

PATENT SPECIFICATION

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(54) POLYTRIAZINE COMPOUNDS

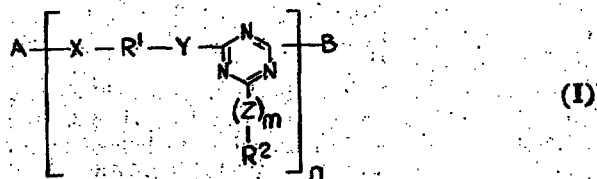
(71) We, CHIMOSA CHIMICA ORGANICA S.P.A., an Italian Joint Stock company of 6/3° Via Pila, 40044 Pontecchio Marconi, Italy, do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to polytriazine compounds which are useful for improving the stability to light, heat and oxidation of polymeric substances.

It is known that synthetic polymers are liable to undergo a severe deterioration of their physical and chemical properties when they are exposed to sunlight or other ultraviolet light sources.

In order to improve the stability to light of said synthetic polymers, various stabilizers have been proposed, some of which have found a wide commercial acceptance in the field, such as some benzophenones, benzotriazoles, aromatic salicylates, α -cyanoacrylic acid esters and organotin compounds, which, although having a certain efficiency level, have not solved the problem completely, so that there is a much felt need for more efficient stabilizers in this field.

According to the present invention there is provided a compound having the formula:

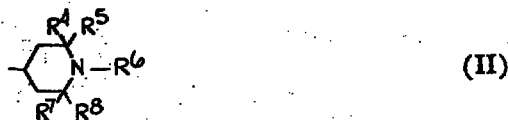


in which:

X, Y and Z are the same or different, and each is —O—, —S— or



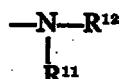
R³ being hydrogen, a straight or branched chain alkyl having 1 to 18 C atoms, a cycloalkyl having 5 to 18 C atoms, a substituted or unsubstituted aryl having 6 to 18 C atoms, an aralkyl having 7 to 18 C atoms, or a piperidine radical of the formula:



wherein R^4 , R^5 , R^7 and R^8 are the same or different and each is C_1 to C_6 alkyl, and R^6 is $-H$, $-O$, a C_1 to C_{18} straight or branched chain alkyl, a C_2 to C_{18} alkenyl or alkynyl, or a C_7 to C_{18} aralkyl;

R^1 is a C_2 to C_{18} straight or branched chain alkylene, a C_5 to C_{18} cycloalkylene, a C_6 to C_{18} arylene, or a C_7 to C_{18} aralkylene or may be a direct bond when X and Y are nitrogen atoms;

R^2 represents $-H$, $-Cl$, $-Br$, $-OH$, a straight or branched chain C_1 to C_{18} (preferably C_1 to C_{12}) alkyl, a C_5 to C_{18} cycloalkyl, a substituted or unsubstituted C_6 to C_{18} aryl, a C_7 to C_{18} aralkyl, a piperidine radical of formula (II), or a



group, in which R^{11} , R^{12} are each hydrogen, a C_1 to C_{12} alkyl, a C_5 to C_{12} cycloalkyl, a C_6 to C_{12} aryl, or a C_7 to C_{12} aralkyl;

m may be 0 or 1, and

when m is 1, the radical R^2-Z can be the same as $-X-R^1-YH$, where X, Y, R^1 have the meaning above indicated;

n is an integer from 2 to 200;

A and B represent terminal groups; and at least one of the radicals $-X-R^1-Y-$ and $-(Z)_m-R^2$ in formula (I) contains a piperidine radical of formula (II).

By the term "terminal groups" is meant the terminal groups of a molecule of formula (I) resulting from the polymerization reaction, which generally are a residue of functional groups. The nature of said residue depends on the reaction conditions, the nature and amount of the reactants used in the reaction, for example, as it is known to one skilled in the art. Said residue is preferably H for A and $-X-R^1-YH$ for B, in that it is preferred using an excess of bifunctional compound in the reaction for controlling the molecular weight, as it will be more fully described later.

$-X-R^1-Y-$ can be a bivalent radical of a heterocycle compound with 6 to 8 members having 2 nitrogen atoms; in such a case X and Y are each a disubstituted nitrogen atom respectively;

$-X-R^1-Y-$ can be also replaced by the radical



in which R^9 , R^{10} are the same or different and each is $-H$, a C_1 to C_{12} alkyl, a C_5 to C_{12} cycloalkyl, a C_6 to C_{12} aryl, or a C_7 to C_{12} aralkyl.

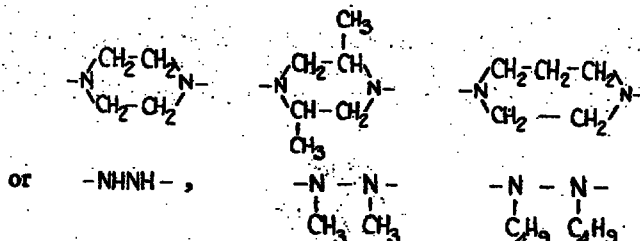
Preferably, R^9 is hydrogen, a C_1 to C_{12} straight or branched chain alkyl, or a radical of the formula (II).

