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PATENT SPECIFICATION

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(54) PIPERIDYL-TRIAZINE DERIVATIVES

(71) We, CHIMOSA CHIMICA ORGANICA S.P.A., an Italian Joint Stock Company of 6/3° Via Pila, 4044 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:—

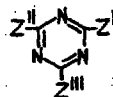
The present invention relates to piperidyl-triazine derivatives which are useful for improving the stability to light, heat and oxidation of polymeric substances.

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 source.

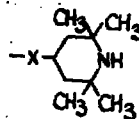
In order to improve the stability to light of said synthetic polymers, various stabilizers have been proposed, some of which have found a wide commercial acceptance in the field, such as some benzophenones, benzotriazoles, aromatic salicylates, α -cyanoacrylic acid esters, organo-tin compounds and the like, which although having a certain efficiency level, are not successful to solve the problem completely.

It is further known that some piperidine derivatives of 1,3,5-triazine can be used to protect a polymeric material from degradation due to ultraviolet light.

In particular, French patent no. 2181 059 describes triazine compounds having the general formula



wherein Z', Z'', Z''' can be, among others, piperidine radicals of the formula



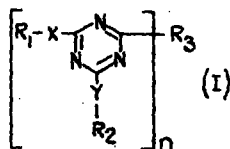
in which X is —O— or —NH—.

The above products considerably improve the light stability of polyolefins, but they are of poor utility in the application to an article of small thickness, such as fibers and films, inasmuch as they tend to be extracted by contact with water or aqueous solutions of surfactants, the stabilizer amount remaining in the polymer being no longer sufficient to provide the required light stabilization.

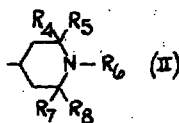
On the other hand the usual commercial light stabilizers, such as benzophenone derivatives, have a reduced effect on light stabilization in polyolefins, when used in articles of small thickness, such as fibers and films.

Therefore there is a need for more efficient light stabilizers for protection against the polymer degradation due to UV light, as well as stabilizers resistant to extraction from the polymer..

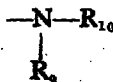
According to the present invention, there is provided a compound having the formula (I):



wherein R_1 and R_2 are the same or different and each is hydrogen, hydroxyl, straight or branched chain C_1 to C_{18} (preferably C_1 — C_{10}) alkyl, C_5 to C_{18} (preferably C_5 — C_{10}) cycloalkyl, substituted or unsubstituted C_6 to C_{18} (preferably C_6 — C_{10}) aryl, C_7 to C_{18} aralkyl, or a piperidine radical of formula (II)



in which R_4 , R_5 , R_7 and R_8 are the same or different, and each is C_1 to C_8 alkyl (preferably methyl) and R_6 is H, O, a C_1 to C_{12} alkyl (preferably methyl), or C_2 to C_{12} alkenyl or alkynyl; or R_1 and R_2 may be



in which R_9 and R_{10} are the same or different and each is hydrogen, C_1 to C_8 alkyl (preferably methyl), C_5 to C_8 cycloalkyl, or C_6 to C_8 aryl; X and Y are the same or different and each is —O—, —S— or



R_{11} being —H, straight or branched chain C_1 to C_{18} (preferably C_1 — C_{10}) alkyl, C_5 to C_{18} (preferably C_5 — C_{10}) cycloalkyl, C_6 to C_{18} (preferably C_6 — C_{10}) aryl, C_7 to C_{18} aralkyl, or a piperidine radical of formula (II); the radicals R_1 —X— and R_2 —Y—, taken as a single substituent group, may be a radical of a nitrogenous heterocyclic compound having 5 to 8 ring atoms linked to the triazine ring by means of a disubstituted nitrogen atom of said radicals, or R_1 —X— and R_2 —Y— may be Cl— or Br—; n is an integer from 2 to 6; R_3 is an n -valent residue derived from a polyalcohol, a polymercaptan or a polyamine by reaction of the active H atoms thereof with a halogen atom of a monohalo triazine; or R_3 may be R_{12} —(Z) $_n$ —, wherein R_{12} is an n -valent C_1 to C_{18} aliphatic, C_5 to C_{18} cycloaliphatic or C_6 to C_{18} aromatic radical, and Z is —O—, —S—, or

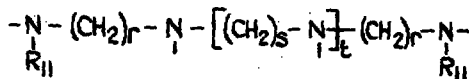


wherein R_{11} is as defined above; when $n=2$, the radical R_3 may be a divalent radical of a nitrogenous heterocyclic compound having 6 to 8 ring atoms, the disubstituted nitrogen atoms of which are linked to a triazine ring; when $n=2$, R_3 may be



in which R_{13} and R_{14} are the same or different and each is hydrogen, C_1 to C_{12} alkyl (e.g. methyl), C_5 to C_{12} cycloalkyl, C_6 to C_{12} aryl, C_7 to C_{12} aralkyl or a piperidine radical of formula (II);

when $n=3, 4, 5$ or 6 , then R_3 may be



in which R_{11} is as defined above; r and s are the same or different and each is an integer from 2 to 6, and t is 0, 1, 2 or 3, provided that at least one piperidine radical of formula (II) is present in at least one of the radicals R_1 —X—, R_2 —Y—, and R_3 .

