

2-(2-Hydroxy-3,5-disubstituted phenyl)-2H-benzotriazole, and mixtures stabilized therewith

The present invention relates to 2-aryl-2H-benzotriazoles and their use as light stabilisers for organic material and to stabilised mixtures.

The invention also relates to a process for the preparation of o-nitroazobenzene intermediates which can be converted to the corresponding 2-aryl-2H-benzotriazole.

UV absorbers of the o-hydroxyphenyl-2H-benzotriazole type have for a long time enjoyed a considerable economic interest as light stabilisers for organic material.

Compounds of this type and their preparation and the use of these valuable 2-aryl-2H-benzotriazoles are known, for example, from the following patent specifications: U.S. 3,004,896, U.S. 3,055,896, U.S. 3,072,585, U.S. 3,074,910, U.S. 3,189,615 and U.S. 3,230,194. However, these stabilisers have poor compatibility in certain substrates. They have a strong tendency to exude and sublime and/or to volatilise during processing to sheets, films, fibres and the like at high temperatures. In this way, a disproportionately large proportion of the benzotriazole stabiliser is lost, especially in the case of extremely thin films and coatings. This also applies if the films or coatings are exposed to elevated temperature during use.

Attempts have been made to improve the compatibility and to reduce the stabiliser loss by structural

modification of the benzotriazole.

U.S. Patent Specification 3,230,194 describes benzotriazoles substituted by a long-chain alkyl group instead of by a methyl group, in particular 2-[2-hydroxy-5-tert.-octylphenyl]-2H-benzotriazole, which has excellent compatibility and an excellent stabilising action in polyethylene.

U.S. Patent Specification 4,127,586 describes other modifications of 2-aryl-2H-benzotriazoles for improvement of the processing characteristics. Thus, the compound 2-[2-hydroxy-3-(1-phenylethyl)-5-methylphenyl]-2H-benzotriazole shows better compatibility and a lower loss due to volatilisation during processing than the benzotriazole compounds known up to that time.

Light stabilisers of the benzotriazole type, for example 2-[2-hydroxy-3- α,α -dimethylbenzyl-5-methylphenyl]-2H-benzotriazole, have likewise been disclosed in Japanese Kokai 158,588/75.

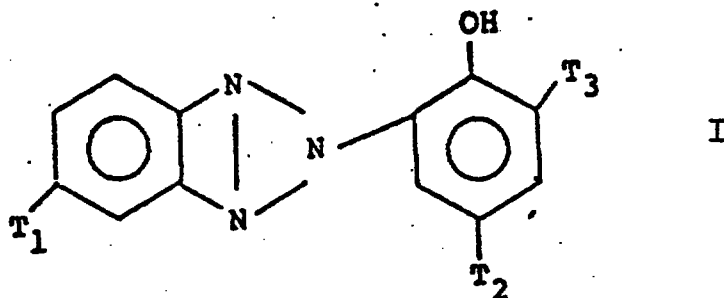
Attempts are also being made to improve the processing characteristics of the benzotriazoles during processing at high temperatures.

The compounds according to the invention, for example 2-[hydroxy-3,5-di-(α,α -dimethylbenzyl)phenyl]-2H-benzotriazole, surprisingly show little loss during high-temperature processing or in the end use of the compounds, where the stabilised mixtures are continually exposed, in the form of films and coatings, to the effects of weathering and light.

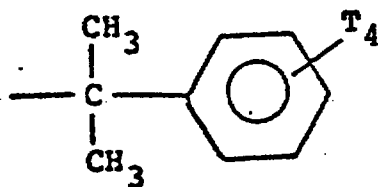
U.S. Patent Specification 4,041,044 describes an improved process for the preparation of the 2-aryl-2H-benzotriazoles, but does not describe the compounds according to the invention.

The present invention relates to 2-aryl-2H-benzotriazoles as light stabilisers and to organic monomers and polymers stabilised with 2-aryl-2H-benzotriazoles.

The invention relates especially to compounds of the formula I



in which T_1 is hydrogen or chlorine and T_2 and T_3 independently of one another are the group



in which T_4 is hydrogen or lower alkyl, and one of T_2 and T_3 can also be t-octyl.

Lower alkyl T_4 is located in particular in the meta- or para-position, preferably in the para-position. Typical alkyl radicals are those having 1-6 C atoms, such as methyl, ethyl, i-propyl, t-butyl, t-amyl and 3-methylpentyl.

Preferred compounds are those in which T_2 and T_3 have the same meaning and T_4 is hydrogen or p-methyl.

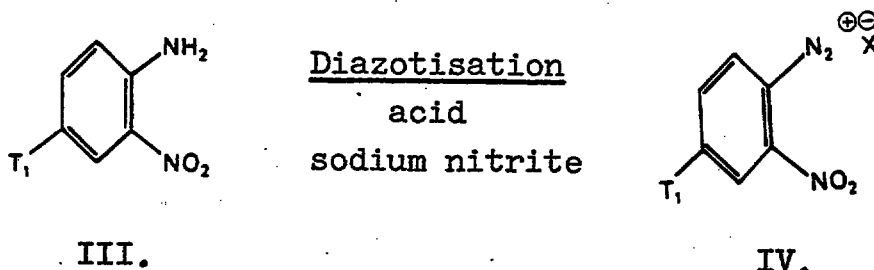
Particularly preferentially, T_4 is hydrogen.

A particularly preferred compound is 2-[2-hydroxy-3,5-di-(α,α -dimethyl-benzyl)-phenyl]-2H-benzotriazole.

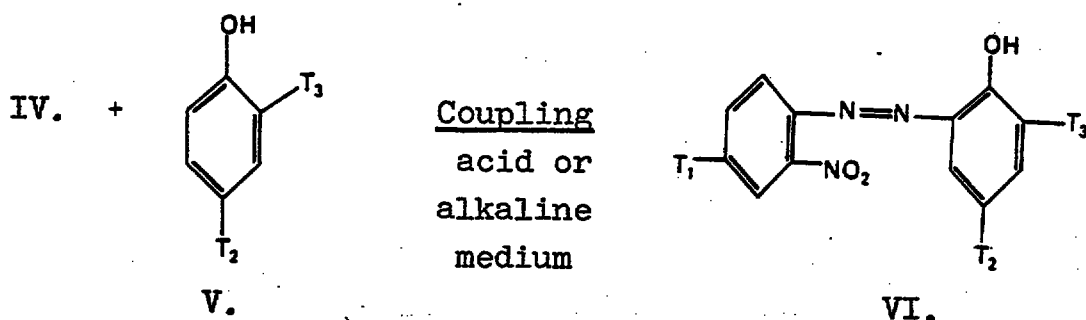
Particularly preferred compounds are 2-[2-hydroxy-3-t-octyl-5-(α,α -dimethyl-benzyl)-phenyl]-2H-benzotriazole and 2-[2-hydroxy-3-(α,α -dimethyl-benzyl)-5-t-octylphenyl]-2H-benzotriazole.

The compounds according to the invention are prepared as follows:

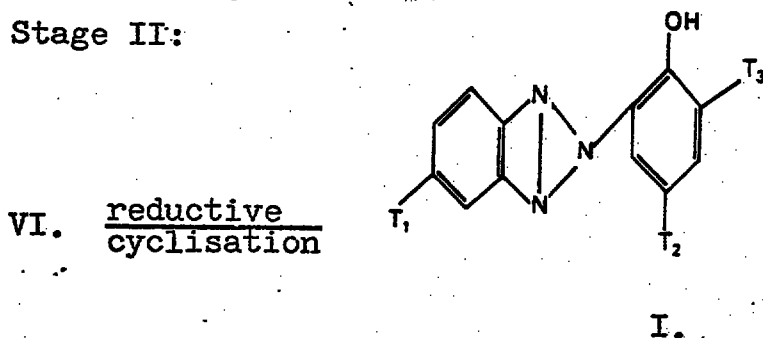
Stage I:



X is an anion, for example chloride or sulfate.



Stage II:



T₁, T₂ and T₃ are as defined above.

Stage 1 The coupling of the diazonium compound can be effected in an acid or alkaline medium. If the coupled phenol carries an aralkyl group in the ortho-position relative to the hydroxyl group and the reaction is carried out in an acid medium, the yield of o-nitroazobenzene VI. is 50% less than theory.

Surprisingly, more than 80% of theory of the intermediate VI. is obtained if the coupling reaction is carried out in a strongly alkaline medium (pH > 11).

Stage 2 The reductive cyclisation of VI. to 2-aryl-2H-benzotriazole can be effected by one of the known reduction methods, for example zinc and NaOH, hydrazine or catalytic hydrogenation with a noble metal catalyst.

The use of these agents results in good benzotriazole yields.

The invention also relates to a process for the preparation of o-nitroazobenzene intermediates which can be converted to the corresponding 2-aryl-2H-benzotriazole.

The process according to the invention relates to the coupling of a substituted phenol with diazotised aniline in a strongly alkaline alkanol. A minimum of water in the reaction mixture is advantageous for the solubility of the substituted phenol.

The process according to the invention differs from the prior art in the use of alkali metal hydroxide in an excess which far exceeds the stoichiometric amount which is necessary to neutralise the resulting diazonium salt and to form a salt with the phenol. Accordingly, the coupling reaction is carried out in the presence of excess hydroxyl ions and at a pH value of more than 11.

The teaching of the prior art is that strongly alkaline coupling processes should be avoided. The success with which the coupling process of this specification has been carried out is therefore particularly surprising.

The coupling of phenols with a diazonium salt under weakly alkaline conditions is a known method for the preparation of aromatic azo derivatives. In "Basic Principles of Organic Chemistry" by J.D. Roberts and M.C. Caserio, W.A. Benjamin, Inc. New York (1965), page 893-895, it is emphasised that the coupling process proceeds in an optimum manner at about pH 10 but virtually ceases at higher pH values.

It is also known that o-nitrobenzenediazonium salt solutions are unstable in the presence of alcohol and alkali metal hydroxide and decompose rapidly with the evolution of N_2 . For this reason, the teaching of the prior art is that coupling reactions in excess alkali metal hydroxide should be avoided. cf. Fierz-David et al., "Fundamental Processes of Dye Chemistry", Inter-

science, New York (1949), page 239-241, 252-253.

H. Zollinger in "Azo and Diazo Chemistry", Interscience, New York (1961), page 249-250, reports that when a coupling reaction is carried out under strongly alkaline conditions the equilibrium shifts away from the diazonium ions.

Soviet Union Patent Specification 360,357 describes the coupling of a sodium phenolate in weakly alkaline solution with excess acid diazonium salt so that the pH rapidly falls below the value of 11 during the reaction, which is absolutely contrary to the reaction conditions according to the invention.

In contrast to the teaching of the prior art, o-nitroazobenzene is obtained in high yield and in high purity if the reaction is carried out in a strongly alkaline medium and in the presence of a lower alkanol as the solvent.

The preparation of a o-nitroazobenzene intermediate which is used to prepare 2-aryl-2H-benzotriazole light stabilisers is the subject of a part application.

The compounds according to the invention are effective light stabilisers for a large number of organic polymers. Such polymers are:

1. Polymers which are derived from mono- or diolefins, for example polyethylene, which can be cross-linked, polypropylene, polyisobutylene, polymethylbut-1-ene, polymethylpent-1-ene, polyisoprene and polybutadiene.
2. Mixtures of the homopolymers listed under 1), for example mixtures of polypropylene and polyethylene, of polypropylene and polybut-1-ene and of polypropylene and polyisobutylene.
3. Copolymers of the monomers for the homopolymers listed under 1), for example ethylene/propylene copolymer, propylene/but-1-ene copolymer, propylene/isobutylene copolymer and ethylene/but-1-ene copolymer and also terpolymers of ethylene and propylene with a diene, for example hexadiene, dicyclopentadiene or ethylidene-

norbornene, and copolymers of α -olefins, for example ethylene with acrylic acid or methacrylic acid.

4. Polystyrene.

5. Copolymers of styrene and of α -methylstyrene, for example styrene/butadiene copolymer, styrene/acrylonitrile copolymer, styrene/acrylonitrile/methacrylate copolymer and styrene/acrylonitrile copolymer modified with acrylate polymer, for example styrene/butadiene/styrene block copolymer.

6. Graft copolymers of styrene, for example the graft polymer of styrene on polybutadiene, the graft polymer of styrene with acrylonitrile on polybutadiene and mixtures thereof with the copolymers listed under 5), known as acrylonitrile/butadiene/styrene or ABS.

7. Halogen-containing vinyl polymers, for example polyvinyl chloride, polyvinylidene chloride, polyvinyl fluoride, polychloroprene, chlorinated rubber, vinyl chloride/vinylidene chloride copolymer, vinyl chloride/vinyl acetate copolymer and vinylidene chloride/vinyl acetate copolymer.

8. Polymers which are derived from α, β -unsaturated acids and their derivatives, such as polyacrylates and polymethacrylates, polyacrylamides and polyacrylonitrile. The compounds according to the invention are advantageously used in heat-curable acrylic resin lacquers which consist of an acrylic acid and a melamine/formaldehyde resin.

9. Polymers prepared from unsaturated alcohols and amines and from their acyl derivatives or acetals, for example polyvinyl alcohol, polyvinyl acetate, polyvinyl stearate, polyvinyl benzoate, polyvinyl maleate, polyvinylbutyral, polyallyl phthalate, polyallylmelamine and their copolymers with other vinyl compounds, for example ethylene/vinyl acetate copolymer.

10. Homopolymers and copolymers prepared from epoxides, for example polyethylene oxide or the polymers of the bisglycidyl ethers.

11. Polyacetals, for example polyoxymethylene, and also polyoxymethylenes which contain ethylene oxide as the comonomer.
12. Polyalkylene oxides, for example polyoxyethylene, polypropylene oxide or polyisobutylene oxide.
13. Polyphenylene oxides.
14. Polyurethanes and polyureas, such as in urethane coatings.
15. Polycarbonates.
16. Polysulfones.
17. Polyamides and copolyamides prepared from diamines and dicarboxylic acids and/or from aminocarboxylic acids or their lactams, for example polyamide 6, polyamide 6/6, polyamide 6/10, polyamide 11, polyamide 12 and poly-m-phenylene-isophthalamide.
18. Polyesters of dicarboxylic acids and dialcohols and/or of hydroxycarboxylic acids or their lactones, for example polyethylene glycol terephthalate and poly-1,4-dimethylol-cyclohexane terephthalate.
19. Crosslinked polymers obtained from aldehydes on the one hand and from phenols, ureas and melamine on the other hand, for example phenol/formaldehyde, urea/formaldehyde and melamine/formaldehyde resin.
20. Alkyd resins, for example glycerol/phthalic acid resins and their mixtures with melamine/formaldehyde resins.
21. Unsaturated polyester resins obtained from the copolyesters of saturated and unsaturated dicarboxylic acids with polyhydric alcohols and also from vinyl compounds as crosslinking agents, and their halogen-containing, flame-resistant modifications.
22. Naturally occurring polymers, for example cellulose and rubber and also their chemically modified homologue derivatives, for example cellulose acetates, cellulose propionates and cellulose butyrates and the cellulose ethers, for example methylcellulose.

The compounds according to the invention are not only effective light stabilisers, like the 2-aryl-2H-

benzotriazoles in general, but, by virtue of their surprisingly low loss due to volatilisation at high temperature, are also particularly valuable for stabilising polymeric substrates which have to be processed at high temperatures.

The compounds according to the invention are therefore particularly suitable for stabilising polymers, for example polyethylene terephthalate and polybutylene terephthalate or copolymers thereof, polycarbonates, for example obtained from bisphenol A and phosgene, or copolymers thereof, polysulfones, polyamides, for example nylon-6, nylon-6,6, nylon-6/10 and the like, and also copolyamides, thermosetting acrylic resins, thermoplastic acrylic resins, polyolefins, for example polyethylene and polypropylene, copolyolefins and the like, and other polymers which require high-temperature processing and production.

The stabilisers of the formulae I. and II. are incorporated in the polymer by the conventional methods and in particular are incorporated in any phase during the production of shaped products. For example, they can be mixed in the form of a powder, suspension or emulsion into the polymer, which can be in the form of a powder, suspension or emulsion.

If desired, 0.1 to 5% by weight and preferably 0.5 to 3% by weight of the conventional additives, especially antioxidants and light stabilisers, or mixtures thereof, can be added to the stabilised polymeric mixtures of the invention. Examples of such additives are: antioxidants, UV-absorbers and light stabilisers, such as 2-(2'-hydroxyphenyl)-benzotriazoles, 2,4-bis-(2'-hydroxyphenyl)-6-alkyl-s-triazines, 2-hydroxybenzophenones, 1,3-bis-(2'-hydroxybenzoyl)-benzenes, esters of substituted or unsubstituted benzoic acids, and acrylates, and also nickel compounds, sterically hindered amines, oxalic acid diamides, metal deactivators, phosphites, compounds which destroy peroxide, polyamide stabilisers, basic co-

stabilisers, nucleating agents or other additives, for example plasticisers, lubricants, emulsifiers, fillers, carbon black, asbestos, kaolin, talc, glass fibres, pigments, fluorescent brighteners, flameproofing agents and antistatic agents.

Certain hydrophobic, non-diffusing hydroxyphenyl-benzotriazoles are known as UV absorbers in photographic gelatin. (U.S. Patent Specification 3,253,921 and U.S. Patent Specification 4,042,394). By virtue of their low volatility, by virtue of their good absorption characteristics in the UV range and by virtue of their photographic inactivity, the compounds according to the invention are particularly suitable for stabilising coloured images.

The thermosetting and thermoplastic acrylic resins, which are used for lacquer coatings on vehicles, are of particular interest. These substances are described on pages 273-276 of Volume 1 (1964) and on pages 530-532 of Volume 13 (1970) of the Encyclopedia of Polymer Science and Technology, Interscience Publishers, New York, and also in "Understanding Paint" by W.R. Fuller, in American Paint Journal Co., St. Louis, 1965, pages 124-135.

Acrylic resin lacquers, which are stabilised according to the invention against the action of light, oxygen and humidity, are the customary stoving lacquers, such as are described, for example, in H. Kittel's "Lehrbuch der Lacke und Beschichtungen" ("Textbook on Lacquers and Coatings"), Volume 1, part 2, pages 735 and 742 (Berlin, 1972) and in H. Wagner and H.F. Sarx "Lackkunstharze" ("Synthetic Resins for Lacquers"), pages 229-235.

