

PATENT SPECIFICATION

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 281 282 28X 290 29X 29Y 304 30Y 313 314 31Y
 323 326 32Y 338 339 340 342 34Y 351 355 358 35X
 35Y 360 361 362 364 365 366 368 36Y 373 375
 37Y 380 386 387 388 38Y 390 391 392 395 39Y 401
 40Y 42Y 43X 464 465 491 500 502 50Y 550 552
 556 558 560 570 574 577 580 584 589 58X 594
 596 605 60X 612 620 623 624 625 627 628 62X
 62Y 633 634 635 637 638 63X 63Y 643 644 645
 647 648 64X 650 652 656 658 65X 662 665 668
 672 675 678 67X 68X 699 70Y 71Y 728 72Y 73X
 750 751 752 753 754 755 75X 76X 76Y 770 771
 772 773 777 778 780 78X 78Y 793 797 79Y BA
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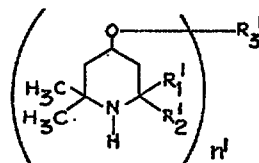
(72) Inventors BRIAN HOLT and DONALD RICHARD RANDELL

(54) NEW PIPERIDINE DERIVATIVES

(71) We, CIBA-GEIGY AG, a Swiss Body Corporate, of Basle, Switzerland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

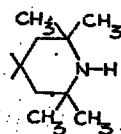
5 The present invention relates to new piperidine derivatives, and in particular to new piperidine derivatives substituted at the 1- and 4- positions and having value as stabilisers for polymeric materials. 5

In German Patent Specification No. 1,929,928 there are described compounds having the general formula:

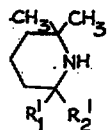


10 wherein R₁' and R₂' are the same or different and each is an alkyl group, or, together with the carbon atom to which they are bound, they form a saturated alicyclic group or a group having the formula: 10

[Price 33p]



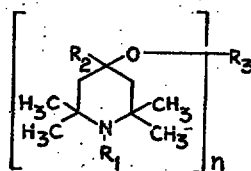
n' is a whole number from 1 to 3 inclusive; and when n' is 1, R_3 is an acyl group derived from an aliphatic, alicyclic or heterocyclic mono-carboxylic acid, an N-substituted carbamoyl group derived from an N-substituted carbamic acid, an N-substituted thiocarbamoyl group derived from an N-substituted thiocarbamic acid, a monovalent group obtained by removing an hydroxyl group from an oxo-acid, an alkyl group, a cycloalkyl group, an aralkyl group, an aryl group or a group having the formula:



wherein R_1' and R_2' have their previous significance; when n' is 2, R_3 is a diacyl group derived from an aliphatic, alicyclic, aromatic or heterocyclic dicarboxylic acid, a di-carbamoyl group derived from dicarbamic acid, a bis-thiocarbamoyl group derived from a bis-thiocarbamic acid, a carbonyl group, a divalent group obtained by removing two hydroxyl groups from an oxo-acid, an alkylene group, an arylene group, or an arylene-dialkylene group; and when n' is 3, R_3 is a triacyl group, derived from an aliphatic, alicyclic, aromatic or heterocyclic tricarboxylic acid, a tricarbamoyl group derived from tricarbamic acid, a tris-thiocarbamoyl group derived from a tris-thiocarbamic acid, a trivalent group obtained by removing three hydroxyl groups from an oxo-acid, an alkanetriyl group, arenetriyl group or an arenetriyl trialkylene group.

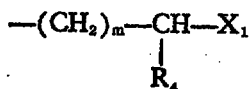
We have now found that certain piperidine derivatives substituted in the 1- and 4- positions are effective stabilisers for polymers, especially against photo- and thermal degradation.

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

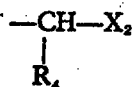


and their salts wherein n is 1, 2, 3 or 4;

R_1 is a monovalent residue and is an alkyl residue having from 1 to 20, preferably 1 to 12 or 5 to 20 carbon atoms, an alkenyl or alkynyl residue having from 3 to 20, preferably 3 to 12 carbon atoms, an aralkyl residue having from 7 to 12 carbon atoms, or a residue having the formula:



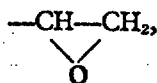
or



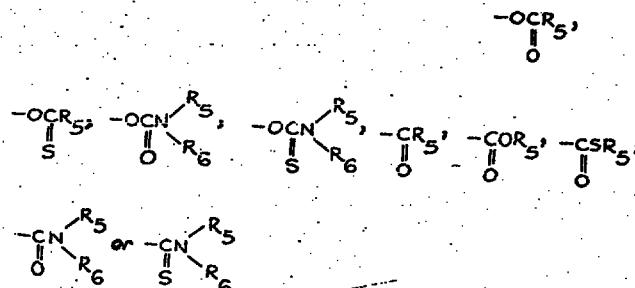
wherein m is 1, 2 or 3,

R_4 is hydrogen or a methyl or phenyl residue,

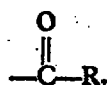
X_2 is halogen, cyano,



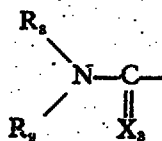
—COR₅, —CO.OR₅, —CO.SR₅, or —CONR₅R₆ and X₁ is hydroxyl, halogen, cyano, —OR₅,



wherein R₅ is an alkyl residue having from 1 to 20 carbon atoms, an alkenyl residue having from 2 to 20 carbon atoms, a cycloalkyl residue having from 5 to 12 carbon atoms, an aryl residue having from 6 to 11 carbon atoms, or an aralkyl residue having from 7 to 14, preferably 7 to 11, more preferably 7 to 8 carbon atoms, or, when R₅ is joined to a nitrogen atom, also hydrogen and R₆ is preferably hydrogen or an alkyl residue having from 1 to 4 carbon atoms, or R₅ and R₆ together with the nitrogen atom to which they are bound form a 5- or 6-membered ring which contains no other heteroatoms or contains one or more other heteroatoms, or R₁ is an acyl group



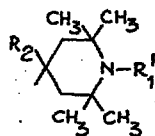
wherein R₁ is hydrogen, an unsubstituted alkyl or substituted alkyl residue having from 1 to 20 carbon atoms, an alkenyl or alkynyl residue having from 2 to 20 carbon atoms, a cycloaliphatic (particularly cycloalkyl) residue having from 5 to 12 (preferably 5 or 6) carbon atoms, an araliphatic residue having from 7 to 14 carbon atoms, an aromatic residue having from 6 to 20, preferably 6 to 12, carbon atoms (more preferably an aralkyl residue having from 7 to 11 carbon atoms) or an heterocyclic residue, or R₁ is a carbamoyl or thiocarbamoyl residue having the formula:



wherein X₃ is —O— or —S—,

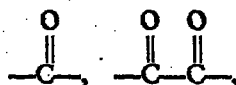
R₂ is hydrogen or an alkyl residue having from 1 to 4 carbon atoms, and R₃ is hydrogen, an alkyl residue having from 1 to 20 carbon atoms, an alkenyl residue having from 3 to 20 carbon atoms, a cycloalkyl residue having from 5 to 12 carbon atoms or an unsubstituted aryl or substituted aryl residue having from 6 to 12 carbon atoms;

R₂ is an alkyl residue having from 1 to 4 carbon atoms, an alkenyl or alkynyl residue having from 3 to 20 carbon atoms, preferably 3 or 4 carbon atoms, a cycloalkyl residue having from 5 to 12 carbon atoms, an aryl residue having from 6 to 10 carbon atoms or an aralkyl residue having from 7 to 9 carbon atoms or preferably hydrogen; and when n is 1, R₃ is a monovalent radical having the same significance as R₁, or R₃ represents a monovalent group obtained by removing a hydroxyl group from a sulphinic acid, a sulphonic acid, a phosphorus containing acid or sulphuric or a boric acid, or R₃ is an aryl residue, a cycloalkyl group having from 5 to 12 carbon atoms, or a residue having the formula:

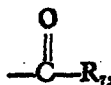


wherein R_1' is hydrogen or R_1' has the same significance as R_1 ;

when n is 2, R_2 is a divalent residue and is an alkylene residue having from 1 to 20 carbon atoms, an alkenylene residue having from 2 to 20, preferably 3 to 20, carbon atoms, an alkynylene residue having from 2 to 20, preferably 3 to 20, carbon atoms, cycloalkylidene residue having from 5 to 12 carbon atoms, an arylene residue having 6 to 14 carbon atoms, an aralkylene residue having from 8 to 14 carbon atoms or an aliphatic, aromatic or heterocyclic diacyl residue,



an aliphatic or aromatic dicarbonyl or dithiocarbonyl residue, sulphinyl or sulphonyl residue or a divalent residue obtained by removing two hydroxyl groups from a disulphonic acid, a phosphorus containing acid or sulphuric or a boric acid; when n is 3, R_3 is a trivalent residue and is an alkanetriyl an arenetriyl or an arenetriyl-trialkylene residue, an aliphatic or aromatic triacyl residue or a triacyl residue derived from *o*-phosphoric, *o*-phosphorous or *o*-boric acid; and when n is 4, R_4 is a tetravalent residue and is an alkane-tetrayl residue, or a tetraacyl residue derived from an aliphatic or aromatic tetracarboxylic acid or from *o*-silicic acid; provided that when R_2 represents an acyl group



an aliphatic, aromatic or heterocyclic diacyl residue, the group —CO— or —CO.CO— , an aliphatic or aromatic triacyl or tetraacyl residue, a triacyl residue derived from *o*-phosphonic, *o*-phosphorous or *o*-boric acid or a tetraacyl residue derived from *o*-silicic acid, the number of carbon atoms in the alkyl group designated by R_1 is from 5 to 20; as well as, when n is 2, 3 or 4, partial ethers, esters and carbamoyloxy and thiocarbamoyloxy compounds related to the fully-reacted compounds of formula 1.

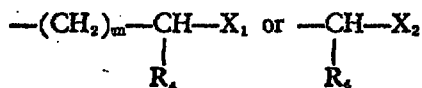
When n is 1, R_1 and/or R_2 may be an alkyl residue having from 1 to 20 carbon atoms, preferred 1 to 18, examples of this substituent are methyl, ethyl, *n*-propyl, *n*-butyl, *sec*-butyl, *t*-butyl, *n*-hexyl, *n*-octyl, 2-ethylhexyl, *n*-nonyl, *n*-decyl, *n*-undecyl, *n*-dodecyl, *n*-tridecyl, *n*-tetradecyl, *n*-hexadecyl or *n*-octadecyl residue and eicosyl. In terms of accessibility and activity however for optimal compatibility with polyolefines substrates, alkyl substituents R_1 and/or R_2 having from 5 to 20, especially 5 to 12 carbon atoms are preferred. A sub-group of alkyl residues R_1 is that containing from 1 to 4 carbon atoms, preferably methyl.

In those cases in which R_1 and/or R_2 is an alkenyl residue having from 3 to 20 carbon atoms, examples of these substituents are allyl, methallyl, 3-hexenyl, 4-octenyl, 6-decenyl, 10-undecenyl, and 8-octadecenyl residues, however the preferred substituents in this group are allyl and methallyl residues.

