cd, Pb, Sn and/or Ni,

M^{3+} = Al, B or Bi,

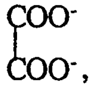
A^n is an anion of valency n,

n is a number from 1 to 4,

x is a number from 0 to 0.5,

m is a number from 0 to 2, and

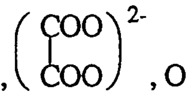
A $= OH^-, Cl^-, Br^-, I^-, ClO_4^-, HCO_3^-, CH_3COO^-, C_6H_5COO^-, CO_3^{2-}, SO_4^{2-}$,



$\begin{matrix} COO^- \\ | \\ COO^- \end{matrix}$, $(CHOHCOO)_2^{2-}$, $(CHOH)_4CH_2OHCOO^-$. $C_2H_4(COO)_2^{2-}$, $(CH_2COO)_2^{2-}$, $CH_3CHOHCOO^-$, SiO_3^{2-}, SiO_4^{4-}, $Fe(CN)_6^{3-}$, $Fe(CN)_6^{4-}$ or HPO_4^{2-},

or

$$M_x^{2+}Al_2(OH)_{2x+6nz}(A^{n-})_2\cdot mH_2O \qquad (Ia)$$



wherein M^{2+} is at least one metal of the series of Mg and Zn, Mg being preferred, A^{n-} is an anion of the series of CO_3^{2-}, $\left(\begin{matrix} COO \\ | \\ COO \end{matrix}\right)^{2-}$, OH^- and S^{2-}, and n is the valency of the anions, m is a positive number, preferably from 0.5 to 5, and x and z are positive numbers, and x is preferably 2 to 6 and z is smaller than 2.

7. A process according to claim 1, wherein the zeolite conforms to the general formula

$$M_{x/n}[(AlO_2)_x(SiO_2)_y]\cdot wH_2O \qquad (X)$$

wherein n is the charge of the cation M,
M is an element of the first or second main group of the Periodic Table,
y : x is a number from 0.8 to 1.2, and
w is a number from 0.5 to 10.

8. A process according to claim 1, which comprises the use of an oxide of a divalent metal.

9. A process according to claim 1, which comprises the use of an oxide of a metal of the second main group and subgroup of the Periodic Table.

10. A process according to claim 1, which comprises the use of an oxide of zinc or magnesium.

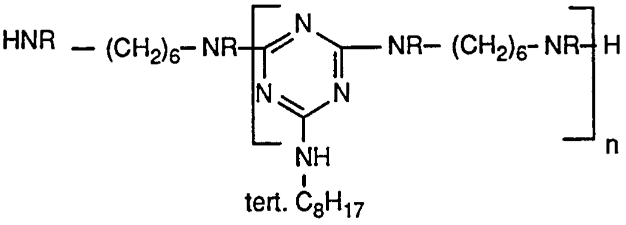
11. A process according to claim 1, wherein a 2,2,6,6,-tetramethylpiperidine having a molecular weight above 500 or a phosphorus(III) compound is added as additional

stabiliser during the polymerisation.

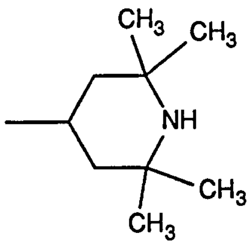
12. A process according to claim 1, wherein a 2,2,6,6,-tetramethylpiperidine having a molecular weight above 500 is used as additional stabiliser.

13. A process according to claim 1, wherein a 2,2,6,6,-tetramethylpiperidine having a molecular weight above 500 that contains in its molecule at least one s-triazine group is used as additional stabiliser.

14. A process according to claim 1, wherein a compound of formula

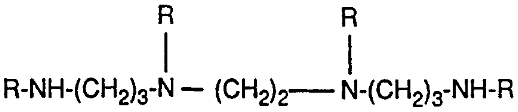


, where R is



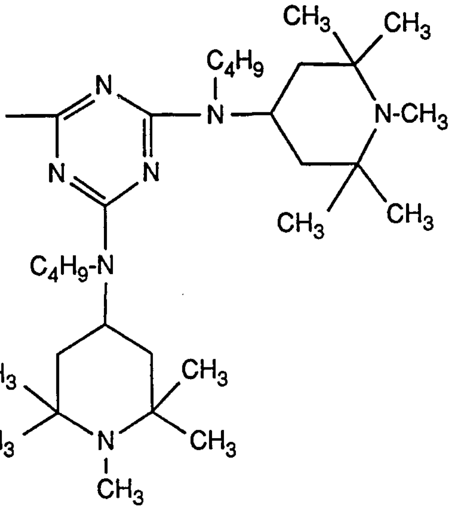
;

$\overline{M}_n > 2500$

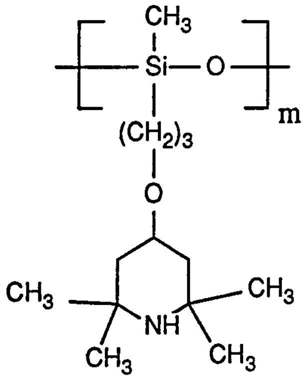


$$R\text{-}NH\text{-}(CH_2)_3\text{-}\underset{}{\overset{R}{N}} - (CH_2)_2 - \overset{R}{N}\text{-}(CH_2)_3\text{-}NH\text{-}R$$

R =



; or



M_n>1500

is used as additional stabiliser.

15. A process according to claim 1, wherein a phosphorus(III) compound is used as additional stabiliser.

16. A process according to claim 1, which comprises the use of a phosphorus(III) compound as additional stabiliser that contains at least one P-O-Ar group, where Ar is a mono-, di- or trialkylphenyl radical.

17. A process according to claim 1, which comprises the use of tris(2,4-di-tert-butylphenyl)phosphite or tetrakis(2,4-di-tert-butylphenyl)-4,4'-biphenylenediphosphonite as an additional stabiliser.

18. A process according to claim 1, wherein an antioxidant of the sterically hindered phenol type is used as additional stabiliser.

19. A process according to claim 1, which comprises the use of octadecyl ß-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate and 1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl)-2,4,6-trimethylbenzene as additional stabiliser.

20. A stabilised polyolefin prepared according to the process of claim 1.

21. Stabilised polypropylene prepared according to the process of claim 1.

INTERNATIONAL SEARCH REPORT

Inter ıal Application No
PCT/EP 93/02419

A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 C08F2/44 C08F10/00

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)
IPC 5 C08F

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	WO,A,92 13899 (AWAPATENT) 20 August 1992 see claims 1-10 see the whole document ---	1-3,5
X	EP,A,0 266 074 (BP CHEMICALS) 4 May 1988 see claims 1,2. see examples ---	1
A	EP,A,0 500 073 (MITSUBISHI) 26 August 1992 see claims 1,6. -----	1

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

☒ Patent family members are listed in annex.

° Special categories of cited documents :

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"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
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1

Date of the actual completion of the international search
3 December 1993

Date of mailing of the international search report
17. 12. 93

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INTERNATIONAL SEARCH REPORT

Information on patent family members

Inter nal Application No
PCT/EP 93/02419

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO-A-9213899	20-08-92	AU-A- 1241992	07-09-92
		EP-A- 0570458	24-11-93
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