Stabilisation, with the compounds according to the invention, of the lacquers based on hot-crosslinkable acrylic resin and styrene is of particular interest. Despite the excellent physical and chemical properties, metal-effect lacquer produced from these resins is unsuitable, since the styrene present results in crazing.

Other lacquers and coatings based on acrylic/melamine resin and alkyd/acrylic/melamine resin are also of interest.

In order to achieve the metal effect, the customary aluminium pigments are used in amounts of 1-10% by weight, based on the solvent-free binder (lacquer resin). The stabilised lacquers can be applied by the conventional one-coat or two-coat processes. In the latter case, the base-coat lacquer containing pigment is first applied and is then coated with clear lacquer.

Further additives which can be contained in the lacquer are other customary light stabilisers, phenolic antioxidants, pigments, dyes, metal deactivators and the like.

In general, the stabilisers used according to the invention make up 0.1 to 5% by weight and preferably 0.5 to 3% by weight, based on the lacquer resin.

The combination of sterically hindered amines and the stabilisers according to the invention enables not only excellent gloss retention but also resistance to flaking off to be imparted to the metallised stoving lacquers which are based on acrylic resin and are used for the top lacquer coats on motorcars.

The sterically hindered amines act as light stabilisers in the acrylic resin lacquers and are responsible for their gloss retention on weathering. However, if no UV absorber is present, UV light can pass through the top coat without hindrance and result in damage in the lower epoxy ester coating. This is successfully prevented by the addition of the benzotriazole UV absorbers according to the invention.

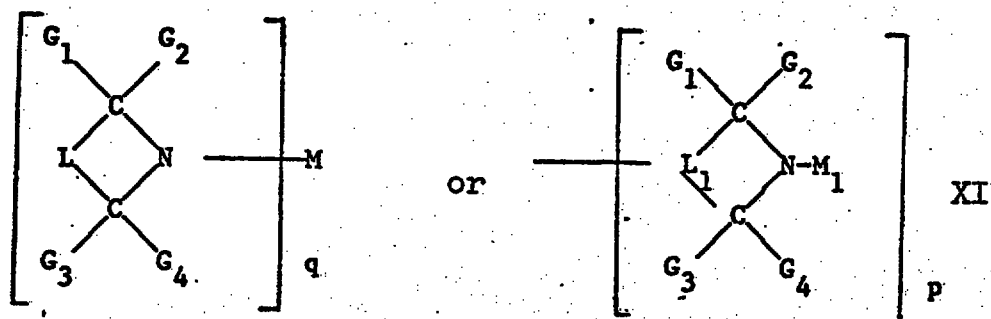
In this way, the combination of sterically hindered amines with benzotriazoles offers not only gloss retention but also resistance to flaking off in metallised top coat lacquers based on acrylic resins.

The amines employed are effective in amounts of 0.1 to 5% by weight, preferably of 0.5 to 2% by weight

and especially of 0.5 to 1% by weight, based on the acrylic resin.

The benzotriazoles according to the invention are effective in amounts of 0.1 to 5% by weight, preferably of 0.5 to 2% by weight and especially of 0.5 to 1% by weight, based on the acrylic resin.

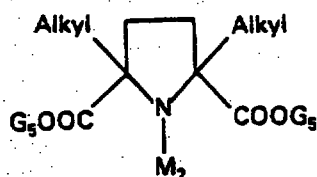
The amine light stabilisers which are used in this invention have the formula XI.



in which q is 1 or 2, p is 2 to 14 and G_1 , G_2 , G_3 and G_4 independently of one another are alkyl, or G_1 and G_3 together form an alkylene, or are each carboalkoxy or carbophenethoxy, or G_1 and G_2 or G_3 and G_4 , independently of one another, together form an alkylene or azaalkylene; if q is 1, M is hydrogen, hydroxyl, oxyl, substituted or unsubstituted alkyl, alkenyl, alkynyl, aralkyl, alkanoyl, alkenoyl, benzoyl, glycidyl or $-\text{CH}_2\text{CHOHZ}$, in which Z is hydrogen, methyl or phenyl, and if q is 2, M is alkylene, alkenylene, alkynylene, arylenedialkylene or the group $-(\text{CH}_2)_{18}\text{OOCR}_{18}\text{COO}(\text{CH}_2)_2-$ or the group $-\text{CH}_2\text{OOOCR}_{19}\text{COOCH}_2-$, in which R_{18} is alkylene and R_{19} is alkylene, xylylene or cyclohexylene, and M_1 has the meaning defined for M where q is 1, L is a divalent organic radical which makes up the N-containing ring to a 5-membered to 7-membered ring, or

is two monovalent radicals, and L_1 is a divalent organic radical which makes up the N-containing ring to a 5-membered to 7-membered ring and which additionally can be linked by a linking group to other amine groupings.

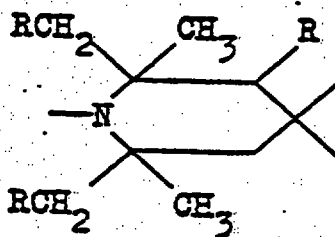
Suitable amines are the compounds of the following formula



XII

in which G_5 is hydrogen, alkyl or phenethyl and M_2 is hydrogen, hydroxyl, oxyl, alkyl, 2-methoxyethyl, alkenyl or propargyl.

2,2,6,6-Tetraalkylpiperidine compounds are preferably used and these preferably contain a group of the formula XIII

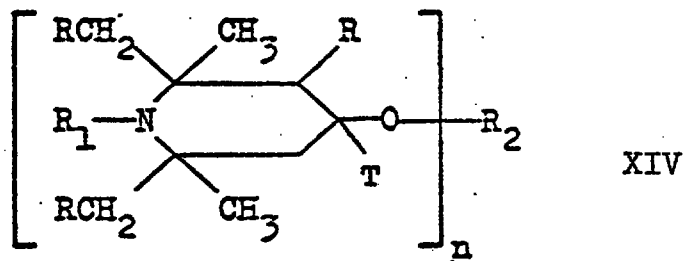


XIII

in which R is hydrogen or methyl.

The light stabilisers to be used according to the invention include, in particular, the following categories of compounds:

a) light stabilisers of the formula XIV



in which n is the numbers 1-4 and preferably 1 or 2, T is hydrogen or $-\text{CONH}_2$, R is as defined for formula XIII, R_1 is hydrogen, oxyl, $\text{C}_1\text{-C}_{18}$ alkyl, $\text{C}_3\text{-C}_8$ alkenyl, $\text{C}_3\text{-C}_8$ alkynyl, $\text{C}_7\text{-C}_{12}$ aralkyl, $\text{C}_1\text{-C}_8$ alkenoyl, glycidyl or a group $-\text{CH}_2\text{CH}(\text{OH})\text{-Z}$, in which Z is hydrogen, methyl, ethyl or phenyl, R_1 preferably being hydrogen, $\text{C}_1\text{-C}_{12}$ alkyl, allyl, benzyl, acetyl or acryloyl, and R_2 , if $n=1$, is hydrogen, $\text{C}_1\text{-C}_{18}$ alkyl, which can be interrupted by one or more oxygen atoms, cyanoethyl, benzyl, glycidyl, a monovalent radical of an aliphatic, cycloaliphatic, araliphatic, aromatic or heterocyclic carboxylic acid, carbamic acid or phosphorus-containing acid or a monovalent silyl radical, preferably a radical of an aliphatic carboxylic acid having 2-18 C atoms, of a cycloaliphatic carboxylic acid having 5-12 C atoms or of an aromatic carboxylic acid having 5-15 C atoms, and, if $n = 2$, is $\text{C}_1\text{-C}_{12}$ alkylene, $\text{C}_4\text{-C}_{12}$ alkenylene, xylylene, a divalent radical of an aliphatic, cycloaliphatic, araliphatic, aromatic or heterocyclic dicarboxylic acid, dicarbamic acid or phosphorus-containing acid or a divalent silyl radical, preferably a radical of an aliphatic dicarboxylic acid having 2-36 C atoms, of a cycloaliphatic or aromatic dicarboxylic acid having 8-10 C atoms or of an aliphatic, cycloaliphatic or aromatic dicarbamic acid having 8-10 C atoms, and, if $n = 3$, is a trivalent radical of an aliphatic, cycloaliphatic, aromatic or heterocyclic

tricarboxylic acid, of an aromatic tricarbamic acid or of a phosphorus-containing acid or a trivalent silyl radical and, if $n=4$, is a tetravalent radical of an aliphatic, cycloaliphatic or aromatic tetracarboxylic acid.

Any C_1-C_{12} alkyl substituents are, for example, methyl, ethyl, n-propyl, n-butyl, sec.-butyl, tert.-butyl, n-hexyl, n-octyl, 2-ethyl-hexyl, n-nonyl, n-decyl, n-undecyl or n-dodecyl.

C_1-C_{18} Alkyl R_1 or R_2 can be, for example, the groups listed above and also, for example, n-tridecyl, n-tetradecyl, n-hexadecyl or n-octadecyl.

C_2-C_8 Alkenyl R_1 can be, for example, 1-propenyl, allyl, methallyl, 2-butenyl, 2-pentenyl, 2-hexenyl, 2-octenyl or 4-tert.-butyl-2-butenyl.

C_3-C_8 Alkynyl R_1 is preferably propargyl.

C_7-C_{12} Aralkyl R_1 is especially phenethyl or in particular benzyl.

C_1-C_8 Alkanoyl R_1 is, for example, formyl, propionyl, butyryl or octanoyl, but preferably acetyl, and C_3-C_5 alkenoyl R_1 is in particular acryloyl.

As a monovalent radical of a carboxylic acid, R_2 is, for example, an acetic acid, stearic acid, salicylic acid, methacrylic acid, maleic acid, benzoic acid or β -(3,5-di-tert.-butyl-4-hydroxyphenyl)-propionic acid radical.

As a divalent radical of a dicarboxylic acid, R_2 is, for example, an adipic acid, suberic acid, sebacic acid, phthalic acid, dibutylmalonic acid, dibenzylmalonic acid, butyl-(3,5-di-tert.-butyl-4-hydroxybenzyl)-malonic acid or bicycloheptenedicarboxylic acid radical.

As a trivalent radical of a tricarboxylic acid, R_2 is, for example, a trimellitic acid radical or a nitrilotriacetic acid radical.

R_2 can also be radicals of di- and tri-carboxylic acids such as are prepared industrially by oligomerisation of higher unsaturated fatty acids or by a Diels-Alder addition of acrylic acid onto linoleic acid. Further-

more, R_2 can also be radicals which are formed by the reaction of mono-, di- and poly-epoxides, for example bis-phenol A diglycidyl ether, butanediol diglycidyl ether, tris-glycidyl isocyanurate or 1,3-diglycidyl-4,4-dimethylhydantoin, with 4-hydroxy-1,2,2,6,6-pentamethylpiperidine.

As a tetravalent radical of a tetracarboxylic acid, R_2 is, for example, a pyromellitic acid radical.

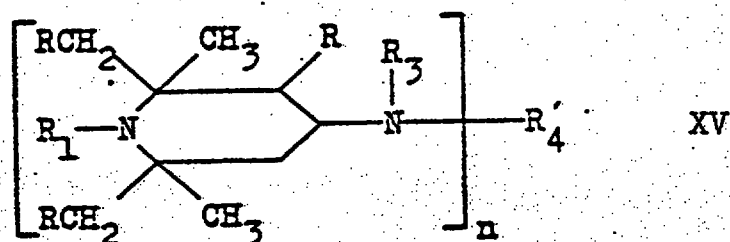
As a divalent radical of a dicarbamic acid, R_2 is, for example, a hexamethylenedicarbamic acid radical or a 2,4-toluylene-dicarbamic acid radical.

Examples of polyalkylpiperidine light stabilisers of this category are the following compounds:

- 1) 4-hydroxy-2,2,6,6-tetramethylpiperidine
- 2) 1-allyl-4-hydroxy-2,2,6,6-tetramethylpiperidine
- 3) 1-benzyl-4-hydroxy-2,2,6,6-tetramethylpiperidine
- 4) 1-(4-tert.-butyl-2-butenyl)-4-hydroxy-2,2,6,6-tetramethylpiperidine
- 5) 4-stearoyloxy-2,2,6,6-tetramethylpiperidine
- 6) 1-ethyl-4-salicyloyloxy-2,2,6,6-tetramethylpiperidine
- 7) 4-methacryloyloxy-1,2,2,6,6-pentamethylpiperidine
- 8) 1,2,2,6,6-pentamethylpiperidin-4-yl β -(3,5-di-tert.-butyl-4-hydroxyphenyl)-propionate
- 9) 1-benzyl-2,2,6,6-tetramethyl-4-piperidinyl maleate
- 10) bis-(2,2,6,6-tetramethylpiperidin-4-yl) adipate
- 11) bis-(2,2,6,6-tetramethylpiperidin-4-yl) sebacate
- 12) bis-(1,2,3,6-tetramethyl-2,6-diethyl-piperidin-4-yl) sebacate
- 13) bis-(1-allyl-2,2,6,6-tetramethyl-piperidin-4-yl) phthalate
- 14) 1-propargyl-4- β -cyanoethyloxy-2,2,6,6-tetramethylpiperidine
- 15) 1-acetyl-2,2,6,6-tetramethylpiperidin-4-yl acetate
- 16) tri-(2,2,6,6-tetramethylpiperidin-4-yl) trimellitate
- 17) 1-acryloyl-4-benzyloxy-2,2,6,6-tetramethylpiperidine
- 18) di-(1,2,2,6,6-pentamethylpiperidin-4-yl) dibutylmalonate
- 19) di-(1,2,2,6,6-pentamethylpiperidin-4-yl) butyl-(3,5-

- di-tert.-butyl-4-hydroxybenzyl)-malonate
- 20) di-(1,2,2,6,6-pentamethylpiperidin-4-yl) dibenzyl-malonate
- 21) di-(1,2,3,6-tetramethyl-2,6-diethyl-piperidin-4-yl) dibenzyl-malonate
- 22) hexane-1',6'-bis-(4-carbamoyloxy-1-n-butyl-2,2,6,6-tetramethylpiperidine)
- 23) toluene-2',4'-bis-(4-carbamoyloxy-1-n-propyl-2,2,6,6-tetramethylpiperidine)
- 24) dimethyl-bis-(2,2,6,6-tetramethylpiperidin-4-oxy)-silane
- 25) phenyl-tris-(2,2,6,6-tetramethylpiperidin-4-oxy)-silane
- 26) tris-(1-propyl-2,2,6,6-tetramethylpiperidin-4-yl) phosphite
- 27) tris-(1-propyl-2,2,6,6-tetramethylpiperidin-4-yl) phosphate
- 28) phenyl bis-(1,2,2,6,6-pentamethylpiperidin-4-yl) phosphonate
- 29) bis-(1,2,2,6,6-pentamethylpiperidin-4-yl) sebacate
- 30) bis-(1-benzyl-2,2,6,6-tetramethylpiperidin-4-yl) sebacate
- 31) bis-(1-allyl-2,2,6,6-tetramethylpiperidin-4-yl) sebacate
- 31a) 2,2,6,6-tetramethyl-4-hydroxy-4-carbamoyl-piperidine
- 32) 4-benzoyloxy-2,2,6,6-tetramethylpiperidine
- 33) 4-acryloxy-2,2,6,6-tetramethylpiperidine
- 34) 4-(p-chlorobenzoyloxy)-1,2,2,6,6-pentamethylpiperidine
- 35) 4-lauroyloxy-1,2,2,6,6-pentamethylpiperidine
- 36) 1-allyl-2,2,6,6-tetramethyl-4-piperidinyl salicylate
- 37) 1-(2-benzoyloxyethyl)-2,2,6,6-tetramethyl-4-piperidinyl benzoate
- 38) bis-(1,2,2,6,6-pentamethyl-4-piperidinyl) isophthalate
- 39) bis-(1,2,2,6,6-pentamethyl-4-piperidinyl) adipate
- 40) bis-(1-acetyl-2,2,6,6-tetramethyl-4-piperidinyl) sebacate
- 41) bis-(1-hydroxyethyl-2,2,6,6-tetramethyl-4-piperidinyl)

- succinate
- 42) tris-(2,2,6,6-tetramethyl-4-piperidiny) nitrilotriacetate
- 43) tris-(1-butyl-2,2,6,6-tetramethyl-4-piperidiny) trimellitate
- 44) tris-(1-butyl-2,2,6,6-tetramethyl-4-piperidiny) phosphate
- 45) diphenyl-bis-(2,2,6,6-tetramethylpiperidin-4-oxy)-silane
- 46) 0,0'-di-(2,2,6,6-tetramethyl-4-piperidiny) tolylene-1,4-dicarbamate
- 47) 1-methylcarbamoyl-2,3,6-trimethyl-2,6-diethyl-4-piperidiny methylcarbamate.
- b) Light stabilisers of the formula XV



in which n is the number 1 or 2, R is as defined for formula XIII, R₁ is as defined under a), R₃ is hydrogen, C₁-C₁₂ alkyl, C₅-C₇ cycloalkyl, C₇-C₈ aralkyl, C₂-C₁₈ alkanoyl, C₃-C₅ alkenoyl, or benzoyl and R₄, if n = 1, is hydrogen, C₁-C₁₈ alkyl, C₅-C₇ cycloalkyl, C₂-C₈ alkenyl, which is unsubstituted or substituted by a cyano, carbonyl or carbamide group, glycidyl or a group of the formula -CH₂-CH(OH)-Z or of the formula -CONH-Z, in which Z is hydrogen, methyl or phenyl; and, if n = 2, is C₂-C₁₂ alkylene, C₆-C₁₂ arylene, xylylene, a -CH₂-CH(OH)-CH₂ group or a group -CH₂-CH(OH)-CH₂-O-X-O-CH₂-CH(OH)-CH₂-, in which X is C₂-C₁₀ alkylene, C₆-C₁₅ arylene or C₆-C₁₂ cycloalkylene, or, if R₃ is not alkanoyl, alkenoyl or benzoyl, R₄ can also be a divalent radical of an aliphatic, cycloaliphatic or aromatic dicarboxylic acid or dicarbamic acid or the group -CO-, or R₃ and R₄ together, if n = 1, can be the imide radical of an aliphatic, cycloaliphatic

or aromatic 1,2- or 1,3-dicarboxylic acid.

