

Stabilization of metallic effect paints against the action of light, moisture and oxygen, by adding polyalkylpiperidine derivatives.

The present invention relates to the stabilization of metallic effect paints based on alkyd or acrylic resins which can be crosslinked by heat, against the action of light and moisture, by adding polyalkylpiperidine derivatives, and to the metallic effect paints thus stabilized.

It has been found that the problems which constantly occur in applying metallic effect paints, in particular in respect of crazing and loss of gloss, when metallic effect paints based on alkyd or acrylic resins which can be crosslinked by heat are used, can be solved satisfactorily by adding light stabilizers based on polyalkylpiperidine derivatives, if appropriate together with further stabilizers.

Admittedly, it is known from Belgian Patent Specification 854,444 to add 2,2,6,6-tetraalkylpiperidine derivatives to thermoplastic polyacrylates as stabilizers. However, these are not resins such as can be used for metallic effect paints. The addition of such piperidine derivatives to acrylic resin paints containing nitrocellulose is disclosed in Japanese Preliminary Published Applications 52-51,427 and 52-22,029. These are paints which dry physically and in which the tendency to discoloration is reduced by the addition. It has not been possible to draw any conclusion from these publications regarding the specific problems arising when light acts on metal-pigmented

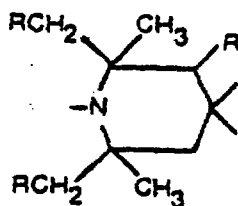


metallic effect paints - in particular crazing and ⁶²loss of gloss.

The present invention therefore relates to the use of 2,2,6,6-tetraalkylpiperidine compounds, their acid addition salts or their complexes with metal compounds, if appropriate together with further stabilizers, for stabilizing metallic effect paints based on alkyd or acrylic resins which can be crosslinked by heat against the action of light, moisture and oxygen.

10 The 2,2,6,6-tetraalkylpiperidine compounds to be used in accordance with the invention are generally known and are already employed against degradation caused by light. They are, for example, compounds which contain a group of the formula (I)

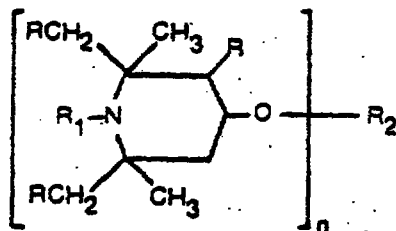
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wherein R denotes hydrogen or methyl.

The light stabilizers to be used in accordance with the invention include, in particular, the following classes of compounds:

20 a) Light stabilizers of the formula (II)



wherein n denotes the numbers 1-4, preferably 1 or 2, R has the meaning indicated for formula (I), R₁ denotes hydrogen, amine oxide, C₁-C₁₈-alkyl, C₃-C₈-alkenyl, C₃-C₈-alkynyl,

C₇-C₁₂-aralkyl, C₁-C₈-alkanoyl, C₃-C₈-alkenoyl, glycidyl, a group -CH₂CH(OH)-Z wherein Z is hydrogen, methyl or phenyl, R₁ being preferably hydrogen, C₁-C₁₂-alkyl, allyl, benzyl, acetyl or acryloyl, and, if n=1, R₂ denotes hydrogen, C₁-C₁₈-
5 alkyl which is optionally interrupted by one or more oxygen atoms, cyanoethyl, benzyl, glycidyl, a monovalent radical of an aliphatic, cycloaliphatic, araliphatic or aromatic carboxylic acid, carbamic acid or an acid containing phosphorus, or a monovalent silyl radical, preferably a radical of an
10 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 7-15 C atoms, or, if n=2, R₂ denotes C₁-C₁₂-alkylene, C₄-C₁₂-alkenylene, xylylene, a divalent radical of an aliphatic, cycloaliphatic, araliphatic
15 or aromatic dicarboxylic acid, dicarbamic acid or an acid containing phosphorus, 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 8-14 C atoms, or of an aliphatic, cycloaliphatic or
20 aromatic dicarbamic acid having 8-14 C atoms, or, if n=3, R₂ denotes a trivalent radical of an aliphatic, cycloaliphatic or aromatic tricarboxylic acid, an aromatic tricarbamic acid or an acid containing phosphorus, or a trivalent silyl radical, or, if n=4, R₂ denotes a tetravalent radical of an
25 aliphatic, cycloaliphatic or aromatic tetracarboxylic acid.

If any substituents are denoted by C₁-C₁₂-alkyl, they 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.

30 When they denote C₁-C₁₈-alkyl, R₁ or R₂ can represent, for example, the groups listed above and additionally thereto, for example, n-tridecyl, n-tetradecyl, n-hexadecyl or n-octadecyl.

If R₁ denotes C₃-C₈-alkenyl, it can be, for example,
35 1-propenyl, allyl, methallyl, 2-butenyl, 2-pentenyl, 2-hexenyl, 2-octenyl or 4-tert.-butyl-2-butenyl.

As C₃-C₈-alkynyl, R₁ is preferably propargyl.

As C₇-C₁₂-aralkyl, R₁ is, in particular, phenethyl or, above all, benzyl.

As C₁-C₈-alkanoyl, R₁ is, for example, formyl, propionyl, butyryl or octanoyl or, preferably, acetyl, and as
5 C₃-C₅-alkenoyl R₁ is, in particular, acryloyl.

If R₂ denotes a monovalent radical of a carboxylic acid, it represents, for example, an acetic acid, stearic acid, salicylic acid, methacrylic acid, maleic acid, benzoic acid, or β-(3,5-ditert.-butyl-4-hydroxyphenyl)-propionic
10 acid radical.

If R₂ denotes a divalent radical of a dicarboxylic acid, it represents, for example, an adipic acid, suberic acid, sebacic acid, phthalic acid, dibutylmalonic acid, dibenzylmalonic acid, butyl-(3,5-ditert.-butyl-4-hydroxybenzyl)-malonic
15 acid radical or bicycloheptenedicarboxylic acid.

If R₂ represents a trivalent radical of a tricarboxylic acid, it denotes, for example, a trimellitic acid radical or a nitrilotriacetic acid radical.

If R₂ represents a tetravalent radical of a tetracarboxylic acid, it denotes, for example, a pyromellitic acid radical.
20 acid radical.

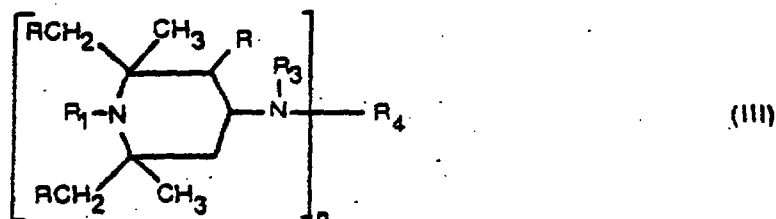
If R₂ denotes a divalent radical of a dicarbamic acid, it represents, for example, a hexamethylenedicarbamic acid radical or a 2,4-toluylenedicarbamic acid radical.

25 The following compounds are examples of polyalkylpiperidine light stabilizers of this class:

- 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
- 30 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
- 35 8) 1,2,2,6,6-Pentamethylpiperidin-4-yl β-(3,5-ditert.-butyl-4-hydroxyphenyl)-propionate
- 9) 1-Benzyl-2,2,2,6,6-tetramethyl-4-piperidinyl maleate

- 10) Di-2,2,6,6-tetramethylpiperidin-4-yl adipate
- 11) Di-2,2,6,6-tetramethylpiperidin-4-yl sebacate
- 12) Di-1,2,3,6-tetramethyl-2,6-diethylpiperidin-4-yl sebacate
- 13) Di-1-allyl-2,2,6,6-tetramethylpiperidin-4-yl phthalate
- 5 14) 1-Propargyl-4- β -cyanoethoxy-2,2,6,6-tetramethylpiperidine
- 15) 1-Acetyl-2,2,6,6-tetramethylpiperidine-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
- 10 19) Di-(1,2,2,6,6-pentamethylpiperidin-4-yl) butyl-(3,5-ditert.-butyl-4-hydroxybenzyl)-malonate
- 20) Di-(1,2,2,6,6-pentamethylpiperidin-4-yl) dibenzylmalonate
- 21) Di-(1,2,3,6-tetramethyl-2,6-diethylpiperidin-4-yl) dibenzylmalonate
- 15 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
- 20 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) Bis-(1,2,2,6,6-pentamethylpiperidin-4-yl) phenyl-phosphonate

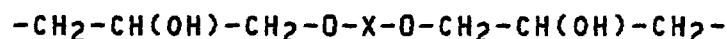
25 b) Light stabilizers of the formula (III)



wherein n denotes the numbers 1 or 2, R has the meaning indicated for formula I, R₁ has the meaning indicated under a), R₃ is hydrogen, C₁-C₁₂-alkyl, C₅-C₇-cycloalkyl, C₇-C₈-aralkyl, C₂-C₁₈-alkanoyl, C₃-C₅-alkenoyl or benzoyl,

and, if $n=1$, R_4 denotes hydrogen, C_1 - C_{18} -alkyl, C_5 - C_7 -cycloalkyl, C_2 - C_8 -alkenyl which is optionally substituted by a cyano, carbanoyl or carboxamide group, glycidyl or a group of the formula $-CH_2-CH(OH)-Z$ or of the formula $-CONH-Z$ wherein
 5 Z denotes hydrogen, methyl or phenyl; if $n=2$, R_4 denotes C_2 - C_{12} -alkylene, C_6 - C_{12} -arylene, xylilene (sic), a group
 $-CH_2-CH(OH)-CH-$ (sic)

or a group



10 wherein X is C_2 - C_{10} -alkylene, C_6 - C_{15} -arylene or C_6 - C_{12} -cycloalkylene, or, provided that R_3 does not denote alkanoyl, alkenoyl or benzoyl, R_4 can also denote a divalent radical of an aliphatic, cycloaliphatic or aromatic dicarboxylic acid or dicarbamic acid or the group $-CO-$, or, if $n=1$, R_3 and R_4 together can be the cyclic radical of an aliphatic or aromatic
 15 1,2-dicarboxylic or 1,3-dicarboxylic acid.

If any substituents represent C_1 - C_{18} -alkyl, they have the meaning already indicated under a).

If any substituents denote C_5 - C_7 -cycloalkyl, they represent, in particular, cyclohexane.
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As C_7 - C_8 -aralkyl, R_3 is, in particular, phenethyl or, above all, benzyl.

As C_2 - C_{18} -alkanoyl, R_3 is, for example, propionyl, butyryl, octanoyl, dodecanoyl, hexadecanoyl or octadecanoyl,
 25 but preferably acetyl, and as C_3 - C_5 -alkenoyl, R_3 is, in particular, acryloyl

If R_4 represents C_2 - C_8 -alkenyl which is optionally substituted by a cyano, carbonyl or carboxamide group, it is, for example, 1-propenyl, allyl, methallyl, 2-butenyl, 2-
 30 pentenyl, 2-hexenyl, 2-octenyl, 2,2-dicyanovinyl, 1-methyl-2-cyano-2-methoxycarbonyl-vinyl or 2,2-diacetylaminovinyl.

If any substituents represent C_2 - C_{12} -alkylene, they are, for example, ethylene, propylene, 2,2-dimethylpropylene, tetramethylene, hexamethylene, octamethylene, decamethylene
 35 or dodecamethylene.

If any substituents denote C_6 - C_{15} -arylene, they represent, for example, o-, m- or p-phenylene, 1,4-naphthylene

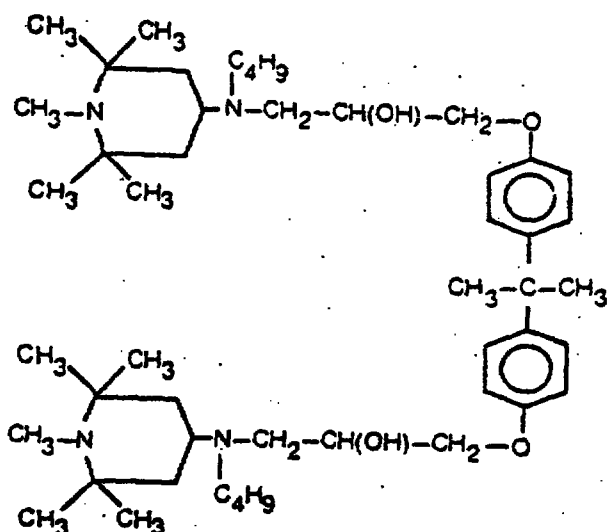
or 4,4'-diphenylene.

As C₆-C₁₂-cycloalkylene, X is, in particular, cyclohexylene.

The following compounds are examples of polyalkyl-5 piperidine light stabilizers of this class:

- 29) N,N'-Bis-(2,2,6,6-tetramethylpiperidin-4-yl)-hexamethylene-1,6-diamine
- 30) N,N'-Bis-(2,2,6,6-tetramethylpiperidin-4-yl)-hexamethylene-1,6-diacetamide
- 10 31) 1-Acetyl-4-(N-cyclohexylacetamido)-2,2,6,6-tetramethylpiperidine
- 32) 4-Benzylamino-2,2,6,6-tetramethylpiperidine
- 33) N,N'-bis-(2,2,6,6-tetramethylpiperidin-4-yl)-N,N'-dibutyladipamide
- 15 34) N,N'-Bis-(2,2,6,6-tetramethylpiperidin-4-yl)-N,N'-di-cyclohexyl-(2-hydroxypropylene)
- 35) N,N'-Bis-(2,2,6,6-tetramethylpiperidin-4-yl)-p-xylylene-diamine
- 36) The compound of the formula

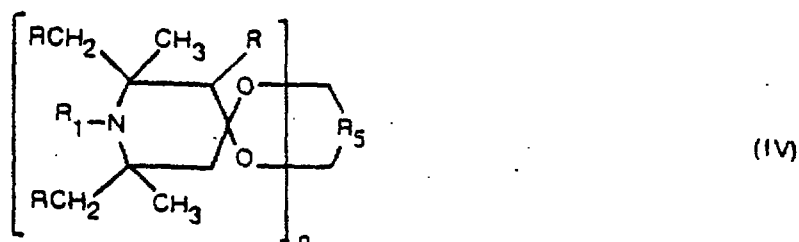
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- 37) 4-(Bis-2-hydroxyethyl)-amino-1,2,2,6,6-pentamethylpiperidine
- 38) 4-(3-Methyl-4-hydroxy-5-tert.-butylbenzamido)-2,2,6,6-tetramethylpiperidine
- 39) 4-Methacrylamido-1,2,2,6,6-pentamethylpiperidine

40) Methyl α -cyano- β -methyl- β -[N-(2,2,6,6-tetramethylpiperidin-4-yl)]-aminoacrylate.

c) Light stabilizers of the formula (IV)



5 wherein n denotes the numbers 1 or 2, R has the meaning indicated for formula (I), R₁ has the meaning indicated under a), and, if n=1, R₅ denotes C₂-C₈-alkylene or C₂-C₈-hydroxyalkylene or C₄-C₂₂ acyloxyalkylene, and, if n=2, R₅ denotes the group (-CH₂)₂C(CH₂)₂.

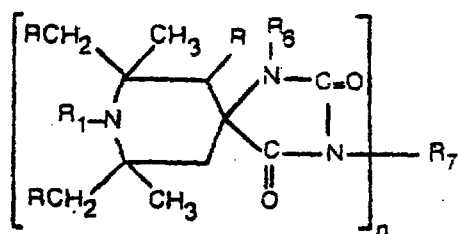
10 If R₅ denotes C₂-C₈-alkylene or C₂-C₈-hydroxyalkylene, it represents, for example, ethylene, 1-methylethylene, 1-methylethylene, propylene, 2-ethylpropylene or 2-ethyl-2-hydroxymethylpropylene.

As C₄-C₂₂-acyloxyalkylene, R₅ denotes, for example,
15 2-ethyl-2-acetoxymethylpropylene.