When the residues R_1 and/or R_2 are alkynyl they may be for example propargyl, but-1- and -2-ynyl, pent-1-ynyl, hex-1-ynyl, oct-1-ynyl, dec-1-ynyl, dodec-1-ynyl, tetradec-1-ynyl and octadec-1-ynyl. The preferred alkynyl substituents however are propargyl and methylpropargyl.

When R_1 and/or R_2 is an aralkyl residue, suitable examples are benzyl, β -phenethyl, α -methylbenzyl, α,α -dimethylbenzyl, α -naphthylmethyl and *p*-methyl- α -methylbenzyl residues. Benzyl is preferred.

A further sub-group of R_1 and/or R_2 substituents is substituted alkyl derivatives having the formula:—



wherein m , R_1 , X_1 and X_2 have their previous significance but wherein, however, R_2 is preferably hydrogen and m is preferably 1.

When X_1 is a hydroxyl residue, examples of the substituents R_1 and/or R_2 are 2-hydroxyethyl, 2- and 3-hydroxypropyl, 3- and 4-hydroxybutyl, 4-hydroxypentyl and 2-hydroxy-2-phenylethyl, preferably 2-hydroxyethyl, 2-hydroxypropyl and 2-hydroxy-2-phenylethyl.

When X_1 and/or X_2 are halogen atoms, examples of R_1 and/or R_2 include 2-chloro- and 2-bromo ethyl, 2- and 3-chloro- and 2- and 3-bromopropyl, 3- and 4-chlorobutyl and 2-chloro-2-phenyl, preferably 2-chloroethyl, 2-chloropropyl and 2-chloro-2-phenylethyl.

When X_1 and/or X_2 are cyano groups, R_1 and/or R_2 include cyanomethyl, 1- and 2-cyanobutyl, 4-cyanopentyl, 2-cyano-2-phenylethyl groups, preferably a 2-cyanoethyl group.

When X_2 is a 1,2-epoxy group, R_1 and/or R_2 may be 2,3-epoxy-n-propyl, 2,3-epoxy-methylpropyl, but the preferred epoxyalkyl substituent is 2,3-epoxy-n-propyl.

When X_1 is $-\text{OR}_3$, $-\text{OCOR}_3$, $-\text{OSR}_3$, $-\text{OCONR}_3$, $-\text{CSNR}_3$, or when X_1 and/or X_2 are $-\text{COR}_3$, $-\text{COOR}_3$, $-\text{COSR}_3$, $-\text{CONR}_3$ and the group R_3 is alkyl, then the alkyl group preferably has from 1 to 12, most preferred 1 to 2, carbon atoms; when R_3 is an alkenyl residue, then it preferably contains 2 to 4 carbons; when R_3 is a cycloalkyl group it preferably contains 6 carbon atoms; when R_3 is an aryl residue it preferably contains 6 or 7 carbons; and when R_3 is an aralkyl residue, it preferably has 7 or 8 carbon atoms.

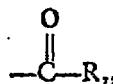
R_3 and R_4 together with the nitrogen atom to which they are bound can form a 5- or 6-membered ring such as the pyrrolidinyl-, imidazolidinyl-, pyrazolidinyl-, piperidinyl-, piperazinyl- or morpholinyl ring.

Examples of R_1 and/or R_2 within this sub-group are 2-methoxyethyl, 2-ethoxyethyl, 2-propoxyethyl, 2-butoxyethyl, 2-methoxypropyl, 2- and 3-ethoxypropyl, 2- and 3-n-butoxypropyl, 3- and 4-methoxybutyl, 3- and 4-ethoxybutyl, 3- and 4-butoxybutyl, 4-methoxypentyl, 4-ethoxypentyl, 4-n-butoxypentyl, 2-methoxy-2-phenylethyl, 2-ethoxy-2-phenylethyl; 2-acetoxyethyl, 2-n-propionoxyethyl, 2-benzoyloxyethyl, 2-acetoxypentyl, 2-n-propionoxypentyl, 4-acetoxybutyl, 4-n-propionoxybutyl, 4-acetoxypentyl, 4-n-propionoxypentyl, 2-phenyl-2-acetoxyethyl, 2-(methylcarbamoyloxy)ethyl, 2-(ethylcarbamoyloxy)ethyl, 2-(phenylcarbamoyloxy)ethyl, 2-(methylcarbamoyloxy)propyl, 2-(ethylcarbamoyloxy)propyl, 2-phenyl-2-(carbamoyloxy)ethyl, 2-(allylthiocarbamoyloxy)ethyl, 2-phenyl-2-(methylcarbamoyloxy)ethyl, 2-phenyl-2-(phenylcarbamoyloxy)ethyl, methylcarbonylmethyl, 2-(methylcarbonyl)ethyl, 2-(ethylcarbonyl)ethyl, 2-(methylcarbonyl)propyl, and 2-(methylcarbonyl)-2-phenylethyl; methoxycarbonylmethyl, 2-(ethoxycarbonyl)ethyl, 2-(methoxycarbonyl)-propyl, and 2-(methoxycarbonyl)-2-phenylethyl, 2-(ethylthiocarbonyl)ethyl, 2-(methylthiocarbonyl)-propyl and 2-(methylthiocarbonyl)-2-phenylethyl, carbamoylmethyl, 2-carbamoylethyl, 2-methylcarbamoylethyl, 2-ethylcarbamoylethyl, dimethylcarbamoylmethyl, 2-diethylcarbamoylethyl, thiocarbamoylmethyl, 2-(thiocarbamoyl)ethyl, 2-methylthiocarbamoylethyl, dimethylthiocarbamoylmethyl, 2-(phenylcarbamoyl)ethyl.

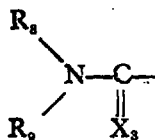
When n is 1 and R_1 and/or R_2 is an acyl group $-\text{COR}$, wherein R is an unsubstituted alkyl or substituted alkyl residue usually having from 1 to 20, preferably 1 to 19, carbon atoms, R may be a methyl, ethyl, propyl, butyl, hexyl, n-octyl, 2-ethylhexyl, n-decyl, n-undecyl, n-tridecyl, n-tetradecyl, n-hexadecyl, n-heptadecyl and eicosyl, chloroethyl, chlorohexyl, methylthioethyl, ethylthioethyl, octylthioethyl, or dodecylthioethyl residue; alkenyl residues R , usually have from 2 to 20, preferably 2 to 17, most preferred 2 to 6, carbon atoms such as vinyl, allyl, methallyl, isobutenyl or hexenyl group; alkynyl residues R , usually have from 2 to 20, preferably 2 to 6, carbon atoms such as a propargyl group; cycloaliphatic residues R , usually have from 5 to 12, preferably 6 to 10, most preferred 5 or 6, carbon atoms, such as a cyclopentyl or cyclohexyl residue; araliphatic residues R , usually have from 7 to 14, preferably 7 to 13, most preferred 7 to 9, carbon atoms such as a benzyl, β -phenylethyl, diphenylmethyl or styryl residue; unsubstituted aromatic residues R , usually have from 6 to 14, preferably 6 to 10, carbon atoms such as a phenyl or naphthyl residue, a substituted aromatic residue, substituted by for example alkyl having 1 to 4 carbon atoms such as tolyl, *p*-tert-butylphenyl; and heterocyclic residues R , may be for example a furan or thiophene residue. As examples of compounds wherein R_1 and/or R_2 are unsaturated acyl groups those are preferred wherein only one of R_1 and R_2 denotes an unsaturated acyl group.

Examples of acyl groups R_1 and/or R_2 are formyl, acetyl, propionyl, n-butyryl, hexanoyl, heptanoyl, octanoyl, 2-ethylhexanoyl, 2,2,4-trimethylpentanoyl, n-decanoyl, n-dodecanoyl, n-tetradecanoyl, n-hexadecanoyl, n-octadecanoyl, n-eicosoyl, acryloyl,

- 5 α -methacryloyl, crotonoyl, undec-10-enoyl, octadec-9-enoyl, β -methylthiopropionyl, methylthioacetyl, β -octylthiopropionyl, β -dodecylthiopropionyl, cyclopentanoyl, cyclohexanoyl, benzoyl, α - and β -naphthoyl, cyclopentylacetyl, cyclohexylacetyl, phenylacetyl, β -phenylpropionyl, diphenyloctanoyl, β -phenylacryloyl, *o*-, *m*- and *p*-toluoyl, *o*-, *m*- or *p*-methoxybenzoyl and *o*-, *m*- and *p*-chlorobenzoyl, 2-furoyl and 2-picolinoyl; provided that when R_3 represents an acyl group 5



- 10 an aliphatic, aromatic or heterocyclic diacyl residue, the group $-\text{CO}-$ or $-\text{CO.CO}-$, an aliphatic or aromatic triacyl or tetraacyl residue, a triacyl residue derived from *o*-phosphonic, *o*-phosphorous or *o*-boric acid or a tetraacyl residue derived from *o*-silicic acid, the number of carbon atoms in the alkyl group designated by R_1 is from 5 to 20. 10
- When n is 1, R_1 and/or R_3 may also be a carbamoyl or thiocarbamoyl residue having the formula:—



- 15 wherein X_3 is $-\text{O}-$ or $-\text{S}-$, R_2 is hydrogen or an alkyl residue having from 1 to 4 carbon atoms and R_3 is hydrogen, an alkyl residue having from 1 to 20, preferably 1 to 8, carbon atoms, an alkenyl residue having from 3 to 20 carbon atoms, a cycloalkyl residue having from 5 to 12 carbon atoms or an unsubstituted alkyl, or substituted aryl, for instance, alkyl or halogen-substituted aryl residue having from 6 to 12, preferably 6 to 10, carbon atoms. Examples of suitable residues within this group are carbamoyl, 15
- 20 N-methylcarbamoyl, N-ethyl-carbamoyl, N-n-propylcarbamoyl, N-isopropylcarbamoyl, N-n-butylcarbamoyl, N-n-pentylcarbamoyl, N-n-octylcarbamoyl, N-n-decylcarbamoyl, N-n-dodecylcarbamoyl, N-n-octadecyl, N-n-eicosylcarbamoyl, N-allylcarbamoyl, N-methallylcarbamoyl, N-undecenylcarbamoyl, N-cyclopentylcarbamoyl, N-cyclohexyl- 20
- 25 carbamoyl, N-methylcyclohexylcarbamoyl, N-cyclododecylcarbamoyl, N-(1- and 2-perhydronaphthyl)carbamoyl, N-adamantylcarbamoyl, N-cyclopentylmethylcarbamoyl, N-benzylcarbamoyl, N-(β -phenethyl)carbamoyl, N-(1- and 2-naphthylmethyl)carbamoyl, N-phenylcarbamoyl, N-(*o*-, *m*- and *p*-tolyl)carbamoyl, N-(2,4- and 2,6-xylyl)- 25
- 30 carbamoyl, N-(α - and β -naphthyl)carbamoyl, N,N-dimethylcarbamoyl, N-methyl, N-ethylcarbamoyl, N,N-diethylcarbamoyl, N,N-diisopropylcarbamoyl, N,N-di-n-propyl- 30
- carbamoyl, N,N-di-n-butyl-carbamoyl and N,N-di-isobutyl-carbamoyl residues as well as the corresponding thiocarbamoyl residues.