More specifically, R^9 may be hydrogen, methyl, ethyl, n-butyl, isobutyl, n-octyl, 2-ethylhexyl, n-dodecyl, n-octadecyl, cyclohexyl, 3,3,5-trimethylcyclohexyl, phenyl, o-, m-, p-tolyl, α - or β -naphthyl, benzyl, p-methylbenzyl, 2,2,6,6-tetramethyl-4-piperidyl, 1,2,2,6,6-pentamethyl-4-piperidyl, 1-ethyl-2,2,6,6-tetramethyl-4-piperidyl, or 1-propyl-2,2,6,6-tetramethyl-4-piperidyl.

R^1 is preferably a straight or branched chain C_2 to C_{10} alkylene or a C_5 to C_{10} arylene.

More specifically, R^1 may be ethylene, 1,2-propylene, trimethylene, hexamethylene, 2,2,4-trimethylhexamethylene, 2,4,4-trimethylhexamethylene, decamethylene, 1,4-cyclohexylene, 4,4'-methylenedicyclohexylene, o-, m-, p-phenylene or o-, m-, p-xylylene.

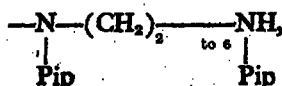
The radical $-X-R^1-Y-$ can be



As an alternative to being hydrogen, chlorine, bromine or $-OH$, R^2 may be $-NH_2$, $-N(CH_3)_2$, methyl, ethyl, isopropyl, n-butyl, isobutyl, n-octyl, 1,1,3,3-tetra-

methylbutyl, n-dodecyl, n-octadecyl, cyclohexyl, 3,3,5-trimethylcyclohexyl, phenyl, 2,6-dimethylphenyl, o-, m-, p-toluy, α -, or β -naphthyl, benzyl, p-methylbenzyl, 2,2,6,6-tetramethyl-4-piperidyl, 1,2,2,6,6-pentamethyl-4-piperidyl, 1-ethyl-2,2,6,6-tetramethyl-4-piperidyl, 6-(2,2,6,6-tetramethyl-4-piperidylamino)-hexyl, or 2-(2,2,6,6-tetramethyl-4-piperidylamino)-ethyl.

Preferably the radical R^2-Z is



Pip being a radical of formula (II).

R^4, R^5, R^7 and R^8 may each be methyl and R^6 may be hydrogen or methyl.

In a convenient embodiment, R^1 is a C_2 to C_{10} alkylene or a C_6 to C_8 arylene;
 R^2 is $-H$, a C_1 to C_{12} alkyl or a piperidyl of formula (II);

R^3 is $-H$, a C_1 to C_{12} alkyl or a piperidyl of formula (II);

R^4, R^5, R^7 and R^8 are methyl;

R^6 is hydrogen or methyl;

$R^9, R^{10}, R^{11}, R^{12}$ are hydrogen;

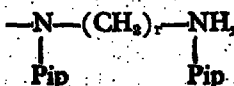
X, Y, Z represents $-O-$, $-NH-$, or



Pip being a piperidyl of formula (II);

A is H;

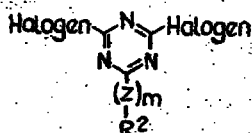
B is



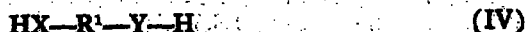
r being an integer from 2 to 6;

m is zero or one; and n is an integer from 2 to 100.

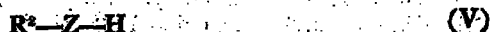
Reacting a 2,4-dihalogen-1,3,5-triazine of formula (III).



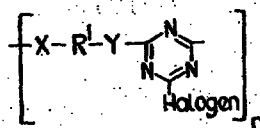
in which halogen is preferably chlorine, with a bifunctional compound (IV)



When in formula (I), m is one, dihalogen-triazines of formula (III) can be prepared by reacting a cyanuric halide, preferably chloride, with 1 mole of a compound of formula (V)

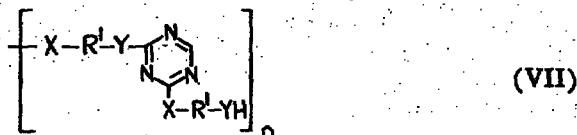


An alternative procedure is reacting a cyanuric halide with a bifunctional compound of formula (IV); depending on the mole ratios in use, it is possible to obtain compounds according to either formula (VI)



(VI)

or formula (VII)



The polytriazines of formula (VI) can be successively reacted with a compound of formula (V).

The reaction of the halogen triazines with the compounds of formula (IV) or compounds of formula (V) is carried out in the presence of an inert solvent for example acetone, dioxane, toluene or xylene, in a temperature range from -10°C and the solvent boiling temperature. The reaction is carried out in the presence of organic or inorganic bases for fixing hydrogen halide. Preferred examples of base useful to said purpose are triethylamine or tributylamine, sodium hydroxide, carbonate or bicarbonate, potassium hydroxide or carbonate, sodium alcoholates when the compounds of formula (IV) or (V) are alcohols or glycols, sodium mercaptides when the reactants of formula (IV) or (V) the mono- or di-mercaptans; it is further possible to use an excess of amine, when reacting a compound of formula (VI) with a compound of formula (V), in which Z is



The mole ratio of compounds (III) to compounds (IV) can range from 1:1.5 to 1.5:1, preferably from 1:1 to 1:1.2.

When reacting a cyanuric halide with a compound (IV) to obtain products of formula (VI), the mole ratio between said compounds is preferably in a range from 1:1 to 1:1.2.