The following compounds are examples of polyalkylpiperidine light stabilizers of this class:

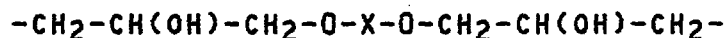
- 41) 9-Aza-8,8,10,10-tetramethyl-1,5-dioaspiro-[5.5]undecane
- 42) 9-Aza-8,8,10,10-tetramethyl-3-ethyl-1,5-dioxaspiro[5.5]decane
- 20 43) 8-Aza-2,7,7,8,9,9-hexamethyl-1,4-dioxyspiro[4.5]decane (sic)
- 44) 9-Aza-3-hydroxymethyl-3-ethyl-8,8,9,10,10-pentamethyl-1,5-dioxaspiro[5.5]decane
- 45) 9-Aza-3-ethyl-3-acetoxymethyl-9-acetyl-8,8,10,10-tetramethyl-1,5-dioxaspiro[5.5]undecane
- 25 46) 2,2,6,6-Tetramethylpiperidine-4-spiro-2'-(1'3-dioxane)-5'-spiro-5''-(1'',3''-dioxane)-2''-spiro-4'''-(2''',2''',6''',6'''-tetramethylpiperidine).

d) Light stabilizers of the formula (V)



(V)

wherein n denotes the numbers 1 or 2, R has the meaning indicated for formula (I), R_1 has the meaning indicated under a), R_6 is hydrogen, C_1 - C_{12} -alkyl, allyl, benzyl, glycidyl or C_2 - C_6 -alkoxyalkyl, and, if $n=1$, R_7 denotes hydrogen, C_1 - C_{12} -alkyl, C_3 - C_5 -alkenyl, C_7 - C_9 -aralkyl, C_5 - C_7 -cycloalkyl, C_2 - C_4 -hydroxyalkyl, C_2 - C_6 -alkoxyalkyl, C_6 - C_{10} -aryl, glycidyl or a group of the formula $-(CH)-COO-Q$ (sic) or of the formula $-(CH_2)_m-O-CO-Q$ wherein m is 1 or 2 and Q is C_1 -
 5 C_4 -alkyl or phenyl, and, if $n=2$, R_7 denotes C_2 - C_{12} -alkylene C_6 - C_{12} -arylene, a group



wherein X is C_2 - C_{10} -alkylene, C_6 - C_{15} -arylene or C_6 - C_{12} -cycloalkylene, or denotes a group



wherein Z' is hydrogen, C_1 - C_{18} -alkyl, allyl, benzyl, C_2 - C_{12} alkanoyl or benzoyl.

If any substituents denote C_1 - C_{12} -alkyl, they represent for example, methyl, ethyl, n -propyl, n -butyl, sec .-butyl,
 20 $tert$.-butyl, n -hexyl, n -octyl, 2-ethylhexyl, n -nonyl, n -decyl, n -undecyl or n -dodecyl.

Of Z' denotes C_1 - C_{18} -alkyl, it can represent, for example, the groups listed above and additionally, for example, n -tridecyl, n -tetradecyl, n -hexadecyl or n -octadecyl.

25 If any substituents denote C_2 - C_6 -alkoxyalkyl, they represent, for example, methoxymethyl, ethoxymethyl, propoxymethyl, $tert$.-butoxymethyl, ethoxyethyl, ethoxypropyl, n -butoxyethyl, $tert$.-butoxyethyl, isopropoxyethyl or propoxypropyl.

If R_7 represents C_3 - C_5 -alkenyl, it denotes, for example, 1-propenyl, allyl, methallyl, 2-butenyl or 2-pentenyl.

As C_7 - C_9 -aralkyl, R_7 is, in particular, phenethyl or, above all, benzyl, and as C_5 - C_7 -cycloalkyl R_7 is, in particular, cyclohexyl.

If R^7 denotes C_2 - C_4 -hydroxyalkyl, it represents, for example, 2-hydroxyethyl, 2-hydroxypropyl, 3-hydroxypropyl, 2-hydroxybutyl or 4-hydroxybutyl.

As C_6 - C_{10} -aryl, R_7 denotes, in particular, phenyl, α -naphthyl or β -naphthyl which are optionally substituted by halogen or C_1 - C_4 -alkyl.

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

If R^7 represents C_6 - C_{12} -arylene, it represents, for example, o-, m- or p-phenylene, 1,4-naphthylene or 4,4'-diphenylene.

If Z' denotes C_2 - C_{12} -alkanoyl, it represents, for example, propionyl, butyryl, octanoyl or dodecanoyl, but preferably acetyl.

As C_2 - C_{10} -alkylene, C_6 - C_{15} -arylene or C_6 - C_{12} -cycloalkylene, X has the meaning indicated under b).

The following compounds are examples of polyalkyl-piperidine light stabilizers of this class:

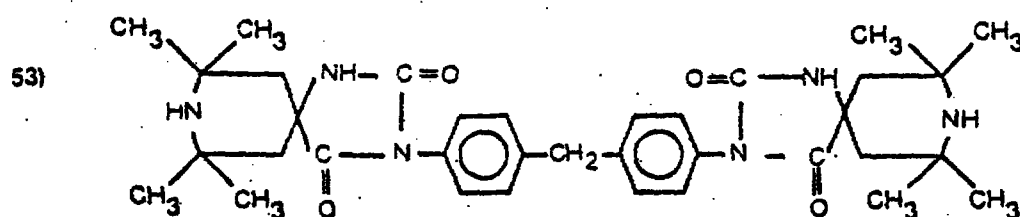
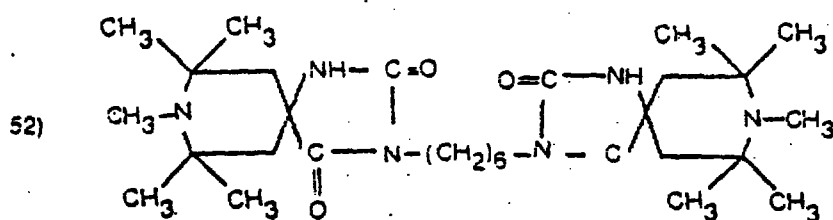
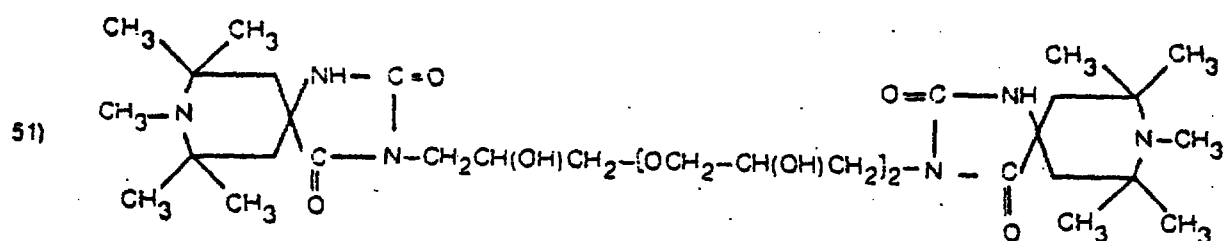
47) 3-Benzyl-1,3,8-triaza-7,7,9,9-tetramethylspiro[4.5]decane-2,4-dione

48) 3-n-Octyl-1,3,8-triaza-7,7,9,9-tetramethylspiro[4.5]decane-2,4-dione

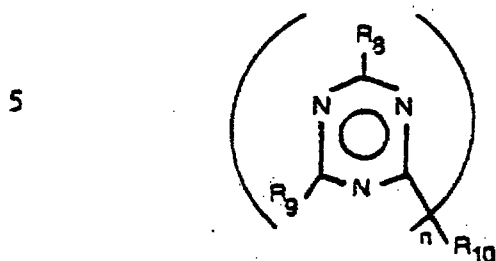
49) 3-Allyl-1,3,8-triaza-1,7,7,9,9-pentamethylspiro[4.5]decane-2,4-dione

50) 3-Glycidyl-1,3,8-triaza-7,7,8,9,9-pentamethylspiro[4.5]decane-2,4-dione

or the compounds of the following formulae:

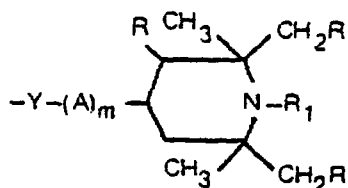


e) Light stabilizers of the formula (VI)

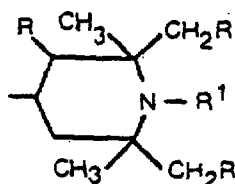


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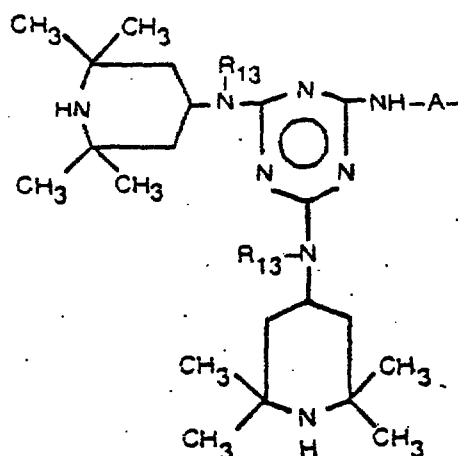
wherein n is the numbers 1 or 2 and R₈ denotes a group of the formula



wherein R has the meaning indicated for formula (I), R₁ has the meaning indicated under a), Y is -O- or -NR₁₁-, A denotes C₂-C₆-alkylene and m denotes the numbers 0 or 1, R₉ is the groups
 5 R₈, NR₁₁R₁₂, -OR₁₃, -NHCH₂OR₁₃ or -N(CH₂OR₁₃)₂, and, if n=1, R₁₀ denotes the groups R₈ or R₉, and, if n=2, R₁₀ denotes the group -Y-Q-Y- wherein Q denotes C₂-C₆ alkylene which is optionally interrupted by -N(R₁₄)-, R₁₁ is C₁-C₁₂-alkyl, cyclohexyl, benzyl or C₁-C₄-hydroxyalkyl or a group of the for-
 10 mula



R₁₂ denotes C₁-C₁₂-alkyl, cyclohexyl, benzyl or C₁-C₄-hydroxyalkyl, R₁₃ denotes hydrogen, C₁-C₁₂-alkyl or phenyl and R₁₄ denotes hydrogen or the group -CH₂OR₁₃, or R₁₁
 15 and R₁₂ together are C₄-C₅-alkylene or C₄-C₅-oxa-alkylene, or R₁₁ and R₁₂ each denote a group of the formula



If any substituents denote C₁-C₁₂-alkyl, they represent, for example, methyl, ethyl, n-propyl, n-butyl, sec.-butyl, tert.-butyl, n-hexyl, n-octyl, 2-ethylhexyl, n-nonyl, 5 n-decyl, n-undecyl or n-dodecyl.

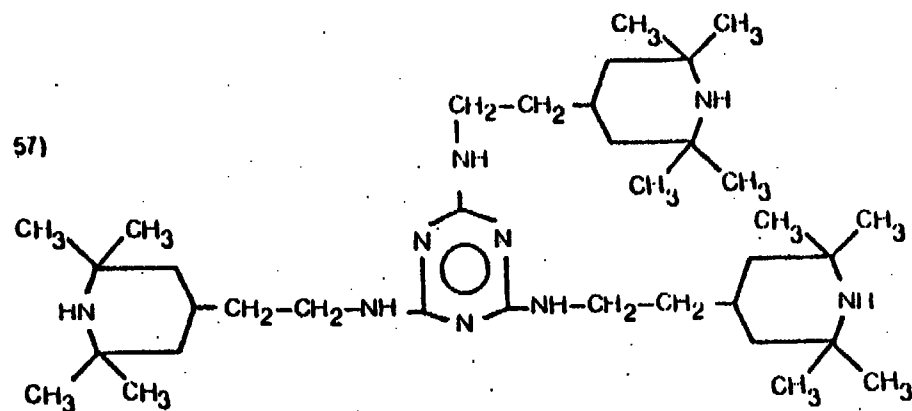
If any substituents denote C₁-C₄-hydroxyalkyl, they represent, for example, 2-hydroxyethyl, 2-hydroxypropyl, 3-hydroxypropyl, 2-hydroxybutyl or 4-hydroxybutyl.

If A denotes C₂-C₆-alkylene, it represents, for example, ethylene, propylene, 2,2-dimethylpropylene, tetramethylene or hexamethylene.

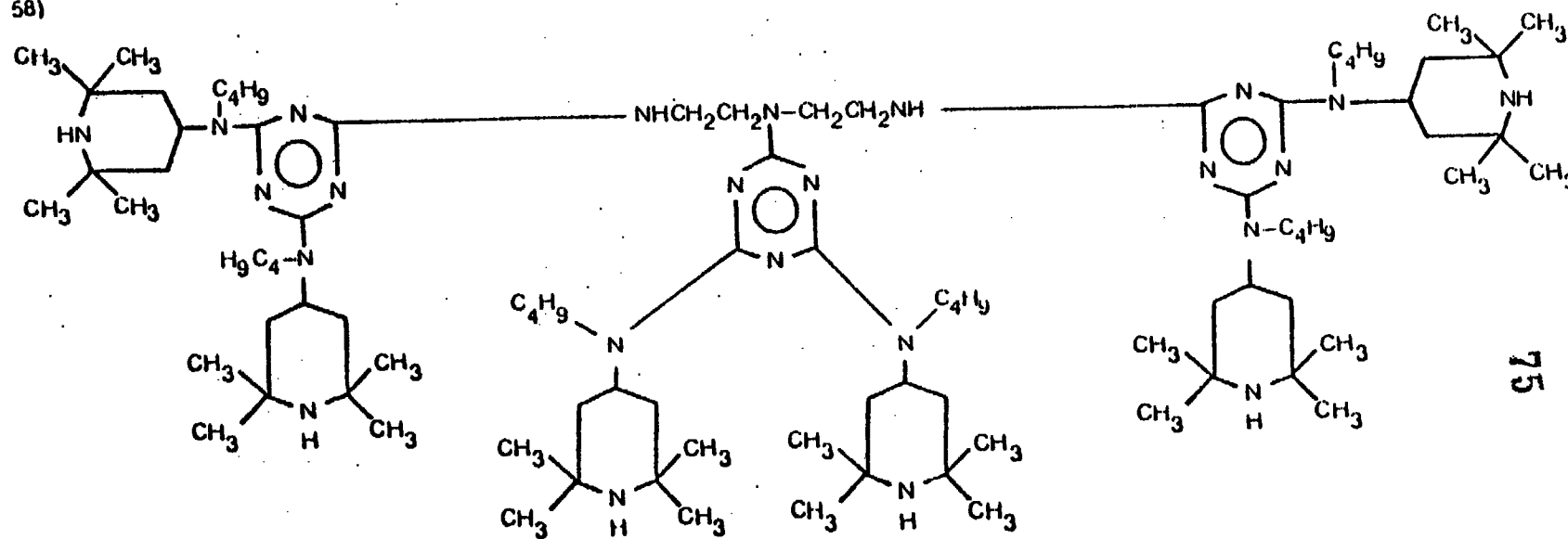
If R₁₁ and R₁₂ together represent C₄-C₅-alkylene or C₄-C₅-oxaalkylene, this denotes, for example, tetramethylene, pentamethylene or 3-oxa-pentamethylene.

15 The compounds of the following formulae are examples of polyalkylpiperidine light stabilizers of this class:

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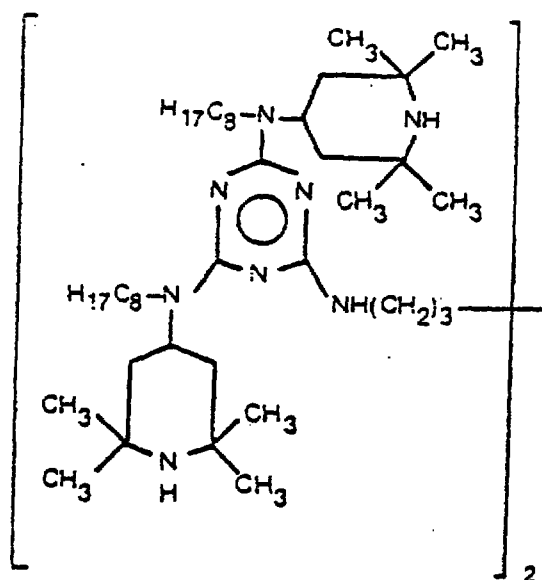


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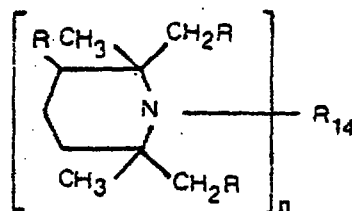


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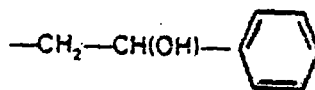
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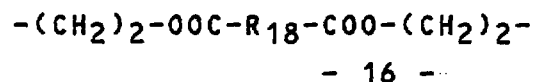
f) Light stabilizers of the formula (VII)



wherein n denotes the numbers 1 or 2, R has the meaning indicated for formula (I), and, if $n=1$, R_{14} denotes C_4 - C_{18} -alkyl, C_7 - C_{12} -aralkyl, the group $-CO-R_{15}$ or C_1 - C_4 -alkyl which is substituted by $-CN$, $-COOR_{16}$, $-OH$, $-OCOR_{17}$ or



wherein R_{15} is C_1 - C_{12} -alkyl, C_2 - C_4 -alkenyl or phenyl, R_{16} is C_1 - C_{18} -alkyl and R_{17} is C_1 - C_{18} -alkyl, C_2 - C_{10} -alkenyl, cyclohexyl, benzyl or C_6 - C_{10} -aryl, or, if $n=2$, R_{14} is C_4 - C_{12} -alkylene, 2-butenyl-1,4-ene, xylylene, the group



or the group $-\text{CH}_2-\text{OOC}-\text{R}_{18}-\text{COO}-\text{CH}_2-$ wherein R_{18} denotes ⁷⁷ C_2-C_{10} -alkylene, phenylene or cyclohexylene and R_{19} denotes C_2-C_{10} -alkylene, xylylene or cyclohexylene.