Any C₁-C₁₈ alkyl substituents have the meaning already defined under a).

Any C₅-C₇ cycloalkyl substituents are in particular cyclohexyl.

C₇-C₈ Aralkyl R₃ is especially phenethyl or in particular benzyl.

C₂-C₁₈ Alkanoyl R₃ is, for example, propionyl, butyryl, octanoyl, dodecanoyl, hexadecanoyl or octadecanoyl, but preferably acetyl, and C₃-C₅ alkenoyl R₃ is in particular acryloyl.

As C₂-C₈ alkenyl which is unsubstituted or substituted by a cyano, carbonyl or carbamide group, R₄ is, for example, 1-propenyl, allyl, methallyl, 2-butenyl, 2-pentenyl, 2-hexenyl, 2-octenyl, 2,2-dicyanovinyl, 1-methyl-2-cyano-2-methoxycarbonyl-vinyl or 2,2-diacetylaminovinyl.

Any C₂-C₁₂ alkylene substituents are, for example, ethylene, propylene, 2,2-dimethylpropylene, tetramethylene, hexamethylene, octamethylene, decamethylene or dodecamethylene.

Any C₆-C₁₅ arylene substituents are, for example, o-, m- or p-phenylene, 1,4-naphthylene or 4,4'-diphenylene.

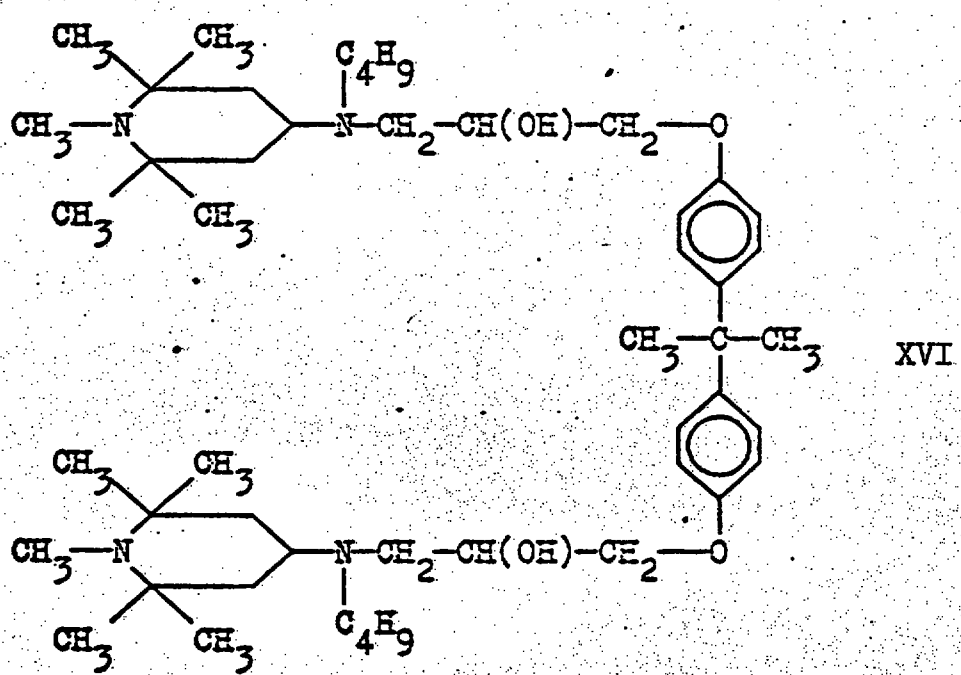
C₆-C₁₂ Cycloalkylene X is in particular cyclohexylene.

Examples of polyalkylpiperidine light stabilisers of this category are the following compounds:

- 48) N,N'-bis-(2,2,6,6-tetramethylpiperidin-4-yl)-hexamethylene-1,6-diamine
- 49) N,N'-bis-(2,2,6,6-tetramethylpiperidin-4-yl)-hexamethylene-1,6-diacetamide
- 50) 4-acetylamino-1,2,2,6,6-pentamethylpiperidine
- 51) 1-benzyl-2,2,6,6-tetramethyl-4-diethanolamino-piperidine
- 52) 4-acrylamido-1,2,2,6,6-pentamethylpiperidine
- 53) 1-acetyl-4-(N-cyclohexylacetamido)-2,2,6,6-tetramethylpiperidine
- 54) 4-benzylamino-2,2,6,6-tetramethylpiperidine

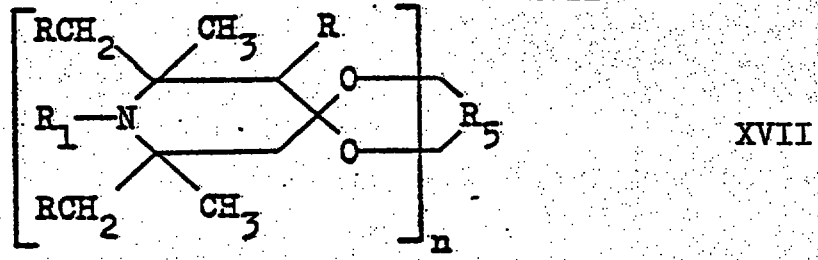
- 55) N,N'-bis-(2,2,6,6-tetramethylpiperidin-4-yl)-N,N'-dibutyl-adipamide
- 56) N,N'-bis-(2,2,6,6-tetramethylpiperidin-4-yl)-N,N'-dicyclohexyl-(2-hydroxypropylene)
- 57) N,N'-bis-(2,2,6,6-tetramethylpiperidin-4-yl)-p-xylylene-diamine
- 58) N,N'-bis-(1,2,2,6,6-pentamethyl-4-piperidiny1)-1,6-diaminohexane.

The compound of the formula XVI



- 59) 4-(bis-2-hydroxyethyl)-amino-1,2,2,6,6-pentamethyl-piperidine
- 60) 4-(3-methyl-4-hydroxy-5-tert.-butyl-benzoamido)-2,2,6,6-tetramethylpiperidine
- 61) 4-methacrylamido-1,2,2,6,6-pentamethylpiperidine
- 62) methyl α -cyano- β -methyl- β -[N-(2,2,6,6-tetramethylpiperidin-4-yl)]-amino-acrylate.

c) Light stabilisers of the formula XVII



in which n is the number 1 or 2, R is as defined for formula XIII, R_1 is as defined under a) and R_5 , if $n = 1$, is C_2-C_8 alkylene or hydroxyalkylene or C_4-C_{22} acyloxyalkylene, and if $n = 2$ is the group $(-CH_2)_2C(CH_2)_2$.

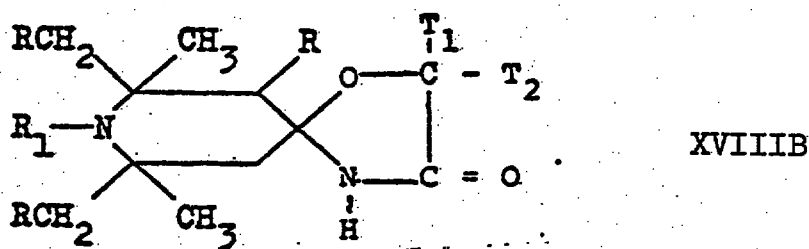
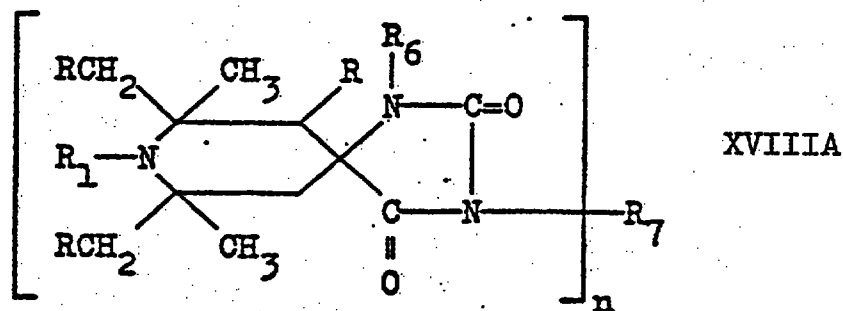
C_2-C_8 Alkylene or hydroxyalkylene R_5 is, for example, ethylene, 1-methyl-ethylene, propylene, 2-ethylpropylene or 2-ethyl-2-hydroxymethylpropylene.

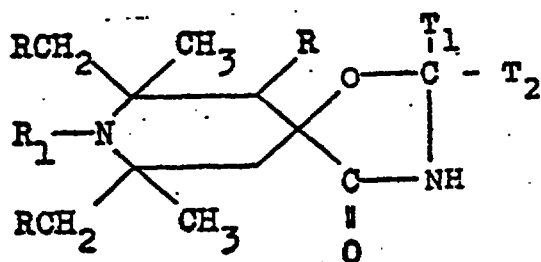
C_4-C_{22} Acyloxyalkylene R_5 is, for example, 2-ethyl-2-acetoxymethylpropylene.

Examples of polyalkylpiperidine light stabilisers of this category are the following compounds:

- 63) 9-aza-8,8,10,10-tetramethyl-1,5-dioxaspiro[5.5]undecane
- 64) 9-aza-8,8,10,10-tetramethyl-3-ethyl-1,5-dioxaspiro[5.5]decane
- 65) 8-aza-2,7,7,8,9,9-hexamethyl-1,4-dioxaspiro[4.5]decane
- 66) 9-aza-3-hydroxymethyl-3-ethyl-8,8,9,10,10-pentamethyl-1,5-dioxaspiro[5.5]undecane
- 67) 9-aza-3-ethyl-3-acetoxymethyl-9-acetyl-8,8,10,10-tetramethyl-1,5-dioxaspiro[5.5]undecane
- 68) 2,2,6,6-tetramethylpiperidine-4-spiro-2'-(1',3'-dioxan)-5'-spiro-5''-(1'',3''-dioxan)-2''-spiro-4'''-(2''',2''',6''',6'''-tetramethylpiperidine).

d) Light stabilisers of the formulae XVIII A, XVIII B and XVIII C





XVIIIIC

in which n is the number 1 or 2, R is as defined for formula XIII, R₁ is as defined under a), R₆ is hydrogen, C₁-C₁₂ alkyl, allyl, benzyl, glycidyl or C₂-C₆ alkoxyalkyl and R₇, if n=1, is hydrogen, C₁-C₁₂ alkyl, C₃-C₅ alkenyl, C₇-C₉ aralkyl, C₅-C₇ cycloalkyl, C₂-C₄ hydroxyalkyl, C₂-C₆ alkoxyalkyl, C₆-C₁₀ aryl, glycidyl or a group of the formula -(CH₂)_m-COO-Q or of the formula -(CH₂)_m-O-CO-Q, in which m is 1 or 2 and Q is C₁-C₁₈ alkyl or phenyl, and if n = 2 is C₂-C₁₂ alkylene, C₆-C₁₂ arylene, C₄-C₁₂ alkenylene, a group -CH₂-CH(OH)-CH₂-O-X-O-CH₂-CH(OH)-CH₂-, in which X is C₂-C₁₀ alkylene, C₆-C₁₅ arylene or C₆-C₁₂ cycloalkylene, or a group -CH₂CH(OZ')CH₂-(OCH₂-CH(OZ')CH₂)₂-, in which Z' is hydrogen, C₁-C₁₈ alkyl, allyl, benzyl, C₂-C₁₂ alkanoyl or benzoyl, and T₁ and T₂ independently of one another are hydrogen, C₁-C₁₈ alkyl or C₆-C₁₀ aryl, which is unsubstituted or substituted by halogen or C₁-C₄ alkyl, or C₇-C₉ aralkyl, or T₁ and T₂ together with the C atom which links them form C₅-C₇ cycloalkyl, pyrrolidinyl or piperidinyl, which are unsubstituted or substituted by C₁-C₄ alkyl.

Any C₁-C₁₂ alkyl substituents are, for example, methyl, ethyl, n-propyl, n-butyl, sec.-butyl, tert.-butyl, n-hexyl, n-octyl, 2-ethyl-hexyl, n-nonyl, n-decyl, n-undecyl or n-dodecyl.

Any C₁-C₁₈ alkyl substituents can be, for example, the groups listed above and in addition also, for example, n-tridecyl, n-tetradecyl, n-hexadecyl or n-octadecyl.

Any C₂-C₆ alkoxyalkyl substituents are, for example, methoxymethyl, ethoxymethyl, propoxymethyl, tert.-butoxymethyl, ethoxyethyl, ethoxypropyl, n-butoxyethyl, tert.-butoxyethyl, isopropoxyethyl or propoxypropyl.

C_3-C_5 Alkenyl R_7 is, for example, 1-propenyl, allyl, methallyl, 2-butenyl or 2-pentenyl.

C_7-C_9 Aralkyl R_7 , T_1 or T_2 is especially phenethyl or in particular benzyl and C_5-C_7 cycloalkyl R_7 or T_1 and T_2 (T_1 and T_2 together with the C atom which links them) is in particular cyclohexyl.

C_2-C_4 Hydroxyalkyl R_7 is, for example, 2-hydroxyethyl, 2-hydroxypropyl, 2-hydroxybutyl or 4-hydroxybutyl.

C_6-C_{10} Aryl R_7 , T_1 or T_2 is in particular phenyl or α - or β -naphthyl, which can be substituted by halogen or C_1-C_4 alkyl.

C_2-C_{12} Alkylene R_7 is, for example, ethylene, propylene, 2,2-dimethylpropylene, tetramethylene, hexamethylene, octamethylene, decamethylene or dodecamethylene.

C_4-C_{12} Alkenylene R_7 is in particular 2-butenylene, 2-pentenylene or 3-hexenylene.

C_6-C_{12} Arylene R_7 is, for example, o-, m- or p-phenylene, 1,4-naphthylene or 4,4'-diphenylene.

C_2-C_{12} Alkanoyl Z' is, for example, propionyl, butyryl, octanoyl or dodecanoyl, but preferably acetyl.

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

Examples of polyalkylpiperidine light stabilisers of this category are the following compounds:

- 69) 3-benzyl-1,3,8-triaza-7,7,9,9-tetramethylspiro[4.5]-decane-2,4-dione
- 70) 3-n-octyl-1,3,8-triaza-7,7,9,9-tetramethylspiro[4.5]-decane-2,4-dione
- 71) 3-allyl-1,3,8-triaza-1,7,7,9,9-pentamethylspiro[4.5]-decane-2,4-dione
- 72) 3-glycidyl-1,3,8-triaza-7,7,8,9,9-pentamethylspiro[4.5]decane-2,4-dione
- 73) 2-iso-propyl-7,7,9,9-tetramethyl-1-oxa-3,8-diaza-4-oxo-spiro[4.5]decane
- 74) 2-butyl-7,7,9,9-tetramethyl-1-oxa-3,8-diaza-4-oxo-spiro[4.5]decane
- 75) 2-isopropyl-7,7,9,9-tetramethyl-1-oxa-4,8-diaza-3-

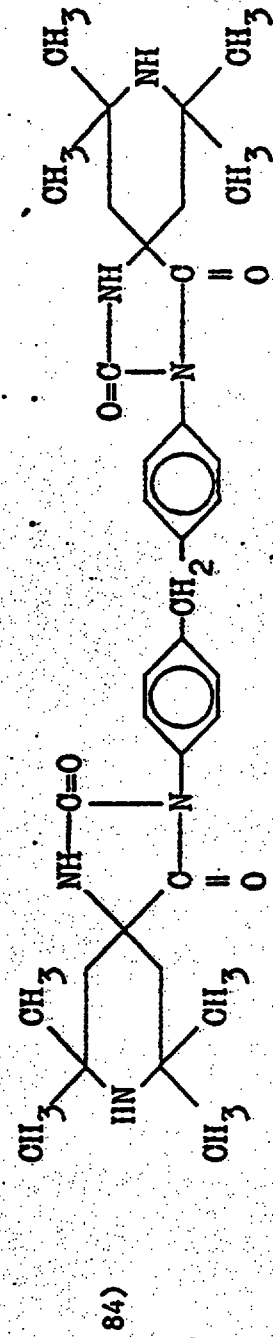
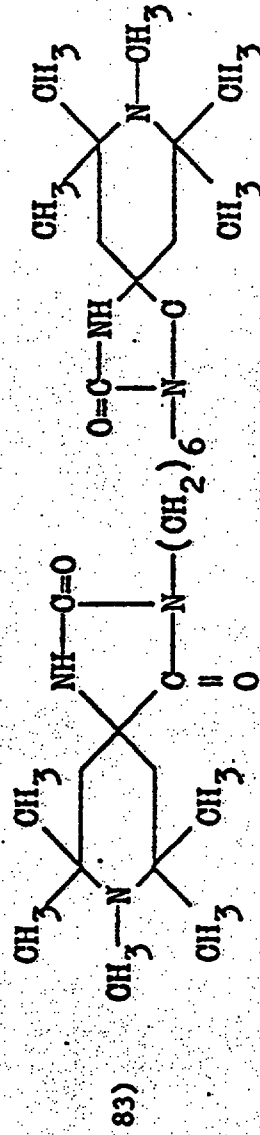
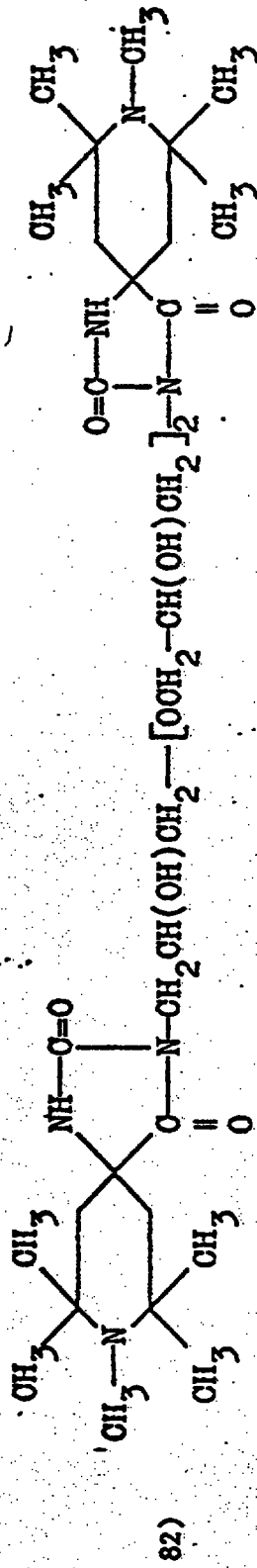
oxo-spiro[4.5]decane

- 76) 2-butyl-7,7,9,9-tetramethyl-1-oxa-4,8-diaza-3-oxo-spiro[4.5]decane

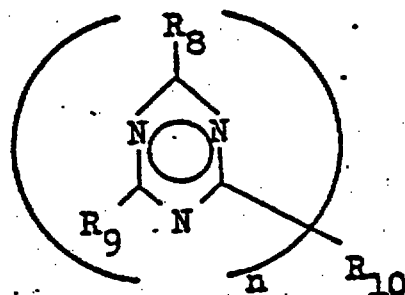
and also the following compounds:

- 77) 2,2,4,4-tetramethyl-7-oxa-3,20-diaza-21-oxo-dispiro-[5,1,11,-2]heneicosane
- 78) 1,3-di-(2,2,6,6-tetramethyl-4-piperidiny1)-imidazolidin-2-one
- 79) 2,4,6-tri-[N-(2,2,6,6-tetramethyl-4-piperidiny1)-butylamino]-s-triazine
- 80) di-[2-(2,2,6,6-tetramethyl-1-piperidino)-ethyl]adipate
- 81) n-octyl 2,2,6,6-tetramethylpiperidine-1-acetate.