When reacting a cyanuric halide with a compound (IV) to obtain products of formula (VII), the mole ratio between said compounds is in a range from 1:2.5 to 1:2, more preferably from 1:2.4 to 1:2.1.

Particular examples of dihalogen triazines (III) which can be employed to obtain products of formula (I), are:

2,4-dichloro-1,3,5-triazine,
2,4-dichloro-6-methyl-1,3,5-triazine,
2,4-dichloro-6-ethyl-1,3,5-triazine,
2,4-dichloro-6-phenyl-1,3,5-triazine,
2,4-dichloro-6-n-butoxy-1,3,5-triazine,
2,4-dichloro-6-n-octyloxy-1,3,5-triazine,
2,4-dichloro-6-cyclohexyloxy-1,3,5-triazine,
2,4-dichloro-6-phenoxy-1,3,5-triazine,
2,4-dichloro-6-(2,6-dimethylphenoxy)-1,3,5-triazine,
2,4-dichloro-6-benzyloxy-1,3,5-triazine,
2,4-dichloro-6-(2,2,6,6-tetramethyl-4-piperidyloxy)-1,3,5-triazine,
2,4-dichloro-6-n-octylthio-1,3,5-triazine,
2,4-dichloro-6-amino-1,3,5-triazine,
2,4-dichloro-6-n-butylamino-1,3,5-triazine,
2,4-dichloro-6-n-octylamino-1,3,5-triazine,
2,4-dichloro-6-cyclohexylamino-1,3,5-triazine,
2,4-dichloro-6-phenylamino-1,3,5-triazine,
2,4-dichloro-6-diethylamino-1,3,5-triazine,
2,4-dichloro-6-(2,2,6,6-tetramethyl-4-piperidylamino)-1,3,5-triazine,
2,4-dichloro-6-[N(2,2,6,6-tetramethyl-4-piperidyl)-n-butylamino]-1,3,5-triazine,
2,4-dichloro-6-[N(2,2,6,6-tetramethyl-4-piperidyl)-n-octylamine]-1,3,5-triazine,

Representatives of compounds of formula (IV) are:

hydrazine,
1,2-dimethylhydrazine,
ethyleneglycol,
1,3-dihydroxypropane,

1,6-dihydroxyhexane,
resorcinol,
2,2-bis (4-hydroxyphenyl) propane,
bis (3,5-dimethyl-4-hydroxyphenyl)-methane,
1,4-bis-(hydroxymethyl)-cyclohexane,
1,2-dimercaptoethane,
2-hydroxyethylamine,
2-mercaptoethylamine,
1,2-diaminoethane,
1,3-diaminopropane,
1,6-diaminohexane,
1,4-diaminocyclohexane,
1,4-bis (aminomethyl) cyclohexane,
p-phenylenediamine,
4,4'-diaminodiphenylmethane,
p-xylylenediamine,
m-xylylenediamine,
1,2-bis-(n-butylamino)-ethane,
1,6-bis-(ethylamino)-hexane,
piperazine,
2,5-dimethylpiperazine, homopiperazine,
1,2-bis-(2,2,6,6-tetramethyl-4-piperidylamino)-ethane,
1,3-bis-(2,2,6,6-tetramethyl-4-piperidylamino)-propane,
1,6-bis-(2,2,6,6-tetramethyl-4-piperidylamino)-hexane.

Representatives of compounds of formula (V) are: methyl-, ethyl-, n-butyl-, n-octyl-, 2-ethylhexyl-, n-dodecyl-, cyclohexyl-, benzyl-alcohol; 2,2,6,6-tetramethyl-4-piperidinol, phenol, 2,6-dimethylphenol, n-butylmercaptan, n-octylmercaptan, ethylamine, n-butylamine, n-octylamine, 1,1,3,3-tetramethylbutylamine, cyclohexylamine, 3,3,5-trimethylcyclohexylamine, aniline, p-toluidine, benzylamine, diethylamine, di-n-butylamine, 2,2,6,6-tetramethyl-4-piperidylamine, 1,2,2,6,6-pentamethyl-4-piperidylamine, 2,2,6,6-tetramethyl-4-n-butylaminopiperidine, 2,2,6,6-tetramethyl-4-n-octylaminopiperidine, hydrazine, 1,1-dimethyl-hydrazine, hydroxylamine.

In order to illustrate further the present invention, some examples of preparation are given in the following for an illustrative and not limitative purpose.

Example 1.

22.1 g (0.1 moles) of 2,4-dichloro-6-n-butylamino-1,3,5-triazine, 43.34 g (0.11 moles) of 1,6-bis (2,2,6,6-tetramethyl-4-piperidylamino) hexane, 8 g (0.2 moles) of NaOH and 300 ml of toluene were refluxed for 16 hours.

After filtering to remove sodium chloride and evaporating the solvent, a light colored resinous substance of reduced viscosity (1% in chloroform at 25° C) = 0.10 was obtained.

Example 2.

a) 2,4-dichloro-6[N(2,2,6,6-tetramethyl-4-piperidyl)-n-butylamino]-1,3,5-triazine was primarily prepared as a starting compound for producing a polytriazine according to the invention.

A solution of 18.4 g (0.1 moles) of cyanuric chloride in 180 ml of acetone was added at 0° C to 21.2 g (0.1 moles) of 2,2,6,6-tetramethyl-4-n-butylaminopiperidine dissolved in 100 ml of acetone and 4 g of sodium hydroxide dissolved in 40 ml of water.