- When R_2 is an alkyl residue it is for example methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, t-butyl, preferably methyl, as alkenyl residue R_2 is for example allyl, 35
- 35 methallyl, 3-hexenyl, 4-octenyl, 6-decenyl, 10-undecenyl or 8-octadecenyl, preferably allyl or methallyl and as alkynyl residue for example propargyl, but-1- and -2-ynyl, penta-1-ynyl, hex-1-ynyl, oct-1-ynyl, dec-1-ynyl, dodec-1-ynyl, tetradec-1-ynyl and octadec-1-ynyl, preferably propargyl, R_2 as cycloalkyl is for example cyclopentyl, cyclohexyl, cyclooctyl, cyclododecyl, preferably cyclohexyl as aryl residue R_2 is for example phenyl, *p*-tolyl, t-butylphenyl, naphthyl, preferably phenyl or *p*-tolyl and as aralkyl 40
- 40 residue it is for example benzyl, alpha-methylbenzyl, *p*-alphadimethylbenzyl, preferably benzyl.

When n is 1

- 45 R_3 may be the same as R_1 . If R_3 is alkyl it is preferably an alkyl group having from 3 to 18 carbon atoms. 45
- When R_3 represents an aryl residue it is for example an aromatic residue having 6 to 20 carbon atoms, preferably an aryl residue having 6 to 12 carbon atoms, most preferred phenyl.

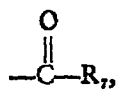
When n is 2

- 50 R_3 is, for example an alkylene residue having from 1 to 20, preferably 2 to 6, carbon atoms such as methylene, ethylene, trimethylene, tetramethylene, hexamethylene or cyclohexane-1,4-bis-methylene residue. Alkenylene residues R_3 preferably contain 3 to 20, most preferred 3 or 4 carbons, and may be, for instance a 1,3-propen-ene or 1,4- 50

buten-2-ene residue. Alkynylene residues R_3 preferably contain 3 to 20, most preferred 4 carbon atoms and may be, for instance a 1:4 but-2-ynylene residue. When R_3 is a cycloalkylidene residue, it preferably contains 7 or 8 carbon atoms.

When R_3 is aralkylene it may be for example α,α -*p*-xylylene.

Diacyl residues R_3 include those derived from an aliphatic, aromatic or heterocyclic dicarboxylic acid. Examples of aliphatic dicarboxylic acids are those having from 2 to 20, preferably alkane dicarboxylic acids having 6 to 10 carbon atoms such as malonic, succinic, glutaric, adipic, pimelic, suberic, azelaic, sebacic, 1,12-dodecanedioic, 1,18-octadecanedioic, 1,20-docosanedioic acid and *N*-methyliminodiacetic acid. Examples of aromatic diacyl residues are those derived from phthalic, isophthalic and terephthalic acids, each optionally ring-substituted, for instance by halogen, an alkyl or alkoxy group each having from 1 to 20 carbon atoms, a hydroxy or tertiary amino group; provided that when R_3 represents an acyl group



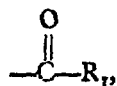
an aliphatic, aromatic or heterocyclic diacyl residue, the group $-\text{CO}-$ or $-\text{CO.CO}-$, an aliphatic or aromatic triacyl or tetraacyl residue, a triacyl residue derived from *o*-phosphonic, *o*-phosphorous or *o*-boric acid or a tetraacyl residue derived from *o*-silicic acid, the number of carbon atoms in the alkyl group designated by R_1 is from 5 to 20.

Examples of heterocyclic dicarboxylic acids are 2,5-thiophene dicarboxylic acid or 2,5-furandicarboxylic acid.

R_3 is for example an aliphatic or aromatic dicarbamoyl residue such as a divalent alkyl dicarbamoyl residue for example the divalent residue of butan-1,4-dicarbamoyl or hexan-1,6-dicarbamoyl or such as a divalent aryl dicarbamoyl residue such as the divalent residue of phenyl-1,4-dicarbamoyl. R_3 is for example an aliphatic or aromatic dithiocarbamoyl residue such as a divalent alkyl dithiocarbamoyl residue for example the divalent residue of butan-1,4-dithiocarbamoyl or hexan-1,6-dithiocarbamoyl or such as an divalent aryl dithiocarbamoyl residue such as the divalent residue of phenyl-1,4-dithiocarbamoyl.

When n is 3

R_3 is, for instance, a triacyl group derived from an aliphatic tricarboxylic acid such as nitrilotriacetic acid, tricarballylic acid, from an aromatic tricarboxylic acid such as benzenetricarboxylic acid or from an inorganic acid such as *o*-phosphorous, *o*-phosphoric or *o*-boric acid, or oxyacids for example, benzene-1,3,5-trisulphonic acid; provided that when R_3 represents an acyl group

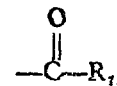


an aliphatic, aromatic or heterocyclic diacyl residue, the group $-\text{CO}-$ or $-\text{CO.CO}-$, an aliphatic or aromatic triacyl or tetraacyl residue, a triacyl residue derived from *o*-phosphonic, *o*-phosphorous or *o*-boric acid or a tetraacyl residue derived from *o*-silicic acid, the number of carbon atoms in the alkyl group designated by R_1 is from 5 to 20.

When n is 4

R_3 is, for instance, a tetracyl group derived from a tetracarboxylic acid, such as ethylenediaminetetracarboxylic acid, from the tetracarboxylic acids described in British Patent Specification No. 1080335, 1,2,4,5-benzene tetracarboxylic acid or from *o*-silicic acid.

R_3 preferably represents an acyl or an *N*-substituted carbamoyl, an alkylene group, a substituted alkylene or an aralkyl group; provided that when R_3 represents an acyl group



an aliphatic, aromatic or heterocyclic diacyl residue, the group $-\text{CO}-$ or $-\text{CO.CO}-$, an aliphatic or aromatic triacyl or tetraacyl residue, a triacyl residue derived from *o*-phosphonic, *o*-phosphorous or *o*-boric acid or a tetraacyl residue derived from *o*-silicic

acid, the number of carbon atoms in the alkyl group designated by R₁ is from 5 to 20.

R₁ preferably represents an alkyl, alkenyl or substituted alkyl group such as hydroxyalkyl, alkylcarbonyloxy or aralkyl group.

Examples of compounds of the present invention are:—

5	<i>Examples where n = 1</i>	5
	4-Methoxy-1,2,2,6,6-pentamethylpiperidine	
	4-n-Butoxy-1,2,2,6,6-pentamethylpiperidine	
	4-n-Dodecyloxy-1,2,2,6,6-pentamethylpiperidine	
	4-n-Octadecyloxy-1,2,2,6,6-pentamethylpiperidine	
10	4-(2'-Cyanooethoxy)-1,2,2,6,6-pentamethylpiperidine	10
	4-(2'-Hydroxyethyl)-1,2,2,6,6-pentamethylpiperidine	
	1-n-Propyl-4-methoxy-2,2,6,6-tetramethylpiperidine	
	1-n-Propyl-4-n-dodecyloxy-2,2,6,6-tetramethylpiperidine	
	1-n-Propyl-4-n-octadecyloxy-2,2,6,6-tetramethylpiperidine	
15	1-sec-Butyl-4-n-dodecyloxy-2,2,6,6-tetramethylpiperidine	15
	1-n-Octyl-4-methoxy-2,2,6,6-tetramethylpiperidine	
	1-n-Dodecyl-4-n-dodecyloxy-2,2,6,6-tetramethylpiperidine	
	1-n-Octadecyl-4-methoxy-2,2,6,6-tetramethylpiperidine	
	1-n-Octadecyl-4-n-octadecyloxy-2,2,6,6-tetramethylpiperidine	
20	1-n-Eicosyl-4-methoxy-2,2,6,6-tetramethylpiperidine	20
	1-Allyl-4-methoxy-2,2,6,6-tetramethylpiperidine	
	1-Allyl-4-allyloxy-2,2,6,6-tetramethylpiperidine	
	1-(1'-Undec-10'-enyl)-4-n-butoxy-2,2,6,6-tetramethylpiperidine	
	1-(1'-Undec-10'-enyl)-4-(1'-undec-10'-enyloxy)-2,2,6,6-tetramethylpiperidine	
25	1-Oleyl-4-methoxy-2,2,6,6-tetramethylpiperidine	25
	1-Oleyl-4-oleyloxy-2,2,6,6-tetramethylpiperidine	
	1-Propargyl-4-ethoxy-2,2,6,6-tetramethylpiperidine	
	1-Propargyl-4-propargyloxy-2,2,6,6-tetramethylpiperidine	
	1-Benzyl-4-n-dodecyloxy-2,2,6,6-tetramethylpiperidine	
30	1-Benzyl-4-allyloxy-2,2,6,6-tetramethylpiperidine	30
	1-Benzyl-4-propargyloxy-2,2,6,6-tetramethylpiperidine	
	1-Benzyl-4-benzyloxy-2,2,6,6-tetramethylpiperidine	
	1-(2'-Hydroxyethyl)-4-methoxy-2,2,6,6-tetramethylpiperidine	
	1-(2'-Hydroxypropyl)-4-allyloxy-2,2,6,6-tetramethylpiperidine	
35	1-(2'-Hydroxyethyl)-4-propargyloxy-2,2,6,6-tetramethylpiperidine	35
	1-(2'-Hydroxypropyl)-4-benzyloxy-2,2,6,6-tetramethylpiperidine	
	1-(2'-Hydroxyethyl)-4-(2'-hydroxyethoxy)-2,2,6,6-tetramethylpiperidine	
	1-(2'-Hydroxypropyl)-4-(2'-hydroxypropoxy)-2,2,6,6-tetramethylpiperidine	
	1-(2'-Hydroxy-2'-phenylethyl)-4-n-butoxy-2,2,6,6-tetramethylpiperidine	
40	1-(2'-Hydroxy-2'-phenylethyl)-4-(2'-hydroxy-2'-phenylethoxy)-2,2,6,6-tetramethylpiperidine	40
	1-(2'-Chloroethyl)-4-n-dodecyloxy-2,2,6,6-methylpiperidine	
	1-(2'-Chloropropyl)-4-benzyloxy-2,2,6,6-tetramethylpiperidine	
	1-(2'-Bromoethyl)-4-(2'-bromoethoxy)-2,2,6,6-tetramethylpiperidine	
45	1-(2'-Chloro-2'-phenylethyl)-4-n-octyloxy-2,2,6,6-tetramethylpiperidine	45
	1-(2'-Cyanoethyl)-4-phenoxy-2,2,6,6-tetramethylpiperidine	
	1-(2'-Cyanoethyl)-4-benzyloxy-2,2,6,6-tetramethylpiperidine	
	1-(2'-Cyanoethyl)-4-(2'-cyanoethoxy)-2,2,6,6-tetramethylpiperidine	
	1-(2'-Cyanopropyl)-4-methoxy-2,2,6,6-tetramethylpiperidine	
50	1-(2',3'-epoxypropyl)-4-n-butoxy-2,2,6,6-tetramethylpiperidine	50
	1-(2',3'-epoxypropyl)-4-benzyloxy-2,2,6,6-tetramethylpiperidine	
	1-(2',3'-epoxypropyl)-4-(2',3'-epoxypropoxy)-2,2,6,6-tetramethylpiperidine	
	1-(2'-methoxyethyl)-4-ethoxy-2,2,6,6-tetramethylpiperidine	
	1-(2'-methoxyethyl)-4-(2'-methoxyethoxy)-2,2,6,6-tetramethylpiperidine	
55	1-(2'-ethoxypropyl)-4-allyloxy-2,2,6,6-tetramethylpiperidine	55
	1-(2'-ethoxy-2'-phenylethyl)-4-benzyloxy-2,2,6,6-tetramethylpiperidine	
	1-(2'-acetoxyethyl)-4-n-butoxy-2,2,6,6-tetramethylpiperidine	
	1-(2'-benzoyloxyethyl)-4-(2'-benzoyloxyethoxy)-2,2,6,6-tetramethylpiperidine	
	1-(2'-propionyloxypropyl)-4-allyloxy-2,2,6,6-tetramethylpiperidine	
60	1-[2'-(methylcarbamoxyloxy)ethyl]-4-benzyloxy-2,2,6,6-tetramethylpiperidine	60
	1-[2'-(methylcarbamoxyloxy)ethyl]-4-[2'-(methylcarbamoxyloxy)ethoxy]-2,2,6,6-tetramethylpiperidine	
	1-[2'-(Phenylcarbamoxyloxy)ethyl]-4-[2'-cyanoethoxy]-2,2,6,6-tetramethylpiperidine	