Further compounds of the formula:

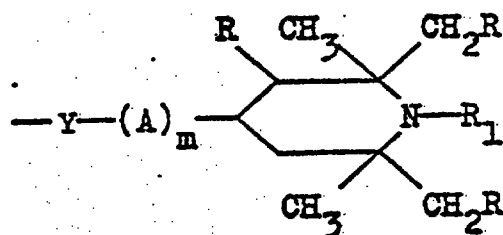


e) Light stabilisers of the formula XIX

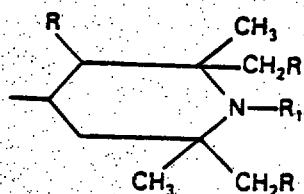


XIX

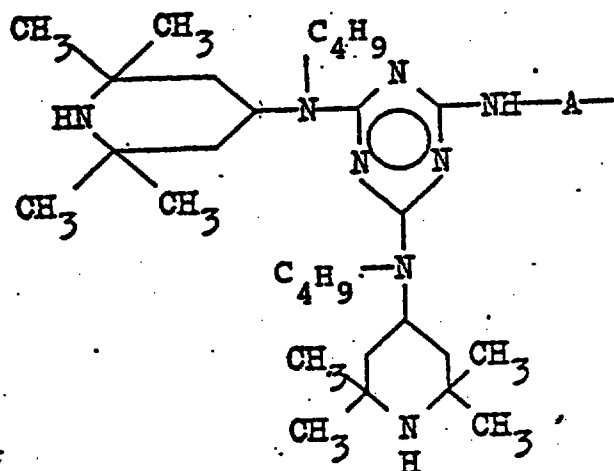
in which n is the number 1 or 2 and R_8 is a group of the formula



in which R is as defined for formula (I), R_1 is as defined under a), Y is $-O-$ or $-NR_{11}-$, A is C_2-C_6 alkylene or $-(CH_2)_3-O-$ and m is the number 0 or 1, R_9 is the group R_8 , $NR_{11}R_{12}$, $-OR_{13}$, $-NHCH_2OR_{13}$ or $-N(CH_2OR_{13})_2$ and R_{10} , if $n = 1$, is the group R_8 or R_9 , and if $n = 2$ is the group $-Y-Q-Y-$, in which Q is C_2-C_6 alkylene which can be interrupted by $-N(R_{14})-$, and R_{11} is C_1-C_{12} alkyl, cyclohexyl, benzyl or C_1-C_4 hydroxyalkyl or a group of the formula



R_{12} is C_1-C_{12} alkyl, cyclohexyl, benzyl or C_1-C_4 hydroxyalkyl, R_{13} is hydrogen, C_1-C_{12} alkyl or phenyl and R_{14} is hydrogen, C_1-C_{12} alkyl, cyclohexyl, benzyl or phenyl, or R_{11} and R_{12} together are C_4-C_5 alkylene or oxaalkylene, or R_{11} and R_{12} are each a group of the formula



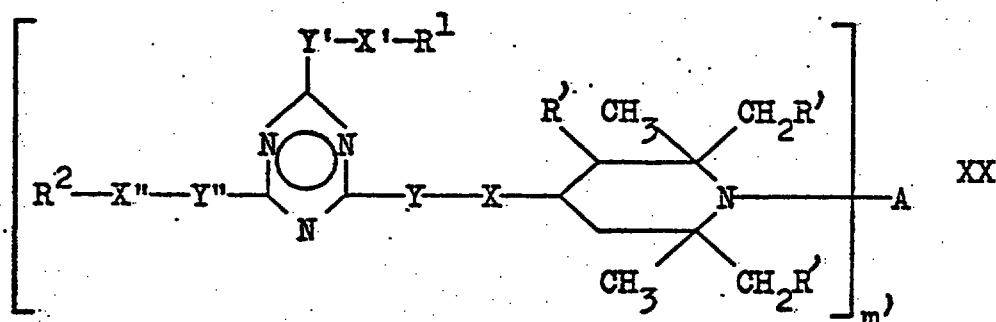
Any C_1 - C_{12} alkyl substituents are, for example, methyl, ethyl, n-propyl, n-butyl, sec.-butyl, tert.-butyl, n-hexyl, n-octyl, 2-ethylhexyl, n-nonyl, n-decyl, n-undecyl or n-dodecyl.

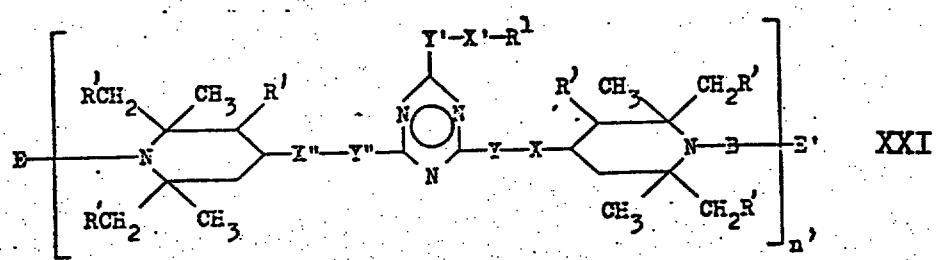
Any C_1 - C_4 hydroxyalkyl substituents are, for example, 2-hydroxyethyl, 2-hydroxypropyl, 3-hydroxypropyl, 2-hydroxybutyl or 4-hydroxybutyl.

C_2 - C_6 Alkylene A is, for example, ethylene, propylene, 2,2-dimethylpropylene, tetramethylene or hexamethylene.

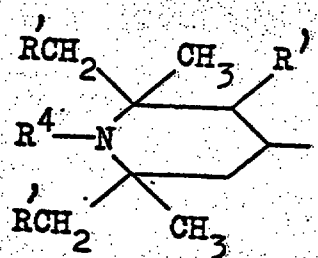
C_4 - C_5 Alkylene or oxaalkylene formed by R_{11} and R_{12} together is, for example, tetramethylene, pentamethylene or 3-oxa-pentamethylene.

Compounds of the formulae XX or XXI

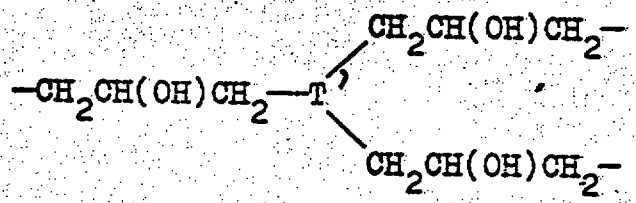




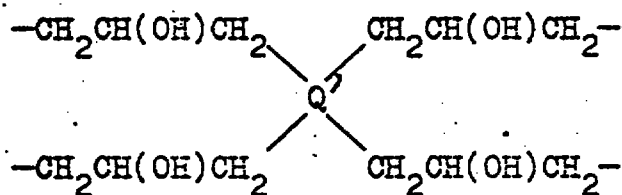
in which m' is 2, 3 or 4, n' is 2 to 50, X, X' and X'' are a direct bond, C_1-C_4 alkylene or $-OCH_2CH_2CH_2-$, the O of which is not bonded to Y, Y' or Y'', and Y, Y' and Y'' are $-O-$, $-S-$, $-NH-$ or $-NR^3-$, R' is hydrogen or C_1-C_4 alkyl and R^1 , R^2 and R^3 are C_1-C_{12} alkyl, C_2-C_8 alkoxyalkyl, C_2-C_4 hydroxyalkyl, C_5-C_{10} cycloalkyl, C_6-C_{10} aryl, phenyl which is substituted by 1 or 2 C_1-C_8 alkyl groups and/or OH and/or C_1-C_4 alkoxy, or a polyalkylpiperidiny group of the formula



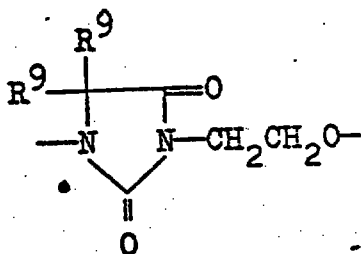
or, if Y' or Y'' is $-NR^3-$ and X' or X'' is a direct bond, R^1 and R^3 together with the N atom form a pyrrolidine, piperidine or morpholine ring, and R^4 is hydrogen, O , C_1-C_{12} alkyl, allyl or benzyl, and A, if m is 2, is C_2-C_{12} alkylene, C_4-C_8 alkenylene, xylylene or a radical of the formula $-\text{CH}_2-\text{COO}-R^5-\text{OOC}-\text{CH}_2-$, $-\text{CH}_2-\text{CH}(\text{OH})-\text{CH}_2-$ or $-\text{CH}_2\text{CH}(\text{OH})\text{CH}_2-\text{D}-\text{CH}_2\text{CH}(\text{OH})\text{CH}_2-$, and if m is 3 is a group of the formula



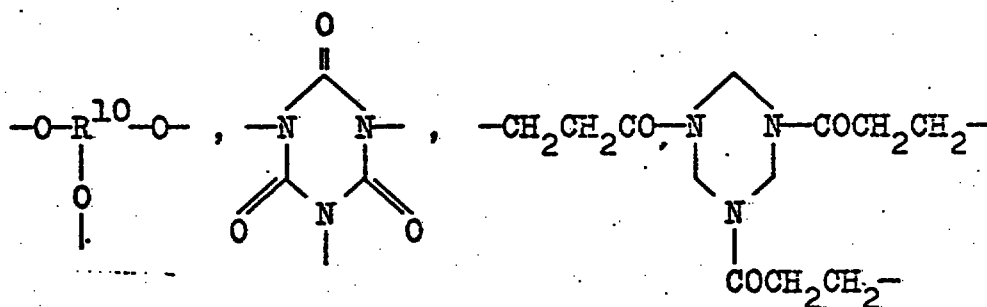
and if m is 4 is a group of the formula



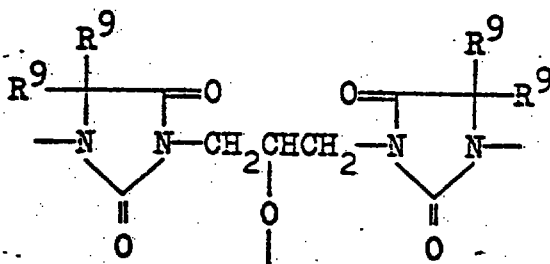
and B is C₂-C₁₂ alkylene, C₄-C₈ alkenylene, xylylene or a radical of the formula -CH₂-COO-R⁵-OOC-CH₂-, -CH₂CH(OH)-CH₂- or -CH₂CH(OH)CH₂-D-CH₂CH(OH)CH₂-, R⁵ is C₂-C₈ alkylene, C₄-C₈ oxaalkylene or cyclohexylene, D is a divalent radical of the formula -O-R⁶-O-, -O-C(O)-R⁷-C(O)-O-, -OCH(R⁸)CH₂O-R⁶-OCH₂CH(R⁸)O- or



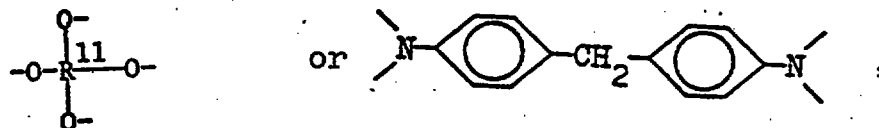
R⁶ is C₂-C₁₂ alkylene, C₆-C₁₂ cycloalkylene, C₆-C₁₂ arylene or -phenylene-Z'-phenylene-, in which Z' is -CH₂-, >C(CH₃)₂-, -SO₂- or -O-, R⁷ is a direct bond, C₁-C₁₂ alkylene, C₂-C₆ alkenylene or C₆-C₁₂ arylene, R⁸ and R⁹ are hydrogen or C₁-C₄ alkyl, T' is a trivalent radical of the formulae



or



R^{10} is a trivalent aliphatic hydrocarbon radical having 3-10 C atoms, Q' is a tetravalent radical of the formula



R^{11} is a tetravalent aliphatic hydrocarbon radical with 4-10 C atoms and E and E' are end groups.

C_1 - C_{12} Alkyl R^1 , R^2 , R^3 or R^4 can be branched or unbranched alkyl radicals, for example methyl, ethyl, isopropyl, tert.-butyl, hexyl, isooctyl, decyl or dodecyl.

Alkoxyalkyl R^1 , R^2 or R^3 can be, for example, methoxymethyl, 2-methoxyethyl, 2-ethoxyethyl, 2-isopropoxyethyl, 2-n-, -sec.- or -tert.-butoxyethyl or 2-butoxypropyl.

Hydroxyalkyl R^1 , R^2 or R^3 can be, for example, 2-hydroxyethyl, 2-hydroxypropyl, 2-hydroxybutyl or 3-hydroxypropyl.

C_5 - C_{10} Cycloalkyl R^1 , R^2 or R^3 can be, for example, cyclopentyl, cyclohexyl, 3-methylcyclohexyl or 4-tert.-butyl-cyclohexyl.

C_6 - C_{10} Aryl R^1 , R^2 or R^3 can be phenyl or naphthyl, phenyl being preferred.

Substituted phenyl R^1 , R^2 or R^3 can be, for example, p-tolyl, 4-hydroxyphenyl, 4-tert.-butylphenyl or 3,5-di-tert.-butyl-4-hydroxyphenyl.

C_1 - C_4 Alkylene X can be, for example, methylene, ethylene, 1,3-propylene, 1,2-propylene, 1,1-dimethylethylene or 2,2-propylene.

Alkylene A, B or R^6 can be a branched or unbranched alkylene group, for example ethylene, tri-, tetra-, hexa-, octa-, deca- or dodeca-methylene, 2,2-dimethyl-1,3-propylene, 1,2-butylenes or 1,2-propylene. R^5 is a divalent aliphatic or cycloaliphatic radical, for example ethylene, 1,2-propylene, 1,2-butylenes, 1,3-propylene, 1,4-butylenes, 1,6-hexylene, 1,4-cyclohexylene or 3-oxa-1,5-pentylene.

Alkenylene A or B can be, for example, 1,4-buten-

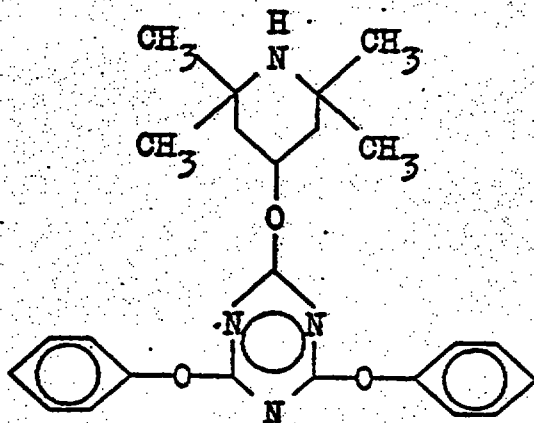
2-ylene or 1,6-hexen-3-ylene.

Cycloalkylene R^6 can be, for example, 1,4-cyclohexylene or 1,4-cyclooctylene. Arylene R^6 can be phenylene, naphthylene or diphenylene.

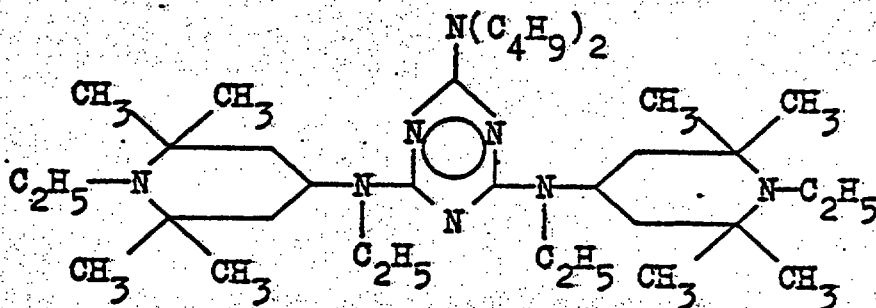
Alkylene or alkenylene R^7 can be, for example, methylene, 1,3-propylene, tetramethylene, 2,2-dimethyl-1,3-propylene, octamethylene, dodecamethylene, vinylene or 1,4-buten-2-ylene. A cyclic radical R^7 can be, for example, 1,2-cyclopentylene, 1,2-cyclohexylene, 1,2-cyclohexen-4-ylene, 3,6-endomethylene-1,2-cyclohexen-4-ylene, 1,2-phenylene, 1,4-phenylene or 1,4-naphthylene.