Also according to the present invention, there is provided a method of producing a compound of the formula (I) as defined above, comprising reacting a 4,6-disubstituted 2-halogen-triazine with a polyalcohol, a polymercaptan or a polyamine in an inert solvent, at the boiling temperature of the solvent, in the presence of an organic or inorganic base, to form the corresponding compound, and recovering said compound from the mixture.

Also according to the present invention, there is provided a method of producing a compound of the formula (I) as defined above comprising reacting a 6-substituted-2,4-dihalogen-1,3,5-triazine with a compound of the formulae R_1 —XH and a compound of the formula R_2 —YH, R_1 , R_2 , X and Y being as defined above, in a molar ratio of 1:2 n, in an inert solvent, at the boiling temperature of the solvent, in the presence of an organic or inorganic base, to form the corresponding compound, and recovering said compound from the mixture.

Each of R_1 and R_2 may be H, OH, NH_2 , $\text{N}(\text{CH}_3)_2$, methyl, ethyl, isopropyl, n-butyl, isobutyl, n-hexyl, n-octyl, n-dodecyl, n-octadecyl, cyclohexyl, 3,3,5-trimethylcyclohexyl, phenyl, o-, m-, p-tolyl, 2,6-dimethylphenyl, 2,4,6-trimethylphenyl, α - or β -naphthyl, benzyl, p-methylbenzyl, 2,2,6,6-tetramethyl-5-piperidyl, 1,2,2,6,6-pentamethyl-4-piperidyl or 1-allyl-2,2,6,6-tetramethyl-4-piperidyl.

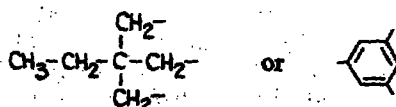
R_{11} may be hydrogen, methyl, ethyl, n-butyl, isobutyl, n-hexyl, n-octyl, n-dodecyl, n-octadecyl, cyclohexyl, 3,3,5-trimethylcyclohexyl, phenyl, p-tolyl, benzyl, 2,2,6,6-tetramethyl-4-piperidyl, 1,2,2,6,6-pentamethyl-4-piperidyl or 1-propyl-2,2,6,6-tetramethyl-4-piperidyl.

R_1 —X— and R_2 —Y—, when they represent radicals of nitrogenous heterocyclic compounds having 5 to 8 ring atoms, are preferably 1-pyrrolidinyl, 1-piperidinyl, 4-morpholinyl, 4-methyl-1-piperazinyl or 4-methyl-1-homopiperazinyl.

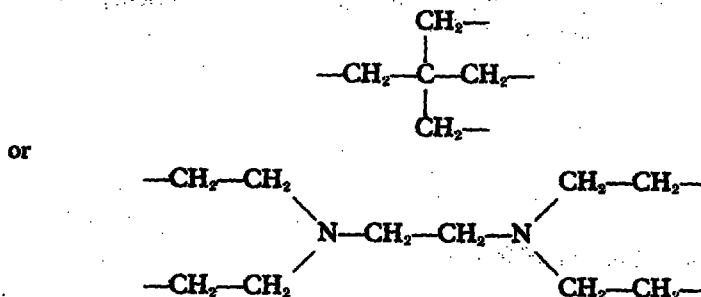
R_{12} may be C_1 to C_{10} , C_6 to C_{10} , cycloalkylene, C_6 to C_{10} , cycloalkylene, C_6 to C_{10} , arylene or C_7 to C_{10} , aralkylene.

When $n=2$, R_{12} is preferably methylene, ethylene, 1,2-propylene, trimethylene, hexamethylene, 2,2,4-trimethylhexamethylene, 2,4,4-trimethylhexamethylene, decamethylene, 1,4-cyclohexylene, 4,4'-methylenedicyclohexylene, o-, m- or p-phenylene, or o-, m- or p-xylylene.

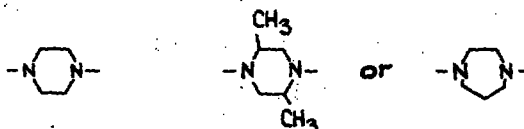
When $n=3$, R_{12} is preferably



When $n=4$, R_{12} is preferably



When $n=2$, R_3 may be a radical of a heterocyclic compound having 6 to 8 members containing 2 nitrogen atoms, such as:



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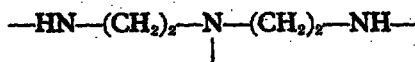
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or it can be substituted by a hydrazine radical such as —NH—NH— ,

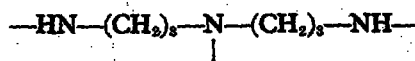


When $n=3$, R_3 may be a radical from a dialkylenetriamine, such as:



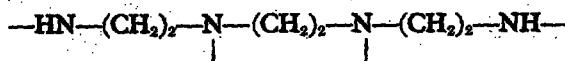
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or

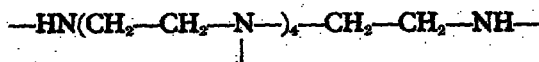


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When $n=4$, R_3 may be a radical from a trialkylenetetramine, such as:



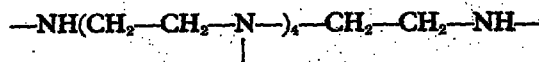
When $n=5$, R_3 may be a radical from a tetra-alkylenepentamine, such as:



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When $n=6$, R_3 may be a radical from a pentaalkylenehexamine, such as:



Preferably each of r and s is 2, 3 or 6, t is 0 and n is 2 or 3.