If any substituents denote C_1-C_{12} -alkyl, they represent, 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 substituents which denote C_1-C_{18} -alkyl can represent, for example, the groups listed above and additionally, for example, n-tridecyl, n-tetradecyl, n-hexadecyl or n-octadecyl.

If any groups represent C_2-C_{10} -alkylene, they denote, for example, ethylene, propylene, 2,2-dimethylpropylene, tetramethylene, hexamethylene, octamethylene or decamethylene.

As C_4-C_{18} -alkyl, R_{14} denotes, for example, n-butyl, sec.-butyl, tert.-butyl, n-hexyl, n-octyl, 2-ethylhexyl, 1,1-dimethyl-2-tert.-butylethyl, n-nonyl, n-decyl, n-dodecyl, n-tridecyl, n-tetradecyl, n-hexadecyl or n-octadecyl.

If R_{14} denotes C_1-C_4 -alkyl which is substituted by -CN, it represents, for example, cyanomethyl, cyanoethyl, 3-cyano-n-propyl or 4-cyano-n-butyl.

If R_{14} denotes C_4-C_{12} -alkylene, it is, for example, 2,2-dimethylpropylene, tetramethylene, hexamethylene, octamethylene, decamethylene or dodecamethylene.

If R_{14} represents C_7-C_{12} -aralkyl, it denotes, in particular, phenethyl, p-methylbenzyl or, above all, benzyl.

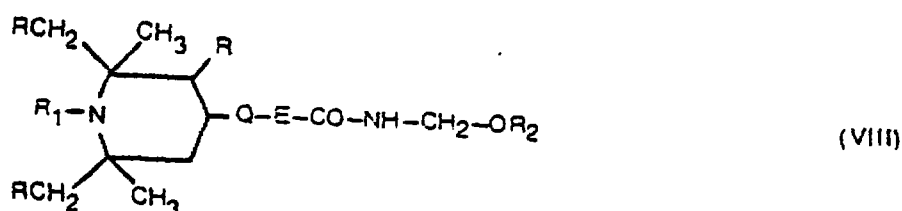
As C_2-C_4 -alkenyl, R_{15} denotes, for example, vinyl, 1-propenyl, allyl, methallyl or 2-butenyl.

As C_2-C_{10} -alkenyl, R_{17} denotes, for example, the groups listed for R_{15} when the latter denotes alkenyl, and additionally denotes, for example, crotyl, 2-hexenyl, 2-octenyl or 2-decenyl.

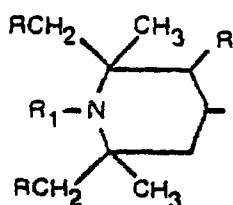
If R_{17} represents C_6-C_{10} -aryl, it denotes, for example, phenyl which is optionally substituted in the o-position or p-position by methyl, ethyl, isopropyl, n-butyl or tert.-butyl.

The following compounds are examples of polyalkyl-piperidine light stabilizers of this class:

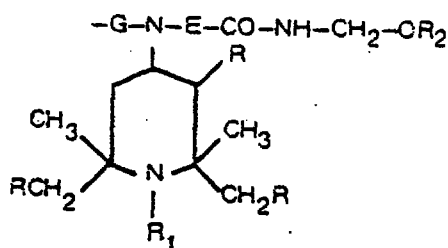
- 60) Bis- β -(2,2,6,6-tetramethylpiperidino)-ethyl] sebacate
 61) n-Octyl α -(2,2,6,6-tetramethylpiperidino)-acetate
 5 62) 1,4-Bis-(2,2,6,6-tetramethylpiperidino)-2-butene.
 g) Light stabilizers of the formula (VIII)



wherein Q is $-N(R_3)-$ or $-O-$, E denotes C₁-C₃-alkylene, the group $-CH_2-CH(R_4)-O-$ wherein R₄ is hydrogen, methyl or phenyl,
 10 or E denotes the group $-(CH_2)_3-NH-$ or a single bond, R denotes hydrogen or methyl, R₁ denotes hydrogen, C₁-C₁₈-alkyl, C₃-C₈-alkenyl, C₃-C₈-alkynyl, C₇-C₁₂-aralkyl, C₁-C₈-alkanoyl, C₃-C₅-alkenoyl or glycidyl, R₂ denotes hydrogen or C₁-C₁₈-alkyl, and R₃ denotes hydrogen, C₁-C₁₈-alkyl, C₅-C₇-cycloalkyl, C₇-
 15 C₁₂-aralkyl, cyanoethyl, C₆-C₁₀-aryl, the group $-CH_2-CH(R_4)-OH$ wherein R₄ has the meaning indicated above, a group of the formula



or a group of the formula



wherein G can be C₂-C₆-alkylene or C₆-C₁₂-arylene, or R₃ is a group -E-CO-NH-CH₂-OR₂.

If any substituents denote C₁-C₁₈-alkyl, they represent, for example, methyl, ethyl, n-propyl, n-butyl, sec.-butyl, tert.-butyl, n-hexyl, n-octyl, 2-ethylhexyl, n-nonyl, n-decyl, n-undecyl, n-dodecyl, n-tridecyl, n-tetradecyl, n-hexadecyl or n-octadecyl.

If any substituents represent C₇-C₁₂-aralkyl, they denote, for example, phenethyl or, in particular, benzyl.

If R₁ denotes C₃-C₈-alkenyl, this can be, for example, 1-propenyl, allyl, methallyl, 2-butenyl, 2-pentenyl, 2-hexenyl, 2-octenyl or 4-tert.-butyl-2-butenyl.

As C₃-C₈-alkynyl, R₁ is preferably propargyl. As C₁-C₈-alkanoyl, R₁ denotes, for example, formyl, propionyl, butyryl or octanoyl, but preferably acetyl, and as C₃-C₅-akenoyl (sic), R₁ denotes, in particular, acryloyl.

As C₅-C₇-cycloalkyl, R₃ denotes, in particular, cyclohexyl.

As C₆-C₁₀-aryl, R₃ denotes, in particular, phenyl, α-naphthyl or β-naphthyl which are optionally substituted by halogen or C₁-C₄-alkyl. As C₁-C₃-alkylene, E denotes, for example, methylene, ethylene or propylene.

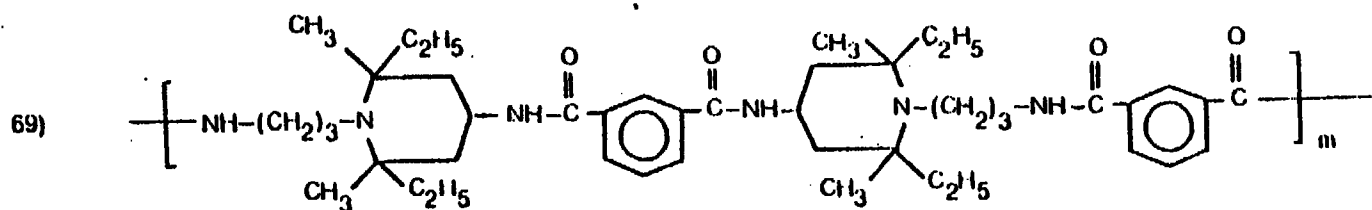
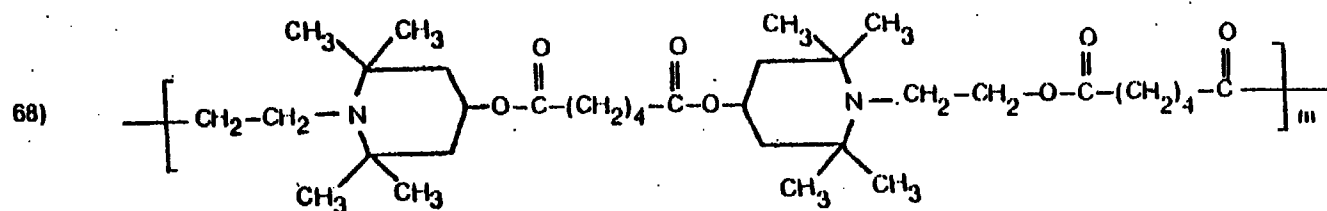
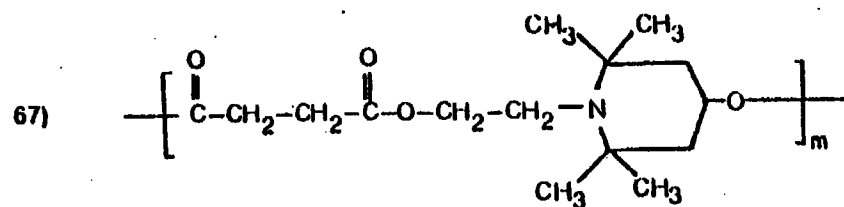
As C₂-C₆-alkylene, G represents, for example, ethylene, propylene, 2,2-dimethylpropylene, tetramethylene or hexamethylene, and as C₆-C₁₂-arylene, G represents o-, m- or p-phenylene, 1,4-naphthylene or 4,4'-diphenylene.

The following compounds are examples of polyalkylpiperidine light stabilizers of this class:

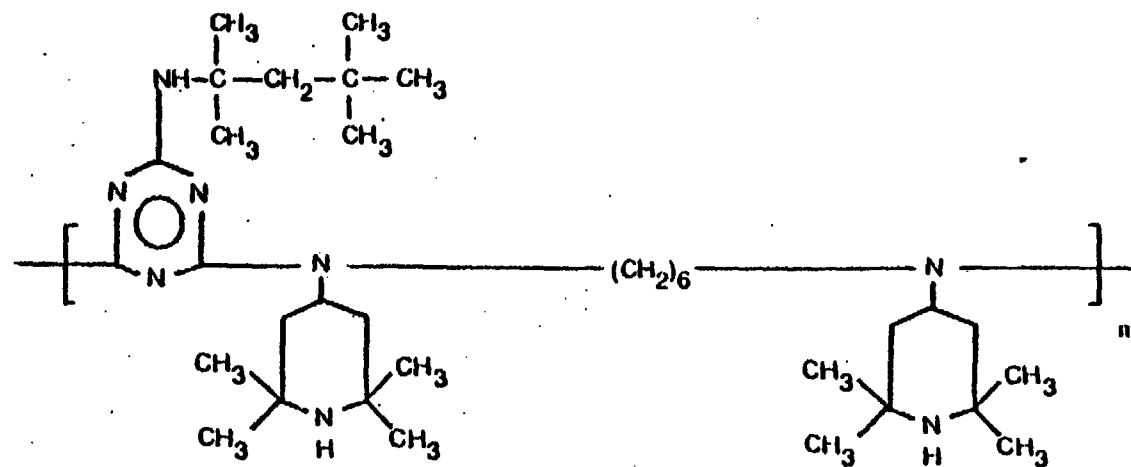
- 63) N-Hydroxymethyl-N'-2,2,6,6-tetramethylpiperidin-4-ylurea.
64) N-Methoxymethyl-N'-2,2,6,6-tetramethylpiperidin-4-ylurea.
65) N-Methoxymethyl-N'-n-dodecyl-N'-2,2,6,6-tetramethyl-
piperidin-4-ylurea.
5 66) O-(2,2,6,6-Tetramethylpiperidin-4-yl)-N-methoxymethyl-
urethane.

f) Polymeric compounds in which the recurring structural unit contains a polyalkylpiperidine radical of the formula (I), in particular polyesters, polyethers, polyamides, 10 polyamines, polyurethanes, polyureas, polyaminotriazines, poly(meth)acrylates, poly(meth)acrylamides and copolymers thereof containing such radicals.

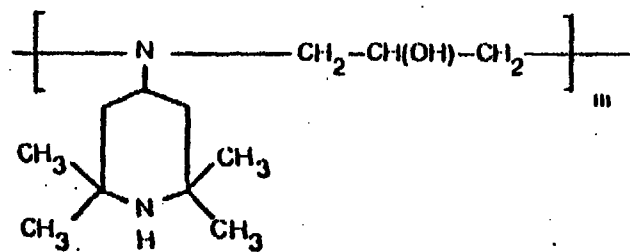
The compounds of the following formulae wherein m denotes the numbers 2 to about 200 are examples of poly- 15 alkylpiperidine light stabilizers of this class:



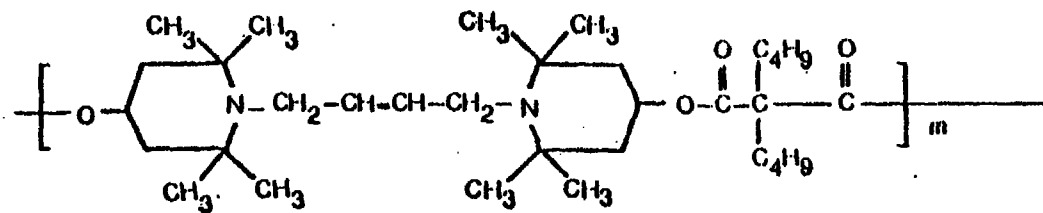
70)

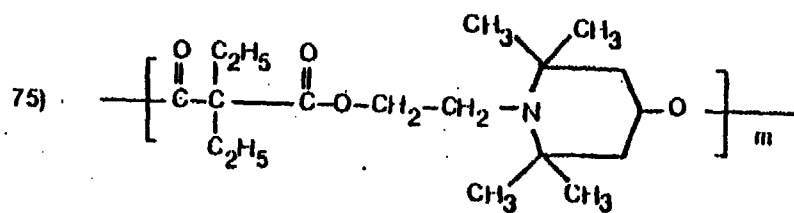
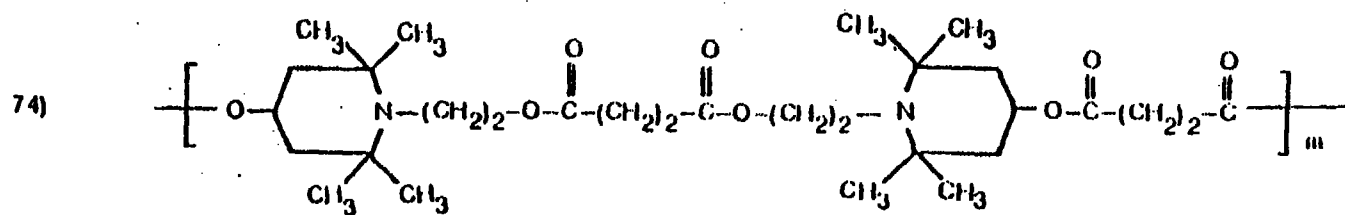
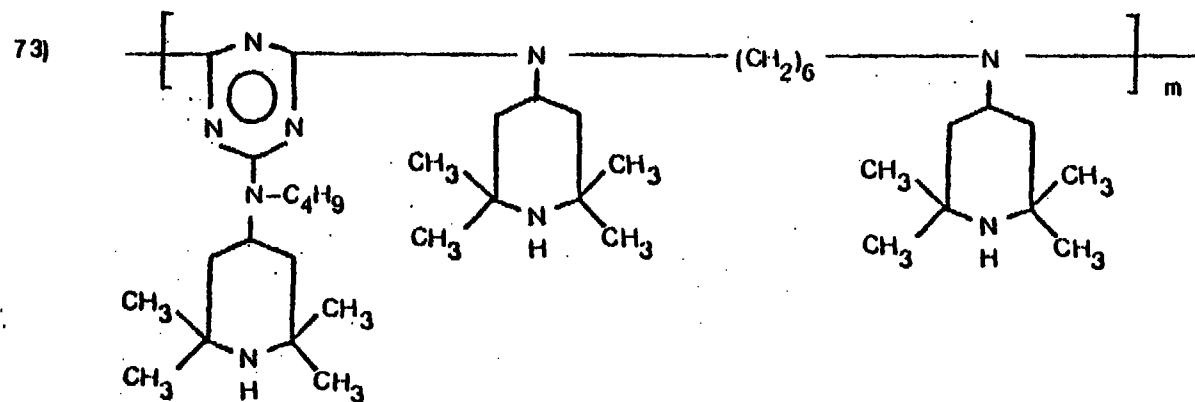


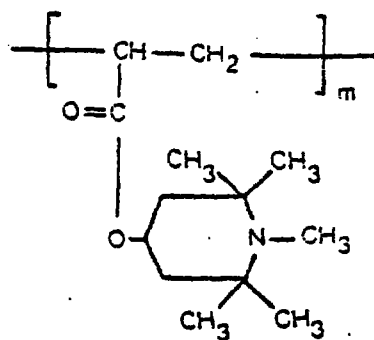
71)



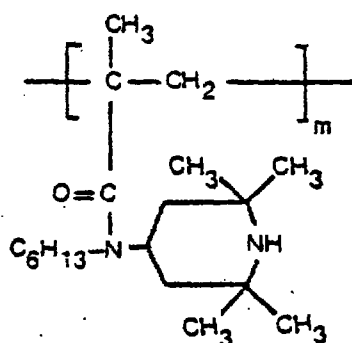
72)







0. 84



It is also possible to use polyalkylpiperidine derivatives of the classes a) - f) which form chemical bonds with the binder of the paint. This is the case if the polyalkylpiperidine derivative contains a reactive group suitable for this purpose, such as, for example, a glycidyl group or a methylol group.