Examples of polyalkylpiperidine light stabilisers of this category are the compound of the following formulae:

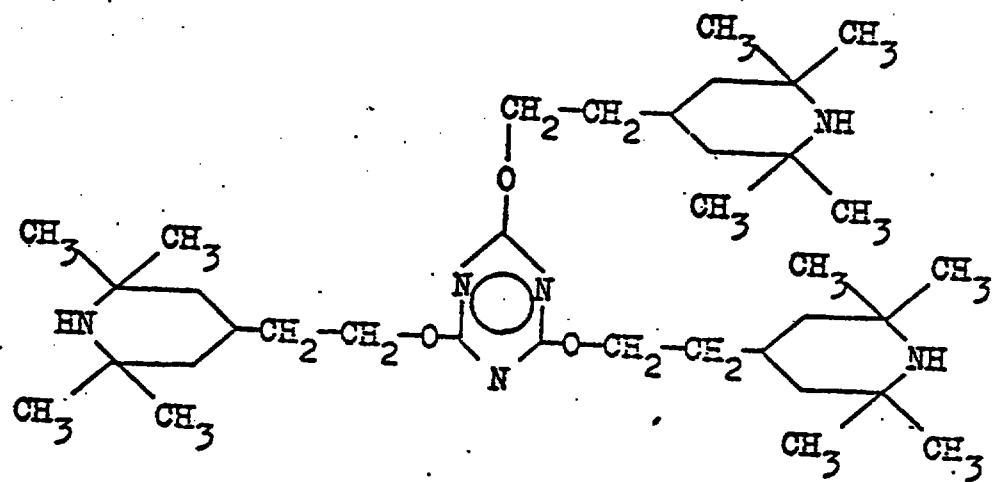
85)



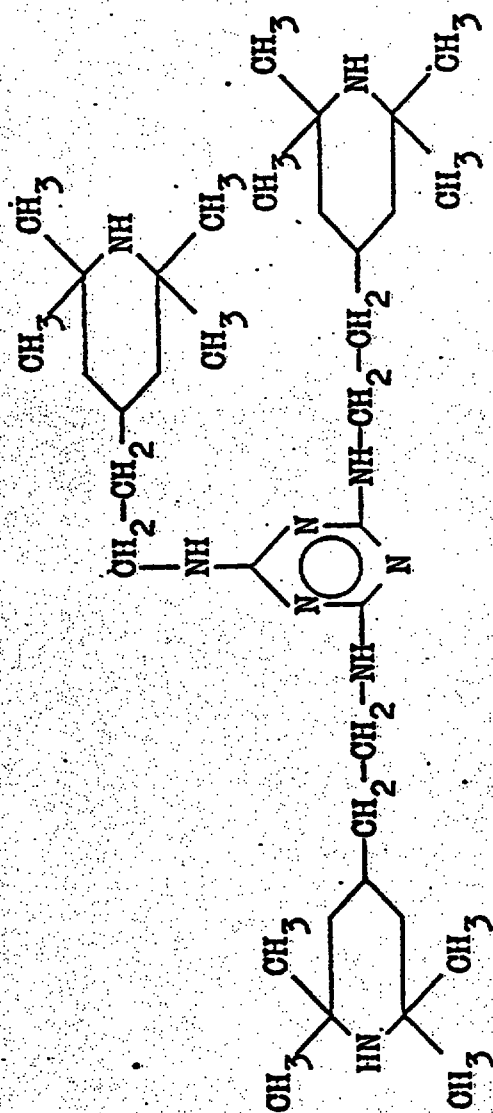
86)



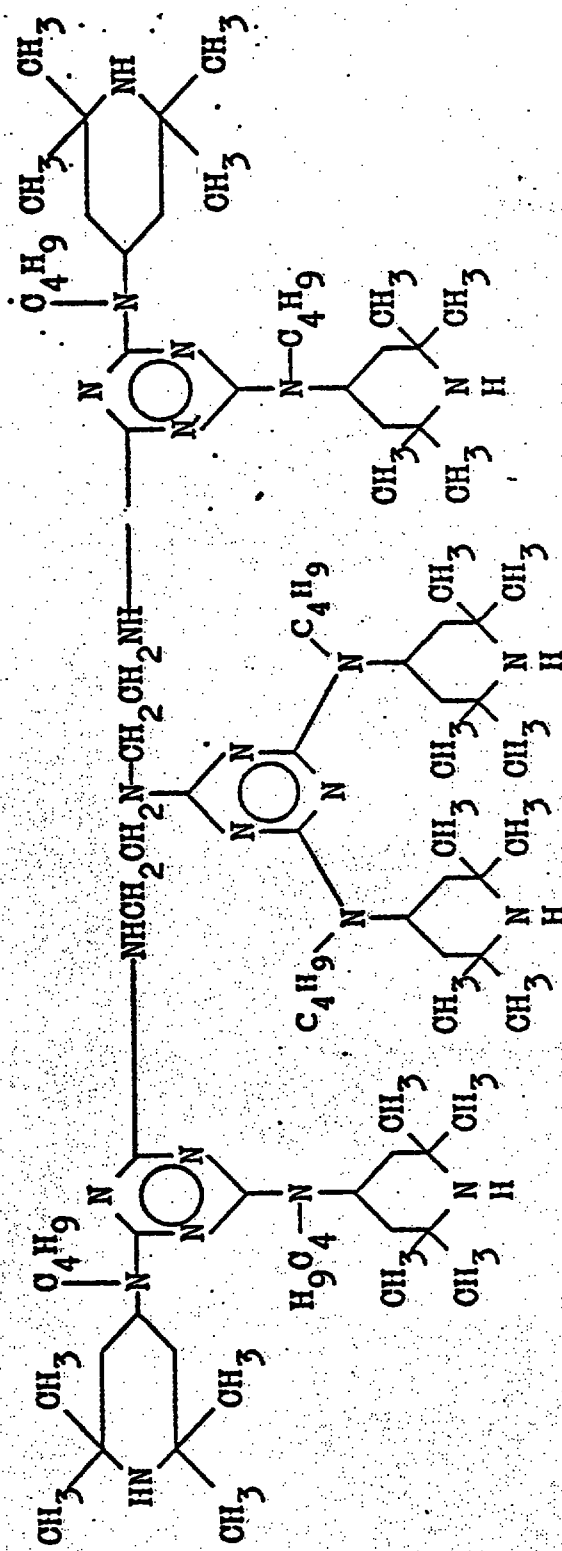
87)



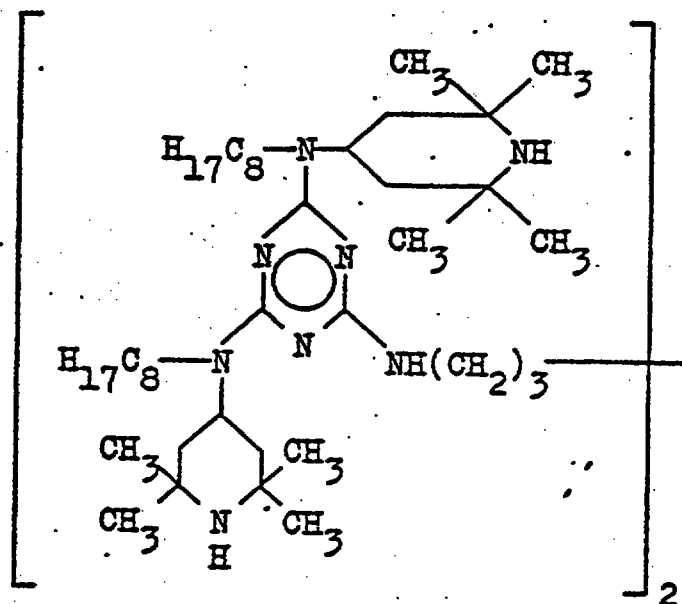
88)



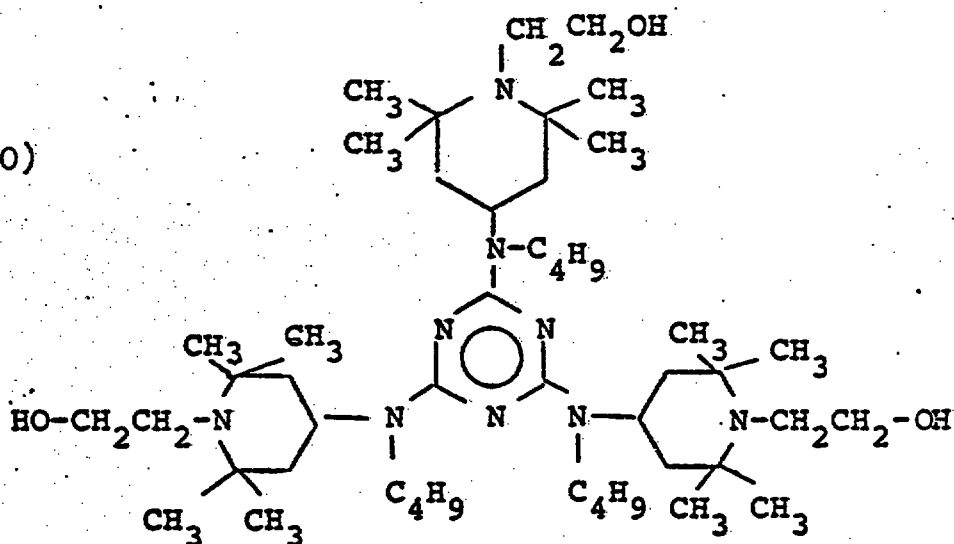
88a)



89)

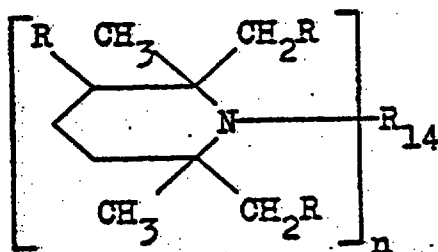


90)



g)

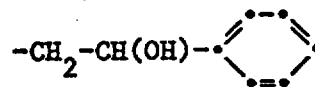
Light stabilisers of the formula XXII



XXII

in which n is the number 1 or 2, R is as defined for formula XIII and R_{14} , if $n = 1$, is C_4 - C_{18} alkyl, C_7 - C_{12} aralkyl, the group $-CO-R_{15}$, C_1 - C_4 alkyl substituted by

CN, $-\text{COOR}_{16}$, $-\text{OH}$, $-\text{OCOR}_{17}$ or



where R_{15} is $\text{C}_1\text{-C}_{12}$ alkyl, $\text{C}_2\text{-C}_4$ alkenyl or phenyl, R_{16} is $\text{C}_1\text{-C}_{18}$ alkyl and R_{17} is $\text{C}_1\text{-C}_{18}$ alkyl, $\text{C}_2\text{-C}_{10}$ alkenyl, cyclohexyl, benzyl or $\text{C}_6\text{-C}_{10}$ aryl, or R_{14} , if $n = 2$, is $\text{C}_4\text{-C}_{12}$ alkylene, 1,4-buten-2-ylene, xylylene, the group $-(\text{CH}_2)_2\text{-OOC-R}_{18}\text{-COO-(CH}_2)_2-$ or the group $-\text{CH}_2\text{-OOC-R}_{19}\text{-COO-CH}_2-$, where R_{18} is $\text{C}_2\text{-C}_{10}$ alkylene, phenylene or cyclohexylene and R_{19} is $\text{C}_2\text{-C}_{10}$ alkylene, xylylene or cyclohexylene.

Any $\text{C}_1\text{-C}_{12}$ alkyl substituents are, for example, methyl, ethyl, n-propyl, n-butyl, sec.-butyl, tert.-butyl, n-hexyl, n-octyl, 2-ethyl-hexyl, n-nonyl, n-decyl, n-undecyl or n-dodecyl.

Any $\text{C}_1\text{-C}_{18}$ alkyl substituents can be, for example, the groups listed above and in addition also, for example, n-tridecyl, n-tetradecyl, n-hexadecyl or n-octadecyl.

Any $\text{C}_2\text{-C}_{10}$ alkylene groups are, for example, ethylene, propylene, 2,2-dimethylpropylene, tetramethylene, hexamethylene, octamethylene or decamethylene.

$\text{C}_4\text{-C}_{18}$ Alkyl R_{14} is, for example, n-butyl, sec.-butyl, tert.-butyl, n-hexyl, n-octyl, 2-ethyl-hexyl, 1,1-dimethyl-2-tert.-butylethyl, n-nonyl, n-decyl, n-dodecyl, n-tridecyl, n-tetradecyl, n-hexadecyl or n-octadecyl.

As $\text{C}_1\text{-C}_4$ alkyl substituted by $-\text{CN}$, R_{14} is, for example, cyanomethyl, cyanoethyl, 3-cyano-n-propyl or 4-cyano-n-butyl.

$\text{C}_4\text{-C}_{12}$ Alkylene R_{14} is, for example, 2,2-dimethylpropylene, tetramethylene, hexamethylene, octamethylene, decamethylene or dodecamethylene.

$\text{C}_7\text{-C}_{12}$ Aralkyl R_{14} is especially phenethyl or p-methyl-benzyl or in particular benzyl.

$\text{C}_2\text{-C}_4$ Alkenyl R_{15} is, for example, vinyl, 1-propenyl, allyl, methallyl or 2-butenyl.

$\text{C}_2\text{-C}_{10}$ Alkenyl R_{17} is, for example, one of the groups listed for alkenyl R_{15} and in addition also, for

example, crotyl, 2-hexenyl, 2-octenyl or 2-decenyl.

C₆-C₁₀ Aryl R₁₇ is, for example, phenyl, which is unsubstituted or substituted in the o-position or p-position by methyl, ethyl, isopropyl, n-butyl or tert.-butyl.

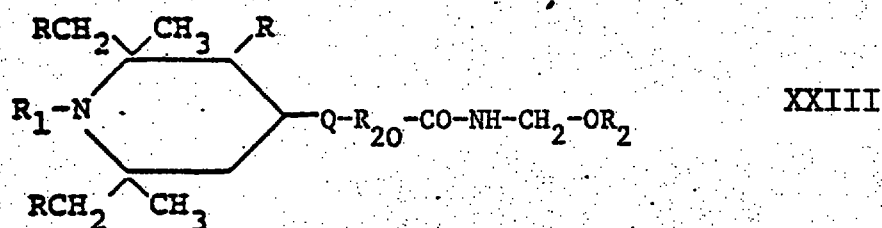
Examples of polyalkylpiperidine light stabilisers of this category are the following compounds:

91) bis-[β-(2,2,6,6-tetramethylpiperidino)-ethyl] sebacate

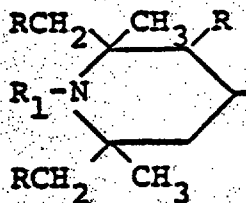
92) n-octyl α-(2,2,6,6-tetramethyl-piperidino)-acetate

93) 1,4-bis-(2,2,6,6-tetramethylpiperidino)-2-butene.

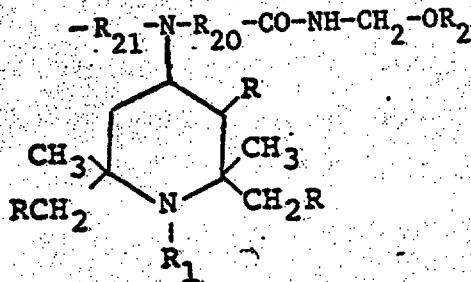
h) Light stabilisers of the formula XXIII



in which Q is -N(R₃)- or -O-, R₂₀ is C₁-C₃ alkylene, the group -CH₂-CH(R₄)-O-, in which R₄ is hydrogen, methyl or phenyl, the group -(CH₂)₃-NH- or a single bond, R is hydrogen or methyl, R₁ is as defined under a), R₂ is hydrogen or C₁-C₁₈ alkyl and R₃ is hydrogen, C₁-C₁₈ alkyl, C₅-C₇ cycloalkyl, C₇-C₁₂ aralkyl, cyanoethyl, C₆-C₁₀ aryl, the group -CH₂-CH(R₄)-OH, in which R₄ is as defined above, a group of the formula



or a group of the formula



in which R_{21} can be C_2-C_6 alkylene or C_6-C_{12} arylene, or R_3 is a group $-R_{20}-CO-NH-CH_2-OR_2$.

Any C_1-C_{18} alkyl substituents are, for example, methyl, ethyl, n-propyl, n-butyl, sec.-butyl, tert.-butyl, n-hexyl, n-octyl, 2-ethyl-hexyl, n-nonyl, n-decyl, n-undecyl, n-dodecyl, n-tridecyl, n-tetradecyl, n-hexadecyl or n-octadecyl.

Any C_7-C_{12} aralkyl substituents are, for example, phenethyl or in particular benzyl.

C_3-C_8 Alkenyl R_1 can be, for example, 1-propenyl, allyl, methallyl, 2-butenyl, 2-pentenyl, 2-hexenyl, 2-octenyl or 4-tert.-butyl-2-butenyl.

C_3-C_8 Alkynyl R_1 is preferably propargyl. C_1-C_8 Alkanoyl R_1 is, for example, formyl, propionyl, butyryl or octanoyl, but preferably acetyl, and C_3-C_5 alkenoyl R_1 is in particular acryloyl.

C_5-C_7 Cycloalkyl R_3 is in particular cyclohexyl.

C_6-C_{10} Aryl R_3 is in particular phenyl or α - or β -naphthyl, which can be substituted by halogen or C_1-C_4 alkyl. C_1-C_3 Alkylene E is, for example, methylene, ethylene or propylene.

C_2-C_6 Alkylene R_{21} is, for example, ethylene, propylene, 2,2-dimethylpropylene, tetramethylene or hexamethylene and C_6-C_{12} arylene R_{21} is o-, m- or p-phenylene, 1,4-naphthylene or 4,4'-diphenylene.