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Advantageously, each of X , Y and Z is —O— , >NH , N -alkyl having 1 to 6 C atoms or >N-Pip , Pip being 2,2,6,6-tetramethyl-4-piperidyl; each of R_1 and R_2 is hydrogen, C_1 to C_6 alkyl or 2,2,6,6-tetramethyl-4-piperidyl; R_3 , R_5 , R_7 and R_8 are methyl; R_6 is hydrogen; R_9 and R_{10} are hydrogen; R_{11} is hydrogen, C_1 to C_6 alkyl or 2,2,6,6-tetramethyl-4-piperidyl; and C_{12} is C_2 to C_6 alkylene.

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Alternatively, each of X , Y and Z is —O— , >NH , >N-alkyl having 1 to 6 C atoms, >N-Pip , Pip being 2,2,6,6-tetramethyl-4-piperidyl; each of R_1 and R_2 is hydrogen, C_1 to C_6 alkyl or 2,2,6,6-tetramethyl-4-piperidyl; R_3 , R_5 , R_7 and R_8 are methyl; R_6 is hydrogen; R_9 and R_{10} are hydrogen; R_{11} is hydrogen, C_1 to C_6 alkyl or 2,2,6,6-tetramethyl-4-piperidyl; and R_{13} and R_{14} are hydrogen.

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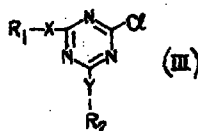
Alternatively, each of X , Y and Z is —O— , >NH , >N-alkyl having 1 to 6 C atoms, >N-Pip , Pip being 2,2,6,6-tetramethyl-4-piperidyl; each of R_1 and R_2 is hydrogen, C_1 to C_6 alkyl or 2,2,6,6-tetramethyl-4-piperidyl; R_3 , R_5 , R_7 and R_8 are methyl; R_6 is hydrogen; R_9 and R_{10} are hydrogen; R_{11} is hydrogen, C_1 to C_6 alkyl or 2,2,6,6-tetramethyl-4-piperidyl; each of r and s is 2 or 3, t is 0, and n is 2 or 3.

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The triazine compounds of formula (I) can be prepared by reacting a 4,6-disubstituted-2-halogen-1,3,5-triazine of formula

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with a polyfunctional compound of formula



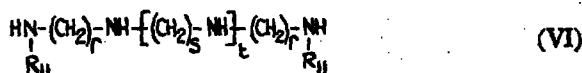
or with a hydrazine of formula



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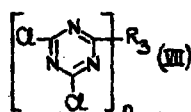
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or with a polyamine of formula



The molar ratio of the reactant of formula (III) to the reactant of formula (IV) is preferably n:1, the molar ratio of the reactant of formula (III) to the reactant of formula (V) is preferably 2:1, the molar ratio of the reactant of formula (III) to the reactant of formula (VI) is preferably one mole of (III) per one amine group of the polyamine (VI); in each case it is possible to employ the reactant of formula (III) in excess to ensure complete reaction.

An alternative process for the preparation of compounds of formula (I) comprises reacting a 6-substituted-2,4-dichloro-1,3,5-triazine of formula



with a compound having the formula



and a compound having the formula



In such a case, the molar ratio of reactants (VIII) and (IX) to dichlorotriazine (VII) is 2n:1, but it is possible to employ an excess of reactants R_1-XH , R_2-YH to assure a complete reaction.

The reactions of halogenotriazines (III) or (VII) with the compounds of formula (IV), (V), (VI), (VIII, IX) respectively are carried out in the presence of inert solvents such as acetone, dioxane, toluene, xylene, at the boiling temperature of the solvent.

The reactions are carried out in the presence of an organic or inorganic base in order to fix hydrogen halide; there can be used for example: triethylamine, or tributylamine; sodium hydroxide, carbonate or bicarbonate; potassium hydroxide or carbonate; sodium alcoholates in the case of the compounds of formula (IV) or formulae (VIII) and (IX) are alcohols; sodium mercaptides in the case where the reactants of formula (IV) or formulae (VIII and IX) are mercaptans; it is also possible to use an amine excess in the case where a product of formula (VII) is reacted with the compounds of formulae (VIII and IX) in which X and Y represent



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

Example 1

A) 2-chloro-4,6-bis(2,6-dimethylphenoxy)-1,3,5-triazine was prepared according to the teachings of German patent publication no. 2307 777.

55.3 g (0.3 moles) of cyanuric chloride dissolved in 300 ml of acetone were added within 30 minutes at 20-25°C to a solution of 73.2 g (0.6 moles) of 2,6-dimethylphenol, 24 g (0.6 moles) of sodium hydroxide and 340 ml of water.

The mixture was stirred for three hours at the same temperature and the precipitate so obtained was removed by filtration, washed, dried and crystallized from petroleum ether: a white powder melting at 159-160°C was obtained.

B) Preparation of N,N' - bis(2,2,6,6 - tetramethyl - 4 - piperidyl) - N,N' - bis[2,4 - bis(2,6 - dimethylphenoxy) - 1,3,5 - triazin - 6 - yl]hexamethylene diamine.