Examples of such compounds are the polyalkylpiperidine derivatives of class g) containing methylol or methylol ether groups.

Insofar as polyalkylpiperidine compounds are basic compounds, they can form salts with acids. Examples of acids suitable for this purpose are inorganic acids or organic carboxylic, sulfonic, phosphonic or phosphinic acids, such as, for example, hydrochloric acids, 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.

The acrylic resin paints which can be stabilized in accordance with the invention against light, moisture and oxygen are the conventional acrylic resin stoving paints, such as are described, for example, in H. Kittel's Lehrbuch der Lacke und Beschichtungen ("Textbook of paints and coatings"), volume 1, part 2 on pages 735 and 742 (Berlin, 1972) or in H. Wagner, H.F. Sarx, Lackkunstharze ("Synthetic resins for paint") on pages 229 - 235.

The stabilization, according to the invention, of metallic effect paints based on polyacrylate resins which can be crosslinked by heat and contain copolymerized styrene is of particular interest. These resins would make it possible to prepare metallic effect paints having excellent physical and chemical properties if, depending on the content of styrene present in the structure, crazing were not to take place during weathering. Surprisingly, however, excellent stabilization against the crazing mentioned is possible as a result of the addition, according to the invention, of polyalkylpiperidine derivatives.

The stabilization, according to the invention, of metallic effect paints based on alkyd resins is also of particular interest. The stabilization of metallic effect paints based on alkyd resins by means of the conventional light stabilizers of the UV absorber type is also beset with problems and does not result in a satisfactory technical solution.

As a result of the addition, according to the invention, of light stabilizers based on polyalkylpiperidine derivatives, if appropriate together with further stabilizers, it is now also possible to stabilize metallic effect paints based on alkyd resins in an entirely satisfactory manner against light and moisture, in particular against crazing.

The alkyd resin paints which can be stabilized in accordance with the invention against the action of light and moisture are the customary stoving paints which are used, in

particular, for painting automobiles (so-called automotive paints), for example paints based on alkyd-melamine resins and alkyd-acrylic-melamine resins.

Metallic effect paints based on oil-free polyesters
5 can also be stabilized successfully in accordance with the invention.

The metallic effect is achieved by using the aluminium pigments customary for this purpose in an amount of 1 to 10% by weight, relative to the solvent-free binder
10 (paint resin). The application of the metallic effect paints which have been stabilized in accordance with the invention is preferably effected in the customary manner by two processes, either by the single-coat process or by the two-coat process. In the latter case, the coat containing the
15 aluminium pigment is first applied and a topcoat of clear lacquer is then applied above it.

The amount of added polyalkylpiperidine derivative is 0.01 to 5% by weight, relative to the solvent-free binder, preferably 0.5 to 1% by weight. The paints can contain the
20 customary organic solvents or can be dissolved or dispersed in water or can be solvent-free.

When used in two-layer coatings, the polyalkyl piperidine derivative to be used for stabilization according to the invention can be incorporated either only in the unpigmented
25 topcoat or both in the unpigmented topcoat and in the undercoat containing aluminium pigment. When acrylic resins or acrylic-modified alkyd resins are prepared, it is possible to copolymerize polymerizable polyalkylpiperidine derivatives (for example the compound 7 and the compound 39) into the
30 resin.

Incorporation into the paint binder can, however, also be effected via polycondensation when the melamine, alkyd or polyester resins are prepared, or, if necessary, stoved. Examples of co-condensable polyalkylpiperidine derivatives are
35 the compounds 1, 26 and 27 and also 1-hydroxyethyl-4-hydroxy-2,2,6,6-tetramethylpiperidine. Incorporation via polyaddition can follow, for example, via the reaction of free carboxyl

groups in the acrylic resin with glycidyl groups in the polyalkylpiperidine derivative. These carboxyl groups can be incorporated by copolymerizing acrylic acid or derivatives thereof.

5 In these cases there is the additional advantage that the light stabilizers cannot be removed by extraction or migration, so that their effect lasts for a very long time.

The concomitant use of other customary light stabilizers can be advantageous for achieving maximum light stability. Examples of these are UV absorbers of the type of benzophenones, oxalanilides, benzotriazoles or acrylic acid derivatives or light stabilizers containing metal, such as, for example, organic nickel compounds.

15 In the case of such combinations, the total of all the light stabilizers is 0.02 to 5% by weight, preferably 0.5 to 2% by weight, relative to the paint resin.

Further additives which can be present in the paint are antioxidants, for example those of the type of sterically hindered phenol derivatives, organic phosphorus compounds, 20 such as, for example, phosphites, phosphonites or phosphines, plasticizers, flow control auxiliaries, curing accelerators, such as, for example, organic Co, Mn or Zr salts, thickeners, dispersing agents or adhesion promoters.

The following examples describe the use according to 25 the invention of polyalkylpiperidine derivatives in metallic effect paints based on binder systems containing alkyd resins. In these examples, parts denote parts by weight and percentages denote percentages by weight.

Examples

30

Example 1

Light stabilization of a two-layer metallic effect coat of paint (crazing test) based on binder systems containing alkyd resins.

Base formulation of the paints

35 a) Metallic effect undercoat

Alftalat[®] VAN 21/1 alkyd resin

	(Hoechst)	13.15 parts
	CAB 381.01 cellulose acetobutyrate, 18% in butyl acetate (Eastman Chemical Corp.)	55 parts
5	Uresin [®] B carbamic acid resin (Hoechst)	2.5 parts
	Maprenal [®] VMF 80/15 melamine resin (Hoechst)	3.45 parts
10	Alcoa [®] 726 aluminium powder (Aluminium Corp. of America)	6.5 parts
	15% solution of BYK 300 (BYK Mallinckrodt) in butyl acetate/xylene (flow control auxiliary based on silicones)	2 parts
15	Xylene	6 parts
	Butylglycol	5 parts
	Butyl acetate/xylene, 1:1	6.4 parts
b) Unpigmented topcoat		
20	Alfatalat [®] AC 451 n alkyd resin (Hoechst)	28.5 parts
	Synthacryl [®] SC 303 acrylic resin (Hoechst)	30.7 parts
	Maprenal [®] VMF 80/15 melamine resin (Hoechst)	22.8 parts
25	Butylglycol	4.3 parts
	Butylglycol acetate	1.7 parts
	Solvesso 150 (Esso)	8.5 parts
	Solvesso 100 (Esso)	3.5 parts

The undercoat was sprayed onto an aluminium sheet
30 coated by the coil-coat process (15-20 μ). After a brief
flash-off period, the topcoat was sprayed on wet-in-wet at a
layer thickness of 30-40 μ m, and, after a flash-off period of
15 minutes was stoved at 135°C for 20 minutes.

Before the application, the polyalkylpiperidine com-
35 pound indicated in column 2 was added to the topcoat in
the % amount (relative to the paint resin) indicated in each

case in column 1 of the following table (the numbers refer to the examples mentioned in the description).

After being stored for 4 weeks in an air-conditioned chamber (23°C/50% relative humidity), the painted sheets 5 were weathered for 930 hours in a QUV tester as specified in ASTM G-53/77 test method. In this test, each of the samples was moistened for 4 hours at 50°C and was irradiated with UV light for 4 hours in a moist atmosphere at 60°C.

The weathered samples of paint were evaluated as specified in the TNO crazing scale, type 353, the crazing pattern 10 being compared with standardized samples. The capital letters indicate the nature and type of crazing. The numbers indicate the intensity of crazing. 10 stages have been chosen to describe the intensity; the stage of highest intensity is always 15 indicated as 10. The small letters are a measure of the crack depth: a represents surface damage to the topcoat, b and c represent crazing in the topcoat or the topcoat and the basecoat; d indicates the case where, although the lower coat is crazed, the topcoat is not. The particular crazing 20 pattern is characterized in column 3 of Table 1.

TABLE I

	%	Polyalkylpiperidine compound	Crazing pattern
5	-	-	J 8 a
	1	Compound 1	no crazing
	1	Compound 3	J 2 a
	1	Compound 4	J 3 a
	1	Compound 11	no crazing
10	1	Compound 19	no crazing
	1	Compound 20	no crazing
	1	Compound 67	no crazing
	1	Compound 70	no crazing
	1	Compound 75	no crazing

Comparison test

Metallic effect paints based on binder systems containing
 15 alkyd resins, containing a UV absorber as the light stabilizer.

The procedure described for Example 1 was repeated exactly in a comparison test with the sole exception that a UV absorber was used instead of the polyalkylpiperidine
 20 compound. In Table II below, column 1 indicates the % amount of light stabilizer (relative to the paint resin), column 2 indicates the light stabilizer used and column 3 indicates the crazing pattern.

TABLE II

	%	Light stabilizer	Crazing pattern
5	1	2-(2-Hydroxy-3,5-di-tert.amylphenyl)-benzotriazole	J 10 b
	3	2-(2-Hydroxy-3,5-di-tert.amylphenyl)-benzotriazole	J 9 b.
10	1	2-(2,4-Dihydroxyphenyl)-benzotriazole	J 9 b
	3	2-(2,4-Dihydroxyphenyl)-benzotriazole	J 4 a
	1	2,4-Dihydroxybenzophenone	J 7 a
	3	2,4-Dihydroxybenzophenone	J 2 a
15	1	2-Hydroxy-4-octylbenzophenone	J 8 b
	3	2-Hydroxy-4-octylbenzophenone	J 7 a
	1	2-Hydroxy-4-dodecylbenzophenone	J 9 b
	3	2-Hydroxy-4-dodecylbenzophenone	J 9 b
	1	2-(2-Hydroxy-5-isooctylphenyl)-benzotriazole	J 4 a
	3	2-(2-Hydroxy-5-isooctylphenyl)-benzotriazole	J 2 a
20	1	2-Ethoxy-2'-ethyloxalanilide	J 4 b
	1	2-Ethoxy-2'-ethyloxalanilide	J 7 b

Example 2

Combination of polyalkylpiperidine derivatives/UV absorbers for stabilizing a two-layer metallic effect coat of paint
 25 (crazing test) based on binder systems containing alkyd resins.

Metallic effect coats of paint were produced and tested exactly as described in Example 1, with the sole exception that a UV absorber was also incorporated together with the
 30 polyalkylpiperidine derivative. In Table III below, column 1 indicates the % amount of light stabilizer (relative to the paint resin, column 2 indicates the light stabilizer used and column 3 indicates the crazing pattern.

TABLE III

5	%	Light stabilizer	Crazing pattern
5	0.5	Compound 1	J 1 a
	0.5	2-(2-Hydroxy-3,5-di-tert.-amylphenyl)-benzotriazole	
10	0.5	Compound 20	no crazing
	0.5	2-(2-Hydroxy-3,5-di-tert.-amylphenyl)-benzotriazole	
10	0.5	Compound 67	no crazing
	0.5	2-(2-Hydroxy-5- α -methylstyrylphenyl)-benzotriazole	

Example 3

Combination of polyalkylpiperidine derivatives with a metal compound for stabilizing a two-layer metallic effect coat of paint (crazing test) based on binder systems containing alkyd resins.

Metallic effect coats of paint were produced and tested exactly as in Example 1, with the sole exception that a metal salt was also infatuated (sic) together with the polyalkyl- piperidine derivative. In Table IV below, column 1 indicates the % amount of light stabilizer or metal compound (relative to the paint resin, column 2 indicates the light stabilizers and metal compounds used and column 3 indicates the crazing pattern.

TABLE IV

5	%	Light stabilizer	Crazing pattern
		Metal compound	
	0.5	Compound 11	no
	0.2	Nickel acetylacetonate	crazing
	0.5	Compound 11	no
	0.2	Aluminium acetylacetonate	crazing

Example 4

A metallic effect coat of paint was produced and tested exactly as described in Example 1, with the sole exception that both a UV absorber and a metal compound were infatuated (sic) together with the polyalkylpiperidine derivative.

0.5% of 2-hydroxy-3,5-di-tert.-amylphenylbenzotriazole and 0.2% of aluminium acetylacetonate (% relative to the paint resin) were added to 0.5% of compound 11. No crazing could be seen after weathering.

Example 5

Stabilization to light of a 2-layer metallic effect coat of paint (gloss retention test) based on binder systems containing acrylic resins.

Base formulation of the paints

a) Metallic effect undercoat

25	L 1850 oil-free alkyd resin	
	polyester resin (Dynamit Nobel AG)	27.0 parts
	Maprenal [®] RT melamine resin	
	(Farbwerke Hoechst AG)	3.0 parts
	CAB 531 cellulose acetobutyrate (Eastman Chem. Corp.)	
		2.0 parts
30	Alcoa [®] 726 aluminium powder	
	(Aluminium Corp. of America)	8.0 parts
	Toluene	10.0 parts
	xylene	7.0 parts
	Butanol	3.0 parts

	Butyl acetate	25.0 parts
	Aromatic solvent	
	Solvesso 150 (Esso)	15.0 parts
b)	Unpigmented topcoat	
5	Synthacryl [®] SC 303 acrylic resin (Hoechst)	59.0 parts
	Maprenal [®] MF 590 melamine resin (Hoechst)	17.4 parts
	Butylglycol acetate	2.0 parts
10	Solvesso 150 (Esso)	2.0 parts
	Solvesso 100 (Esso)	2.0 parts
	Xylene	6.6 parts
	Silicone oil AL/1% in xylene (as flow control auxiliary)	0.2 parts
15	A commercially available base surface (PRIMER), fol- lowed by a commercially available intermediate filler were applied to an aluminium sheet 0.4 mm thick, and were stoved. The undercoat containing aluminium pigment was sprayed onto this paint substrate at a coating thickness of approx. 15 µm, 20 and the unpigmented topcoat was sprayed onto the latter wet- in-wet at a coating thickness of approx. 30-40 µm. After a short flash-off period, the paints were stoved in a paint- drying cabinet for 30 minutes at 125°C. 2 samples were pre- pared; the first without added stabilizer, the second with 25 1% (relative to the paint resin) of compound 11 added in the topcoat. The sheets thus obtained were stored for four weeks in a standard environment (23°C/5% relative humidity) and were then subjected to weathering in the QUV apparatus as specified in ASTM G 53-77. Diagram I below shows the gloss 30 values obtained (ASTM D 523) for the stabilized (O) sample and the unstabilized (X) sample, as a function of the weather- ing time.	

Example 6

Stabilization to light of a two-layer metallic effect coat of
35 paint based on polyacrylate resins which can be cross-linked
by heat and contain copolymerized styrene.