	1-[2'-(ethylthiocarbamoyloxy)ethyl]-4-{2'-(ethylthiocarbamoyloxy)ethoxy}-2,2,6,6-tetramethylpiperidine	
	1-Methylcarbonylmethyl-4-methoxy-2,2,6,6-tetramethylpiperidine	
	1-[(methylcarbonyl)ethyl]-4-n-octyloxy-2,2,6,6-tetramethylpiperidine	
5	1-Methylcarbonylmethyl-4-methylcarbonylmethoxy-2,2,6,6-tetramethylpiperidine	5
	1-(2'-methoxycarbonyl)ethyl-4-(2'-methoxycarbonylethoxy)-2,2,6,6-tetramethylpiperidine	
	1-(2'-methoxycarbonylethyl)-4-ethoxy-2,2,6,6-tetramethylpiperidine	
10	1-[2'-(ethoxycarbonyl)ethyl]-4-(2'-hydroxyethoxy)-2,2,6,6-tetramethylpiperidine	10
	1-[2'-(thioethoxycarbonyl)ethyl]-4-methoxy-2,2,6,6-tetramethylpiperidine	
	1-Carbamoylmethyl-4-benzyloxy-2,2,6,6-tetramethylpiperidine	
	1-(2'-Carbamoyl)ethyl-4-dodecoxy-2,2,6,6-tetramethylpiperidine	
	1-[2'-(Methylcarbamoyl)ethyl]-4-[2'-methylcarbamoylethoxy]-2,2,6,6-tetramethylpiperidine	
15	1-[2'-(Diethylcarbamoyl)ethyl]-4-methoxy-2,2,6,6-tetramethylpiperidine	15
	1-Thiocarbamoylmethyl-4-allyloxy-2,2,6,6-tetramethylpiperidine	
	1-(Dimethylthiocarbamoyl)methyl-4-benzyloxy-2,2,6,6-tetramethylpiperidine	
	1-Acetyl-4-benzyloxy-2,2,6,6-tetramethylpiperidine	
	1-Lauroyl-4-(2'-hydroxyethoxy)-2,2,6,6-tetramethylpiperidine	
20	1-Stearoyl-4-methoxy-2,2,6,6-tetramethylpiperidine	20
	1-Benzoyl-4-n-butoxy-2,2,6,6-tetramethylpiperidine	
	1-Carbamoyl-4-n-octadecyloxy-2,2,6,6-tetramethylpiperidine	
	1-Methylcarbamoyl-4-benzyloxy-2,2,6,6-tetramethylpiperidine	
	1-Phenylcarbamoyl-4-(2'-hydroxyethoxy)-2,2,6,6-tetramethylpiperidine	
25	1-Phenylthiocarbamoyl-4-(cyclohexyloxy)-2,2,6,6-tetramethylpiperidine	25
	1-Dimethylcarbamoyl-4-methoxy-2,2,6,6-tetramethylpiperidine	
	1-Methylthiocarbamoyl-4-n-octyloxy-2,2,6,6-tetramethylpiperidine	
	1-Phenylthiocarbamoyl-4-methoxy-2,2,6,6-tetramethylpiperidine	
30	1,2,2,6,6-Pentamethylpiperidinyl-4-formate	30
	1,2,2,6,6-Pentamethylpiperidinyl-4-acetate	
	1,2,2,6,6-Pentamethylpiperidinyl-4-isobutyrate	
	1,2,2,6,6-Pentamethylpiperidinyl-4-n-octanoate	
	1,2,2,6,6-Pentamethylpiperidinyl-4-pivalate	
35	1,2,2,6,6-Pentamethylpiperidinyl-4-stearate	35
	1,2,2,6,6-Pentamethylpiperidinyl-4-eicosanoate	
	1,2,2,6,6-Pentamethylpiperidinyl-4-(2'-ethylhexanoate)	
	1,2,2,6,6-Pentamethylpiperidinyl-4-acrylate	
	1,2,2,6,6-Pentamethylpiperidinyl-4-oleate	
40	1,2,2,6,6-Pentamethylpiperidinyl-4-cyclohexanecarboxylate	40
	1,2,2,6,6-Pentamethylpiperidinyl-4-adamantane-1-carboxylate	
	1,2,2,6,6-Pentamethylpiperidinyl-4-benzoate	
	1,2,2,6,6-Pentamethylpiperidinyl-4-p-toluate	
	1,2,2,6,6-Pentamethylpiperidinyl-4-p-t-butylbenzoate	
45	1,2,2,6,6-Pentamethylpiperidinyl-4-p-methoxybenzoate	45
	1,2,2,6,6-Pentamethylpiperidinyl-4-o-chloro-benzoate	
	1,2,2,6,6-Pentamethylpiperidinyl-4-p-chloro-benzoate	
	1,2,2,6,6-Pentamethylpiperidinyl-4-α-naphthoate	
	1,2,2,6,6-Pentamethylpiperidinyl-4-phenylacetate	
50	1,2,2,6,6-Pentamethylpiperidinyl-4-(1'-naphthylacetate)	50
	1,2,2,6,6-Pentamethylpiperidinyl-4-cinnamate	
	1,2,2,6,6-Pentamethylpiperidinyl-4-diphenylacetate	
	1,2,2,6,6-Pentamethylpiperidinyl-4-n-dodecylthioacetate	
	1,2,2,6,6-Pentamethylpiperidinyl-4-(furan-2'-carboxylate)	
	1,2,2,6,6-Pentamethylpiperidinyl-dimethyl trimesate	
55	1-n-Propyl-2,2,6,6-tetramethylpiperidinyl-acetate	55
	1-n-Propyl-2,2,6,6-tetramethylpiperidinyl-4-octanoate	
	1-n-Propyl-2,2,6,6-tetramethylpiperidinyl-4-stearate	
	1-n-Octyl-2,2,6,6-tetramethylpiperidinyl-4-benzoate	
	1-n-Dodecyl-2,2,6,6-tetramethylpiperidinyl-4-n-octanoate	
60	1-n-Dodecyl-2,2,6,6-tetramethylpiperidinyl-4-p-chlorobenzoate	60
	1-n-Octadecyl-2,2,6,6-tetramethylpiperidinyl-4-benzoate	
	1-Allyl-2,2,6,6-tetramethylpiperidinyl-4-n-octanoate	
	1-Allyl-2,2,6,6-tetramethylpiperidinyl-4-cyclohexanecarboxylate	
	1-Allyl-2,2,6,6-tetramethylpiperidinyl-4-benzoate	
65	1-α-Methylallyl-2,2,6,6-tetramethylpiperidinyl-4-acetate	65