35.5 g (0.1 mole) of 2-chloro-4,6-bis(2,6-dimethylphenoxy)-1,3,5-triazine, 19.7 g (0.05 moles) of 1,6-bis(2,2,6,6-tetramethyl-4-piperidylamino)hexane, 4 g (0.1 mole) of sodium hydroxide and 250 ml of xylol were boiled for 16 hours under stirring. The

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reaction solvent was removed, the residue was washed with water, dried at 100°C/1 mm and crystallized from anhydrous ethanol.

A white solid melting at 224—229°C, N % = 13.34 (calculated for $C_{62}H_{84}N_{10}O_4 = 13.55\%$) was obtained.

Example 2

A) 2 - chloro - 4,6 - bis(2,2,6,6 - tetramethyl - 4 - piperidylamino) - 1,3,5 - triazine was prepared according to the French patent 2181 059.

18.45 (0.1 mole) cyanuric chloride, slurried into 600 ml water, were added to 31.2 g (0.2 moles) of 4-amino-2,2,6,6-tetramethylpiperidine and a solution of 8 g (0.2 moles) of sodium hydroxide in 20 ml water. The mixture was stirred for 30 minutes at room temperature, then it was heated to 90°C for 16 hours.

After cooling, the precipitate was removed by filtration, washed and dried under vacuum. A white powder melting at 277—278°C was obtained.

Preparation of

B) N,N' - bis[2,4 - bis(2,2,6,6 - tetramethyl - 4 - piperidylamino) - 1,3,5 - triazin - 6 - yl]hexamethylenediamine:

42.3 (0.1 mole) of 2-chloro-4,6-bis(2,2,6,6-tetramethyl-4-piperidylamino)-1,3,5-triazine, 5.8 g (0.05 moles) of hexamethylenediamine, 4 g (0.1 moles) of sodium hydroxide and 500 ml of xylene were boiled for 16 hours under stirring. After removing the reaction solvent, the residue was washed with water, dried at 100°C/1 mm and crystallized from methylethylketone.

A white solid melting at 153—156°C was obtained. N % = 24.66 (calculated for $C_{48}H_{80}N_{16} = 25.16\%$).

Example 3

A) Preparation of 2 - chloro - 4,6 - bis - (n - butylamino) - 1,3,5 - triazine as starting compound:

a mixture of 18.45 g (0.1 mole) of cyanuric chloride, 180 ml of acetone and 160 g of ice was added to 14.6 (0.2 moles) of n-butylamine dissolved in 100 ml acetone. The mixture temperature was raised to 30°C, then 8 g (0.2 moles) of sodium hydroxide dissolved in 100 ml of water were added.

The mixture was stirred for 6 hours at 30—35°C, then the precipitate so obtained was filtered, washed with water and dried on anhydrous $CaCl_2$. A white powder melting at 209—212°C was obtained, chlorine % = 13.70 calculated, for $C_{11}H_{20}ClN_3 = 13.81\%$.

B) Preparation of N,N' - bis(2,2,6,6 - tetramethyl - 4 - piperidyl) - N,N' - bis[2,4 - bis - (n - butylamino) - 1,3,5 - triazin - 6 - yl]ethylene diamine:

51.5 (0.2 moles) of 2 - chloro - 4,6 - bis - n - butylamino - 1,3,5 - triazine, 33.8 g (0.1 mole) of 1,2 - bis(2,2,6,6 - tetramethyl - 4 - piperidylamino)ethane, 8 g (0.2 moles) of sodium hydroxide and 500 ml of xylene were boiled for 16 hours under stirring. After removing the reaction solvent, the residue was washed with water, dried at 100°C/1 mm and crystallized from methyl-ethyl-ketone.

A white solid melting at 143—45°C was obtained. N % = 24.51 (calculated for $C_{42}H_{80}N_{14} = 25.12\%$).

Example 4

Preparation of N,N' - bis(2,2,6,6 - tetramethyl - 4 - piperidyl) - N,N' - bis[2,4 - bis(2,2,6,6 - tetramethyl - 4 - piperidylamino) - 1,3,5 - triazin - 6 - yl]ethylene diamine.

21.15 g (0.05 moles) of 2-chloro-4,6-bis(2,2,6,6-tetramethyl-4-piperidylamino)-1,3,5-triazine (prepared according to example 2A), 8.45 g (0.025 moles) of 1,2-bis(2,2,6,6-tetramethyl-4-piperidylamino)ethane, 2 g (0.05) of sodium hydroxide and 150 ml of xylene were boiled for 16 hours under stirring. After removing the reaction solvent, the residue was washed with water, dried at 100°C/1 mm and crystallized from benzene.

A white solid melting at 325—328°C was obtained. N % = 22.14 (calculated for $C_{62}H_{110}N_{18} = 22.66\%$).

Example 5

Preparation of N,N' - bis[2,4 - bis(2,2,6,6 - tetramethyl - 4 - piperidylamino) - 1,3,5 - triazin - 6 - yl]ethylenediamine.

42.3 (0.1 mole) of 2-chloro-4,6-bis(2,2,6,6-tetramethyl-4-piperidylamino)-1,3,5-triazine (prepared according to example 2A), 3 g (0.05 moles) of ethylenediamine, 4 g of sodium hydroxide and 150 ml of xylene were boiled for 16 hours under stirring.