Base formulation of the paints

9 95

a) Metallic effect undercoat

	L 1850 polyester resin (Dynamit Nobel AG)	27.0 parts
5	Maprenal [®] RT melamine resin (Farbwerke Hoechst AG)	3.0 parts
	CAB 531 cellulose acetobutyrate (Eastman Chem. Corp.)	2.0 parts
10	Alcoa [®] 726 (Aluminium Corp. of America)	8.0 parts
	Toluene	10.0 parts
	Xylene	7.0 parts
	Butanol	3.0 parts
	Butyl acetate	25.0 parts
15	Aromatic solvent solvesso 150 (Esso)	15.0 parts

b) Unpigmented topcoat

	Commercially available acrylic resin containing copolymerized styrene (60%)	59.0 parts
20	Maprenal [®] MF 590 (Hoechst)	17.4 parts
	Butylglycol acetate	2.0 parts
	Solvesso ^R 150 (Esso)	2.0 parts
	Solvesso ^R 100 (Esso)	2.0 parts
	Xylene	6.6 parts
25	Silicone oil OL/1% in xylene	0.2 parts

The undercoat containing aluminium pigment is sprayed at a coating thickness of approx. 15 μm onto an aluminium sheet coated by the coil-coat process, and the unpigmented topcoat is sprayed onto the latter wet-in wet at a coating thickness of approx. 30-40 μm . After a short flash-off period, the paints are stoved in a paint-drying cabinet for 30 minutes at 140°C. The sheets thus obtained are stored for 4 weeks in a standard environment (23°C/50% relative humidity) and are then subjected to weathering in the QUV apparatus as specified in ASTM G 53-77, as already mentioned in Example 1.

The light stabilizers indicated in column 2 of Table V below had previously been added to the unpigmented topcoat in the % amount (relative to the laugh (sic) resin) indicated in each case in column 1. Column 3 of Table V indicates the weathering time, and column 4 characterizes the appropriate crazing pattern.

TABLE V

%	Light stabilizer	Weathering time	Crazing pattern
10 -	-	1400 hrs.	J 10 b
1	Compound 11	2800 hrs.	no crazing
15 0.5 0.5	Compound 11 2-(2-Hydroxy- 3,5-di-tert.- amylphenyl)- benzotriazole	2800 hrs.	no crazing

Comparsion test

Metallic effect paints based on polyacrylate resins which can be crosslinked by heat and contain copolymerized styrene; stabilization by means of a UV absorber.

The procedure described for Example 6 was repeated exactly in a comparison test, with the sole exception that a UV absorber was used instead of the polyalkylpiperidine compound. In Table VI below, column 1 indicates the % amount of light stabilizer (relative to the paint resin), column 2 indicates the light stabilizer used, column 3 indicates the weathering time and column 4 indicates the appropriate crazing pattern.

TABLE VI

%	Light stabilizer	Weathering time	Crazing pattern
-	-	1400 hrs.	J 10 b
1	2,4-Dihydroxy-benzophenone	2800 hrs.	J 10 a
2	2-(2-Hydroxy-3,5-di-tert.amylphenyl)-benzotriazole	2800 hrs.	J 10 a

10 It can be seen from Table V that, when a polyalkyl-
piperidine compound is added as the stabilizer, no crazing
in contrast with the zero sample was obtained, even when the
weathering time in the QUV apparatus was doubled. As Table
VI shows, this surprisingly good stabilizing effect was not
15 achieved with the UV absorbers tested in comparison.

It can be seen from diagrams II and III below that
the result of combining a polyalkylpiperidine compound with
a UV absorber is to achieve a synergistic stabilizing ef-
fect which is reflected in a markedly better gloss retention
20 (determined as specified in ASTM D 523) and a markedly lower
loss in weight.

Example 7

Stabilisation to light of a single-layer metallic effect coat
of paint (gloss retention test) based on binder systems con-
25 taining acrylic resins.

Base formulation of the paint

	Mobil R very fine aluminium paste (Eckhart-Werke, Fürth/Bavaria, Germany)	1.29 parts
30	Xylene (for making a paste of the aluminium paste)	1.29 parts
	Synthacryl [®] SC 300 acrylic resin, 50% (Hoechst)	59.35 parts

	Maprenal [®] MF 650 melamine resin, 55% (Cassella-Hoechst)	25.22 parts
	Polysolvan [®] D butyl glycollate (Hoechst)	3.97 parts
5	Ethylglycol acetate	1.98 parts
	Xylene	6.90 parts

The spraying viscosity was adjusted to 19 seconds as specified in DIN 53,211 by means of 29.7 parts of DKH synthetic resin thinner (Dr. K. Herberts, Wuppertal, Germany).

10 A commercially available base surface (PRIMER) followed by a commercially available intermediate filler were applied to an aluminium sheet 0.4 mm thick, and were stoved. The paint containing aluminium pigment was sprayed at a coating thickness of approx. 40 μ m onto this paint substrate in
15 3 cross-coatings with 15 seconds flashing off in each case. After a flash-off period of 20 minutes, the paint was stoved in a paint-drying cabinet for 25 minutes at 120°C.

Before the application, the stabilizer(s) indicated in column 2 of Table VII below had been added to the paint in
20 the % amount (relative to the paint resin) indicated in column 1 (polyalkylpiperidine compounds numbered as in the examples mentioned in the description). The sheets thus obtained were stored for four weeks in a standard environment (23°C/5% relative humidity) and were then subjected to
25 weathering in the QUV apparatus as specified in ASTM G-53/77. Table VII below indicates the gloss values (ASTM D 523) obtained as a function of the weathering time (prior to weathering and after 350, 480 and 570 hours).

TABLE VII

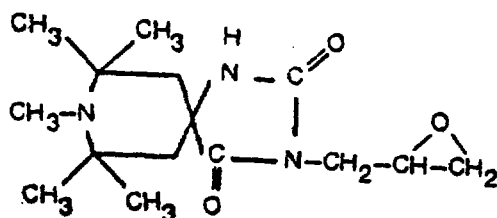
	%	Light stabilizer	20° gloss after weathering			
			0 hrs.	350 hrs.	480 hrs.	570 hrs.
5	-	-	70	25	19	17
	1	Compound 3	76	64	57	47
	1	Compound 11	75	60	55	52
	1	Compound 19	75	63	51	48
10	0.5	Compound 11	75	60	59	59
	0.5	2-(2-Hydroxy-3,5-di-tert.-amyl-phenyl)-benzotriazole				
	0.5	Compound 19	77	70	71	71
15	0.5	2-(2-Hydroxy-3-methylbenzyl-5-methylphenyl)-benzotriazole				

20 Analogous results are also obtained if polyalkyl-piperidine derivatives are used in combination with 2-(2-hydroxy-3,5-di- α,α -dimethylbenzylphenyl)-benzotriazole or with 2-[2-hydroxy-3,5-di-(1,1,3,3-tetramethylbutylphenyl)-benzotriazole.

25 Example 8

Light stabilizer which can be incorporated by addition.

The stabilization to light of a 2-layer metallic effect coat of paint (gloss retention test) by means of the compound A of the formula



(A)

Incorporation of compound A into the unpigmented topcoat.

Compound A is added to a commercially available clear lacquer based on an acrylic resin which can be crosslinked by means of melamine/formaldehyde resins and contains copolymerized acrylic acid as well as acrylic acid esters and styrene, and the mixture is stirred overnight at 40°C. In the course of this the incorporation of the light stabilizer takes place by reaction between the glycidyl group of the light stabilizer and the acid groups in the acrylic resin. Subsequently, it is possible to add further light stabilizers, if desired, (compare Table VIII below, column 2).

Preparation of the test samples

The topcoat, prepared as described above, is sprayed wet-in-wet onto an aluminium sheet onto which a commercially available filling primer and the metallic effect undercoat have previously been applied, and the sheet is stoved for 30 minutes at 130°C. The coating thickness of the undercoat paint is approx. 15 µm, while that of the topcoat is approx. 35 µm.

Weathering tests

After the sheets have been stored for 2 weeks in a standard environment, the samples are weathered for 1,000 hours in a QUV tester as specified in ASTM G 53-77 test method.

The light stabilizers indicated in column 2 of Table VIII below were added to the unpigmented topcoat in the % amount (relative to the paint resin) indicated in each

case in column 1. The gloss of the paint surface was then measured as specified in ASTM D 523 test method, the values from which are recorded in column 3:

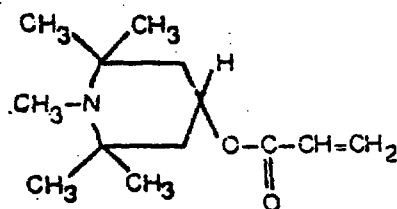
TABLE VIII

5	% Light stabilizer	20° gloss (determined)	
		not weathered	after 1,000 hours of weathering
10	- -	98	43
	1 Compound A	96	80
15	0.5 Compound A	99	92
	0.5 2-(2-Hydroxy-3,5-di- α,α -dimethylbenzylphenyl)-benzotriazole		
20	1 Compound A 1 2-(2-hydroxy-3, 5-di- α,α -dimethylbenzylphenyl)-benzotriazole	99	98

Example 9

Light stabilizer which can be incorporated by polymerization.

The stabilization to light of a two-layer metallic effect coat of paint by means of the compound B of the formula



(B)

Incorporation of compound B into the unpigmented topcoat.

The compound of the formula B is incorporated in a concentration of approx. 30% by weight (relative to the paint resin) into an acrylic resin (a copolymer formed from acrylic acid esters and styrene). In this reaction the compound of the formula B is used as a comonomer together with other (meth)acrylic acid esters and styrene, the solution being introduced into boiling xylene and the polymerization being initiated by means of di-tert.-butyl peroxide. The reaction time is approx. 4 hours. The acrylic resin thus prepared is used as a stabilizer concentrate for the preparation of the topcoat. This is effected by adding the stabilizer concentrate, if desired together with further light stabilizers (compare Table IX), to a commercially available clear lacquer (acrylic/melamine resin mixture).

Preparation of the test samples

The topcoat prepared as described above is sprayed wet-in-wet onto an aluminium sheet onto which a commercially available filling primer and the metallic effect undercoat have previously been applied, and the sheet is stoved for 30 minutes at 130°C. The coating thickness of the undercoat is approx. 15 µm, while that of the topcoat is approx. 35 µm.

Weathering tests

After the sheets had been stored for two weeks in a standard environment, the samples were weathered in the Xenotest 1200, and the time for the appearance of crazing in the topcoat was determined.

The light stabilizers indicated in column 2 of Table IX below were added to the unpigmented topcoat in the % amount (relative to the paint resin) indicated in column 1. Column 3 indicates the time in hours until crazing appeared.

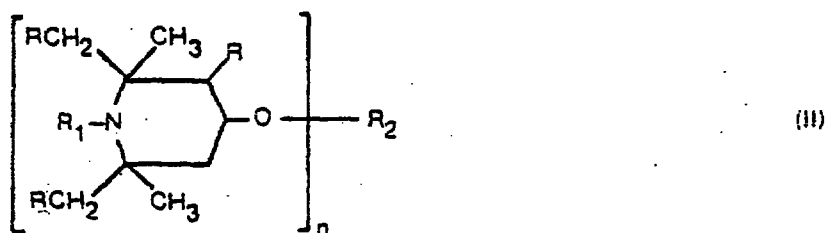
TABLE IX

% Light stabilizer	Crazing after...hours
- -	1300
1 2-(2-Hydroxy-3,5-di- tert.-amylphenyl)- benzotriazole	1600
0.5 Compound B 0.5 2-(2-Hydroxy-3, 5- di-tert.-amyl- phenyl)-benzotriazole	1900

Patent claims

1. The use of 2,2,6,6-tetraalkylpiperidine compounds, their acid addition salts or their complexes with metal compounds, if desired together with further stabilizers, for stabilizing metallic effect stoving paints based on alkyd or acrylic resins which can be crosslinked by heat, against the effect of light, moisture and oxygen.

2. The use, according to claim 1, of light stabilizers of the formula (II)



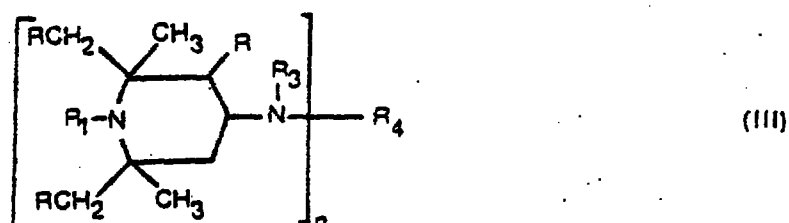
wherein n denotes the numbers 1 - 4, R is hydrogen or methyl, R_1 is hydrogen, amine oxide, C_1 - C_{18} -alkyl, C_3 - C_8 -alkenyl, C_3 - C_8 -alkynyl, C_7 - C_{12} -aralkyl, C_1 - C_8 -alkanoyl, C_3 - C_5 -alkenoyl, glycidyl or a group $-CH_2-CH(OH)-Z$ wherein Z denotes hydrogen, methyl or phenyl, and, if $n=1$, R_2 denotes hydrogen, C_1 - C_{18} -alkyl which is optionally interrupted by one or more oxygen atoms, cyanoethyl, benzyl, glycidyl, a mono-valent radical of an aliphatic, cycloaliphatic, araliphatic or aromatic carboxylic acid, carbamic acid or an acid containing phosphorus, or a monovalent silyl radical, and, if $n=2$, R_2 denotes C_2 - C_{12} -alkylene, C_4 - C_{12} -alkenylene, xylylene, a divalent radical of an aliphatic, cycloaliphatic, araliphatic or aromatic dicarboxylic acid, dicarbamic acid or an acid containing phosphorus, or a divalent silyl radical, and, if $n=3$, R_2 denotes a trivalent radical of an aliphatic, cycloaliphatic or aromatic tricarboxylic acid, of an aromatic tricarbamic acid or of an acid containing phosphorus, or denotes a trivalent silyl radical, and, if $n=4$, R_2 denotes a



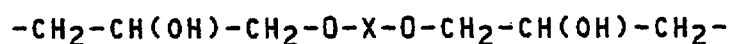
tetravalent radical of an aliphatic, cycloaliphatic or aromatic tetracarboxylic acid.

3. The use, according to claim 2, of light stabilizers of the formula (II) wherein n denotes the numbers 1 or 2, R is hydrogen or methyl, R_1 is hydrogen, C_1 - C_{12} -alkyl, allyl, benzyl, acetyl or acryloyl, and, if $n=1$, R_2 denotes 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 7-15 C atoms, and, if $n=2$, R_2 denotes a radical of an aliphatic dicarboxylic acid having 2-36 C atoms, of a cycloaliphatic or aromatic dicarboxylic acid having 8-14 C atoms, or of an aliphatic, cycloaliphatic or aromatic dicarbamic acid having 8-14 C atoms.