The precipitate so obtained was filtered after 6 hours at 0° C. After drying a solid product was obtained, which was purified by distillation: b.p. 151—2°/0.1, m.p. 56—58° C. Cl% 19.65 (calculated for C₁₆H₂₈Cl₂N₅: 19.72%).

b) 36 g (0.1 moles) of 2,4-dichloro-6[N(2,2,6,6-tetramethyl-4-piperidyl)-n-butylamino]1,3,5-triazine as prepared in example 2 a), 12.7 g (0.11 moles) of hexamethylenediamine, 8 g of sodium hydroxide and 200 ml of toluene were refluxed for 16 hours.

After filtering to remove sodium chloride and evaporating the reaction solvent a light colored resinous substance of reduced viscosity (1% in chloroform at 25° C) = 0.12 was obtained.

Example 3.

18.4 g (0.1 moles) of cyanuric chloride, 39.4 g (0.1 moles) of 1,6-bis(2,2,6,6-

tetramethyl-4-piperidylamino) hexane, 8 g of sodium hydroxide and 250 ml of toluene were heated 8 hours at 40° C.

The mixture was added to 26.8 g (0.1 moles) of 2,2,6,6-tetramethyl-4-n-octyl-amino-piperidine and 4 g of sodium hydroxide and refluxed for 16 hours.

After filtering to remove sodium chloride and evaporating the reaction solvent a resinous substance of reduced viscosity (1% in chloroform at 25° C)=0.13 was obtained.

Example 4.

a) 2,4-dichloro-6-(2,6-dimethylphenoxy)1,3,5-triazine, was primarily prepared as a starting compound for producing a polytriazine according to the invention.

A solution of 18.4 g (0.1 moles) of cyanuric chloride in 200 ml of acetone was added at 0° C to a solution of 12.2 g (0.1 moles) of 2,6-dimethylphenol, 4 g of sodium hydroxide (0.1 moles) and 100 ml of water. The precipitate so obtained was filtered at 0° C 6 hours after.

After drying and crystallizing from hexane, a white powder was obtained melting at 114—115° C, Cl% 26.18 (calculated for $C_{11}H_8Cl_2N_3O$: 26.29%).

b) 27 g (0.1 moles) of 2,4-dichloro-6-(2,6-dimethylphenoxy)1,3,5-triazine as prepared in example 4 a), 33.8 g (0.1 moles) of 1,2-bis (2,2,6,6-tetramethyl-4-piperidylamino)-ethane, 8 g of sodium hydroxide and 250 ml of toluene were refluxed for 16 hours.

After filtering to remove sodium chloride and evaporating the reaction solvent a resinous substance of reduced viscosity (1% in chloroform at 25° C)=0.14 was obtained.

Example 5.

29.4 g (0.1 moles) of 2,4-dichloro-6-n-octylthio-1,3,5-triazine, 33.8 g (0.1 moles) of 1,2-bis-(2,2,6,6-tetramethyl-4-piperidylamino)-ethane, 8 g of sodium hydroxide and 250 ml of toluene were refluxed for 16 hours.

After filtering to remove sodium chloride and evaporating the reaction solvent, a resinous substance of reduced viscosity (1% in chloroform at 25° C)=0.17 was obtained.

Example 6.

35.4 g (0.09 moles) of 1,6-bis-(2,2,6,6-tetramethyl-4-piperidylamino)-hexane, 7.36 g (0.04 moles) of cyanuric chloride, 4.8 g of sodium hydroxide and 250 ml of toluene were refluxed for 16 hours.

After filtering to remove sodium hydroxide and evaporating the reaction solvent, a solid substance of reduced viscosity (1% in chloroform at 25° C)=0.10 was obtained.

Example 7.

36 g (0.1 moles) of 2,4-dichloro-6[N(2,2,6,6-tetramethyl-4-piperidyl)-n-butyl-amino]1,3,5-triazine as prepared in example 2 a) dissolved in 200 ml of acetone were added to 100 ml of water, containing in solution 12.1 g (0.11 moles) of resorcinol and 8 g of sodium hydroxide and refluxed for 16 hours.

Acetone was removed, the precipitate was filtered, washed with water and dried.

A solid product of reduced viscosity (1% in chloroform at 25° C)=0.10 was obtained.

Example 8.

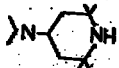
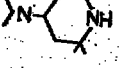
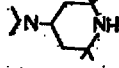
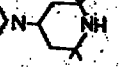
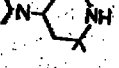
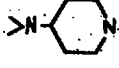
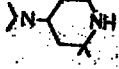
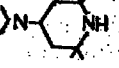
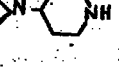
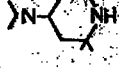
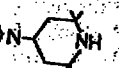
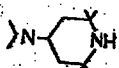
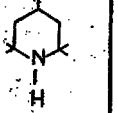
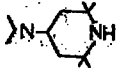
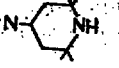
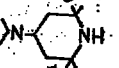
A solution of 18.4 g (0.1 moles) of cyanuric chloride in 200 ml of toluene was added at 10° C to a solution of 39.4 (0.1 moles) of 1,6-bis (2,2,6,6-tetramethyl-4-piperidylamino) hexane in 100 ml of toluene and 8 g of sodium hydroxide.