After removing the reaction solvent, the residue was washed with water, dried at

100°C/1 mm and crystallized from methanol. A white solid melting at 290—292°C was obtained. N % = 26.09 (calculated for $C_{44}H_{82}N_{16}$ = 26.83%).

Example 6

A) Preparation of N,N'-bis(2,4-dichloro-1,3,5-triazin-6-yl)piperazine.

36.9 (0.2 moles) of cyanuric chloride dissolved in 200 ml of acetone were added to a solution of 8.6 g (0.1 mole) of anhydrous piperazine in 50 ml of acetone at 0—5°C within 30 minutes. It was stirred for 30 minutes at 0—5°C, then a solution of 8 g (0.2 moles) of NaOH in 50 ml of water were added within 30 minutes at the same temperature. It was stirred again for 4 hours at 0—5°C, then it was diluted with 100 ml of ice water, filtered, washed with water and dried on anhydrous $CaCl_2$. A white powder melting at >300°C was obtained, chlorine % 37.32 (calculated for $C_{10}H_8Cl_4N_8$ = 37.17%).
(CH_2)₂-N-(CH

B) Preparation of N,N' - bis[2,4 - bis[N(2,2,6,6 - tetramethyl - 4 - piperidyl) - n - butylamino] - 1,3,5 - triazin - 6 - yl] - piperazine.

19.1 g (0.05 moles) of N,N' - bis(2,4 - dichloro - 1,3,5 - triazin - 6 - yl)piperazine, 46.6 g (0.22 moles) of 2,2,6,6-tetramethyl-4-(n-butyl-amino)piperidine, 80 ml of xylene and 8 g (0.2 moles) of NaOH were heated at reflux temperature for 16 hours. After removing the reaction solvent, the residue was washed with water, dried at 100°C/1 mm and crystallized from methylethylketone.

A white crystalline product melting at 272—275°C was obtained, N % 20.37 (calculated for $C_{82}H_{116}N_{16} \cdot H_2O$ = 20.32%).

Example 7

A) Preparation of 2 - chloro - 4,6 - bis - [N(2,2,6,6 - tetramethyl - 4 - piperidyl) - ethylamino] - 1,3,5 - triazine.

A mixture of 92.2 g (0.5 moles) of cyanuric chloride, 500 ml of acetone and 160 g of ice was added to 184 g (1 mole) of 2,2,6,6 - tetramethyl - 4 - ethylaminopiperidine dissolved in 100 ml of acetone.

The mixture temperature was raised to 35°C, then 40 g (1 mole) of sodium hydroxide dissolved in 100 ml of water were added. The mixture was stirred for 6 hours at 35—40°C, then the precipitate so obtained was filtered, washed with water and dried on anhydrous $CaCl_2$. After crystallization from acetone a white crystalline powder melting at 127—129°C was obtained, chlorine % = 7.36 (calculated for $C_{26}H_{46}ClN_7$ = 7.40).

B) Preparation of N,N',N'' - tris[2,4 - bis[N(2,2,6,6 - tetramethyl - 4 - piperidyl)ethylamino]1,3,5 - triazin - 6 - yl] - diethylenetriamine.

143.8 g (0.3 moles) of 2 - chloro - 4,6 - bis - [N(2,2,6,6 - tetramethyl - 4 - piperidyl)ethylamino]1,3,5 - triazine, 10.3 g (0.1 mole) of diethylenetriamine, 12 g of sodium hydroxide and 450 ml of xylene were boiled for 16 hours under stirring.

After filtration, the solution was stirred at room temperature with 50 ml of water. A white precipitate, melting at 145—150°C, was obtained. N % = 22.78 calculated for $C_{79}H_{149}N_{24} \cdot H_2O$ = 23.13%).

The piperidyl triazine derivatives of formula (I) are useful and valuable agents for improving the stability to light, heat and oxidation of synthetic polymers such as, 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, unsaturated polyesters.

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 be optionally added with other additives, such as 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 compounds of formula (I) are:

phenolic antioxidants, such as 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, tris-(3,5 - ditert - butyl - 4 - hydroxybenzyl)isocyanurate;

esters of thiodipropionic acid, such as di - n - dodecyl - thiodipropionate, di - n - octadecyl - thiodipropionate, aliphatic sulfides and disulfides, such as di - n - dodecyl - sulfide, di - n - octadecyl - sulfide, di - n - octadecyl - disulfide;

aliphatic, aromatic or aliphatic - aromatic phosphites and thiophosphites, such as tri - n - dodecyl - phosphite, tris - (n - nonylphenyl)phosphite, tri - n - dodecyl - tri - thiophosphite, phenyl - di - n - decylphosphite, di - n - octadecylpentaerythritoldi - phosphite;