4. The use, according to claim 1, of light stabilizers of the formula (III)

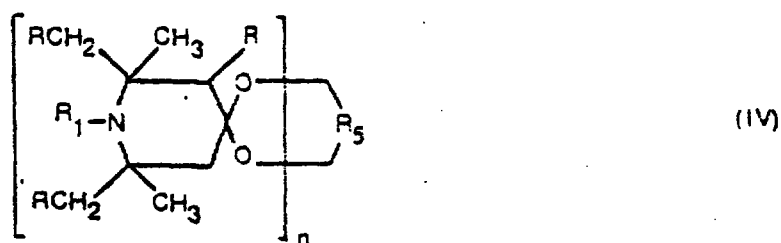


wherein n denotes the numbers 1 or 2, R is hydrogen or methyl, R_1 is hydrogen, amine oxide, C_1 - C_{18} -alkyl, C_3 - C_8 -alkenyl, C_3 - C_8 -alkynyl, C_7 - C_{12} -aralkyl, C_1 - C_8 -alkanoyl or C_3 - C_5 -alkenoyl and R_3 is hydrogen, C_1 - C_{12} -alkyl, C_5 - C_7 -cycloalkyl, C_7 - C_8 -aralkyl, C_2 - C_{18} -alkanoyl, C_3 - C_5 -alkenoyl or benzoyl, and, if $n=1$, R_4 denotes hydrogen, C_1 - C_{18} -alkyl, C_5 - C_7 -cycloalkyl, C_2 - C_8 -alkenyl which is optionally substituted by a cyano, carbonyl or carboxamide group, glycidyl or a group of the formula $-\text{CH}_2-\text{CH}(\text{OH})-\text{Z}$ or of the formula $-\text{CONH}-\text{Z}$ wherein Z denotes hydrogen, methyl or phenyl, and, if $n=2$, R_4 is C_2 - C_{12} -alkylene, C_6 - C_{12} -arylene, xylilene (sic) or a $-\text{CH}_2-\text{CH}(\text{OH})-\text{CH}_2-$ group or a group



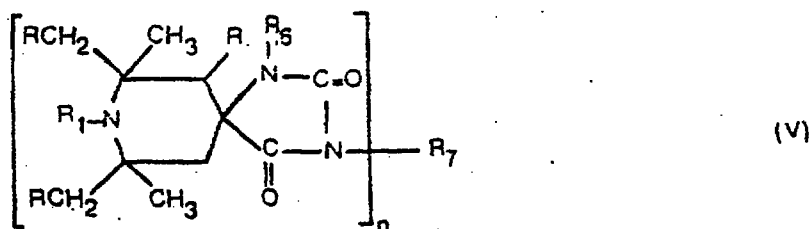
wherein X is C₂-C₁₀-alkylene, C₆-C₁₅-arylene or C₆-C₁₂ cycloalkylene, or, provided that R₃ does not denote alkanoyl, alkenoyl or benzoyl, R₄ can also denote a divalent radical of an aliphatic, cycloaliphatic or aromatic dicarboxylic acid or dicarbamic acid or the group -CO-, or, if n=1, R₃ and R₄ together can be the cyclic radical of an aliphatic or aromatic 1,2-dicarboxylic or 1,3-dicarboxylic acid.

5. The use according to claim 1, of light stabilizers of the formula (IV)



wherein n denotes the numbers 1 or 2, R is hydrogen or methyl, R₁ denotes hydrogen, amine oxide, C₁-C₁₈-alkyl, C₃-C₈-alkenyl, C₃-C₈-alkynyl, C₇-C₁₂-aralkyl, C₁-C₈-alkanoyl or C₃-C₅-alkenoyl, and, if n=1, R₅ denotes C₂-C₈-alkylene or C₂-C₈-hydroxyalkylene or C₄-C₂₂-acyloxyalkylene, and, if n=2, R₅ denotes the group (-CH₂)₂C(CH₂)₂.

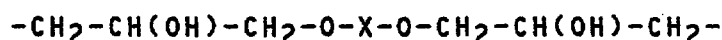
6. The use, according to claim 1, of light stabilizers of the formula (V)



wherein n denotes the numbers 1 or 2, R is hydrogen or methyl, R₁ is hydrogen, amine oxide, C₁-C₁₈-alkyl, C₃-C₈-alkenyl, C₃-C₈-alkynyl, C₇-C₁₂-aralkyl, C₁-C₈-alkanoyl or C₃-C₅-alkenoyl and R₆ is hydrogen, C₁-C₁₂-alkyl, allyl, benzyl



glycidyl or C₂-C₆-alkoxyalkyl, and, if n=1, R₇ denotes 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 $-(CH_2)_m-COO-Q$ or of the formula $-(CH_2)_m-O-CO-Q$ wherein m is 1 or 2 and Q is C₁-C₄-alkyl or phenyl, and, if n=2, R₇ denotes C₂-C₁₂-alkylene, C₆-C₁₂-arylene, a group

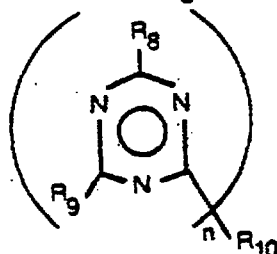


wherein X is C₂-C₁₀-alkylene, C₆-C₁₅-arylene or C₆-C₁₂-cycloalkylene, or denotes a group



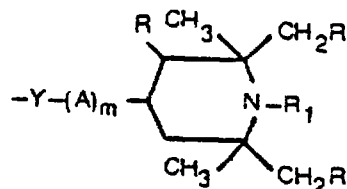
wherein Z is hydrogen, C₁-C₁₈-alkyl, allyl, benzyl, C₂-C₁₂-alkanoyl or benzoyl.

7. The use, according to claim 1, of light stabilizers of the formula VI

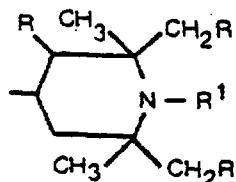


(VI)

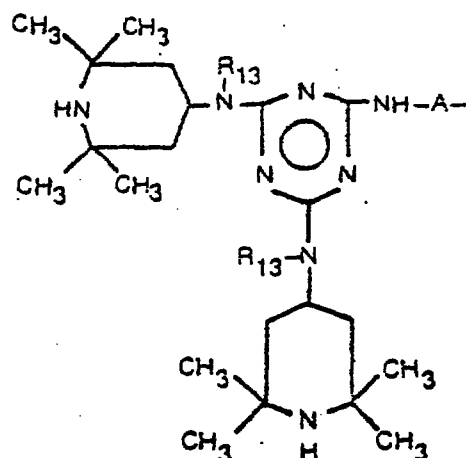
wherein n is the numbers 1 or 2 and R₈ denotes a group of the formula



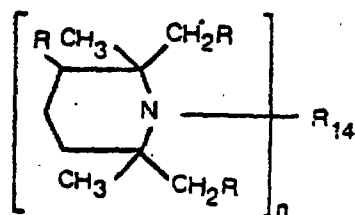
wherein R has the meaning given for formula (I), R₁ has the meaning indicated under a), Y is -O- or -NR₁₁, A denotes C₂-C₆-alkylene and n denotes the numbers 0 or 1, R₉ is the groups R₈, NR₁₁R₁₂, -OR₁₃, -NHCH₂OR₁₃ or -N(CH₂OR₁₃)₂, and, if n=1, R₁₀ denotes the groups R₈ or R₉, and, if n=2, R₁₀ denotes the group -Y-Q-Y- wherein Q denotes C₂-C₆-alkylene which is optionally interrupted by -N(R₁₄)-, R₁₁ is C₁-C₁₂-alkyl, cyclohexyl, benzyl or C₁-C₄-hydroxyalkyl or a group of the formula



R_{12} denotes C_1 - C_{12} -alkyl, cyclohexyl, benzyl or C_1 - C_4 -hydroxyalkyl, R_{13} denotes hydrogen, C_1 - C_{12} -alkyl or phenyl and R_{14} denotes hydrogen or the group $-CH_2OR_{13}$, or R_{11} and R_{12} together are C_4 - C_5 -alkylene or C_4 - C_5 -oxaalkylene, or R_{11} and R_{12} each denote a group of the formula

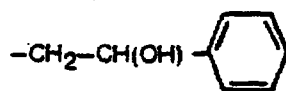


8. The use, according to claim 1, of light stabilizers of the formula (VII)



(VII)

wherein n denotes the numbers 1 or 2, R is hydrogen or methyl, and, if $n=1$, R_{14} denotes C_4 - C_{18} -alkyl, C_7 - C_{12} -aralkyl, the group $-CO-R_{15}$ or C_1 - C_4 -alkyl which is substituted by $-CN$, $-COOR_{16}$, $-OH$, $-OCOR_{17}$ or



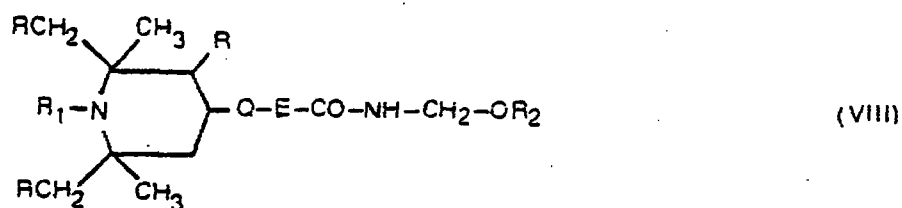
wherein R_{15} is C_1 - C_{12} -alkyl, C_2 - C_4 -alkenyl or phenyl, R_{16} is C_1 - C_{18} -alkyl and R_{17} is C_1 - C_{18} -alkyl, C_2 - C_{10} -alkenyl, cyclohexyl, benzyl or C_6 - C_{10} -aryl, or, if $n=2$, R_{14} is C_4 - C_{12} -alkylene, 2-butenyl-1,4-ene, xylylene, the group $-(CH_2)_2-OOC-R_{18}-COO-(CH_2)_2-$



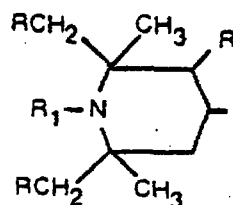
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or the group $-\text{CH}_2-\text{OOC}-\text{R}_{19}-\text{COO}-\text{CH}_2-$ wherein R_{18} denotes C_2 C_{10} -alkylene, phenylene or cyclohexylene and R_{19} denotes C_2 - C_{10} -alkylene, xylylene or cyclohexylene.

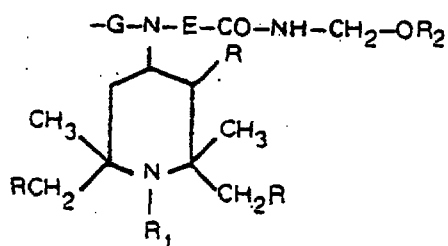
9. The use, according to claim 1, of light stabilizers of the formula (VIII)



wherein Q is $-\text{N}(\text{R}_3)-$ or $-\text{O}-$, E denotes C_1 - C_3 -alkylene, the group $-\text{CH}_2-\text{CH}(\text{R}_4)-\text{O}-$ wherein R_4 is hydrogen, methyl or phenyl, or denotes the group $-(\text{CH}_2)_3-\text{NH}-$ or a single bond, R denotes hydrogen or methyl, R_1 denotes hydrogen, C_1 - C_{18} -alkyl, C_3 - C_8 -alkenyl, C_3 - C_8 -alkynyl, C_7 - C_{12} -aralkyl, C_1 - C_8 -alkanoyl, C_3 - C_5 -alkenoyl or glycidyl, R_2 denotes hydrogen or C_1 - C_{18} -alkyl, and R_3 denotes hydrogen, C_1 - C_{18} -alkyl, C_5 - C_7 -cycloalkyl, C_7 - C_{12} -aralkyl, cyanoethyl, C_6 - C_{10} -aryl, the group $-\text{CH}_2-\text{CH}(\text{R}_4)-\text{OH}$ wherein R_4 has the meaning indicated above, a group of the formula



or a group of the formula



wherein G can be C_2 - C_6 -alkylene or C_6 - C_{12} -arylene, or R_3 is a group $-\text{E}-\text{CO}-\text{NH}-\text{CH}_2-\text{OR}_2$.



10. The use according to claim 1, characterized in that the stabilizers used are polymeric compounds in which the recurring structural unit contains a 2,2,6,6-tetraalkylpiperidine radical, in particular polyesters, polyethers, polyamides, polyamines, polyurethanes, polyureas, polyaminotriazines, poly(meth)acrylates, poly(meth)acrylamides and copolymers thereof containing radicals of this type.

11. The use according to one of the preceding claims, characterized in that an acid addition salt of a 2,2,6,6-tetraalkylpiperidine compound is used.

12. The use according to one of claims 1-10, characterized in that a complex of a 2,2,6,6-tetraalkylpiperidine compound with a metal compound is used.

13. The use according to one of the preceding claims, characterized in that the 2,2,6,6-tetraalkylpiperidine compound is used in an amount of 0.01 to 5% by weight, relative to the solvent-free binder (paint resin).

14. The use according to claim 13, characterized in that additionally other light stabilizers are used, the amount of which is so chosen that the sum of all the light stabilizers is 0.02 to 5% by weight, relative to the solvent-free binder (paint resin).

15. The use according to one of claims 13 or 14, characterized in that antioxidants, plasticizers, flow control agents, curing accelerators, thickeners, dispersing agents or adhesion promoters are added as further additives.

16. The use according to claim 1 for stabilizing metallic effect paints based on polyacrylate resins which can be cured by heat and contain copolymerized styrene.

17. The use according to one of the preceding claims for stabilizing single-coat metallic effect paints.

18. The use according to one of claims 1-16 for stabilizing two-coat metallic effect paints.

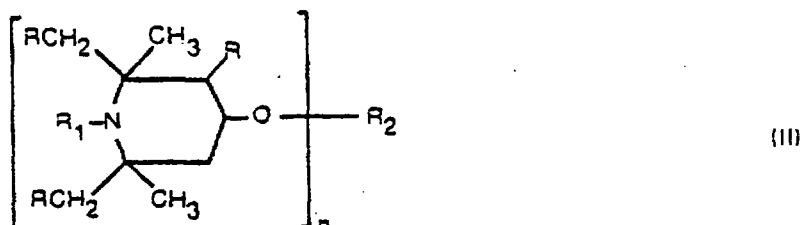
19. The use according to one of the preceding claims for stabilizing automotive paints.



Revendications (as printed)

1. Application de composés tétraalkyl-2,2,6,6 pipéridiniques, de leurs sels d'addition d'acides ou des complexes qu'ils forment avec des composés métalliques, éventuellement en association avec d'autres stabilisants, à la stabilisation de peintures métallisées à cuire à base de résines alkydes ou acryliques thermoréticulables, contre l'action de la lumière, de l'humidité et de l'oxygène.

2. Application selon la revendication 1 de stabilisants à la lumière répondant à la formule (II):



dans laquelle:

n est un nombre de 1 à 4.

R représente l'hydrogène ou un méthyle.

R₁ représente l'hydrogène, un oxyle, un alkyle en C₁—C₈, un alcényle en C₃—C₉, un alcynyle en C₃—C₉, un aralkyle en C₇—C₁₂, un alcanoyle en C₁—C₃, un alcénoyle en C₃—C₅, un glycidyle ou un radical —CH₂CH(OH)—Z dans lequel Z représente l'hydrogène, un méthyle ou un phényle, et

R₂ représente:

—lorsque n est égal à 1, l'hydrogène, un alkyle en C₁—C₈ éventuellement interrompu par un ou plusieurs atomes d'oxygène, un cyanéthyle, un benzyle, un glycidyle, un radical univalent provenant d'un acide carboxylique aliphatique, cycloaliphatique, araliphatique ou aromatique, d'un acide carbamique ou d'un acide contenant du phosphore, ou un radical silyle univalent,

—lorsque n est égal à 2, un alkylène en C₂—C₁₂, un alcénylène en C₄—C₁₂, un xylène, un radical bivalent provenant d'un acide dicarboxylique aliphatique, cycloaliphatique, araliphatique ou aromatique, d'un acide dicarbamique ou d'un acide contenant du phosphore, ou un radical silyle bivalent,

—lorsque n est égal à 3, un radical trivalent provenant d'un acide tricarboxylique aliphatique, cycloaliphatique ou aromatique, d'un acide tricarbamique aromatique ou d'un acide contenant du phosphore, ou un radical silyle trivalent, et

—lorsque n est égal à 4, un radical quadrivalent provenant d'un acide tétracarboxylique aliphatique, cycloaliphatique ou aromatique.

3. Application selon la revendication 2 de stabilisants à la lumière de formule (II) dans lesquels:

n représente le nombre 1 ou le nombre 2,

R représente l'hydrogène ou un méthyle,

R₁ représente l'hydrogène, un alkyle en C₁—C₁₂, un allyle, un benzyle, un acétyle ou un acryloyle,

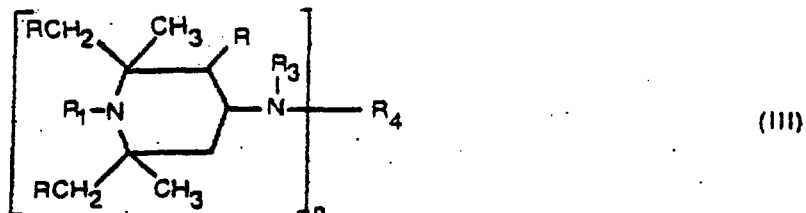
et

R₂ représente:

—lorsque n est égal à 1 un radical d'acide carboxylique aliphatique contenant de 2 à 18 atomes de carbone, d'acide carboxylique cycloaliphatique contenant de 5 à 12 atomes de carbone ou d'acide carboxylique aromatique contenant de 7 à 15 atomes de carbone et

—lorsque n est égal à 2 un radical d'acide dicarboxylique aliphatique contenant de 2 à 36 atomes de carbone, d'acide dicarboxylique cycloaliphatique ou aromatique contenant de 8 à 14 atomes de carbone ou d'acide dicarbamique aliphatique, cycloaliphatique ou aromatique contenant de 8 à 14 atomes de carbone.