The mixture was warmed at 40° C under stirring for 12 hours.

After filtering to remove sodium chloride and evaporating the reaction solvent, a solid substance of reduced viscosity (1% in chloroform at 25° C)=0.16 was obtained.

The products as obtained in the preparation examples are summarized in the following table 1, in which the respective substituent groups are listed according to the definition of the previously specified formula (I).

TABLE 1

Example No.	X	R ¹	Y	Z	R ²	m
1		$-(CH_2)_6-$		NH	n-butyl	1
2	NH	$-(CH_2)_6-$	NH		n-butyl	1
3		$-(CH_2)_6-$			n-octyl	1
4		$-(CH_2)_2-$		-O-	2,6-dimethyl-phenyl	1
5		$-(CH_2)_2-$		-S-	n-octyl	1
6		$-(CH_2)_6-$			$-(CH_2)_6-$ 	1
7	O	m-phenylene	O		n-butyl	1
8		$-(CH_2)_6-$		-	Cl	0

Light stabilization tests.

The polytriazine compounds of formula (I) are useful and valuable agents for improving the stability to light, heat and oxidation of synthetic polymers, for example, high and low density polyethylene, polypropylene, ethylene-propylene copolymers, ethylene-vinylacetate copolymers, polybutadiene, polyisoprene, polystyrene, styrene-butadiene copolymers, acrylonitrile-butadiene-styrene copolymers, vinyl- and vinylidene chloride polymers and copolymers, polyoxymethylene, polyethylene-terephthalate, nylon 66, nylon 6, nylon 12, polyurethanes and unsaturated polyesters.

The compounds of formula (I) are particularly useful as light stabilizers for polyolefins and more particularly for polyolefin articles of manufacturing having a reduced thickness, such as fibers and films. In a surprising manner said compounds are hardly liable to be extracted from said thin articles, when brought in contact with water or an aqueous surfactant solution.

The compounds of formula (I) can be employed in a mixture with the synthetic polymers in various proportions, depending on the polymer nature, final use and presence of additional additives.

Generally it is preferable to employ from 0.01 to 5% by weight of compounds of formula (I) referred to the polymer weight, more preferably from 0.1 to 1%.

The compounds of formula (I) can be included in a polymeric material composition by various procedures, such as dry mixing in the form of powder, or by a wet process in the form of a solution or slurry. In said operation the synthetic polymer can be employed in the form of powder, granulate, solution, slurry or emulsion.

The polymers stabilized by the products of formula (I) can be used for the manufacture of molded articles, films, tapes, fibers and monofilaments.

A mixture of compounds of formula (I) and synthetic polymers can contain other optional additives, for example antioxidants, UV absorbers, nickel stabilizers, pigments, charges, plastifying agents, antistatic agents, flame retardants, lubricating agents, anticorrosive agents and metal inhibitors.

Particular examples of additives which can be employed in a mixture with the polytriazine compounds of formula (I) are:

phenolic antioxidants, for example 2,6-ditert-butyl-p-cresol, 4,4'-thiobis-(3-methyl-6-tertbutylphenol), 1,1,3-tris-(2-methyl-4-hydroxy-5-tertbutylphenyl)butane, octadecyl-3-(3,5-ditertbutyl-4-hydroxyphenyl)propionate, pentaerythritol-tetra-(3,5-ditert-butyl-4-hydroxyphenyl)-propionate, and tris-(3,5-ditert-butyl-4-hydroxybenzyl)isocyanurate;

esters of thiodipropionic acid, for example di-n-dodecyl-thiodipropionate, di-n-octadecyl-thiodipropionate and aliphatic sulfides and disulphides, for example di-n-dodecyl-sulfide, di-n-octadecyl-sulfide, di-n-octadecyl-disulfide;

aliphatic, aromatic or aliphatic-aromatic phosphites and thiophosphites, for example tri-n-dodecyl-phosphite, tris-(n-nonylphenyl)phosphite, tri-n-dodecyl-trithiophosphite, phenyl-di-n-decylphosphite, di-n-octadecyl-pentaerythritoldiphosphite;

UV absorbers, for example, 2-hydroxy-4-n-octyloxybenzophenone, 2-hydroxy-4-n-dodecylbenzophenone, 2-(2'-hydroxy-3',5'-ditert-butylphenyl)-5-chlorobenzotriazole, 2-(2'-hydroxy-3',5'-di-tert-amylphenyl)benzotriazole, 2,4-ditertbutylphenyl-3,5-ditert-butyl-4-hydroxybenzoate, phenyl-salicylate, p-tertbutylphenyl-salicylate, 2,2'-dioctyloxy-5,5'-ditertbutyloxanilide, and 2-ethoxy-5-tertbutyl-2'-ethyloxanilide;

nickel stabilizers, for example Ni monoethyl-3,5-di-tert-butyl-4-hydroxybenzylphosphonate, butylamine-Ni 2,2'-thiobis-(4-tertoctylphenolate) complex, Ni 2,2'-thiobis-(4-tertoctylphenolphenolate), Ni dibutylthiocarbamate, Ni 3,5-ditertbutyl-4-hydroxybenzoate, and Ni complex of 2-hydroxy-4-n-octyloxybenzophenone;

organo-tin compounds, for example dibutyl-tin-maleate, dibutyl-tin-laurate and di-n-octyl-tin-maleate;

acrylic esters, for example ethyl- α -cyano- β , β -diphenylacrylate and methyl- α -cyano- β -methyl-4-methoxy-cinnamate; and

metal salts of higher fat acids, for example calcium, barium, zinc, cadmium, lead and nickel stearates, calcium, cadmium, barium and zinc laurates.