Examples of polyalkylpiperidine light stabilisers of this category are the following compounds:

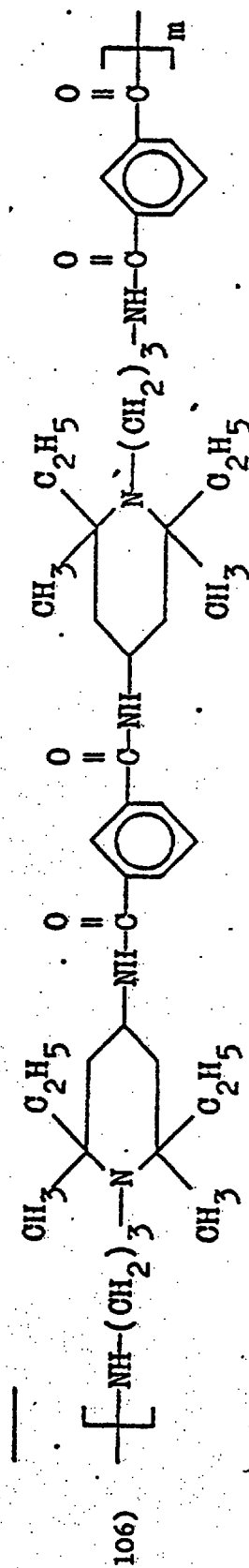
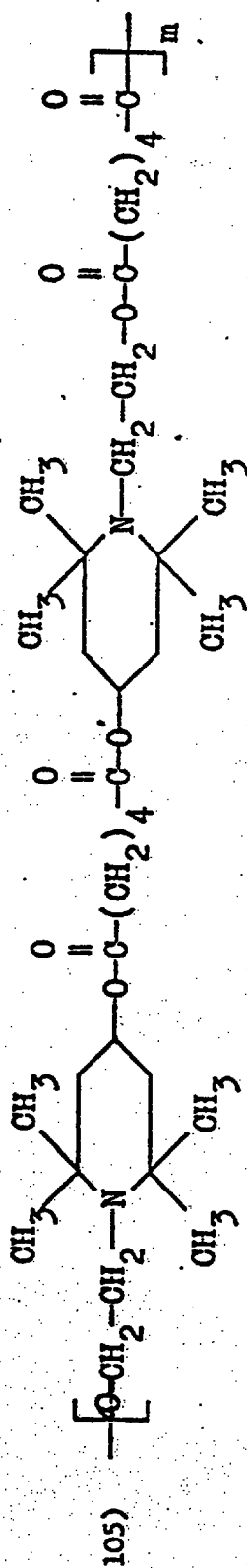
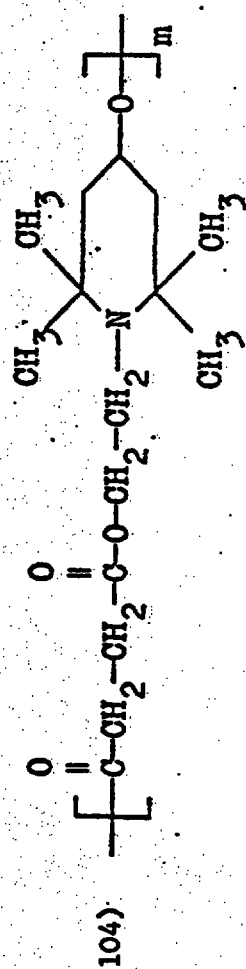
- 94) N-hydroxymethyl-N'-2,2,6,6-tetramethylpiperidin-4-yl-urea
- 95) N-methoxymethyl-N'-2,2,6,6-tetramethylpiperidin-4-yl-urea
- 96) N-methoxymethyl-N'-n-dodecyl-N'-2,2,6,6-tetramethylpiperidin-4-yl-urea
- 97) O-(2,2,6,6-tetramethylpiperidin-4-yl)-N-methoxy-methyl-urethane.

i) Polymeric compounds in which the recurring structural unit contains a polyalkylpiperidine radical of the

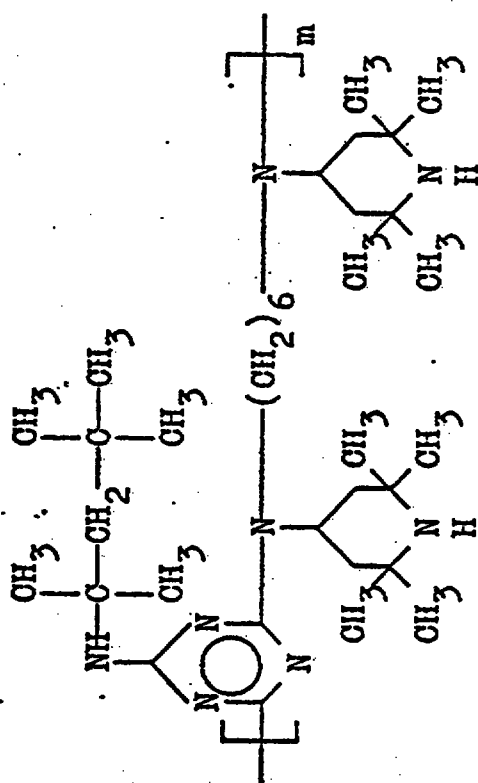
formula (I), especially polyesters, polyethers, polyamides, polyamines, polyurethanes, polyureas, polyaminotriazines, poly(meth)acrylates, poly(meth)acrylamides and their copolymers which contain such radicals.

- 98) Polyester of succinic acid, sebacic acid, di-butylmalonic acid, oxalic acid or isophthalic acid and 1-hydroxyethyl-2,2,6,6-tetramethyl-4-hydroxypiperidine
- 99) Polyamide of succinic acid, adipic acid or phthalic acid and 1-(3-aminopropyl)-2,2,6,6-tetramethyl-4-aminopiperidine
- 100) Polyamide of oxalic acid or p-phenylenediacetic acid and N,N'-bis-(1,2,2,6,6-pentamethyl-4-piperidiny)-1,6-diaminohexane
- 101) Polyamine of 1,2,2,6,6-pentamethyl-4-aminopiperidine and epichlorohydrin or bisphenol A diglycidyl ether
- 102) Polytriazine of 2,4-dichloro-6-N-(1,2,2,6,6-pentamethyl-4-piperidiny)-ethylamino-s-triazine and N,N'-bis-(2,2,6,6-tetramethyl-4-piperidiny)-1,6-diaminohexane
- 103) Copolymer of 1-benzyl-2,2,6,6-tetramethyl-4-acrylamidopiperidine and N-butylacrylamide.

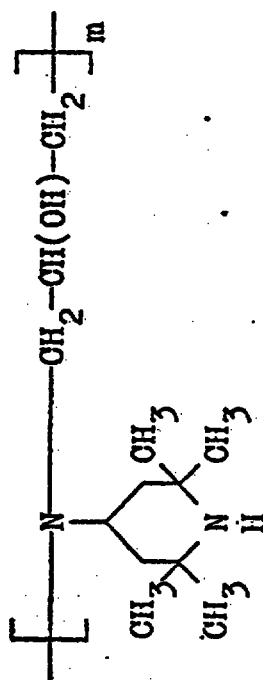
Examples of polyalkylpiperidine light stabilisers of this category are the compounds of the following formulae, in which m is a number between 2 and about 200.



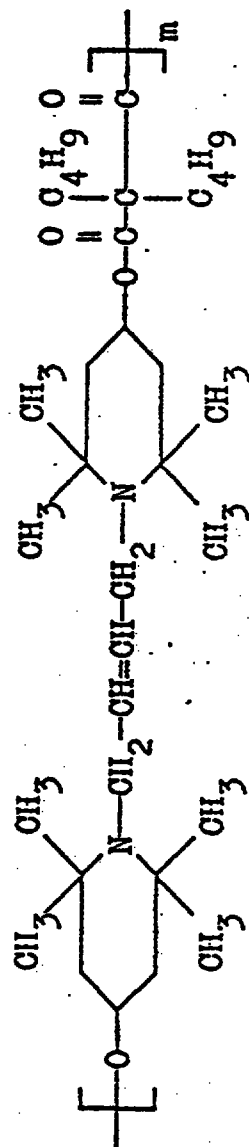
82



107)

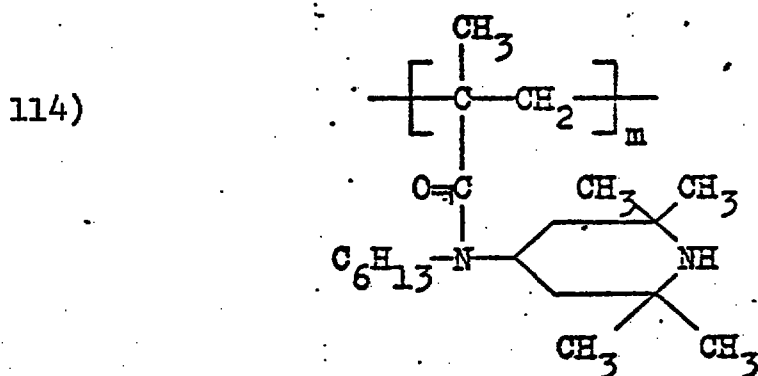
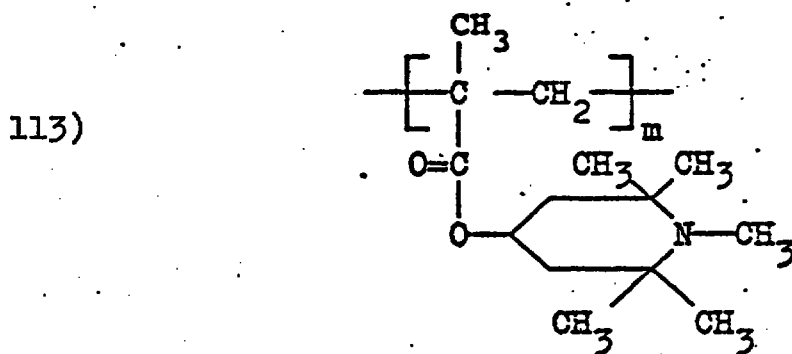


108)



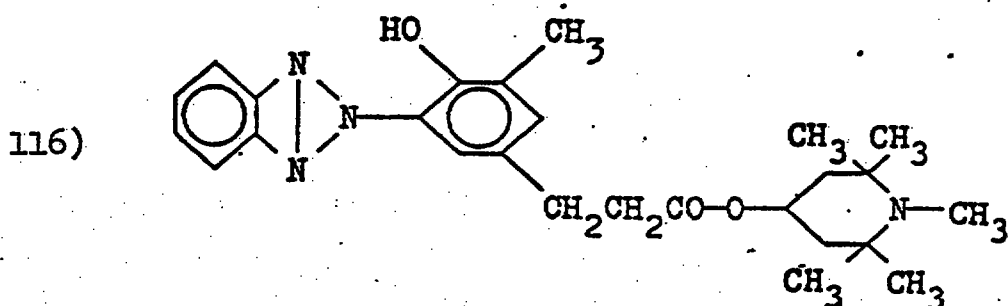
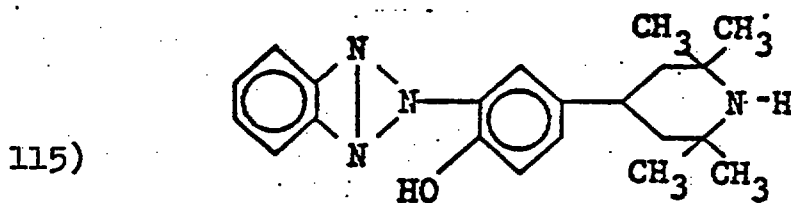
109)

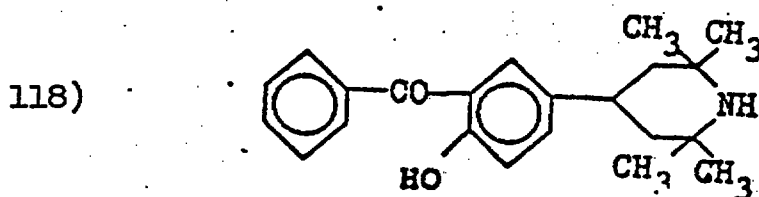
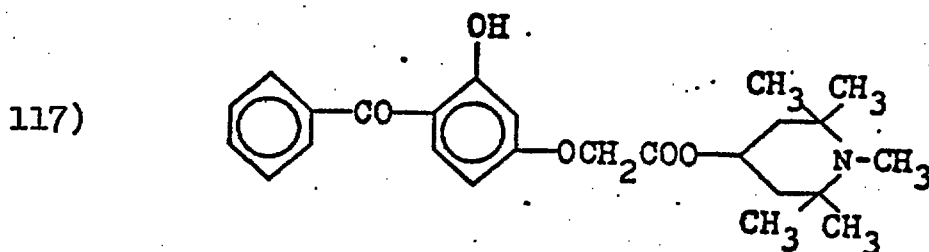
82



j) Compounds which contain in their molecule at least one 2-(2'-hydroxyphenyl)-benzotriazole group or 2-hydroxybenzophenone group and at least one polyalkylpiperidine group.

Examples of polyalkylpiperidine light stabilisers of this category are the compounds of the following formulae





It is also possible to use polyalkylpiperidine derivatives of categories a) - j) which enter into chemical bonds with the binder of the lacquer. This is the case if the polyalkylpiperidine derivative possesses a reactive group suitable for this, for example a glycidyl group or a methylol group.

Examples of such compounds are the polyalkylpiperidine derivatives of category h) which contain methylol or methylol-ether groups.

If the polyalkylpiperidine compounds are basic compounds, they can form salts with acids. Suitable acids are, for example, inorganic acids or organic carboxylic, sulfonic, phosphonic or phosphinic acids, for example hydrochloric acid, boric acid, phosphoric acid, acetic acid, salicylic acid, toluenesulfonic acid or benzenephosphonic acid.

The polyalkylpiperidine compounds can form complexes with complex-forming metal compounds, for example with zinc-II acetate, cobalt-II acetylacetonate, nickel-II acetylacetonate, aluminium-III acetylacetonate, nickel-II benzoate or aluminium-III benzoylacetonate.

Salts and complexes are, for example: the salt of 1 mol of H_3PO_4 and 1 mol of di-(1,2,2,6,6-pentamethyl-4-piperidinyl) adipate, the salt of 2 mols of bis-(3,5-di-

tert.-butyl-4-hydroxybenzyl)-malonic acid and 1 mol of 2,2,6,6-tetramethyl-4-lauroyl-oxypiperidine, the 1:1 complex of bis-(2,2,6,6-tetramethyl-4-piperidinyl) sebacate and nickel-II acetylacetonate and the 1:2 complex of bis-(1,2,2,6,6-pentamethyl-4-piperidinyl) adipate and nickel-II acetate.

The following examples illustrate the invention. Percentages are by weight.

A. Preparation of the precursor: 2,4-di-(α,α -dimethylbenzyl)-phenol

This intermediate was prepared in accordance with the description in U.S. Patent Specification 2,714,120. 705.8 g (7.5 mols) of phenol are mixed with 1,772.7 g (15 mols) of α -methylstyrene in the presence of 25.7 g (0.135 mol) of p-toluenesulfonic acid monohydrate as the catalyst and the mixture is heated at 140°C for 2.5 hours under N₂. After the reaction has ended, the mixture is cooled to 110°C and 1,125 ml of toluene are added. The resulting solution is then washed at 80°C with 750 ml of an aqueous solution consisting of 37.5 g of NaCO₃ and 75 g of NaCl. The organic phase is washed three times with 1,000 ml of aqueous NaCl solution and dried over anhydrous sodium sulfate and the product is then isolated by filtration and vacuum distillation.

The main fraction contains 1,229.8 g (49.6% of theory) of the product. Boiling point 172-175°/0.15-0.18 mm Hg. Melting point 63-65°C.

B. Comparison Example: Preparation of the intermediate 2-nitro-2'-hydroxy-3',5'-di-(α,α -dimethylbenzyl)-azobenzene by an acid coupling reaction

90.6 g of a 26% aqueous solution of naphthalene-sulfonic acid, 1.9 g of Triton X-207 (non-ionic surfactant), 5.6 g of Conoco AAS-90F (sodium dodecylbenzene sulfonate) and 90 ml of water are introduced into a 2 l three-necked round-bottomed flask fitted with a stirrer and a thermometer. The mixture is warmed to 40°C, 16.5 g of 2,4-di-(α,α -dimethylbenzyl)-phenol, which has been preheated

to 90°C, are then added and the mixture is kept at 40°C, with vigorous stirring.

A cold solution of o-nitrobenzenediazonium chloride is prepared from 49.8 g (0.36 mol) of o-nitroaniline and from 24.9 g (0.36 mol) of sodium nitrite in concentrated HCl at -5°C to 0°C. This solution is added dropwise in the course of 3 hours to the reaction mixture and the resulting dark red to black solution is kept at 40°C overnight. The temperature is then raised to 65°C for one hour and to 95°C for a further 30 minutes. After cooling to 85°C, the crude product, which is a deep red viscous mass, is isolated.

The comminuted crude product is mixed with 200 ml of hot water (75°C) and the mixture is then left to stand with 400 ml of methanol overnight. The mixture is stirred with a further 400 ml of methanol to produce fine granules. 81.9 g (48.4% of theory) of the intermediate were obtained. Melting point: 139-141°C.

The thin layer chromatogram shows a homogeneous product with $R_f = 0.61$ on silica gel in 3 parts of cyclohexane and 1 part of ethyl acetate as the solvent.

Example 1: 2-[2-Hydroxy-3,5-di-(α,α -dimethyl-benzyl)-phenyl]-2H-benzotriazole.

386 g (0.805 mol) of o-nitroazobenzene, prepared in Example A, and 1,200 ml of toluene are introduced into a 5 l three-necked round-bottomed flask fitted with a gas inlet, a stirrer and a reflux condenser. 240 ml of isopropanol and 240 ml of water are added to this solution. 160 ml of 50.1% sodium hydroxide solution are added to the solution, whilst passing in nitrogen. A flask containing 158.2 g (2.42 gram atoms) of zinc is connected to the reaction flask. The zinc dust is fed in portions, in the course of 90 minutes, into the reaction mixture and this is carried out in such a way that the reaction temperature remains between 40 and 45°C. After all of the zinc has been added, the reaction mixture is kept at 40°C for 1 hour and is then warmed to 70°C for 3 hours. The

mixture is cooled to room temperature and acidified with 600 ml of concentrated hydrochloric acid.

The residual zinc is removed by filtration. The organic phase, which contains the product, is washed four times with 340 ml of dilute hydrochloric acid. After removing the solvent by vacuum distillation, the viscous crude product is obtained and this crystallises on standing.

In order to purify the crude product, it is first recrystallised from 750 ml of ethyl acetate and then from 1,000 ml of an acetonitrile/ethyl acetate mixture (4 : 1) and is then dissolved in 1,250 ml of toluene. The toluene solution is extracted with 70% aqueous sulfuric acid in order to remove coloured impurities. (Compound 1)

219.3 g (60.9% of theory) of yellowish-white crystals are obtained. Melting point 140-141°C.

Analysis: $C_{30}H_{29}N_3O$

calculated C: 80.51 H: 6.53 N: 9.39

found C: 80.53 H: 6.54 N: 9.51

Example 2: 2-Nitro-2'-hydroxy-3',5'-di-(α,α -dimethylbenzyl)-azobenzene

13.5 g (0.21 mol) of solid potassium hydroxide and 10 ml of water are introduced into a 500 ml three-necked flask fitted with a stirrer, a gas inlet and a pressure relief device. The resulting hot solution is cooled with 80 ml of methanol.