UV absorbers such as 2 - hydroxy - 4 - n - octyloxybenzophenone, 2 - hydroxy - 4 - n - dodecyloxybenzophenone, 2 - (2' - hydroxy - 3',5' - ditert - butylphenyl)5 - chlorobenzotriazole, 2 - (2' - hydroxy - 3',5' - di - tert - amylphenyl)benzotriazole, 2,4 - ditertbutylphenyl - 3,5 - ditertbutyl - 4 - hydroxybenzoate, phenyl - salicylate, p - tert - butylphenyl - salicylate, 2,2' - dioctyloxy - 5,5' - ditertbutyloxanilide, 2 - ethoxy - 5 - tert - butyl - 2' - ethyloxanilide;

nickel stabilizers such as Ni monoethyl - 3,5 - ditertbutyl - 4 - hydroxybenzyl - phosphonate, butylamine - Ni 2,2' - thiobis - (4 - tertoctylphenolate) complex, Ni 2,2' - thio - bis - (4 - tertoctylphenolphenolate), Ni dibutyldithiocarbamate, Ni 3,5 - ditert - butyl - 4 - hydroxybenzoate, Ni complex of 2 - hydroxy - 4 - n - octyloxybenzophenone; organo-tin compounds, such as dibutyl - tin - maleate, dibutyl - tin - laurate, di - n - octyl - tin - maleate;

acrylic esters, such as ethyl - α - cyano - β , β - diphenylacrylate, methyl - α - cyano - β - methyl - 4 - methoxy - cinnamate;

metal salts of higher fat acids, such as calcium, barium, zinc, cadmium, lead, nickel stearates, calcium cadmium, barium, 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—7, for the stabilization of synthetic polymers.

The results of the tests are listed in the tables and compared with tests carried out without using any stabilizer and using a known stabilizer commercially available.

Example 8

2.5 g of each of the compounds listed in table 1 below, dissolved in 100 ml chloroform, were mixed with 1000 g polypropylene Moplen C (Regd. Trade Mark), manufactured by Società Montedison, Italy], 1 g n - octadecyl - 3(3,5 - ditert.butyl-4 - hydroxy - phenyl)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 0.1) 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 1.

TABLE 1

Stabilizer	T 0.1 (hours)
None	280
2-hydroxy-4-n-octyloxybenzophenone	900
Compound of example 1	1170
Compound of example 2	1550
Compound of example 3	1460
Compound of example 4	1780
Compound of example 5	1680
Compound of example 6	1600
Compound of example 7	1570

Example 9

2 g of each of the compounds listed in table 2 below, dissolved in 100 ml chloroform, were mixed with 1000 g of high density polyethylene Moplen (Registered Trade Mark) RO, manufactured by Società Montedison, Italy), 0.5 g of n-octadecyl-3-(3,5-ditert.butyl-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 at 200°C plates 0.2 mm thick were produced, said plates were exposed in a Xenotest 150 apparatus, as in example 8.

The time T 0.05 required to have $\Delta CO\% = 0.05$ at $5.85 \mu m$ was determined.

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

The results are referred in table 2.

TABLE 2

Stabilizer	T 0.05 (hours)
None	320
2-hydroxy-4-n-octyloxybenzophenone	1100
Compound of example 1	1750
Compound of example 2	2300
Compound of example 3	2080
Compound of example 4	2360
Compound of example 5	2210
Compound of example 6	2190
Compound of example 7	2270

Example 10

The polypropylene granules produced in example 8 were made into fibers under the following conditions:

Extruder temperature	250—260°C
Die temperature	250°C
Stretching ratio	1:4
Multifilament count	1080/200 den

The fibers were assembled on a white paperboard and exposed until brittleness in a 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 (Registered Trade Mark), with 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, and
- 0.25% by weight of 2,4,6 - tris(2,2,6,6 - tetramethyl - 4 - piperidylamino)-

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1,3,5 - triazine, as an example of French patent 2181 059. The results obtained are referred in table 3.

TABLE 3

5	Stabilizer	Time to brittleness (hours)		5
		Not treated fibers	Treated fibers	
	a)	670	360	
	b)	1080	380	
10	Compound of example 1	950	780	10
	Compound of example 2	1160	960	
	Compound of example 3	1020	810	
	Compound of example 4	1250	1040	
	Compound of example 5	1090	870	
15	Compound of example 6	1170	920	15
	Compound of example 7	1190	870	

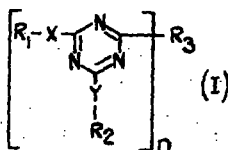
From the test results, a considerable increase in the time required to induce a degradation in a polymer stabilized by the invention compounds can be observed with respect to the same polymer not stabilized.

Furthermore, clearly improved effects induced by the invention compounds can be observed in comparison with a similar proportion of a prior art additive.

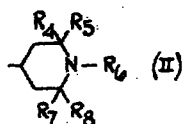
It will be further appreciated from table 3 that the stabilizers of the invention maintain a very high proportion of their activity, when the stabilized fibers have been treated so as to promote the extraction thereof from the polymer, even when the polymer is in the very thin form of a fiber or film.