In the following several examples are described in an illustrative and not limitative way, for illustrating the usefulness of the compounds of formula (I) obtained in examples 1-8, for the stabilization of synthetic polymers.

The results of the tests are listed in Tables 2, 3 and 4 and compared with tests carried out without using any stabilizer and using a known stabilizer commercially available.

Example 9.

2.5 g of each of the compounds listed in Table 2 below, dissolved in 100 ml chloroform, were mixed with 1000 g polypropylene (MOPLen* C, manufactured by

Società Montedison, Italy (* denotes Registered Trade Mark), 1 g n-octadecyl-3(3,5-ditertbutyl-4-hydroxyphenyl)propionate and 1 g calcium stearate.

The solvent was removed in an oven under vacuum at a temperature of 50° C for 4 hours.

The dry mixture so obtained was then extruded at a temperature of 200° C and made into granules, wherefrom 0.2 mm thick plates were produced by diecasting at 200° C.

Said plates were exposed in a XENOTEST* 150 apparatus at a black panel temperature of 60° C and the increase in the content of carbonyl groups was periodically determined using the not exposed specimens for balancing the polymer original absorption. The time (T.O.1) required to have a $\Delta\text{CO}\% = 0.1$ at 5.85 μm was then calculated.

As a comparison, a polymer plate was produced under the same conditions, but without addition of any light stabilizer, and another one with the addition of 2.5 g of 2-hydroxy-4-n-octyloxybenzophenone, a usual commercial stabilizer.

The results are referred in Table 2.

TABLE 2.

Stabilizer	T 0.1 (hours)
None	280
2-hydroxy-4-n-octyloxybenzophenone	900
Compound of example 1	1320
Compound of example 2	1030
Compound of example 3	1170
Compound of example 4	1240
Compound of example 5	980
Compound of example 6	1510
Compound of example 7	1050
Compound of example 8	1180

Example 10.

2 g of each of the compounds listed in Table 3 below, dissolved in 100 ml chloroform, were mixed with 1000 g of high density polyethylene (MOPLIN* RO, manufactured by Società Montedison, Italy), 0.5 g of n-octadecyl-3(3,5-ditertbutyl-4-hydroxy-phenyl)propionate and 1 g of calcium stearate.

The solvent was removed in an oven under vacuum at a temperature of 50° C for 4 hours.

The dry mixture so obtained was then extruded at a temperature of 190° C and made into granules, wherefrom by diecasting plates 0.2 mm thick were produced, said plates were exposed in a XENOTEST* 150 apparatus, as in example 9. (* denotes Registered Trade Mark).

The time T 0.05 required to have $\Delta\text{CO}\% = 0.05$ at 5.85 μm was determined.

As a comparison, under the same conditions a polymer plate was produced without addition of any light stabilizer and another was produced with addition of 2 g of 2-hydroxy-4-n-octyloxybenzophenone.

The results are referred in Table 3.

TABLE 3.

Stabilizer	T 0.05 (hours)
None	320
2-hydroxy-4-n-octyloxybenzophenone	1100
Compound of example 1	2030
Compound of example 2	1460
Compound of example 3	2180
Compound of example 4	2070
Compound of example 5	1520
Compound of example 6	2200
Compound of example 7	1710
Compound of example 8	1890

Example 11.

The polypropylene granules produced in example 9 were made into fibers under the following conditions:

Extruder temperature	250—260° C
Die temperature	250° C
Stretching ratio	1:4
Multifilament count	1020/200 den

The fibers were assembled on a white paperboard and exposed until brittleness in XENOTEST* 150 at a black panel temperature of 60° C.

Another lot of the same fibers were subjected to tests of extraction fastness under the following conditions: the fibers fixed to a stainless steel frame, were soaked into an aqueous solution containing 0.5% b.w. of a commercially available surfactant "DIXAN", under stirring at a temperature of 80° C.

After 10 hours treating, the fibers were rinsed with distilled water, dried and exposed until brittleness to the XENOTEST* 150 under the same conditions as above.

As a comparison under the same conditions, polypropylene fibers were produced and treated with addition of 0.25% by weight of 2-hydroxy-4-n-octyloxybenzophenone.

The results obtained are referred in Table 4.

TABLE 4.

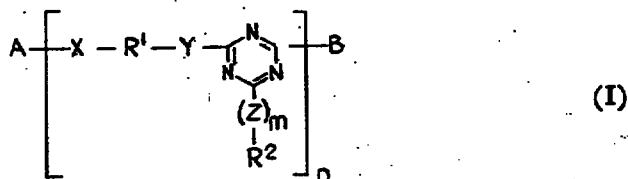
Stabilizer	Time to brittleness (hours)	
	Not treated fibers	Treated fibers
2-hydroxy-4-n-octyloxybenzophenone	670	360
Compound of example 1	1050	860
Compound of example 2	860	750
Compound of example 3	1130	930
Compound of example 4	1170	1090
Compound of example 5	980	810
Compound of example 6	1230	1110
Compound of example 7	920	800
Compound of example 8	970	830

From the test results, a considerable increase in the time required to induce a degradation in a polymer stabilized by the invention compounds can be observed with respect to the same polymer not stabilized. Furthermore, clearly improved effects induced by the invention compounds can be observed in comparison with a similar proportion of a prior art additive.