	1-Oleoyl-2,2,6,6-tetramethylpiperidinyl-4-cyclohexanecarboxylate	
	1-Propargyl-2,2,6,6-tetramethylpiperidinyl-4- <i>p</i> -methoxybenzoate	
	1-Benzyl-2,2,6,6-tetramethylpiperidinyl-4- <i>n</i> -octanoate	
	1-Benzyl-2,2,6,6-tetramethylpiperidinyl-4-(2'-ethylhexanoate)	
5	1-Benzyl-2,2,6,6-tetramethylpiperidinyl-4-stearate	5
	1-Benzyl-2,2,6,6-tetramethylpiperidinyl-4-benzoate	
	1-(2'-Hydroxyethyl)-2,2,6,6-tetramethylpiperidinyl-4-acetate	
	1-(2'-Hydroxyethyl)-2,2,6,6-tetramethylpiperidinyl-4-laurate	
	1-(2'-Hydroxyethyl)-2,2,6,6-tetramethylpiperidinyl-4-stearate	
10	1-(2'-Hydroxyethyl)-2,2,6,6-tetramethylpiperidinyl-4-benzoate	10
	1-(2'-Hydroxypropyl)-2,2,6,6-tetramethylpiperidinyl-4-oleate	
	1-(2'-Hydroxy-2'-phenylethyl)-2,2,6,6-tetramethylpiperidinyl-4-phenylacetate	
	1-(2'-Chloroethyl)-2,2,6,6-tetramethylpiperidinyl-4- <i>n</i> -octanoate	
	1-(2'-Bromopropyl)-2,2,6,6-tetramethylpiperidinyl-4-cyclohexanecarboxylate	
15	1-(2'-Chloro-2'-phenylethyl)-2,2,6,6-tetramethylpiperidinyl-4- <i>p</i> -methoxybenzoate	15
	1-(2'-Cyanoethyl)-2,2,6,6-tetramethylpiperidinyl-4-benzoate	
	1-(2'-Cyanopropyl)-2,2,6,6-tetramethylpiperidinyl-4- <i>p</i> -chlorobenzoate	
	1-(2',3'-epoxypropyl)-2,2,6,6-tetramethylpiperidinyl-4-acetate	
	1-(2'-ethoxypropyl)-2,2,6,6-tetramethylpiperidinyl-4-(2'-ethylhexanoate)	
20	1-(2'-ethoxy-2'-phenylethyl)-2,2,6,6-tetramethylpiperidinyl-4-diphenylacetate	20
	1-(2'-acetoxyethyl)-2,2,6,6-tetramethylpiperidinyl-4-laurate	
	1-[2'-(methylcarbamoyloxy)ethyl]-2,2,6,6-tetramethylpiperidinyl-4-benzoate	
	1-[2'-(phenylcarbamoyloxy)ethyl]-2,2,6,6-tetramethylpiperidinyl-4-isobutyrate	
	1-[2'-(ethylthiocarbamoyloxy)ethyl]-2,2,6,6-tetramethylpiperidinyl-4-pivalate	
25	1-Methylcarbonylmethyl-2,2,6,6-tetramethylpiperidinyl-4-phenylacetate	25
	1-[2'-(methylcarbonyl)ethyl]-2,2,6,6-tetramethylpiperidinyl-4-acetate	
	1-Ethoxycarbonylmethyl-2,2,6,6-tetramethylpiperidinyl-4- <i>p</i> -methoxybenzoate	
	1-[2'-(Methoxycarbonyl)ethyl]-2,2,6,6-tetramethylpiperidinyl-4- <i>p</i> -toluate	
	1-Carbamoylmethyl-2,2,6,6-tetramethylpiperidinyl-4- <i>p</i> -methoxybenzoate	
30	1-(2'-Carbamoyl)ethyl-2,2,6,6-tetramethylpiperidinyl-4-stearate	30
	1-[2'-(methylcarbamoyl)ethyl]-2,2,6,6-tetramethylpiperidinyl-4-octanoate	
	1-(Dimethylthiocarbamoyl)methyl-2,2,6,6-tetramethylpiperidinyl-4-isobutyrate	
	1-Acetyl-2,2,6,6-tetramethylpiperidinyl-4-acetate	
	1-Acetyl-2,2,6,6-tetramethylpiperidinyl-4-(2'-ethylhexanoate)	
35	1-Acetyl-2,2,6,6-tetramethylpiperidinyl-4-stearate	35
	1-Isobutyryl-2,2,6,6-tetramethylpiperidinyl-4- <i>n</i> -octanoate	
	1-Lauroyl-2,2,6,6-tetramethylpiperidinyl-4-cicosanoate	
	1-Stearoyl-2,2,6,6-tetramethylpiperidinyl-4-acetate	
	1-Benzoyl-2,2,6,6-tetramethylpiperidinyl-4-benzoate	
40	1-Carbamoyl-2,2,6,6-tetramethylpiperidinyl-4-(1'-naphthylacetate)	40
	1-Methylcarbamoyl-2,2,6,6-tetramethylpiperidinyl-4- <i>n</i> -octanoate	
	1-Phenylcarbamoyl-2,2,6,6-tetramethylpiperidinyl-4-phenylacetate	
	1-Dimethylcarbamoyl-2,2,6,6-tetramethylpiperidinyl-4-laurate	
	1-Phenylthiocarbamoyl-2,2,6,6-tetramethylpiperidinyl-4- <i>p</i> - <i>t</i> -butylbenzoate	
45	4-carbamoyloxy-1,2,2,6,6-pentamethylpiperidine	45
	4-methylcarbamoyloxy-1,2,2,6,6-pentamethylpiperidine	
	4-dimethylcarbamoyloxy-1,2,2,6,6-pentamethylpiperidine	
	4-isopropylcarbamoyloxy-1,2,2,6,6-pentamethylpiperidine	
	4- <i>t</i> -butylcarbamoyloxy-1,2,2,6,6-pentamethylpiperidine	
50	4- <i>n</i> -hexylcarbamoyloxy-1,2,2,6,6-pentamethylpiperidine	50
	4-[2'-ethylhexylcarbamoyloxy]-1,2,2,6,6-pentamethylpiperidine	
	4- <i>n</i> -dodecylcarbamoyloxy-1,2,2,6,6-pentamethylpiperidine	
	4- <i>n</i> -octadecylcarbamoyloxy-1,2,2,6,6-pentamethylpiperidine	
	4-allylcarbamoyloxy-1,2,2,6,6-pentamethylpiperidine	
55	4-oleylcarbamoyloxy-1,2,2,6,6-pentamethylpiperidine	55
	4-cyclohexylcarbamoyloxy-1,2,2,6,6-pentamethylpiperidine	
	4-[3'-methylcyclohexylcarbamoyloxy]-1,2,2,6,6-pentamethylpiperidine	
	4-[4'- <i>t</i> -butylcyclohexylcarbamoyloxy]-1,2,2,6,6-pentamethylpiperidine	
	4-cyclohexylmethylcarbamoyloxy-1,2,2,6,6-pentamethylpiperidine	
60	4-benzylcarbamoyloxy-1,2,2,6,6-pentamethylpiperidine	60
	4-phenylcarbamoyloxy-1,2,2,6,6-pentamethylpiperidine	
	4-phenylthiocarbamoyloxy-1,2,2,6,6-pentamethylpiperidine	
	4- <i>m</i> -tolylcarbamoyloxy-1,2,2,6,6-pentamethylpiperidine	
	4- <i>p</i> -tolylcarbamoyloxy-1,2,2,6,6-pentamethylpiperidine	
65	4- <i>p</i> -chlorophenylcarbamoyloxy-1,2,2,6,6-pentamethylpiperidine	65

10	11	1,399,239	11
		4- <i>p</i> -t-butylphenylcarbamoyloxy-1,2,2,6,6-pentamethylpiperidine	
		4- α -naphthylcarbamoyloxy-1,2,2,6,6-pentamethylpiperidine	
		4-cyclohexylcarbamoyloxy-1-ethyl-2,2,6,6-tetramethylpiperidine	
5	5	4-methylcarbamoyloxy-1-n-propyl-2,2,6,6-tetramethylpiperidine	
		4-methylcarbamoyloxy-1-secbutyl-2,2,6,6-tetramethylpiperidine	5
		4-n-octadecylcarbamoyloxy-1-n-butyl-2,2,6,6-tetramethylpiperidine	
		4-Methylcarbamoyloxy-1-n-octyl-2,2,6,6-tetramethylpiperidine	
		4-methylcarbamoyloxy-1-n-octadecyl-2,2,6,6-tetramethylpiperidine	
		4-phenylcarbamoyloxy-1-allyl-2,2,6,6-tetramethylpiperidine	
10	10	4- <i>p</i> -tolylcarbamoyloxy-1-oleyl-2,2,6,6-tetramethylpiperidine	10
		4-methylcarbamoyloxy-1-propargyl-2,2,6,6-tetramethylpiperidine	
		4-phenylcarbamoyloxy-1-benzyl-2,2,6,6-tetramethylpiperidine	
		4-methylcarbamoyloxy-1-(2'-hydroxyethyl)-2,2,6,6-tetramethylpiperidine	
		4-cyclohexylcarbamoyloxy-1-(2'-chloropropyl)-2,2,6,6-tetramethylpiperidine	
15	15	4-phenylcarbamoyloxy-1-(2'-hydroxy-2'-phenylethyl)-2,2,6,6-tetramethylpiperidine	15
		4-methylcarbamoyloxy-1-(2',3'-epoxypropyl)-2,2,6,6-tetramethylpiperidine	
		4-carbamoyloxy-1-(2'-methoxyethyl)-2,2,6,6-tetramethylpiperidine	
		4-dimethylcarbamoyloxy-1-(2'-acetoxyethyl)-2,2,6,6-tetramethylpiperidine	
20	20	4-n-hexylcarbamoyloxy-1-[2'-(methylcarbamoyloxy)ethyl]-2,2,6,6-tetramethyl- piperidine	20
		4-methylcarbamoyloxy-1-methylcarbonylmethyl-2,2,6,6-tetramethylpiperidine	
		4-phenylcarbamoyloxy-1-(2'-methylcarbonylethyl)-2,2,6,6-tetramethylpiperidine	
		4-benzylcarbamoyloxy-1-carbamoylmethyl-2,2,6,6-tetramethylpiperidine	
		4-n-dodecylcarbamoyloxy-1-(2'-carbamoylethyl)-2,2,6,6-tetramethylpiperidine	
25	25	4-methylcarbamoyloxy-1-(2'-thiocarbamoylethyl)-2,2,6,6-tetramethylpiperidine	25
		4-methylcarbamoyloxy-1-acetyl-2,2,6,6-tetramethylpiperidine	
		4-phenylcarbamoyloxy-1-stearoyl-2,2,6,6-tetramethylpiperidine	
		4-methylthiocarbamoyloxy-1-lauroyl-2,2,6,6-tetramethylpiperidine	
30	30	4-[2'-ethylhexylcarbamoyloxy]-1-benzoyl-2,2,6,6-tetramethylpiperidine	30
		4-carbamoyloxy-1-carbamoyl-2,2,6,6-tetramethylpiperidine	
		4-methylcarbamoyloxy-1-methylcarbamoyl-2,2,6,6-tetramethylpiperidine	
		4-phenylcarbamoyloxy-1-phenylcarbamoyl-2,2,6,6-tetramethylpiperidine	
		4-methylthiocarbamoyloxy-1-methylthiocarbamoyl-2,2,6,6-tetramethylpiperidine	
		4-phenylthiocarbamoyloxy-1-phenylthiocarbamoyl-2,2,6,6-tetramethylpiperidine	
35	35	4-dimethylcarbamoyloxy-1-dimethylcarbamoyl-2,2,6,6-tetramethylpiperidine	35
		4-stearyl-1,2,2,4,6,6-hexamethylpiperidine	
		4-phenyl-1,2,2,6,6-pentamethyl-piperidinyl-4-n-octanoate	
		<i>Examples where n = 2</i>	
40	40	1,2-Bis-(1',2',2',6',6'-pentamethyl-4'-piperidyloxy)ethane	40
		1,4-Bis-(1'-n-propyl-2',2',6',6'-tetramethyl-4'-piperidyloxy)butene	
		1,6-Bis-(1'-n-octadecyl-2',2',6',6'-tetramethyl-4'-piperidyloxy)hexane	
		1,4-Bis-(1'-allyl-2',2',6',6'-tetramethyl-4'-piperidyloxy)cyclohexane	
		1,4-Bis-(1'-propargyl-2',2',6',6'-tetramethyl-4'-piperidyloxy)but-2-ene	
45	45	α,α -Bis-(1-benzyl-2,2,6,6-tetramethyl-4-piperidyloxy- <i>p</i> -xylene	45
		1,3-Bis-[1'-(2''-hydroxyethyl)-2',2',6',6'-tetramethyl-4'-piperidyloxy]benzene	
		1,2-Bis-[1'-(2''-cyanoethyl)-2',2',6',6'-tetramethyl-4'-piperidyloxy]ethane	
		1,4-Bis-(1'-acetyl-2',2',6',6'-tetramethyl-4'-piperidyloxy)but-2-yne	
50	50	4,4-Bis-(1''-methylcarbamoyl-2'',2'',6'',6''-tetramethyl-4''-piperidyloxy)diphenyl- methane	50
		Bis-(1,2,2,6,6-pentamethyl-4-piperidinyl)carbonate	
		Bis-(1,2,2,6,6-pentamethyl-4-piperidinyl)oxalate	
		Bis-(1,2,2,6,6-pentamethyl-4-piperidinyl)malonate	
55	55	Bis-(1,2,2,6,6-pentamethyl-4-piperidinyl)adipate	55
		Bis-(1,2,2,6,6-pentamethyl-4-piperidinyl)sebacate	
		Bis-(1,2,2,6,6-pentamethyl-4-piperidinyl)fumarate	
		Bis-(1,2,2,6,6-pentamethyl-4-piperidinyl)isophthalate	
		Bis-(1,2,2,6,6-pentamethyl-4-piperidinyl)cyclohexane 1',4'-dicarboxylate	
60	60	Bis-(1,2,2,6,6-pentamethyl-4-piperidinyl)thiodipropionate	60
		Bis-(1,2,2,6,6-pentamethyl-4-piperidinyl)methyltrimesate	
		Bis-(1-n-propyl-2,2,6,6-tetramethyl-4-piperidinyl)adipate	
		Bis-(1-sec butyl-2,2,6,6-tetramethyl-4-piperidinyl)succinate	
		Bis-(1-n-octyl-2,2,6,6-tetramethyl-4-piperidinyl)sebacate	
		Bis-(1-n-dodecyl-2,2,6,6-tetramethyl-4-piperidinyl)adipate	
65		Bis-(1-n-octadecyl-2,2,6,6-tetramethyl-4-piperidinyl)sebacate	