WHAT WE CLAIM IS:—

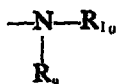
1. A compound having the formula



wherein R_1 and R_2 are the same or different and each is hydrogen, hydroxyl, straight or branched chain C_1 to C_{18} alkyl, C_5 to C_{18} cycloalkyl, substituted or unsubstituted C_6 to C_{18} aryl, C_7 to C_{18} aralkyl, or a piperidine radical of formula (II)



in which R_4 , R_5 , R_7 and R_8 are the same or different and each is C_1 to C_8 alkyl and R_6 is H, O, C_1 to C_{12} alkyl, or C_2 to C_{12} alkenyl or alkynyl, or R_1 and R_2 may be



in which R_9 and R_{10} are the same or different and each is hydrogen, C_1 to C_8 alkyl, C_5 to C_8 cycloalkyl, or C_6 to C_8 aryl;

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



R_{11} being H, straight or branched chain C_1 to C_{18} alkyl, C_5 to C_{18} cycloalkyl, C_6 to C_{18} aryl, C_7 to C_{18} aralkyl or a piperidine radical of formula (II); R_1-X- and R_2-Y- , taken as a single substituent group, may be a radical of a nitrogenous heterocyclic compound having 5 to 8 ring atoms linked to the triazine ring by means of a disubstituted nitrogen atom of said radical, or R_1-X- and R_2-Y- may be Cl— or Br—; n is an integer from 2 to 6; R_3 is an n-valent residue derived from a poly-

1,3,5 - triazine, as an example of French patent 2181 059. The results obtained are referred in table 3.

TABLE 3

Time to brittleness (hours)

5	Stabilizer	Not treated	Treated fibers	5
		fibers		
	a)	670	360	
	b)	1080	380	
10	Compound of example 1	950	780	10
	Compound of example 2	1160	960	
	Compound of example 3	1020	810	
	Compound of example 4	1250	1040	
	Compound of example 5	1090	870	
15	Compound of example 6	1170	920	15
	Compound of example 7	1190	870	

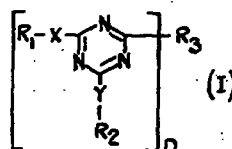
From the test results, a considerable increase in the time required to induce a degradation in a polymer stabilized by the invention compounds can be observed with respect to the same polymer not stabilized.

Furthermore, clearly improved effects induced by the invention compounds can be observed in comparison with a similar proportion of a prior art additive.

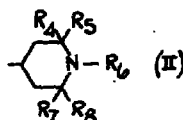
It will be further appreciated from table 3 that the stabilizers of the invention maintain a very high proportion of their activity, when the stabilized fibers have been treated so as to promote the extraction thereof from the polymer, even when the polymer is in the very thin form of a fiber or film.

WHAT WE CLAIM IS:—

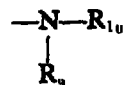
1. A compound having the formula



wherein R_1 and R_2 are the same or different and each is hydrogen, hydroxyl, straight or branched chain C_1 to C_{18} alkyl, C_5 to C_{18} cycloalkyl, substituted or unsubstituted C_6 to C_{18} aryl, C_7 to C_{18} aralkyl, or a piperidine radical of formula (II)



in which 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, C_1 to C_{12} alkyl, or C_2 to C_{12} alkenyl or alkynyl, or R_1 and R_2 may be



in which R_9 and R_{10} are the same or different and each is hydrogen, C_1 to C_6 alkyl, C_5 to C_6 cycloalkyl, or C_6 to C_8 aryl;

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



R_{11} being H, straight or branched chain C_1 to C_{18} alkyl, C_5 to C_{18} cycloalkyl, C_6 to C_{18} aryl, C_7 to C_{18} aralkyl or a piperidine radical of formula (II); R_1-X- and R_2-Y- , taken as a single substituent group, may be a radical of a nitrogenous heterocyclic compound having 5 to 8 ring atoms linked to the triazine ring by means of a disubstituted nitrogen atom of said radical, or R_1-X- and R_2-Y- may be Cl— or Br—; n is an integer from 2 to 6; R_3 is an n-valent residue derived from a poly-



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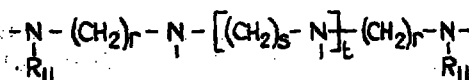
alcohol, a polymercaptan or a polyamine by reaction of the active H atoms thereof with a halogen atom of a monohalo triazine; or R_3 may be $R_{12}-(Z)-n$, where R_{12} is an n -valent C_1 to C_{18} aliphatic, C_5 to C_{18} cycloaliphatic or C_6 to C_{18} aromatic radical, and Z is $-O-$, $-S-$ or



R_{11} being as defined above; when $n=2$, radical R_3 may be a divalent radical of a nitrogenous heterocyclic compound having 6 to 8 ring atoms, the disubstituted nitrogen atoms of which are linked to a triazine ring; when $n=2$, radical R_3 may be



in which R_{13} and R_{14} are the same or different, and each is hydrogen, C_1 to C_{12} alkyl, C_5 to C_{12} cycloalkyl, C_6 to C_{12} aryl, C_7 to C_{12} aralkyl, or a piperidine radical of formula (II); when $n=3, 4, 5$, or 6 then R_3 may be



wherein R_{11} is as defined above, r and s are the same or different and each is an integer from 2 to 6, and t is 0, 1, 2 or 3, provided that at least one piperidine radical of formula (II) is present in at least one of the radicals R_1-X- , R_2-Y- , and R_3 .

2. A compound according to claim 1, in which R_{11} is hydrogen, straight or branched chain C_1 to C_{10} alkyl, C_6 to C_{10} cycloalkyl, C_6 to C_{10} aryl, or a piperidine radical of formula (II).

3. A compound according to claim 1, wherein R_1 and R_2 are the same or different and each is selected from hydrogen, C_1 to C_{10} alkyl, C_5 to C_{10} cycloalkyl, C_6 to C_{10} aryl, or a piperidine radical of formula (II).