16.5 g (0.05 mol) of 2,4-di-(α,α -dimethylbenzyl)-phenol and 85 ml of methanol are added under nitrogen and the mixture is cooled to -4°C. A cooled solution containing 42.9 g (0.06 mol) of o-nitrobenzenediazonium chloride in concentrated HCl is added in the course of 15 minutes, with stirring, and the temperature is kept at -2°C to 0°C. A deep red coloration, caused by the azo dye phenoxide formed, develops immediately. The mixture is stirred for a further 10 minutes at -1°C to +1°C and is then acidified slowly (in the course of 2 minutes) with 20 ml of glacial acetic acid and the temperature is

kept at +1 to +3°C. The brick-red suspension is stirred for a further 15 minutes, during which time a rise in temperature is possible, and is then filtered. The filter residue is washed with a solution of 40 g of ice and 160 ml of methanol and finally with 1,800 ml of water.

The pale red crude product is dried in vacuo at 60°C and 75 mm Hg for 16 hours. The yield is 22.7 g, 82% of theory. Analysis by spectrophotometry indicates a purity of 86.7%. Melting point: 135 - 140°C.

The crude product is recrystallised from hot n-butanol (5 ml per gram). Melting point: 147 - 148°C.

Example 3: 2-Nitro-2'-hydroxy-3',5'-di-(α,α -dimethylbenzyl)-azobenzene

Using the process of Example 2, 13.6 g (0.34 mol) of solid sodium hydroxide are dissolved in 145 ml of methanol, and 16.5 g (0.05 mol) of 2,4-di-(α,α -dimethylbenzyl)-phenol and 20 ml of methanol are added. The solution is cooled to +2°C. In the meantime, a o-nitrobenzenediazonium chloride solution is prepared from 8.3 g (0.06 mol) of o-nitroaniline and 17.3 g of concentrated HCl and 6 ml of water and from 4.3 g of sodium nitrite in 8 ml of water. The diazonium solution is added in the course of 2 hours at +2°C to the alkaline solution. The deep red mixture is stirred for 30 minutes at +2°C and then acidified with 20 ml of glacial acetic acid and the pale red precipitate is isolated by filtration. The product is washed with 3 x 50 ml of methanol and then with 4 x 75 ml of water and is then dried at 75°C/ mm Hg. The yield is 21.6 g (89% with 97% purity. Melting point: 140-142°C.

Examples 4 - 16: Alkaline coupling reaction

The procedure is as in Example 2. However, other phenols are used in place of 2,4-di-(α,α -dimethylbenzyl)-phenol. The yield varies in accordance with the substituents on the phenol.

Example No.	Phenols	Yield of o-nitroazobenzene in %
4	2,4-di-tert.-amyl	66
5	2,4-di-tert.-octyl	70(50) ^a
6	2,4-di-tert.-octyl	47 ^b
7	2,4-di-(α,α -dimethyl-benzyl)	82
8	2,4-di-(α,α -dimethyl-benzyl)	89 ^c
9	2-(1-phenylethyl)-4-methyl	84.3
10	4-methyl	56 ^d
11	2,4-di-n-octyl	56 ^e
12	2-methyl-4-(α,α -dimethyl-benzyl)	85 [*]
13	2-(α,α -dimethyl-benzyl)-4-methyl	66 ^f
14	2-(α,α -dimethyl-benzyl)-4-tert.-butyl	54
15	2-(α,α -dimethyl-benzyl)-4-tert.-octyl	62
16	2-tert.-octyl-4-(α,α -dimethyl-benzyl)	73
	control without phenol	0 ^g

a) The process was as in Example 3 with a higher concentration of alkali. The yield after purification is 50%. Evolution of N_2 gas took place. (= 48% of theory).

b) Evolution of N_2 = 60% of theory.

c) Process was in accordance with Example 3.

d) Evolution of N_2 gas = 29% of theory.

e) The acid coupling reaction gave a yield of only 16 - 19%.

f) Evolution of N_2 gas = 33% of theory.

g) When no phenol is present, about 67% of the N_2 theoretically present is evolved from the decomposed diazonium solution.

^{*} The yield is 47% when 4-chloro-2-nitrobenzenediazonium chloride is coupled with this phenol.

Example 17: 2-Nitro-2'-hydroxy-3',5'-di-(α,α -dimethyl-benzyl)-azobenzene

When Example 2 is repeated using ethanol in place of methanol, evolution of N_2 (50% of theory) is observed.

A low yield (50.5%) of the abovementioned product is obtained.

The same result is obtained when isopropanol is used in place of methanol.

These data show that methanol is the most suitable solvent for the alkaline coupling reaction.

Example 18: 4-Chloro-2-nitro-2'-hydroxy-3',5'-di-(α,α -dimethyl-benzyl)-azobenzene

When Comparison Example B is repeated using, in place of the diazonium solution prepared from 2-nitroaniline, a diazonium solution prepared from 4-chloro-2-nitroaniline in an equivalent amount, 47.3% of dark red product are obtained.

Example 19: 5-Chloro-2-[2'-hydroxy-3',5'-di-(α,α -dimethyl-benzyl)-phenyl]-2H-benzotriazole

When Example 1 is repeated using 4-chloro-2-nitro-2'-hydroxy-3',5'-di-(α,α -dimethyl-benzyl)-azobenzene in place of 2-nitro-2'-hydroxy-3',5'-di-(α,α -dimethyl-benzyl)-azobenzene, 70.0% of product are obtained.

The pale brown crystals melt at 160-161°C. (Compound 2)

Analysis: $C_{30}H_{28}CN_3O$:

calculated C: 74.45; H: 5.86; N: 8.72

found C: 74.53; H: 6.11; N: 8.72.

Example 20: 2-(2-Hydroxy-3-tert.-octyl-5- α,α -dimethyl-benzyl)-phenyl-2H-benzotriazole

When Example 1 is repeated using an equivalent amount of 2-nitro-2'-hydroxy-3'-tert.-octyl-5'- α,α -dimethyl-benzyl-azobenzene in place of the o-nitroazobenzene from Comparison Example B, the abovementioned product is obtained.

Example 21: Resistance of the benzotriazole to loss

A number of 2-aryl-2H-benzotriazoles are subjected to thermogravimetric analysis, both isothermally at 280°C, in order to determine the time in minutes after which 10%, 50% and 100% of the stabiliser are lost, and by a scanning method, in which the temperature is raised continuously by 10°C per minute until a stabiliser loss of 10% and of

50% is determined.

The test results are listed in Table A.

The results show the precise extent of the resistance of the stabiliser to exudation or volatilisation during processing of the polymer to sheets, films, fibres and the like.

Table A

Stabiliser*	Thermogravimetric analytical data isothermally at 280°C				
	Time in minutes taken to reach a loss in weight of			Temperature in °C with a temperature rise of 10°C/minute at which the loss in weight is	
	10%	50%	100%	10%	50%
TINUVIN P	0.4	0.75	1.2	182	215
TINUVIN 350	0.6	1.0	1.8	210	247
CYASORB UV-5411	0.6	1.9	3.5	225	260
Compound 333	0.8	3.0	6.0	250	290
Compound 1	6.0	24.0	56.0	300	340
Compound 2	6.0	29.0	65.0	305	350
Compound 3	1.7	6.3	12.5	273	313
Compound S1	0.8	2.6	4.5	240	282
Compound S2	1.0	4.0	7.0	257	298
Compound S3	1.0	3.4	6.6	258	298
Compound S4	0.8	2.8	5.7	263	298

* TINUVIN P is 2-(2-hydroxy-5-methylphenyl)-2H-benzotriazole. (GB 878.362)

* TINUVIN 350 is 2-(2-hydroxy-3-tert.-butyl-5-sec.-butylphenyl)-2H-benzotriazole. (DE-AS 2.130.322)

CYASORB UV-5411 is 2-(2-hydroxy-5-tert.-octylphenyl)-2H-benzotriazole. (NL 127.157)

Compound 333 is 2-[2-hydroxy-3-(1-phenylethyl)-5-methylphenyl]-2H-benzotriazole. (DE-AS 2.130.322)

Compound S1 is 2-[2-hydroxy-3-methyl-5-(α,α -dimethylbenzyl)-phenyl]-2H-benzotriazole. (JP-OS 158.588/75)

Compound S2 is 2-[2-hydroxy-3-(α,α -dimethylbenzyl)-5-methylphenyl]-2H-benzotriazole. (JP-OS 158.588/75)

Compound S3 is 2-[2-hydroxy-3-(α,α -dimethylbenzyl)-5-tert.-butylphenyl]-2H-benzotriazole. (JP-OS 158.588/75)

Compound S4 is 5-chloro-2-[2-hydroxy-3-methyl-5-(α,α -dimethyl-benzyl)-phenyl]-2H-benzotriazole. (JP-OS 158.588/75)

Compound 1 (from Example 1), is clearly more resistant than the other benzotriazoles. Compound 1, incorporated in the polymer, would therefore offer the polymer better protection against the harmful actions of light and, moreover, display excellent characteristics during processing. The same applies to Compounds 2 (Example 19) and 3 (Example 28).

Example 22: Stability of benzotriazole stabilisers in polycarbonate during the production of sheets.

Polycarbonate resin (Lexan, General Electric) was finished with 0.3% (by weight) of diverse 2-aryl-2H-benzotriazole UV absorbers. The formulated resin was extruded at 316°C to thin sheets. The resulting sheets were dissolved in methylene chloride and the polycarbonate was precipitated with methanol. The amount of benzotriazole stabiliser which remained in the polycarbonate sheet after production was determined by means of analysis by gas chromatography. The results are given in Table B.

Table B

Stabiliser*	% remaining in the polycarbonate sheet after production
TINUVIN 350	82
CYASORB UV-5411	87
Compound 333	100
Compound 1	100

* see Table A for the chemical names of these stabilisers.

These data confirm the results of Table A and the stability to sublimation and stability to exudation of Compound 1 during the production. Compound 33 likewise shows low volatility in this test.

Example 23: Stability of benzotriazole stabilisers in thermosetting acrylic coatings to losses on curing and weathering.

Diverse thermosetting acrylic resins and an alkyd/

acrylic resin system were formulated with 2% (by weight) of diverse benzotriazole UV absorbers and the formulations were cast on glass plates to give 1 μ thick coatings. The coatings were then cured for a specific time at elevated temperature. The loss of benzotriazole UV absorber was then determined by UV absorption analysis of the coatings. A reduction in the absorption of the coatings can be equated with a loss in benzotriazole stabiliser during curing.

These cured coatings were subjected to the accelerated (quick) weathering test (QUV), in which the coatings are subjected to the effect of alternating 4 hour periods of UV radiation at 60°C and 4 hour periods of condensation (rain) at 50°C over a period of 670 hours. Once again, a reduction in the absorption of the weathered coatings can be equated with a loss in benzotriazole stabiliser during curing and during weathering. The results are given in Table C.

Table C

Loss in absorption during curing or weathering (%)

Stabiliser*	Thermosetting acrylic resin systems			Alkyd/acrylic resin			
	Single coat heated after weathering for 25 minutes at 120°C	2-coat system heated after weathering for 20 minutes at 135°C	High-solids heated for 30 minutes at 150°C	heated for 30 minutes at 125°C	after weathering		
TINUVIN 328	25	35	59	69	77	100	
Compound 333	2	17	8	26	37	12	96
Compound 1	0	5	0	10	0	0	73

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* TINUVIN 328 is 2-(2-hydroxy-3,5-di-tert.-amylphenyl)-2H-benzotriazole.

Compound 333 is 2-[2-hydroxy-3-(1-phenylethyl)-5-methylphenyl]-2H-benzotriazole.

acrylic resin or polyamide or a polyurethane,

9. Stabilised polymer according to claim 8 in the form of a lacquer which has gloss retention and resistance to flaking off on weathering, characterised by

- a) a hot-crosslinkable acrylic resin and
- b) 0.1 to 5% by weight, based on the resin, of a compound of the formula I according to claims 1 to 5 and
- c) 0.1 to 5% by weight, based on the resin, of a sterically hindered amine stabiliser.

10. Stabilised organic material according to claim 9, containing 0.5 to 2% by weight of b) and 0.5 to 2% by weight of c).

11. Stabilised organic material according to claim 9, containing, as constituent c), bis-(2,2,6,6-tetramethyl-4-piperidyl) sebacate as a light stabiliser.

12. Stabilised organic material according to claim 9, containing, as component c), bis-(1,2,2,6,6-pentamethyl-4-piperidyl) 2-n-butyl-2-(3,5-di-tert.-butyl-4-hydroxybenzyl)-malonate as a light stabiliser.

Table C shows that the compound according to the invention suffers much smaller losses in the thermosetting acrylic resin and alkyd/acrylic resin systems than do known benzotriazoles. Compound 1 is considerably less volatile than compound 333, which has a comparable structure.

Example 24: Gloss values of acrylic enamel and lacquers containing benzotriazole stabilisers, and weathering.

Diverse thermosetting acrylic enamels and thermoplastic acrylic lacquers were formulated with a benzotriazole UV absorber. The gloss values are compared with those of the original enamel or the lacquer after accelerated weathering (QUV with one cycle of 4 hours UV at 60°C and one cycle of 4 hours condensation at 50°C). The results are given in Table D.

Table D

<u>Stabiliser*</u>	<u>20° gloss values of enamels or lacquers containing benzotriazole stabilisers, before and after weathering</u>					
	<u>Thermosetting acrylic enamel A</u>		<u>Thermosetting acrylic enamel B</u>		<u>Thermoplastic acrylic lacquer</u>	
	<u>before</u>	<u>800 hours QUV</u>	<u>before</u>	<u>800 hours QUV</u>	<u>before</u>	<u>200 hours QUV</u>
no stabilisers	65	15.4	67.3	25.1	77.8	23.1
1% of TINUVIN 328	68.1	15.0	64.6	26.7	-	-
1% of Compound 333	68.7	19.8	65.2	25.6	78.0	24.0
1% of Compound 1	66.9	27.8	68.8	33.2	78.5	41.1
2% of TINUVIN 328	64.8	16.6	59.2	23.1	77.1	33.5
2% of Compound 333	68.6	19.4	63.5	30.3	77.4	41.0
2% of Compound 1	66.7	27.2	69.3	39.0	79.1	41.0

* See Table C for the chemical names of these stabilisers.

Throughout, formulations containing Compound 1 gave better gloss after QUV weathering than those containing benzotriazoles known hitherto.

Example 25: Stabilisation of polyethylene terephthalate.

0.5% of the compound of Example 1 is added, as the

stabiliser, to molten polyethylene terephthalate at 270°C, with stirring and under a nitrogen atmosphere. The resulting, formulated polymer is ground with solid carbon dioxide.

The stabilised mixture is extruded to a film at elevated temperature, with little stabiliser loss. The film is then subjected to UV radiation. The stabilised film retains its desired physical properties longer than the film which has not been stabilised.

Example 26: Stabilisation of polycarbonate.

Polycarbonate (Lexan, General Electric) is mixed in an extruder with 0.3% of the compound of Example 4. The stabilised mixture is extruded to a sheet at elevated temperature, with little loss of stabiliser. The sheet retains its physical properties after UV radiation longer than does a sheet without stabiliser.

Example 27: 2-Nitro-2'-hydroxy-3'-(α,α -dimethylbenzyl)-5-tert.-octylazobenzene.

This compound is obtained, in the form of a red crystalline solid with a melting point of 133-134°C, by the general process of Example 3, by a coupling reaction of o-nitrobenzene-diazonium chloride with 2-(α,α -dimethylbenzyl)-4-tert.-octyl-phenol.

Example 28: 2-(2-Hydroxy-3-(α,α -dimethylbenzyl)-5-tert.-octylphenyl)-2H-benzotriazole.

The general process of Example 1 is carried out using an equivalent amount of 2-nitro-2'-hydroxy-3'-(α,α -dimethylbenzyl)-5'-tert.-octylazobenzene in place of the o-nitroazobenzene intermediate of Comparison Example B. The above compound is obtained in the form of virtually white crystals. Melting point 88-90°C (Compound 3).

Analysis: calculated for $C_{29}H_{35}N_3O$:

	C:	78.87;	H:	7.99;	N:	9.51
found:	C	79.21;	H:	8.01;	N:	9.55.

Example 29: 2-(2-Hydroxy-3-tert.-octyl-5-(α,α -dimethylbenzyl)-phenyl)-2H-benzotriazole.

The process of Example 1 is carried out using an

equivalent amount of 2-nitro-2'-hydroxy-3'-tert.-octyl-5-(α,α -dimethylbenzyl)-azobenzene in place of the o-nitroazobenzene intermediate of Comparison Example B.

The above compound is obtained.

The delamination of UV-transparent top-coat lacquers for motorcars, which lacquers are applied to epoxy ester primer surfaces, is a serious problem for motorcar manufacturers. This problem is particularly relevant if the thickness of the top-coat lacquer is less than the specified thickness. The incorporation of UV absorbers according to the invention in the top-coat lacquer protects this lacquer against delamination and against loss of gloss.

Example 30: Gloss and delamination values of top-coat lacquers of thermoplastic acrylate.

A silver metal-thermoplastic acrylic lacquer was formulated with a benzotriazole UV absorber and then sprayed as the top-coat lacquer onto a primer surface of an epoxy ester on metal sheets. The whole was heated for 10 minutes at 48°C and then for 30 minutes at 155°C. The original coating thickness of the top-coat lacquer was 2.0 to 2.2 mils (50 to 55 microns, 0.0508 to 0.0559 mm).

The sheets were exposed to the sun in an unheated black box at an angle of 5° for one year in southern Florida.

The exposed sheets were placed in a constant humidity chamber at 38°C and 100% relative humidity for 96 hours. They were then dried off and immediately assessed by means of the "cross-hatch tape" adhesion test. The sheets were then left at room temperature for one hour, before the "cross-hatch tape" adhesion test was repeated at another point on the same plate. The samples in general display a somewhat improved stability to delamination after this one hour recovery period, compared with the delamination immediately after the humidity treatment.

In the "cross-hatch tape" adhesion test, a multi-

blade knife is used to apply cuts through the top-coat lacquer to the sheet. An acetate fibre adhesive tape is stuck over the cut areas and then pulled off. The top-coat lacquer is assessed visually to determine whether and to what extent it has been pulled off. This gives a relative assessment of the delamination from 0 (no "cross-hatch" delamination) to 5 (complete "cross-hatch" delamination). The results are given in Tables E and F.