It will further appreciate from Table 4 that the stabilizers of the invention maintain a very high proportion of their activity, when the stabilized fibers have been treated so as to promote the extraction thereof from the polymer, even when the polymer is in the very thin form of a fiber or film.

WHAT WE CLAIM IS:—

1. A compound having the formula (I):



wherein X, Y and Z are the same or different and each is —O—, —S— or



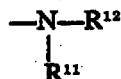
R^3 is hydrogen, a straight or branched chain C_1 to C_{18} alkyl, a C_5 to C_{18} cycloalkyl, a substituted or unsubstituted C_6 to C_{18} aryl, a C_7 to C_{18} aralkyl, or a piperidine radical of formula (II):



wherein R^4 , R^5 , R^7 and R^8 are the same or different, and each is a C_1 to C^8 alkyl, and R^6 is —H, —O, a C_1 to C_{18} straight or branched chain alkyl, a C_2 to C_{18} alkenyl or alkynyl, or a C_7 to C_{18} aralkyl;

R^1 is a C_2 to C_{18} straight or branched chain alkylene, a C_5 to C_{18} cycloalkylene, a C_6 to C_{18} arylene or a C_7 to C_{18} aralkylene or may be a direct bond when X and Y are nitrogen; and

R^2 is —H, —Cl, —Br, —OH, a C_1 to C_{18} straight or branched chain alkyl, a C_5 to C_{18} cycloalkyl, a substituted or unsubstituted C_6 to C_{18} aryl, a C_7 to C_{18} aralkyl, a piperidine radical of formula (II), or a



group wherein

R^{11} , R^{12} are selected from —H, a C_1 to C_{12} alkyl, a C_5 to C_{12} cycloalkyl, a C_6 to C_{12} aryl or a C_7 to C_{12} aralkyl;

m is 0 or 1;

n is an integer from 2 to 200;

A, B are terminal groups; and at least one of the radicals —X— R^1 —Y— and —(Z) $_m$ — R^2 in formula (I) contains a piperidine radical of formula (II).

2. A compound according to claim 1, wherein —X— R^1 —Y— represents a bivalent radical of a heterocyclic compound having 6 to 8 members and containing 2 nitrogen atoms, X and Y each represent a disubstituted nitrogen atom.

3. A compound according to claim 1, wherein the group —X— R^1 —Y— represents a residue





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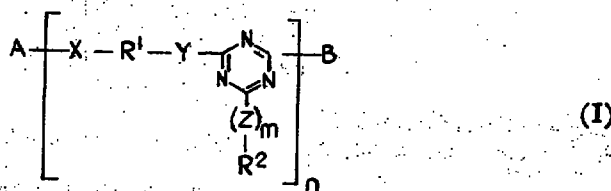
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From the test results, a considerable increase in the time required to induce a degradation in a polymer stabilized by the invention compounds can be observed with respect to the same polymer not stabilized. Furthermore, clearly improved effects induced by the invention compounds can be observed in comparison with a similar proportion of a prior art additive.

It will further appreciate from Table 4 that the stabilizers of the invention maintain a very high proportion of their activity, when the stabilized fibers have been treated so as to promote the extraction thereof from the polymer, even when the polymer is in the very thin form of a fiber or film.

WHAT WE CLAIM IS:—

1. A compound having the formula (I):



wherein X, Y and Z are the same or different and each is —O—, —S— or



R³ is hydrogen, a straight or branched chain C₁ to C₁₈ alkyl, a C₆ to C₁₈ cycloalkyl, a substituted or unsubstituted C₆ to C₁₈ aryl, a C₇ to C₁₈ aralkyl, or a piperidine radical of formula (II):



wherein R⁴, R⁵, R⁷ and R⁸ are the same or different, and each is a C₁ to C⁶ alkyl, and R⁶ is —H, —O, a C₁ to C₁₈ straight or branched chain alkyl, a C₂ to C₁₈ alkenyl or alkynyl, or a C₇ to C₁₈ aralkyl;

R¹ is a C₂ to C₁₈ straight or branched chain alkylene, a C₆ to C₁₈ cycloalkylene, a C₆ to C₁₈ arylene or a C₇ to C₁₈ aralkylene or may be a direct bond when X and Y are nitrogen; and

R² is —H, —Cl, —Br, —OH, a C₁ to C₁₈ straight or branched chain alkyl, a C₆ to C₁₈ cycloalkyl, a substituted or unsubstituted C₆ to C₁₈ aryl, a C₇ to C₁₈ aralkyl, a piperidine radical of formula (II), or a



group wherein

R¹¹, R¹² are selected from —H, a C₁ to C₁₂ alkyl, a C₆ to C₁₂ cycloalkyl, a C₆ to C₁₂ aryl or a C₇ to C₁₂ aralkyl;

m is 0 or 1;

n is an integer from 2 to 200;

A, B are terminal groups; and at least one of the radicals —X—R¹—Y— and —(Z)_m—R² in formula (I) contains a piperidine radical of formula (II).

2. A compound according to claim 1, wherein —X—R¹—Y— represents a bivalent radical of a heterocyclic compound having 6 to 8 members and containing 2 nitrogen atoms, X and Y each represent a disubstituted nitrogen atom.