4. Application selon la revendication 1 de stabilisants à la lumière répondant à la formule (III):



dans laquelle:

n représente le nombre 1 ou le nombre 2,

R représente l'hydrogène ou un méthyle,

R₁ représente l'hydrogène, un oxyle, un alkyle en C₁—C₈, un alcényle en C₃—C₉, un alcynyle en



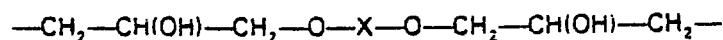
C_3-C_3 , un aralkyle, en C_1-C_{12} , un alcanoyle en C_1-C_9 ou un alcénoyle en C_3-C_9 .

R_3 représente l'hydrogène, un alkyle en C_1-C_{12} , un cycloalkyle en C_5-C_7 , un aralkyle en C_7 ou C_9 , un alcanoyle en C_1-C_{18} , un alcénoyle en C_3-C_9 ou un benzoyle, et

R_4 représente:

—lorsque n est égal à 1, l'hydrogène, un alkyle en C_1-C_9 , un cycloalkyle en C_5-C_7 , un alcényle en C_3-C_9 éventuellement porteur d'un radical cyano, carbonyle ou carbamoyle, un glycidyle, ou un radical de formule $-CH_2CH(OH)-Z$ ou de formule $-CONH-Z$ dans lesquelles Z représente l'hydrogène, un méthyle ou un phényle, et

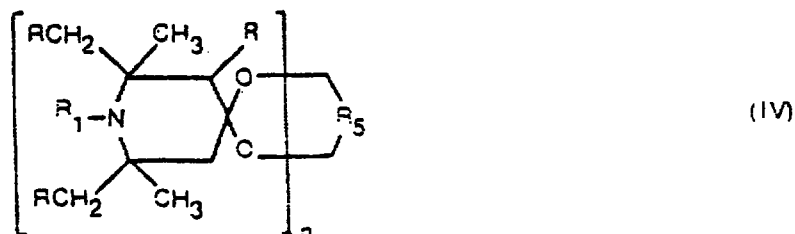
—lorsque n est égal à 2, un alkylène en C_2-C_{12} , un arylène en C_6-C_{12} , un xylène, un radical $-CH_2-CH(OH)-CH_2-$, un radical:



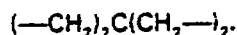
(dans lequel X représente un alkylène en C_2-C_{10} , un arylène en C_6-C_{15} ou un cycloalkylène en C_6-C_{12}), ou, lorsque R_3 n'est ni un alcanoyle ni un alcénoyle ni un benzoyle, R_4 peut aussi représenter un radical bivalent provenant d'un acide dicarbamique ou d'un acide dicarboxylique aliphatique, cycloaliphatique ou aromatique ou encore le radical $-CO-$, ou

R_3 et R_4 peuvent aussi, dans le cas où n est égal à 1, former ensemble le radical cyclique d'un acide dicarboxylique-1,2- ou -1,3 aliphatique ou aromatique.

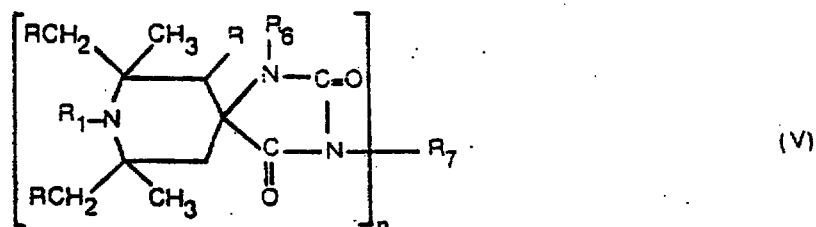
5. Application selon la revendication 1 de stabilisants à la lumière répondant à la formule (IV):



dans laquelle n représente le nombre 1 ou le nombre 2, R l'hydrogène ou un méthyle, R_1 représente l'hydrogène, un oxyde, un alkyle en C_1-C_{18} , un alcényle en C_3-C_9 , un alcynyle en C_3-C_9 , un aralkyle en C_7-C_{12} , un alcanoyle en C_1-C_9 ou un alcénoyle en C_3-C_9 , et R_5 représente, dans le cas où n est égal à 1, un hydroxyalkylène ou un alkylène en C_2-C_8 ou un acyloxyalkylène en C_4-C_{22} et, lorsque n est égal à 2, un radical



6. Application selon la revendication 1 de stabilisants à la lumière répondant à la formule (V):



dans laquelle:

n représente le nombre 1 ou le nombre 2,

R représente l'hydrogène ou un méthyle,

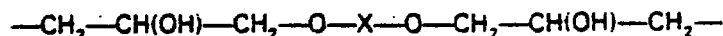
R_1 représente l'hydrogène, un oxyde, un alkyle en C_1-C_{18} , un alcényle en C_3-C_9 , un alcynyle en C_3-C_9 , un aralkyle en C_7-C_{12} , un alcanoyle en C_1-C_9 ou un alcénoyle en C_3-C_9 ,

R_6 représente l'hydrogène, un alkyle en C_1-C_{12} , un allyle, un benzyle, un glycidyle ou un alcoxyalkyle en C_2-C_9 , et

R_7 représente:

—lorsque n est égal à 1, l'hydrogène, un alkyle en C_1-C_{12} , un alcényle en C_3-C_9 , un aralkyle en C_7-C_9 , un cycloalkyle en C_5-C_7 , un hydroxyalkyle en C_2-C_4 , un alcoxyalkyle en C_2-C_8 , un aryle en C_6-C_{10} , un glycidyle ou un radical de formule $-(CH_2)_m-COO-Q$ ou de formule $-(CH_2)_m-O-CO-Q$ dans lesquelles m est égal à 1 ou à 2 et Q représente un alkyle en C_1-C_4 ou un phényle, et

—lorsque n est égal à 2, un alkylène en C_2-C_{12} , un arylène en C_6-C_{12} , un radical:

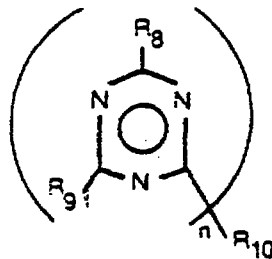


(dans lequel X représente un alkylène en C_2-C_{10} , un arylène en C_6-C_{10} ou un cycloalkylène en C_6-C_{12}), ou un radical:



(dans lequel Z représente l'hydrogène, un alkyle en C_1-C_{18} , un allyle, un benzyle, un alcanoyle en C_2-C_{12} ou un benzoyle).

7. Application selon la revendication 1 de stabilisants à la lumière répondant à la formule (VI):

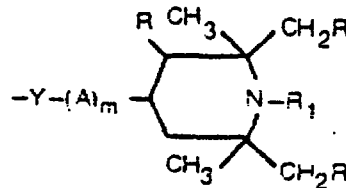


(VI)

dans laquelle:

n représente le nombre 1 ou le nombre 2.

R_8 représente un radical de formule:



dans laquelle R représente l'hydrogène ou un méthyle. R_1 a la signification donnée à la revendication 2. X représente $-O-$ ou $-NR_{11}-$. A représente un alkylène en C_2-C_9 et m représente le nombre 0 ou le nombre 1.

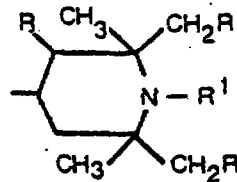
R_8 représente un radical R_8 , $-NR_{11}R_{12}$, $-OR_{13}$, $-NHCH_2OR_{13}$ ou $-N(CH_2OR_{13})_2$, et

R_{10} représente:

—lorsque n est égal à 1, un radical R_8 ou R_9 et

—lorsque n est égal à 2, un radical $-Y-Q-Y-$ dans lequel Q représente un alkylène en C_2-C_9 , éventuellement interrompu par $-N(R_{14})-$.

R_{11} représente un alkyle en C_1-C_{12} , un cyclohexyle, un benzyle, un hydroxyalkyle en C_1-C_4 ou un radical de formule:



R_{12} représente un alkyle en C_1-C_{12} , un cyclohexyle, un benzyle ou un hydroxyalkyle en C_1-C_4 .

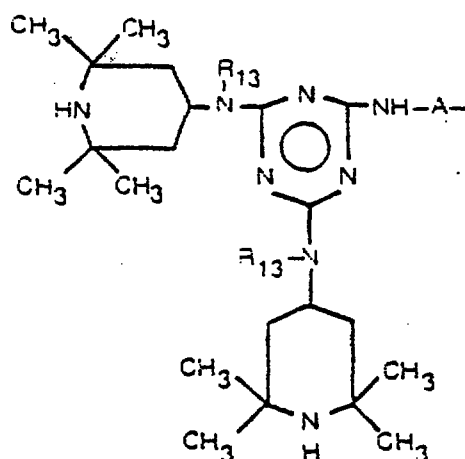
R_{13} représente l'hydrogène, un alkyle en C_1-C_{12} ou un phényle, et

R_{14} représente l'hydrogène ou un radical $-CH_2OR_{13}$, ou

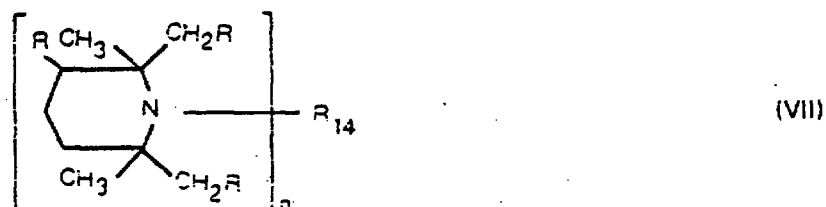
R_{11} et R_{12} forment ensemble un alkylène en C_4 ou C_5 ou un oxa-alkylène ou

R_{11} et R_{12} représentent chacun un radical de formule:





8. Application selon la revendication 1 de stabilisants à la lumière répondant à la formule (VII):



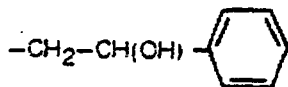
dans laquelle:

n représente le nombre 1 ou le nombre 2.

R représente l'hydrogène ou un méthyle et

R_{14} représente:

—lorsque n est égal 1, un alkyle en C_1-C_8 , un aralkyle en C_7-C_{12} , un radical $—CO—R_{15}$, un alkyle en C_1-C_4 porteur d'un radical $—CN$, $—COOR_{16}$, $—OH$, $—OCOR_{17}$ ou

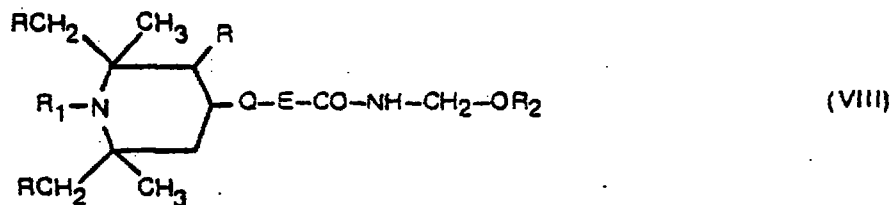


R_{15} représentant un alkyle en C_1-C_{12} , un alcényle en C_2-C_4 ou un phényle, R_{16} un alkyle en C_1-C_{18} , R_{17} un alkyle en C_1-C_8 , un alcényle en C_2-C_{10} , un cyclohexyle, un benzyle ou un aryle en C_6-C_{10} , et —lorsque n est égal à 2, un alkylène en C_4-C_{12} , un butène-2 ylène-1,4, un xylène, un radical



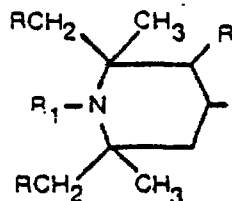
ou un radical $—CH_2—OOC—R_{18}—COO—CH_2—$ dans lesquels R_{18} représente un alkylène en C_2-C_{10} , un phénylène ou un cyclohexylène et R_{19} un alkylène en C_2-C_{10} , un xylène ou un cyclohexylène.

9. Application selon la revendication 1 de stabilisants à la lumière répondant à la formule (VIII):



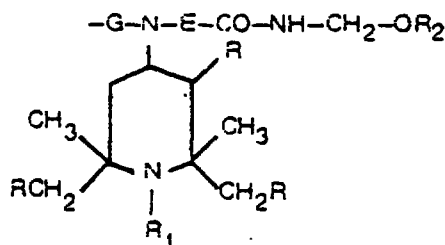
dans laquelle Q représente $—N(R_1)—$ ou $—O—$, E représente un alkylène en C_1-C_3 , un radical $—CH_2—CH(R_4)—O—$ dans lequel R_4 représente l'hydrogène, un méthyle ou un phényle, un radical $—(CH_2)_3—NH—$ ou une liaison simple, R représente l'hydrogène ou un méthyle, R_1 représente l'hydrogène, un alkyle en C_1-C_{18} , un alcényle en C_2-C_8 , un alcynyle en C_3-C_8 , un aralkyle en C_7-C_{12} , un alcanoyle en C_1-C_8 , un alcénoyle en C_3-C_5 ou un glycidyle, R_2 représente l'hydrogène ou un alkyle en C_1-C_{18} , R_3 représente l'hydrogène, un alkyle en C_1-C_{18} , un cycloalkyle en C_5-C_7 , un aralkyle en C_7-C_{12} , un cyanéthyle, un aryle en C_6-C_{10} , un radical $—CH_2CH(R_4)—OH$ dans lequel R_4 a la signification indiquée ci-dessus, un radical de formule:





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ou un radical répondant à la formule:



dans laquelle G représente un alkylène en C_2-C_8 ou un arylène en C_6-C_{12} , ou R_2 représente un radical $-E-CO-NH-CH_2-OR_2$.

10. Application selon la revendication 1 caractérisée en ce qu'on utilise, comme stabilisants à la lumière, des composés polymères dont le motif répété contient un radical tétraalkyl-2,2,6,6 pipéridinique, plus particulièrement des polyesters, des polyéthers, des polyamides, des polyamines, des polyuréthanes, des polyurées, des polyaminotriazines, des polyacrylates, des polyméthacrylates, des polyacrylamides, des polyméthacrylamides et leurs copolymères, qui contiennent de tels radicaux.

11. Application selon l'une quelconque des revendications précédentes, caractérisée en ce qu'on utilise un sel d'addition d'acide d'un composé tétraalkyl-2,2,6,6 pipéridinique.

12. Application selon l'une quelconque des revendications 1 à 10, caractérisée en ce qu'on utilise un complexe formé par un composé tétraalkyl-2,2,6,6 pipéridinique avec un composé métallique.

13. Application selon l'une quelconque des revendications précédentes, caractérisée en ce qu'on utilise le composé tétraalkyl-2,2,6,6 pipéridinique en une quantité de 0,01 à 5% en poids par rapport au feuilligène (résine pour peinture ou vernis) dépourvu de solvant.

14. Application selon la revendication 13, caractérisée en ce qu'on utilise en outre d'autres stabilisants à la lumière dont la quantité est choisie de telle façon que la somme des quantités de tous les stabilisants à la lumière soit comprise entre 0,02 et 5% en poids par rapport au feuilligène (résine pour peinture ou vernis) dépourvu de solvant.

15. Application selon l'une des revendications 13 et 14, caractérisée en ce qu'on ajoute, comme additifs supplémentaires, des anti-oxydants, des plastifiants, des agents de nivellement, des accélérateurs de durcissement, des épaississants, des dispersants ou des renforçateurs d'adhérence.

16. Application selon la revendication 1 à la stabilisation de peintures métallisées à base de résines polyacryliques thermoréticulables qui renferment du styrène incorporé par polymérisation.

17. Application selon l'une quelconque des revendications précédentes pour la stabilisation de peintures métallisées à une seule couche.

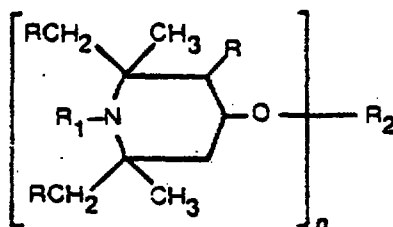
18. Application selon l'une quelconque des revendications 1 à 16, pour la stabilisation de peintures métallisées à deux couches.

19. Application selon l'une quelconque des revendications précédentes pour la stabilisation de peintures pour automobiles.