	Bis-(1-allyl-2,2,6,6-tetramethyl-4-piperidiny) adipate	
	Bis-(1-allyl-2,2,6,6-tetramethyl-4-piperidiny) thiophene-2',5'-dicarboxylate	
	Bis-(1-oleyl-2,2,6,6-tetramethyl-4-piperidiny) thiodipropionate	
5	Bis-(1-propargyl-2,2,6,6-tetramethyl-4-piperidiny) sebacate	5
	Bis-(1-benzyl-2,2,6,6-tetramethyl-4-piperidiny) sebacate	
	Bis-[1-(2'-hydroxyethyl)-2,2,6,6-tetramethyl-4-piperidiny] adipate	
	Bis-[1-(2'-chloropropyl)-2,2,6,6-tetramethyl-4-piperidiny] succinate	
	Bis-[1-(2'-cyanoethyl)-2,2,6,6-tetramethyl-4-piperidiny] sebacate	
10	Bis-[1-(2',3'-epoxypropyl)-2,2,6,6-tetramethyl-4-piperidiny] azelate	10
	Bis-[1-(2'-methoxyethyl)-2,2,6,6-tetramethyl-4-piperidiny] pimelate	
	Bis-[1-(2'-acetoxyethyl)-2,2,6,6-tetramethyl-4-piperidiny] glutarate	
	Bis-[1-(2'-methylcarbamoyloxyethyl)-2,2,6,6-tetramethyl-4-piperidiny] malonate	
	Bis-[1-(methylcarbonylmethyl)-2,2,6,6-tetramethyl-4-piperidiny] terephthalate	
15	Bis-[1-carbamoylmethyl-2,2,6,6-tetramethyl-4-piperidiny] cyclohexane-1',4'-dicarboxylate	15
	Bis-[1-(methylcarbamoyl-ethyl)-2,2,6,6-tetramethyl-4-piperidiny] thiodipropionate	
	Bis-[1-acetyl-2,2,6,6-tetramethyl-4-piperidiny] sebacate	
	Bis-[1-stearoyl-2,2,6,6-tetramethyl-4-piperidiny] succinate	
20	Bis-[1-Benzoyl-2,2,6,6-tetramethyl-4-piperidiny] dodecandioate	20
	Bis-[1-methylcarbamoyl-2,2,6,6-tetramethyl-4-piperidiny] adipate	
	Bis-[1-phenylthiocarbamoyl-2,2,6,6-tetramethyl-4-piperidiny] isophthalate	
	ethane-1',2'-bis-[4-carbamoyloxy-1,2,2,6,6-pentamethylpiperidine]	
	hexane-1',6'-bis-[4-carbamoyloxy-1,2,2,6,6-pentamethylpiperidine]	
25	2',4',4'-trimethylhexane-1',6'-bis-[4-carbamoyloxy-1,2,2,6,6-pentamethylpiperidine]	25
	cyclohexane-1',3'-bis-[4-carbamoyloxy-1,2,2,6,6-pentamethylpiperidine]	
	benzene-1',4'-bis-[4-carbamoyloxy-1,2,2,6,6-pentamethylpiperidine]	
	toluene-2',4'-bis-[4-carbamoyloxy-1,2,2,6,6-pentamethylpiperidine]	
	toluene-2',4'-bis-[4-thiocarbamoyloxy-1,2,2,6,6-pentamethylpiperidine]	
30	naphthalene-1',5'-bis[4-carbamoyloxy-1,2,2,6,6-pentamethylpiperidine]	30
	diphenylmethane-4',4''-bis[4-carbamoyloxy-1,2,2,6,6-pentamethylpiperidine]	
	toluene-2',4'-bis[4-carbamoyloxy-1-n-propyl-2,2,6,6-tetramethylpiperidine]	
	hexane-1',6'-bis[4-carbamoyloxy-1-n-butyl-2,2,6,6-tetramethylpiperidine]	
	Hexane-1',6'-bis[4-carbamoyloxy-1-n-octyl-2,2,6,6-2',4',4'-trimethylhexane-1',6'-bis[4-carbamoyloxy-1-n-octadecyl-2,2,6,6-tetramethylpiperidine]	
35	Cyclohexane-1',4'-bis[4-carbamoyloxy-1-allyl-2,2,6,6-tetramethylpiperidine]	35
	2',4',4'-trimethylhexane-1',6'-bis[4-carbamoyloxy-1-allyl-2,2,6,6-tetramethylpiperidine]	
	Benzene-1',4'-bis[4-carbamoyloxy-1-propargyl-2,2,6,6-tetramethylpiperidine]	
	toluene-2',4'-bis[4-carbamoyloxy-1-benzyl-2,2,6,6-tetramethylpiperidine]	
40	Toluene-2'',4''-bis[4-carbamoyloxy-1-(2'-hydroxyethyl)-2,2,6,6-tetramethylpiperidine]	40
	Diphenylmethane-4',4''-bis[4-carbamoyloxy-1-(2'-cyanoethyl)-2,2,6,6-tetramethylpiperidine]	
	Toluene-2'',4''-bis[4-carbamoyloxy-1-(2''-acetoxyethyl)-2,2,6,6-tetramethylpiperidine]	
	Ethane-1',2'-bis[4-carbamoyloxy-1-methylcarbonylmethyl-2,2,6,6-tetramethylpiperidine]	
45	Hexane-1'',6''-bis[4-carbamoyloxy-1-(2'-methylcarbamoyl-ethyl)-2,2,6,6-tetramethylpiperidine]	45
	Naphthalene-1',5'-bis[4-carbamoyloxy-1-acetyl-2,2,6,6-tetramethylpiperidine]	
	2',4',4'-trimethylhexane-1',6'-[4-carbamoyloxy-1-stearoyl-2,2,6,6-tetramethylpiperidine]	
50	Hexane-1',6'-bis[4-carbamoyloxy-1-methylcarbamoyl-2,2,6,6-tetramethylpiperidine]	50
	Bis[1,2,2,6,6-pentamethyl-4-piperidiny] ether	
<i>Example where n = 3</i>		
	Tris-(1,2,2,6,6-pentamethyl-4-piperidiny) nitrilotriacetate	
55	Tris-(1,2,2,6,6-pentamethyl-4-piperidiny) tricarallylate	55
	Tris-(1,2,2,6,6-pentamethyl-4-piperidiny) trimesate	
	Tris-(1,2,2,6,6-pentamethyl-4-piperidiny) trimellitate	
	Tris-(1,2,2,6,6-pentamethyl-4-piperidiny) phosphite	
	Tris-(1,2,2,6,6-pentamethyl-4-piperidiny) phosphate	
60	Tris-(1,2,2,6,6-pentamethyl-4-piperidiny) borate	60
	Tris-(1-n-octadecyl-2,2,6,6-tetramethyl-4-piperidiny) trimesate	
	Tris-(1-allyl-2,2,6,6-tetramethyl-4-piperidiny) phosphite	
	Tris-(1-propargyl-2,2,6,6-tetramethyl-4-piperidiny) borate	
	Tris-(1-benzyl-2,2,6,6-tetramethyl-4-piperidiny) trimellitate	
	Tris-[1-(2'-hydroxyethyl)-2,2,6,6-tetramethyl-4-piperidiny] trimesate	

Tris-[1-(2'-cyanoethyl)-2,2,6,6-tetramethyl-4-piperidinyl]phosphite
 Tris-[1-acetyl-2,2,6,6-tetramethyl-4-piperidinyl]borate
 Tris-[1-methylcarbamoyl-2,2,6,6-tetramethyl-4-piperidinyl]trimesate

Examples where n = 4

- 5 Tetrakis-(1,2,2,6,6-pentamethyl-4-piperidinyl)ethylenediamine tetracarboxylate 5
 Tetrakis-(1,2,2,6,6-pentamethyl-4-piperidinyl)pyromellitate
 Tetrakis-(1,2,2,6,6-pentamethyl-4-piperidinyl)-o-silicate
 10 Tetrakis-(1-n-octyl-2,2,6,6-tetramethyl-4-piperidinyl)-pyromellitate
 Tetrakis-(1-allyl-2,2,6,6-tetramethyl-4-piperidinyl)pyromellitate
 10 Tetrakis(1-propargyl-2,2,6,6-tetramethyl-4-piperidinyl)-o-silicate 10
 Tetrakis(1-benzyl-2,2,6,6-tetraethyl-4-piperidinyl)ethylenediamine tetracarboxylate
 Tetrakis[1-(2'-hydroxypropyl)-2,2,6,6-tetramethyl-4-piperidinyl]-o-silicate
 15 Tetrakis[1-stearoyl-2,2,6,6-tetramethyl-4-piperidinyl]-pyromellitate
 Tetrakis[1-phenylcarbamoyl-2,2,6,6-tetramethyl-4-piperidinyl]-o-silicate

- 15 The invention also includes salts of the compounds of Formula I, for instance 15
 salts of inorganic acids such as phosphates, carbonates, sulphates and chlorides and
 salts of organic acids such as acetates, stearates, maleates, citrates, tartrates, oxalates,
 20 benzoates and substituted carbamic acids.