4. A compound according to claim 1, in which R_4 , R_5 , R_7 and R_8 are each methyl and R_6 is hydrogen or methyl.

5. A compound according to claim 1, wherein R_9 and R_{10} are hydrogen or methyl.

6. A compound according to claim 1, in which R_{12} is C_1 to C_{10} alkylene, C_6 to C_{10} cycloalkylene, C_6 to C_{10} arylene, or C_7 to C_{10} aralkylene.

7. A compound according to claim 1, in which said divalent heterocyclic radical is piperazin-1,4-diyl.

8. A compound according to claim 1, wherein R_{13} and R_{14} are hydrogen or methyl.

9. A compound according to claim 1, wherein each of r and s is 2, 3 or 6, t is 0 and n is 2 or 3.

10. A compound according to claim 1, in which each of X , Y and Z is $-O-$, $>NH$, $>N$ -alkyl having 1 to 6 C atoms or $>N$ -Pip, Pip being 2,2,6,6-tetramethyl-4-piperidyl; each of R_1 and R_2 is hydrogen, C_1 to C_6 alkyl or 2,2,6,6-tetramethyl-4-piperidyl; R_4 , R_5 , R_7 and R_8 are methyl; R_6 is hydrogen; R_9 and R_{10} are hydrogen; R_{11} is hydrogen, C_1 to C_6 alkyl or 2,2,6,6-tetramethyl-4-piperidyl; and R_{12} is C_2 to C_6 alkylene.

11. A compound according to claim 1, in which each of X , Y and Z is $-O-$, $>NH$, $>N$ -alkyl having 1 to 6 C atoms, $>N$ -Pip, Pip being 2,2,6,6-tetramethyl-4-piperidyl; each of R_1 and R_2 is hydrogen, C_1 to C_6 alkyl or 2,2,6,6-tetramethyl-4-piperidyl; R_4 , R_5 , R_7 and R_8 are methyl; R_6 is hydrogen; R_9 and R_{10} are hydrogen; R_{11} is hydrogen, C_1 to C_6 alkyl or 2,2,6,6-tetramethyl-4-piperidyl; and R_{13} and R_{14} are hydrogen.

12. A compound according to claim 1, wherein each of X , Y and Z is $-O-$, $>NH$, $>N$ -alkyl having 1 to 6 C atoms, $>N$ -Pip, Pip being 2,2,6,6-tetramethyl-4-piperidyl; each R_1 and R_2 is hydrogen, C_1 to C_6 alkyl or 2,2,6,6-tetramethyl-4-piperidyl; R_4 , R_5 , R_7 and R_8 are methyl; R_6 is hydrogen; R_9 and R_{10} are hydrogen; R_{11} is hydrogen, C_1 to C_6 alkyl or 2,2,6,6-tetramethyl-4-piperidyl; each of r and s is 2 or 3, t is 0, and n is 2 or 3.

13. A method for producing a compound of the formula (I) as claimed in claim 1, comprising reacting a 4,6-disubstituted 2-halogen-triazine with a polyalcohol, a poly-

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mercaptan or a polyamine in an inert solvent, at the boiling temperature of the solvent, in the presence of an organic or inorganic base to form the corresponding compound, and recovering said compound from the mixture.

14. A method according to claim 13, wherein the polyalcohol, polymercaptan or the polyamine has the formula $R_{12}-(ZH)_n$, wherein R_{12} and Z are as defined in claim 1, the molar ratio of 4,6-disubstituted-2-halogen-triazine to the compound of formula $R_{12}-(ZH)_n$ being $n:1$.

15. A method according to claim 13, wherein the polyamine is a hydrazine having the formula

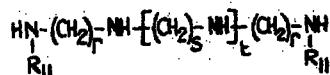
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wherein R_{13} and R_{14} are as defined in claim 1, the molar ratio of 4,6-disubstituted-2-halogen-triazine to hydrazine being 2:1.

16. A method according to claim 13, wherein the polyamine has the formula



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wherein r , s and t are as defined in claim 1, the molar ratio of 4,6-disubstituted-2-halogen-triazine to polyamine being 1 mole of the halogen-triazine per 1 amine group of polyamine, or in excess of that ratio.

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17. A method for producing a compound having the formula (I) as claimed in claim 1, comprising reacting a 6-substituted-2,4-dihalogen-1,3,5-triazine with a compound of the formula R_1-XH and a compound of the formula R_2-YH , R_1 , R_2 , X and Y being as defined in claim 1, in a molar ratio of 1:2 n , in an inert solvent, at the boiling temperature of the solvent, in the presence of an organic or inorganic base, to form the corresponding compound, and recovering said compound from the mixture.

18. 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 claimed in any one of claims 1 to 12 effective to increase the light stability of said synthetic polymer.

19. A method according to claim 18, wherein said synthetic polymer is a polyolefin.

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

21. A method according to claim 19, wherein said synthetic polymer is polyethylene.

22. A method according to claim 19, wherein said synthetic polymer is in the form of fibers or film.

23. A method according to claim 18, wherein said compound is added to the synthetic polymer in an amount from 0.1 to 1% by weight of the synthetic polymer.

24. A method of producing a compound of the formula (I) as claimed in claim 1, substantially as hereinbefore described in any one of Examples 1 to 7.

25. A method as claimed in claim 18, substantially as hereinbefore described in any one of Examples 8 to 10.

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