Claims (as printed)

1. Use of 2,2,6,6-tetraalkylpiperidine compounds, of their acid addition salts or complexes with metal compounds, optionally together with further stabilisers, for stabilising metallic stoving lacquers based on hot-crosslinkable alkyd resins or acrylic resins against the action of light, moisture and oxygen.

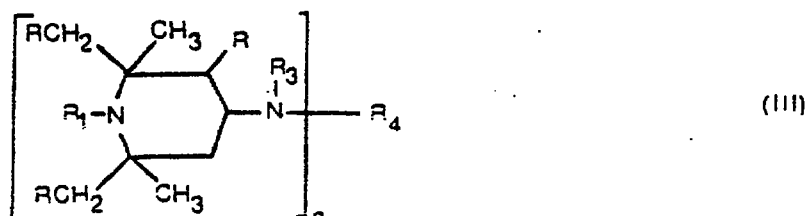
2. Use according to Claim 1 of a light stabiliser of the formula (II)



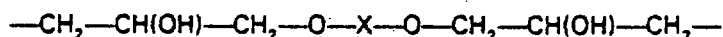
in which n is a number from 1—4 inclusive; R is hydrogen or methyl; R_1 is hydrogen, oxyl, C_1 — C_{18} alkyl, C_3 — C_8 alkenyl, C_3 — C_8 alkynyl, C_7 — C_{12} aralkyl, C_1 — C_8 alkanoyl, C_3 — C_5 alkenoyl, glycidyl or a group $—CH_2—CH(OH)—Z$ wherein Z is hydrogen, methyl or phenyl; and R_2 when n is 1 is hydrogen, C_1 — C_8 alkyl optionally interrupted by one or more oxygen atoms, cyanoethyl, benzyl, glycidyl, a monovalent radical of an aliphatic, cycloaliphatic, araliphatic or aromatic carboxylic acid, or of carbamic acid or of a phosphorus-containing acid, or a monovalent silyl radical; R_2 when n is 2 is C_2 — C_{12} alkylene, C_4 — C_{12} alkenylene, xylilene, a bivalent radical of an aliphatic, cycloaliphatic, araliphatic or aromatic dicarboxylic acid, of dicarbamic acid or of a phosphorus-containing acid, or a bivalent silyl radical; R_2 when n is 3 is a trivalent radical of an aliphatic, cycloaliphatic or aromatic tricarboxylic acid, of an aromatic tricarbamic acid or of a phosphorus-containing acid, or a trivalent silyl radical; and R_2 when n is 4 is a tetravalent radical of an aliphatic, cycloaliphatic or aromatic tetracarboxylic acid.

3. Use according to Claim 2 of a light stabiliser of the formula (III) in which n is the number 1 or 2; R is hydrogen or methyl; R_1 is hydrogen, C_1 — C_{12} alkyl, allyl, benzyl, acetyl or acyloyl; and R_2 when n is 1 is 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 7—15 C atoms; and R_2 when n is 2 is a radical of an aliphatic dicarboxylic acid having 2—36 C atoms, of a cycloaliphatic or aromatic dicarboxylic acid having 8—14 C atoms, or of an aliphatic, cycloaliphatic or aromatic dicarbamic acid having 8—14 C atoms.

4. Use according to Claim 1 of a light stabiliser of the formula (III)

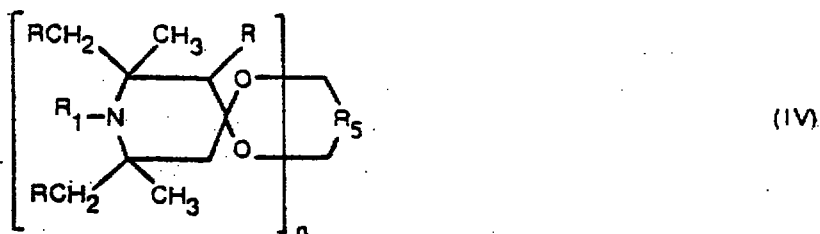


in which n is the number 1 or 2; R is hydrogen or methyl; R_1 is hydrogen, oxyl, C_1 — C_{18} alkyl, C_3 — C_8 alkenyl, C_3 — C_8 alkynyl, C_7 — C_{12} aralkyl, C_1 — C_8 alkanoyl or C_3 — C_5 alkenoyl; R_2 is hydrogen, C_1 — C_{12} alkyl, C_5 — C_7 cycloalkyl, C_7 — C_8 aralkyl, C_2 — C_{18} alkanoyl, C_3 — C_5 alkenoyl or benzoyl; and R_4 when n is 1 is hydrogen, C_1 — C_{18} alkyl, C_5 — C_7 cycloalkyl, C_2 — C_8 alkenyl which is unsubstituted or substituted by a cyano, carbonyl or carbamide group, or it is glycidyl, a group of the formula $—CH_2—CH(OH)—Z$ or of the formula $—CONH—Z$ wherein Z is hydrogen, methyl or phenyl; or R_4 when n is 2 is C_2 — C_{12} alkylene, C_6 — C_{12} arylene, xylilene, a $—CH_2—CH(OH)—CH_2—$ group or a group



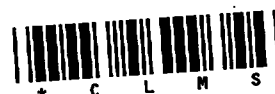
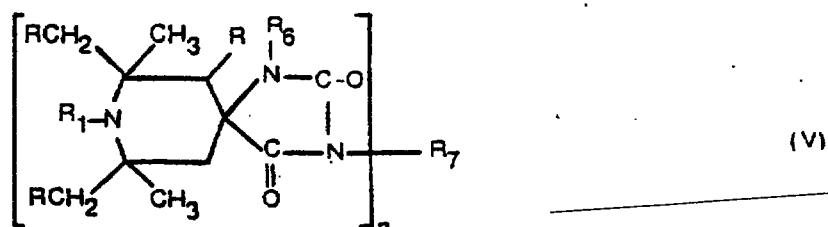
wherein X is C_2 — C_{10} alkylene, C_6 — C_{15} arylene or C_6 — C_{12} cycloalkylene; or, provided that R_3 is not alkanoyl, alkenoyl or benzoyl, R_4 can also be a bivalent radical of an aliphatic, cycloaliphatic or aromatic dicarboxylic acid or dicarbamic acid, or can also be the group $—CO—$; or R_3 and R_4 together when n is 1 can be the cyclic radical of an aliphatic or aromatic 1,2- or 1,3-dicarboxylic acid.

5. Use according to Claim 1 of a light stabiliser of the formula (IV)

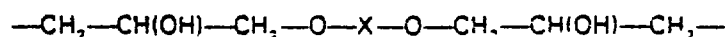


in which n is the number 1 or 2; R is hydrogen or methyl; R_1 is hydrogen, oxyl, C_1 — C_{18} alkyl, C_3 — C_8 alkenyl, C_3 — C_8 alkynyl, C_7 — C_{12} aralkyl, C_1 — C_8 alkanoyl or C_3 — C_5 alkenoyl; and R_5 when n is 1 is C_2 — C_8 alkylene or hydroxyalkylene or C_4 — C_{22} acyloxyalkylene; and R_5 when n is 2 is the group $(—CH_2)_2C(CH_2—)_2$.

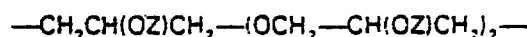
6. Use according to Claim 1 of a light stabiliser of the formula (V)



in which n is the number 1 or 2; R is hydrogen or methyl; R_1 is hydrogen, oxy, C_1-C_{18} alkyl, C_3-C_9 alkenyl, C_3-C_9 alkynyl, C_7-C_{12} aralkyl, C_1-C_3 alkanoyl or C_3-C_9 alkenoyl; R_2 is hydrogen, C_1-C_{12} alkyl, allyl, benzyl, glycidyl or C_2-C_6 alkoxyalkyl; and R_3 when n is 1 is hydrogen, C_1-C_{12} alkyl, C_3-C_9 alkenyl, C_7-C_9 aralkyl, C_3-C_7 cycloalkyl, C_2-C_4 hydroxyalkyl, C_2-C_6 alkoxyalkyl, C_8-C_{10} aryl, glycidyl, a group of the formula $-(CH_2)_m-COO-Q$ or of the formula $-(CH_2)_m-O-CO-Q$ wherein m is 1 or 2, and Q is C_1-C_4 alkyl or phenyl; or R_3 when n is 2 is C_2-C_{12} alkylene or C_8-C_{12} arylene, a group

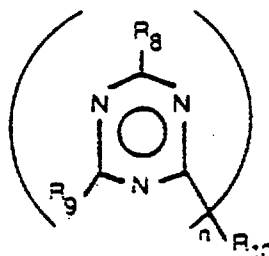


wherein X is C_2-C_{10} alkylene, C_8-C_{15} arylene or C_8-C_{12} cycloalkylene, or a group



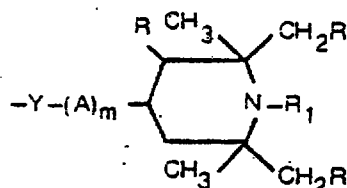
wherein Z is hydrogen, C_1-C_{18} alkyl, allyl, benzyl, C_2-C_{12} alkanoyl or benzoyl.

7. Use according to Claim 1 of a light stabiliser of the formula (VI)

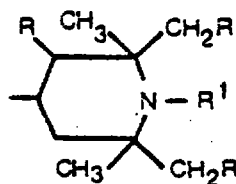


(VI)

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

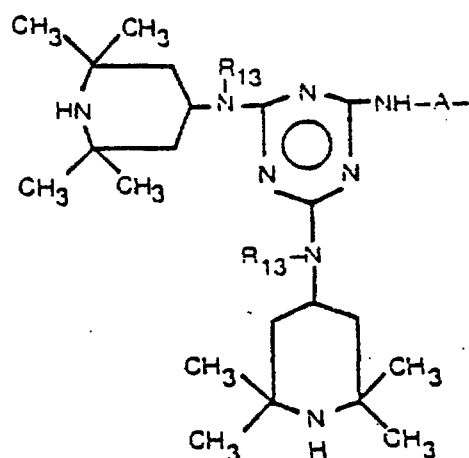


in which R is as defined under the formula (I), R_1 is as defined under a), Y is $-O-$ or $-NR_{11}-$, A is C_2-C_9 alkylene; and m is the number 0 or 1; R_9 is the groups R_8 , $NR_{11}R_{12}$, $-OR_{13}$, $-NHCH_2OR_{13}$ or $-N(CH_2OR_{13})_2$; R_{10} when n is 1 is the groups R_8 or R_9 ; and R_{10} when n is 2 is the group $-Y-Q-Y-$ wherein Q is C_2-C_6 alkylene optionally interrupted by $-N(R_{14})-$; R_{11} is C_1-C_{12} alkyl, cyclohexyl, benzyl or C_1-C_4 hydroxyalkyl, or a group of the formula

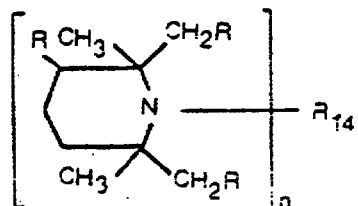


R_{12} is C_1-C_{12} alkyl, cyclohexyl, benzyl, C_1-C_4 hydroxyalkyl; R_{13} is hydrogen, C_1-C_{12} alkyl or phenyl; and R_{14} is hydrogen or the group $-CH_2OR_{13}$; or R_{11} and R_{12} together are C_4-C_9 alkylene or oxaalkylene, or R_{11} and R_{12} are each a group of the formula



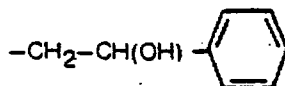


8. Use according to Claim 1 of a light stabiliser of the formula (VII)



(VII)

in which n is the number 1 or 2; R is hydrogen or methyl; and R_{14} when n is 1 is C_4-C_{12} alkyl, C_7-C_{12} aralkyl, the group $-CO-R_{15}$, or C_1-C_4 alkyl which is substituted by $-CN$, $-COOR_{16}$, $-OH$, $-OCOR_{17}$, or

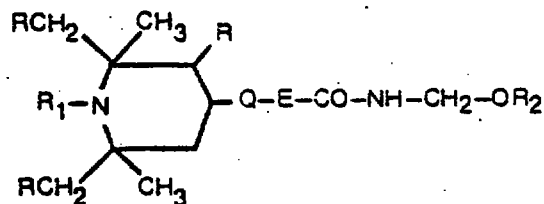


wherein R_{15} is C_1-C_{12} alkyl, C_2-C_4 alkenyl or phenyl, R_{16} is C_1-C_{12} alkyl, R_{17} is C_1-C_{12} alkyl, C_2-C_{12} alkenyl, cyclohexyl, benzyl or C_6-C_{10} aryl; or R_{14} when n is 2 is C_4-C_{12} alkylene, 2-butenylene-1,4, xylylene, the group



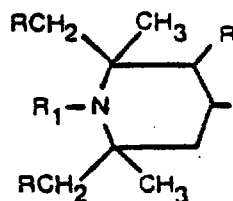
or the group $-CH_2-OOC-R_{19}-COO-CH_2-$ wherein R_{18} is C_2-C_{10} alkylene, phenylene or cyclohexylene, and R_{19} is C_2-C_{10} alkylene, xylylene or cyclohexylene.

9. Use according to Claim 1 of a light stabiliser of the formula (VIII)



(VIII)

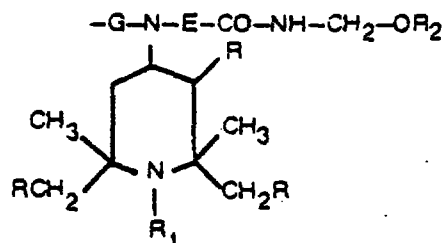
in which Q is $-N(R_3)-$ or $-O-$; E is C_1-C_3 alkylene, the group $-CH_2-CH(R_4)-O-$ wherein R_4 is hydrogen, methyl or phenyl, the group $-(CH_2)_3-NH-$ or a single bond; R is hydrogen or methyl, R_1 is hydrogen, C_1-C_{18} alkyl, C_3-C_8 alkenyl, C_3-C_8 alkynyl, C_7-C_{12} aralkyl, C_1-C_8 alkanoyl, C_3-C_8 alkenoyl or glycidyl; R_2 is hydrogen or C_1-C_{19} alkyl; R_3 is hydrogen, C_1-C_{18} alkyl, C_5-C_7 cycloalkyl, C_7-C_{12} aralkyl, cyanoethyl, C_6-C_{10} aryl, the group $-CH_2-CH(R_4)-OH$ wherein R_4 has the meaning defined above, a group of the formula



or a group of the formula



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wherein G can be C_2-C_8 alkylene or C_6-C_{12} arylene; or R_2 is a group $-E-CO-NH-CH_2-OR_2$.

10. Use according to Claim 1, wherein the light stabilisers used are polymeric compounds of which the recurring structural unit contains a 2,2,6,6-tetraalkylpiperidine radical, particularly polyesters, polyethers, polyamides, polyamines, polyurethanes, polyureas, polyaminotriazines, poly(meth)acrylates, poly(meth)acrylic amides, and copolymers thereof which contain radicals of this type.

11. Use according to any one of the preceding claims, wherein an acid addition salt of a 2,2,6,6-tetraalkylpiperidine compound is used.

12. Use according to any one of Claims 1-10, wherein a complex of a 2,2,6,6-tetraalkylpiperidine compound with a metal compound is used.

13. Use according to any one of the preceding claims, wherein the 2,2,6,6-tetraalkylpiperidine compound is used in an amount of 0.01 to 5 per cent by weight, relative to the solvent-free binder (lacquer resin).

14. Use according to Claim 13, wherein there are additionally used other light stabilisers, the amount of which is so chosen that the sum of all the light stabilisers is 0.02 to 5 per cent by weight, relative to the solvent-free binder (lacquer resin).

15. Use according to any one of Claims 13 or 14, wherein antioxidants, plasticisers, levelling agents, curing accelerators, thickeners, dispersing agents or agents improving adhesion are added as further additives.

16. Use according to Claim 1, for stabilising metallic lacquers based on hot-crosslinkable polyacrylate resins containing styrene incorporated by polymerisation.

17. Use according to any one of the preceding claims, for stabilising single-layer metallic lacquerings.

18. Use according to any one of Claims 1-16 for stabilising two-layer metallic lacquerings.

19. Use according to any one of the preceding claims, for stabilising motor car lacquers.