Examples of salts are

- 20 4-n-butoxy-1,2,2,6,6-pentamethylpiperidine dihydrogen phosphate 20
 4-n-dodecyloxy-1,2,2,6,6-pentamethylpiperidine hydrochloride
 25 bis(1,2,2,6,6-pentamethyl-4-piperidinyl)sebacate sulphate
 1,2,2,6,6-pentamethylpiperidinyl-4-beta-(3',5'-di-t-butyl-4'-hydroxyphenyl)-
 propionate.bicarbonate
 25 4-methylcarbamoyloxy-1,2,2,6,6-pentamethylpiperidine acetate 25
 1,6-bis(4'carbamoyloxy-1',2',2',6',6'-pentamethylpiperidine hexane.stearate
 30 4-phenylcarbamoyloxy-1,2,2,6,6-pentamethylpiperidine.benzoate
 1,2,2,6,6-pentamethyl-4-n-heptacarbonyloxy-piperidinium-3',5'-di-t-butyl-4'-
 hydroxybenzoate
 30 1,4-bis(1',2',2',6',6'-pentamethyl-4'-piperidyloxy)butane hydrogen oxalate 30
 4-(2'-cyanoethoxy)-1,2,2,6,6-pentamethylpiperidine hydrogen maleate
 35 4-stearylcarbamoyloxy-1,2,2,6,6-pentamethylpiperidine.citrate
 1-(2'-hydroxyethyl)-2,2,6,6-tetramethylpiperidinyl-4-n-octanoate.tartrate
 1,2,2,6,6-pentamethylpiperidinyl-4-benzoate.dibutyl carbamate.

- 35 R₁ or R₃ can be represented by a monovalent, divalent or trivalent group obtained 35
 by removing 1 to 3 hydroxyl groups from a sulphonic acid, a sulphinic acid, a disul-
 phonic acid, a phosphorus containing acid, such as o-phosphoric or o-phosphorous acid
 or a boric acid. The following list shows compounds with acid radicals for R₃. However,
 the same radicals are also examples for R₁.

a) when n is 1

- 40 1,2,2,6,6-pentamethylpiperidinyl-4-benzene sulphinat 40
 1,2,2,6,6-pentamethylpiperidinyl-4-benzenesulphonate
 1,2,2,6,6-pentamethylpiperidinyl-4-methyl sulphate
 1,2,2,6,6-pentamethylpiperidinyl-4-dimethylborate
 50 1,2,2,6,6-pentamethylpiperidinyl-4-phenyl phosphonate 45
 1,2,2,6,6-pentamethylpiperidinyl-4-dimethyl phosphite
 1,2,2,6,6-pentamethylpiperidinyl-4-diphenyl phosphate

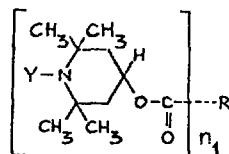
b) when n is 2

- 55 bis(1,2,2,6,6-pentamethyl-4-piperidinyl)sulphate
 50 bis(1,2,2,6,6-pentamethyl-4-piperidinyl)phosphonate 50
 bis(1,2,2,6,6-pentamethyl-4-piperidinyl)phenyl phosphate
 bis(1,2,2,6,6-pentamethyl-4-piperidinyl)benzene-1,3-disulphinat

c) when n is 3

- 60 tris(1,2,2,6,6-pentamethyl-4-piperidinyl)-benzene-1,3,5-trisulphonate
 55 tris(1,2,2,6,6-pentamethyl-4-piperidinyl)-benzene-1,3,5-trisulphinat. 55

A preferred sub-group of compounds of formula I are those compounds having the formula:



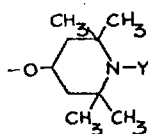
Ia

and their salts,

wherein Y is an alkyl group having from 5 to 20 carbon atoms, alkenyl having from 3 to 20 carbon atoms or an aralkyl residue, preferably having from 7 to 9 carbon atoms, and

n_1 is 1 or 2;

when n_1 is 1, R is hydrogen or a monovalent aliphatic residue having from 1 to 20, preferably 6 to 20 carbon atoms, a monovalent alicyclic residue having from 5 to 12 carbon atoms, or a monovalent aromatic residue having from 6 to 20 carbon atoms; or

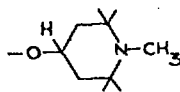


and

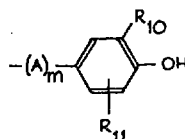
when n_1 is 2, R is a divalent aliphatic residue having from 1 to 20, preferably 4 to 20 carbon atoms, a divalent alicyclic residue having from 5 to 12 carbon atoms, or a divalent aromatic residue having from 6 to 14 carbon atoms.

Examples of substituents Y are n-hexyl, n-octyl, n-dodecyl, n-octadecyl, eicosyl, allyl, methallyl, oleyl, benzyl, α -methylbenzyl, *p*-methylbenzyl and *p*-methyl- α -methylbenzyl. However, it is particularly preferred that Y is methyl.

When n_1 is 1, R can be hydrogen, methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, t-butyl, n-pentyl, 2-ethylpropyl, 2-methylbutyl, n-hexyl, 2-methylpentyl, n-heptyl, 2-ethylpentyl, n-octyl, 2,2,4-trimethylpentyl, n-decyl, n-undecyl, n-tridecyl, n-pentadecyl, n-heptadecyl, eicosyl, vinyl, α - or β -methylvinyl, dec-9-enyl, heptadec-8-enyl, β -methylthioethyl, β -octylthioethyl, β -dodecylthioethyl, cyclopentyl, cyclohexyl, cyclohex-3-enyl, methylcyclohexyl, t-butylcyclohexyl, cyclododecyl, 1- or 2-perhydronaphthyl, adamantyl, cyclopentylmethyl, cyclohexylmethyl, β -cyclohexylethyl, 1- or 2-(perhydronaphthyl)methyl, β -[1- or 2-perhydronaphthyl]ethyl, benzyl, β -phenylethyl, β -phenylvinyl, 1- or 2-naphthylmethyl, β -[1- or 2-naphthyl]ethyl, phenyl, *o*-, *m* or *p*-tolyl, *o*-, *m*- or *p*-ethylphenyl, *o*-, *m*- or *p*-isopropylphenyl, *o*-, *m*- or *p*-t-butylphenyl, phenylphenyl, 4-methyl-1-naphthyl, 4-ethyl-1-naphthyl, 4-isopropyl-1-naphthyl or 4-t-butyl-1-naphthyl or the group



Particularly preferred substituent groups R are those listed above containing from 6 to 20 carbon atoms, as well as the group having the formula:—



III

wherein R_{10} and R_{11} are the same or different and each is an alkyl group having from 1 to 6, preferably 1 to 4 carbon atoms such as methyl, ethyl, n-propyl, isopropyl, sec-butyl, t-butyl, t-pentyl, (1,1-dimethylpropyl), t-hexyl (1,1-dimethylbutyl), but preferably methyl, isopropyl or t-butyl groups;

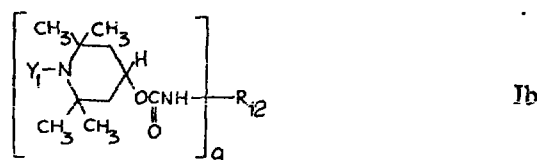
A is $-\text{CH}_2-$, $-\text{CH}_2\text{CH}_2-$ and p is 0 or 1.



When n_1 is 2, R can be methylene, 1,2-ethylene, 1,4-n-butylene, 1,8-n-octylene, 2,2,4-trimethyl-1, 4-butylene, 1,10-n-decylene, 1,2-eicosylene, vinylene, propenylene, 1,2-, 1,3- and 1,4-cyclohexylene, cyclohexyl-3-ene, 1,2-, 1,3- and 1,4-phenylene, *p*-xylylene, 1,4-, and 1,5-naphthylene, diphenylene or diphenylmethylenes.

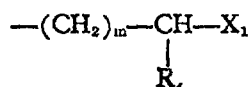
Specific examples of compounds having the formula Ia are shown hereinabove.

A further preferred sub-group of compounds of formula I are those having the formula:—

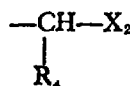


and its salts

wherein Y_1 is an alkyl residue having from 1 to 12 carbon atoms, an alkenyl residue having from 3 to 12 carbon atoms or an aralkyl residue having from 7 to 12 carbon atoms and R_{12} is hydrogen or an alkyl or alkenylene containing up to 20 carbon atoms, a substituted alkyl having the formula



or



wherein m is 1, 2 or 3,

R_4 is hydrogen or methyl,

X_1 is halogen or methoxy and

X_2 is halogen

or R_{12} is an alkenyl or alkenylene having up to 20 carbon atoms, a cycloalkyl or cycloalkylidene having 5 to 12 carbon atoms, an aryl or arylene having 6 to 12 carbon atoms and q is 1 or 2.

Two sub-groups of compounds of the formula Ib are those having as Y_1 alkyl from 1 to 4 and alkyl having 5 to 12 carbon atoms.

When q is 1, R_{12} can be for example hydrogen, methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, secbutyl, *t*-butyl, *n*-pentyl, 2-ethylpropyl, 2-methylbutyl, *n*-hexyl, 2-methylpentyl, *n*-heptyl, 2-ethylpentyl, *n*-octyl, 2-ethylhexyl, 2,2,4-trimethylpentyl, *n*-decyl, *n*-dodecyl, *n*-tetradecyl, *n*-octadecyl, eicosyl, mesityl, allyl, oleyl, cyclopentyl, cyclohexyl, methylcyclohexyl, *t*-butylcyclohexyl, *t*-octylcyclohexyl, cyclododecyl, 1- and 2-perhydronaphthyl, adamantyl, cyclopentylmethyl, cyclohexylmethyl, β -cyclohexylethyl, benzyl, β -phenylethyl, 1- and 2-naphthylmethyl, β -[1- and 2-naphthyl]ethyl, phenyl, *o*-, *m*- and *p*-tolyl, 2,4- and 2,6-xylyl, *p*-chlorophenyl, 3-chloro-*p*-tolyl, *o*-ethylphenyl, *p*-*t*-butylphenyl, 2,3- and 2,5-di-chlorophenyl, α - and β -naphthyl, phenylphenyl. Preferred monovalent groups R_{12} are hydrocarbyl groups such as methyl, ethyl, propyl, isopropyl, *n*-butyl, 2-ethylhexyl, dodecyl, octadecyl, allyl, oleyl, cyclohexyl, benzyl, phenyl, *o*-, *m*- and *p*-tolyl, 2,4- and 2,6-xylyl and naphthyl.

When q is 2, R_{12} can be for example methylene, 1,2-ethylene, 1,4-n-butylene, 1,6-n-hexylene, 1,8-n-octylene, 2,4,4-trimethyl-1,6-hexylene, 1,10-n-decylene, 1,2-eicosylene, 1,2-eicosenylene, 1,3- and 1,4-cyclohexylene, 1,3- and 1,4-phenylene, 2,4-tolylene, 1,5-naphthylene, 4,4'-diphenylene, 4,4'-diphenylmethylenes, 3,3'-dimethyl-4,4'-diphenylene, 3,3'-dimethyl-4,4'-diphenylmethylenes.

Preferred divalent groups R_{12} are 1,2-ethylene, 1,6-hexylene, 2,4,4-trimethyl-1,6-hexylene, 1,3- and 1,4-phenylene, 2,4-tolylene, 1,5-naphthylene, 4,4'-diphenylmethylenes.