Table E

20° gloss values of silver-metallic thermo-plastic acrylic lacquer* after exposure at 5° in a black box in southern Florida

Stabilisers (% by weight) ^{XX}	before	after 6 months (Florida)	after 1 year (Florida)	after 1 year polished ^{XXX}
none	77.8	15.1	1.6	4.4
1% of Compound 333	78.0	33.5	3.7	6.6
1% of Compound 1	78.5	44.0	13.4	29.5
2% of TINUVIN 328	77.1	34.9	8.5	13.7
2% of Compound 333	77.4	41.0	9.5	28.0
2% of TINUVIN 350	77.5	37.5	6.0	24.3
2% of Compound 1	79.1	53.4	15.8	28.9
2% of Compound 2	79.4	50.0	17.7	38.4

* Thermoplastic acrylic lacquer obtained from a binder of 60% of poly(methyl methacrylate), 20% of cellulose acetate-butyrate and 20% of plasticiser and about 3% of metallic pigment.

^{XX} See Tables A and C for the chemical names of these stabilisers.

^{XXX} Half of each sheet was polished with DuPont No. 7 car polish.

Table F

Delamination values for silver-metallic thermoplastic acrylic lacquer^{*} after exposure for one year at 50° in a black box in southern Florida

Stabiliser ^{XX} (% by weight)	Delamination value (0 to 5)	
	Immediately after the humidity treatment	After a recovery period of one hour at room temperature after the humidity treatment
none	5	5
1% of Compound 1	2	1
2% of TINUVIN 328	5	2
2% of TINUVIN 350	3	2
2% of Compound 333	5	4
2% of Compound 1	2	2
2% of Compound 2	4	3

* See the description of the lacquer given under Table E.

XX See Tables A and C for the chemical names of these stabilisers.

The data in Table E confirm that Compound 1 and the compound of Example 10 effect excellent protection against losses during prolonged exposure in the southern Florida black box test, compared with other benzotriazole light stabilisers.

The data in Table F show that the compounds according to the invention, and especially Compound 1, protect a thermoplastic acrylic top-coat lacquer against delamination after 1 year's exposure in a black box in southern Florida under extremely strict test conditions with immediate subsequent humidity treatment.

Example 31: Delamination values of top-coat lacquers of thermosetting acrylic enamels.

Two silver-metallic thermosetting acrylic enamels were formulated with a benzotriazole light stabiliser and then sprayed as the top-coat lacquer onto a primer surface of an epoxy ester on a metal sheet. Curing was

carried out for 17 minutes at 130°C to give an initial top-coat lacquer film 1.7 mil thick (42 microns, 0.0432 mm). The plate was treated for 1,200 hours in the QUV weathering test according to Example 23.

After the QUV weathering, the sheets were subjected to a humidity treatment and the delamination was then determined; the sheets were then allowed a one hour recovery period, after which the stability to delamination was again determined according to Example 30. The results are given in Table G.

Table G

Delamination values of a silver-metallic thermosetting acrylic enamel after 1,200 hours QUV weathering

<u>Stabiliser</u> <u>(% by weight)</u>	Delamination value (0 to 5)			
	Enamel * A		Enamel * B	
	Immedi- ately after the humidity treatment	After a 1 hour recovery period at room tempera- ture after the humidity treatment	Immedi- ately after the humidity treatment	After a 1 hour recovery period at room tempera- ture after the humidity treatment
none	3	1	5	3
1% of Compound 1	0	0	0	0
2% of Compound 1	0	0	0	0

* Thermosetting acrylic enamel consisting of a binder of 70% of acrylic monomers, such as hydroxyethyl acrylate, styrene, acrylonitrile, butyl acrylate and acrylic acid with 30% of a melamine resin. Enamel A is a low-solids (40-45%) ready-to-use solution. Enamel B is a non-aqueous dispersion (NAD) containing about 40-50% of solids and about 3% of metallic pigment.

The combination of sterically hindered amine light stabilisers with the benzotriazole UV absorbers according to the invention is particularly suitable for retaining

the gloss and preventing delamination, especially in the case of metallised thermosetting acrylic enamels and in the case of metallised thermoplastic acrylic lacquers for the top-coat lacquers on motorcars.

Even in low concentration, the hindered amines protect the thermosetting acrylic enamel and the thermoplastic acrylic lacquer against losses in gloss, but they do not act as UV filters. Accordingly, UV light can pass through the acrylic top-coat lacquer if a UV absorber, such as the benzotriazoles according to the invention, is not present, and can cause damage in the epoxy ester primer surface beneath the top-coat lacquer. The incorporation of a benzotriazole, even in low concentrations (0.5% by weight), in combination with a hindered amine effects both gloss retention and resistance to delamination in metallised acrylic top-coat lacquers.

Example 32: Delamination values for top-coat lacquers of thermosetting acrylic enamels.

Two silver-metallised thermosetting acrylic enamels were formulated both with a hindered amine light stabiliser and with a benzotriazole UV absorber. The test sheets were produced and tested as described in Example 31. The results are given in Table H.

Table H

Delamination values of a silver-metallic
thermosetting acrylic enamel after
1,200 hours QUV weathering

<u>Stabiliser^{xx}</u> <u>(% by weight)</u>	Delamination values (0 to 5)			
	Enamel A		Enamel B	
	Immedi- ately after the humidity treatment	After a 1 hour recovery period at room tempera- ture after the humidity treatment	Immedi- ately after the humidity treatment	After a 1 hour recovery period at room tempera- ture after the humidity treatment
none	3	1	5	3
0.5% of Compound A	1	0	5	2
1% of Compound A	3	0	5	1
2% of Compound A	3	0	5	1
0.5% of Compound B	5	2	5	3
1% of Compound B	4	2	5	0
2% of Compound B	2	2	5	0
1% of TINUVIN 328	0	0	0	0
2% of TINUVIN 328	0	0	0	0
1% of Compound 1	0	0	0	0
2% of Compound 1	0	0	0	0
1% of Compound A + 1% of TINUVIN 328	0	0	0	0
1% of Compound B + 1% of TINUVIN 328	0	1	0	0
1% of Compound A + 1% of Compound 333	0	0	0	0
1% of Compound B + 1% of Compound 333	1	0	0	0
1% of Compound A + 1% of Compound 1	0	0	0	0
1% of Compound B + 1% of Compound 1	0	0	0	0

* See the description of the thermosetting acrylic enamel

in Table G.

~~See~~ See Table C for the chemical names of Tinuvin 328 and Compound 333.

Compound A is bis-(2,2,6,6-tetramethyl-4-piperidyl) sebacate

Compound B is bis-(1,2,2,6-pentamethyl-4-piperidyl) 2-n-butyl-2-(3,5-di-tert.-butyl-4-hydroxybenzyl)-malonate.

Example 33: Delamination and 20° gloss values of thermoplastic acrylic lacquers.

The effectiveness of combinations of hindered amine light stabilisers with benzotriazole UV absorbers according to the invention for the protection of top-coat lacquers for motorcars can be seen with thermoplastic acrylic resins, with which not only is gloss retention after prolonged exposure in southern Florida effected by the hindered amine but protection of the thermoplastic acrylic top-coat lacquer against delamination is also effected by the benzotriazole UV absorbers according to the invention.

A silver-metallic thermoplastic acrylic lacquer was formulated both with a hindered amine light stabiliser and with a benzotriazole UV absorber. Test sheets are produced and tested as described in Example 30. The results are given in Table J.

Table J

Delamination and 20° gloss values of a silver-metallic thermoplastic acrylic lacquer* after exposure at 5° in a black box in southern Florida

Stabiliser ^{XX} (% by weight)	20° gloss values				Delamination values (0 to 5)	
	before	after 6 months in Florida	after 1 year in Florida	after 1 year in Florida, polished	immediately after the humidity treatment	after exposure for 1 year after a 1 hour recovery period at room temperature after the humidity treatment
none	77.8	15.1	1.6	4.4	5	5
0.5% of Compound A	77.5	48.0	15.1	35.6	5	3
1% of Compound A	77.2	42.0	36.2	39.7	5	5
2% of Compound A	76.7	44.2	14.3	31.4	5	5
0.5% of Compound B	77.9	45.0	38.5	45.6	5	5
1% of Compound B	77.4	45.4	22.1	37.7	5	2
2% of Compound B	76.8	45.3	26.5	46.0	5	3
2% of TINUVIN 328	77.1	34.9	8.5	13.7	5	2
2% of DOBP	77.5	35.0	6.8	19.7	3	2
1% of Compound 333	78.0	33.5	3.7	6.6	-	-
2% of Compound 333	77.4	41.0	9.5	28.0	5	4
1% of Compound 1	78.5	44.0	13.4	29.5	2	1
2% of Compound 1	79.1	53.4	15.8	28.9	2	2

Table J (Continuation)

Delamination and 20° gloss values of a silver-metallic thermoplastic acrylic lacquer* after exposure at 5° in a black box in southern Florida

Stabiliser** (% by weight)	20° gloss values				Delamination values (0 to 5) after exposure for 1 year	
	before	after 6 months in Florida	after 1 year in Florida	after 1 year in Florida, polished	immediately after a 1 hour after the recovery period at room temperature after the humidity treatment	
1% of Compound 2	79.4	50.0	17.7	38.4	4	3
2% of TINUVIN 350	77.5	37.5	6.0	24.3	3	2
1% of Compound A + 1% of TINUVIN 320	77.6	47.8	19.6	41.3	5	5
0.5% of Compound A + 0.5% of Compound 333	78.3	50.2	21.4	39.4	5	4
0.5% of Compound B + 0.5% of Compound 333	78.2	52.7	18.8	41.3	3	2
1% of Compound A + 1% of Compound 333	78.4	49.6	21.7	39.0	5	4
1% of Compound B + 1% of Compound 333	77.7	47.5	25.4	44.6	4	3

Table J (Continuation)

Delamination and 20° gloss values of a silver-metallic thermoplastic acrylic lacquer* after exposure at 5° in a black box in southern Florida

Stabiliser** (% by weight)	20° gloss values			Delamination values (0 to 5) after exposure for 1 year	
	before	after 6 months in Florida	after 1 year in Florida	after 1 year humidity treatment	immediately after a 1 hour after the recovery period at room temperature after the humidity treatment
			polished		
0.5% of Compound A +	78.2	47.1	16.0	3	2
0.5% of Compound 1					
0.5% of Compound B +	77.7	48.0	33.4	3	2
0.5% of Compound 1					

* See the description of the thermoplastic acrylic lacquer in Table E.

** See Tables A, C and H for the chemical names of the stabilisers.

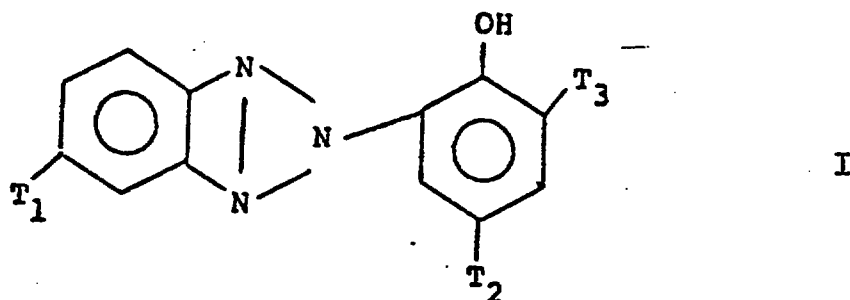
DOB is 4-dodecyloxy-2-hydroxybenzophenone.

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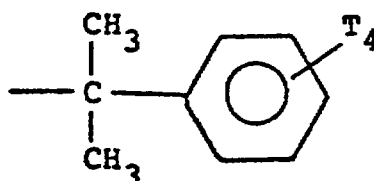


WHAT IS CLAIMED IS:

1. A compound of the formula I



in which T_1 is hydrogen or chlorine and T_2 and T_3 independently of one another are the group



in which T_4 is hydrogen or lower alkyl, and one of T_2 and T_3 can also be t-octyl.

2. A compound according to claim 1, in which T_1 is hydrogen or chlorine, T_2 and T_3 have the same meaning and T_4 is hydrogen or p-methyl.

3. A compound according to claim 1, in which T_4 is hydrogen.

4. A compound according to claim 1, which is 2-[2-hydroxy-3,5-di-(α,α -dimethylbenzyl)-phenyl]-2H-benzotriazole.

5. A compound according to claim 1, which is 5-chloro-2-[2-hydroxy-3,5-di-(α,α -dimethylbenzyl)-phenyl]-2H-benzotriazole.

6. Stabilised organic material containing 0.1 - 5% by weight of a stabiliser according to any one of claims 1 to 5.

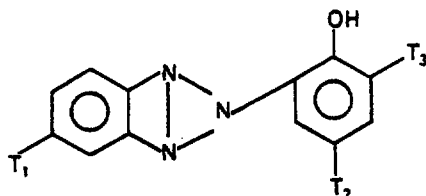
7. Stabilised organic material according to claim 6, wherein the material is a synthetic polymer.

8. Stabilised polymer according to claim 7 and 6, wherein the polymer is a polyester, polycarbonate, hot-crosslinkable

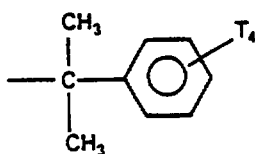


Claims

1. A compound of the formula



wherein T_1 is hydrogen or chlorine and each of T_2 and T_3 independently of the other is the group



wherein T_4 is hydrogen or lower alkyl, whilst one of T_2 and T_3 can also be t-octyl.

2. A compound according to claim 1, wherein T_1 is hydrogen or chlorine, T_2 and T_3 have the same meaning and T_4 is hydrogen or p-methyl.

3. A compound according to claim 1, wherein T_4 is hydrogen.

4. 2-[2-Hydroxy-3,5-di-(α,α -dimethylbenzyl)-phenyl]-2H-benzotriazole, according to claim 1.

5. 5-Chloro-2-[2-hydroxy-3,5-di-(α,α -dimethylbenzyl)-phenyl]-2H-benzotriazole according to claim 1.

6. A stabilised organic material containing 0,1-5% by weight of a stabiliser according to any one

of claims 1 to 5.

7. A stabilised organic material according to claim 6, wherein the material is a synthetic polymer.

8. A stabilised polymer according to claim 6, wherein the polymer is a polyester, polycarbonate, hot-crosslinkable acrylic resin or polyamide or a polyurethane.

9. A lacquer which has gloss retention and resistance to peeling on weathering, said lacquer containing

a) a hot-crosslinkable acrylic resin and

b) 0,1 to 5% by weight, based on the resin, of a compound of the formula I according to any one of claims 1 to 5 and

c) 0,1 to 5% by weight, based on the resin, of a sterically hindered amine stabiliser.

10. A stabilised organic material according to claim 9, containing 0,5 to 2% by weight of b) and 0,5 to 2% by weight of c).

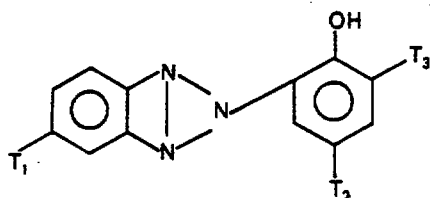
11. A stabilised organic material according to claim 9, containing, as constituent c), bis-(2,2,6,6-tetramethyl-4-piperidyl) sebacate as light stabiliser.

12. A stabilised organic material according to claim 9, containing, as component c), bis-(1,2,2,6,6-pentamethyl-4-piperidyl)-2-n-butyl-2-(3,5-di-tert.-butyl-4-hydroxybenzyl)-malonate as light stabiliser.

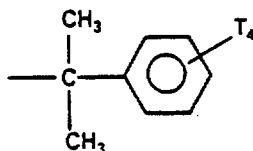


Revendications

1. Composés répondant à la formule I



dans laquelle T_1 représente l'hydrogène ou le chlore, et T_2 et T_3 représentent chacun, indépendamment l'un de l'autre, un radical:



dans lequel T_4 représente l'hydrogène ou un radical alkyle inférieur, l'un des symboles T_2 et T_3 pouvant également être un radical tert-octyle.

2. Composés selon la revendication 1 dans lesquels T_1 représente l'hydrogène ou le chlore, T_2 et T_3 ont la même signification et T_4 représente l'hydrogène ou un radical méthyle en para.

3. Composés selon la revendication 1 dans lesquels T_4 représente l'hydrogène.

4. Composé selon la revendication 1, en l'es-

pèce l'[hydroxy-2-bis-(α,α -diméthylbenzyl)-3,5-phényl]-2-2H-benzotriazole.

5. Composé selon la revendication 1, en l'es-pèce le chloro-5-[hydroxy-2-bis-(α,α -diméthylbenzyl)-3,5-phényl]-2-2H-benzotriazole.

6. Matière organique stabilisée qui contient de 0,1 à 5% en poids d'un stabilisant selon l'une quelconque des revendications 1 à 5.

7. Matière organique stabilisée selon la revendication 6, caractérisée en ce que la matière est un polymère synthétique.

8. Polymère stabilisé selon la revendication 6, caractérisé en ce que le polymère est un polyester, un polycarbonate, une résine acrylique réticulable à chaud, un polyamide ou un polyuréthane.

9. Vernis conservant son brillant et résistant bien à l'écaillage lorsqu'il est exposé aux agents atmosphériques, vernis qui renferme:

a) une résine acrylique réticulable à chaud,

b) de 0,1 à 5% en poids, par rapport à la résine, d'un composé de formule I selon l'une quelconque des revendications 1 à 5 et

c) de 0,1 à 5% en poids, par rapport à la résine, d'un stabilisant qui est une amine à empêchement stérique.

10. Matière organique stabilisée selon la revendication 9, qui contient de 0,5 à 2% en poids de b) et de 0,5 à 2% en poids de c).

11. Matière organique stabilisée selon la revendication 9, qui renferme, comme constituant c), du sébacate de bis-(tétraméthyl-2,2,6,6-pipéridyle-4) jouant le rôle de stabilisant à la lumière.

12. Matière organique stabilisée selon la revendication 9, qui renferme, comme constituant c), du n-butyl-2-(di-tert-butyl-3,5-hydroxy-4-benzyl)-2-malonate de bis-(pentaméthyl-1,2,2,6,6-pipéridyle-4) jouant un rôle de stabilisant à la lumière.