3. A compound according to claim 1, wherein the group —X—R¹—Y— represents a residue





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in which R^9 and R^{10} are the same or different and each is hydrogen, a C_1 to C_{12} alkyl, a C_6 to C_{12} cycloalkyl, a C_6 to C_{12} aryl, or a C_1 to C_{12} aralkyl.

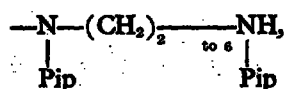
4. A compound according to claim 1, wherein m is one and the radical R^2-Z- is the same as $-X-R^1-YH$.

5. A compound according to claim 1, wherein R^3 is hydrogen, a C_1 to C_{12} straight or branched chain alkyl, or a piperidine radical of formula (II).

6. A compound according to claim 1, wherein R^3 is a straight or branched chain C_2 to C_{10} alkylene or a C_6 to C_{10} arylene.

7. A compound according to claim 1, wherein R^3 is hydrogen, a C_1 to C_{12} straight or branched chain alkyl or a piperidine radical of formula (II).

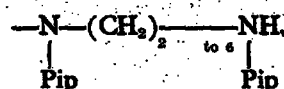
8. A compound according to claim 1, wherein the radical R^2-Z- is



Pip being a radical of formula (II).

9. A compound according to claim 1, wherein A is hydrogen and B is $-X-R^1-YH$.

10. A compound according to claim 9, wherein A is hydrogen and B is



11. A compound according to claim 1, wherein R^4 , R^5 , R^7 , R^8 are each methyl and R^6 is hydrogen or methyl.

12. A compound according to claim 1, wherein:

R^1 is a C_2 to C_{10} alkylene or a C_6 to C_8 arylene;

R^2 is $-H$, a C_1 to C_{12} alkyl or a piperidyl of formula (II);

R^3 is $-H$, a C_1 to C_{12} alkyl or a piperidyl of formula (II);

R^4 , R^5 , R^7 and R^8 are methyl;

R^6 is hydrogen or methyl;

R^9 , R^{10} , R^{11} , R^{12} are hydrogen;

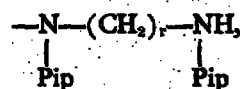
X , Y , Z represents $-O-$, $-NH-$, or



Pip being a piperidyl of formula (II);

A is H ;

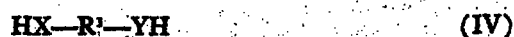
B is



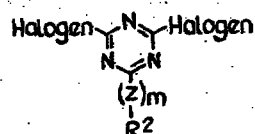
r being an integer from 2 to 6;

m is zero or one; and n is an integer from 2 to 100.

13. A method of producing a compound of the formula (I) as defined in claim 1, comprising reacting a compound of formula (IV)



wherein X , Y and R^1 are as defined in claim 1, with a) a 2,4-dihalogenotriazine of formula (III)



wherein Z and m are as defined in claim 1, or b) cyanuric halide in solution in inert



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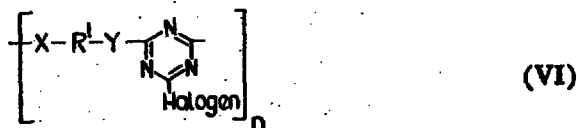
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solvent, at a temperature from -10°C to the solvent boiling temperature, in the presence of an organic or inorganic base.

14. A method according to claim 13, comprising reacting a 2,4-dihalogentriazine of formula (III) with a compound of formula (IV) in a molar ratio from 1:1.5 to 1.5:1.

15. A method according to claim 13, in which said halogen is chlorine.

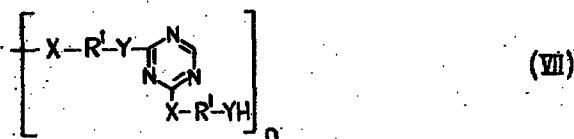
16. A method of producing a compound of the formula (I) as defined in claim 1, comprising reacting a cyanuric halide with a compound of formula (IV) in a molar ratio from 1:1 to 1:1.2, to obtain a product having the formula (VI)



in which m as defined in formula (I) is zero.

17. A method according to claim 16, wherein said product of the formula (VI) is reacted with a compound of the formula $\text{R}^2-\text{Z}-\text{H}$ to obtain a product of formula (I) in which m is one.

18. A method of producing a compound of the formula (I) as defined in claim 1, comprising reacting a cyanuric halide with a compound of formula (IV) in a molar ratio from 1:2.4 to 1:2.1 to obtain a product of formula (VII).



19. A method of increasing the light stability of a synthetic polymer, comprising adding to said synthetic polymer, an amount of a compound having the formula (I) as defined in claim 1 effective to increase the light stability of said synthetic polymer.

20. A method according to claim 19, wherein said synthetic polymer is a polyolefin.

21. A method according to claim 20, wherein said synthetic polymer is polypropylene.

22. A method according to claim 20, wherein said synthetic polymer is polyethylene.

23. A method according to claim 20, wherein said synthetic polymer is in the form of fibres of film.

24. A method according to claim 19, wherein said compound is added to the synthetic polymer in an amount from 0.1 to 1% by weight of the synthetic polymer.

25. A method according to claim 13, substantially as hereinbefore described in any one of Examples 1 to 8.

26. A method according to claim 19, substantially as hereinbefore described in any one of Examples 9 to 11.

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