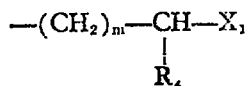
In the above formula Ib, examples of the group Y_1 are methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, secbutyl, *n*-hexyl, *n*-octyl, *n*-dodecyl, allyl, α -methylallyl, 10-undecenyl, benzyl, α -methylbenzyl, *p*-methylbenzyl, *p*-methyl- α -methylbenzyl, α -naphthylmethyl. Particularly preferred are straight or branched alkyl having 1 to 4 carbon atoms and for reasons of ease of preparation the most preferred meaning for Y_1 is methyl.

Specific examples of the carbamoyloxy derivatives of N-substituted-2,2,6,6-

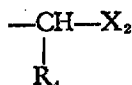
tetrasubstituted piperidin-4-ols of formula Ic are given in the preceding pages 19 and 20.

The following groups A to O are subgroups of compounds of the formula I.

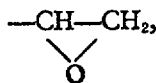
- 5 A) Compounds of formula I wherein when n is 1,
 5 R_3 is a monovalent residue and is an alkyl residue having from 1 to 20 carbon atoms, a cycloalkyl residue having from 5 to 12 carbon atoms, an alkenyl or alkynyl residue having from 3 to 20 carbon atoms, an aralkyl residue having from 7 to 12 carbon atoms, or a residue having the formula:—



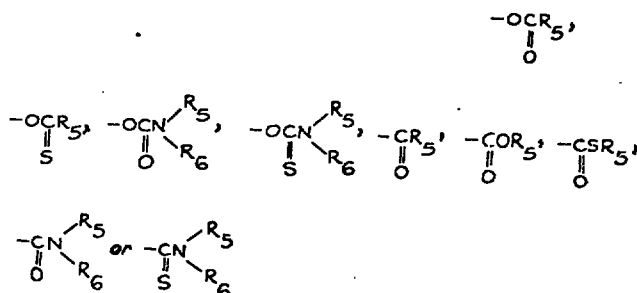
10 or



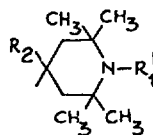
wherein m is 1, 2 or 3, R_4 is a hydrogen, methyl or phenyl residue, X_2 is halogen, cyano,



- 15 ---COR_5 , ---CO.OR_5 , ---CO.SR_5 or ---CONR_5R_6 and
 X_1 is hydroxyl, halogen, cyano, ---OR_5 ,



- 20 wherein R_5 is an alkyl residue having from 1 to 20 carbon atoms, an alkenyl residue having from 2 to 20 carbon atoms, a cycloalkyl residue having from 5 to 12 carbon atoms, an aryl residue having from 6 to 11 carbon atoms or an aralkyl residue having from 7 to 14 carbon atoms or, when R_5 is joined to a nitrogen atom, also hydrogen and R_6 is hydrogen or an alkyl residue having from 1 to 4 carbon atoms, or R_5 and R_6 together with the nitrogen atom to which they are bound form a 5- or 6-membered ring to which contains no other heteroatoms or contains one or more other heteroatoms or R_5 is an aryl residue or a residue having the formula:—



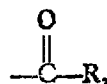
- 25 wherein R_1' is hydrogen or R_1' has the same significance as R_1 of formula I; when n is 2, R_3 is a divalent residue and is an alkylene residue having from 1 to 20 carbon atoms, an alkenylene residue having from 2 to 20 carbon atoms, an alkynylene residue having from 2 to 20 carbon atoms, a cycloalkylidene residue having from 3 to 12 carbon atoms, an arylene residue having 6 to 14 carbon atoms, an aralkylene residue having from 8 to 14 carbon atoms; when n is 3, R_3 is a trivalent residue and is an alkanetriyl, an arenetriyl or an arenetriyl-trialkylene residue, and when n is 4, R_3 is a tetravalent residue and is an alkanetetrayl residue.

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and

B) Compounds of the formula I wherein when n is 1
 R_3 is an acyl group



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wherein R_7 is hydrogen, an unsubstituted alkyl or substituted alkyl residue having from 1 to 20 carbon atoms, an alkenyl or alkynyl residue having from 2 to 20 carbon atoms, a cycloaliphatic residue having from 5 to 12 carbon atoms, an araliphatic residue having from 7 to 14 carbon atoms, an aromatic residue having from 6 to 20 carbon atoms or an heterocyclic residue,

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or R_3 represents a monovalent group obtained by removing a hydroxyl group from a sulphuric acid, a sulphonic acid, a phosphorus containing acid, sulphuric acid or a boric acid,

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when n is 2, R_3 is a divalent residue of an aliphatic, aromatic or heterocyclic diacyl, the group $-\text{CO}-$ or $-\text{CO}\cdot\text{CO}-$, a sulphinyl or sulphonyl residue or a divalent residue obtained by removing two hydroxyl groups from a disulphonic acid, a phosphorus containing acid or a boric acid;

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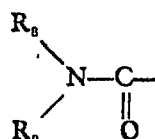
ano,

when n is 3, R_3 is a trivalent residue of an aliphatic or aromatic triacyl residue or a triacyl residue derived from o-phosphoric, o-phosphorous or o-boric acid; and when n is 4, R_3 is a tetravalent residue of a tetraacyl residue derived from an aliphatic or aromatic tetracarboxylic acid or from o-silicic acid.

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C) Compounds of the formula I wherein n is 1 or 2 and when n is 1
 R_3 is a carbamoyl residue having the formula:

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wherein R_8 is hydrogen or an alkyl residue having from 1 to 4 carbon atoms, and R_9 is hydrogen, an alkyl residue having from 1 to 20 carbon atoms, an alkenyl residue having from 3 to 20 carbon atoms, a cycloalkyl residue having from 5 to 12 carbon atoms or an unsubstituted aryl or substituted aryl residue having from 6 to 12 carbon atoms;

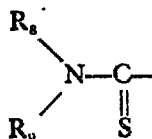
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and when n is 2 R_3 is a divalent aliphatic or aromatic dicarbamoyl residue.

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D) Compounds of the formula I wherein n is 1 or 2 and when n is 1
 R_3 is a thiocarbamoyl residue having the formula:

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wherein R_8 is hydrogen or an alkyl residue having from 1 to 4 carbon atoms, and R_9 is hydrogen, an alkyl residue having from 1 to 20 carbon atoms, an alkenyl residue having from 3 to 20 carbon atoms, a cycloalkyl residue having from 5 to 12 carbon atoms or an unsubstituted aryl or substituted aryl residue having from 6 to 12 carbon atoms;

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and when n is 2, R_3 is a divalent aliphatic or aromatic dithiocarbamoyl residue.

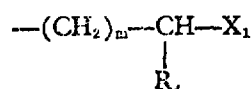
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E) Compounds of the formula I wherein when n is 1

R_3 is a monovalent residue and is an alkyl residue having from 1 to 20 carbon atoms, a cycloalkyl residue having from 5 to 12 carbon atoms, an alkenyl or alkynyl residue having from 3 to 20 carbon atoms, an aralkyl residue having from 7 to 9 carbon atoms, or a residue having the formula:

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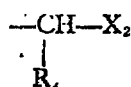


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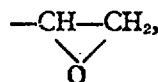
residue
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or

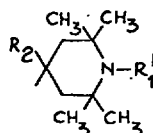


wherein m is 1, 2 or 3, R₄ is a hydrogen, methyl or phenyl residue, X₂ is halogen, cyano,



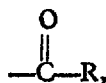
5 —COR₅, —CO.OR₅, —CO.SR₅ or —CONR₅R₆ and X₁ is hydroxyl, halogen, cyano, 5
 —OR₅, —O—CO.R₅, —OCSR₅, —O.CO.NR₅R₆, —CO.R₅, —CO.OR₅, —CO.SR₅,
 —CO.NR₅R₆ or —CS.NR₅R₆,

10 wherein R₅ is an alkyl residue having from 1 to 20 carbon atoms, an alkenyl residue 10
 having from 2 to 20 carbon atoms, a cycloalkyl residue having from 5 to 12 carbon
 atoms, an aryl residue having from 6 to 11 carbon atoms, or an aralkyl residue having
 7 to 11 carbon atoms, or, when R₅ is joined to a nitrogen atom, also hydrogen and R₆
 is hydrogen or an alkyl residue having from 1 to 4 carbon atoms, or R₅ and R₆ together
 with the nitrogen atom to which they are bound form a 5- or 6-membered ring which
 contains no other heteroatoms or contains one or more other heteroatoms or R₅ is an
 15 aryl residue or a residue having the formula: 15



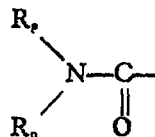
20 wherein R₁' is hydrogen or R₁' has the same significance as R₁ of claim 2; 20
 when n is 2, R₃ is a divalent residue and is an alkylene residue having from 1 to 20
 carbon atoms, an alkenylene residue having from 3 to 20 carbon atoms, an alkynylene
 residue having from 3 to 20 carbon atoms, an arylene residue having 6 to 14 carbon 20
 atoms, an aralkylene residue having from 8 to 14 carbon atoms;
 when n is 3, R₃ is a trivalent residue of an alkanetriyl, an arenetriyl, or arenetriyl-
 trialkylene group; and when n is 4, R₃ is a tetravalent residue of an alkanetetrayl group.

25 F) Compounds of the formula I wherein when n is 1 25
 R₃ is an acyl group



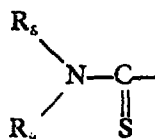
30 wherein R₇ is an alkyl or substituted alkyl residue having from 1 to 20 carbon atoms, 30
 an alkenyl or alkynyl residue having from 2 to 20 carbon atoms, a cycloaliphatic residue
 having from 5 to 12 carbon atoms, an aliphatic residue having from 7 to 14 carbon
 atoms, an aromatic residue having from 6 to 12 carbon atoms or an heterocyclic residue,
 with the proviso that only one of R₁ and R₃ can represent an unsaturated acyl group
 or R₃ represents a monovalent group obtained by removing a hydroxyl group from
 a sulphinic acid, a sulphonic acid, a phosphorus containing acid or a boric acid,
 35 when n is 2, R₃ is a divalent residue of an aliphatic, aromatic or heterocyclic diacyl 35
 residue, a carbonyl, sulphinyl or sulphonyl residue or a divalent residue obtained by
 removing two hydroxyl groups from a disulphonic acid a phosphorus containing acid,
 sulphuric acid or a boric acid;
 when n is 3, R₃ is a trivalent residue of an aliphatic or aromatic triacyl residue or a
 triacyl residue derived from o-phosphoric, o-phosphorous or o-boric acid and when n
 40 is 4, R₃ is a tetravalent residue of a tetraacyl residue derived from an aliphatic or 40
 aromatic tetracarboxylic acid or from o-silicic acid

G) Compound of the formula I wherein n is 1 or 2 and when n is 1, R_3 is a carbamoyl residue having the formula:



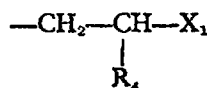
5 wherein R_1 is hydrogen or an alkyl residue having from 1 to 4 carbon atoms, and R_2 is hydrogen, an alkyl residue having from 1 to 20 carbon atoms, an alkenyl residue having from 3 to 20 carbon atoms, a cycloalkyl residue having from 5 to 12 carbon atoms or an aryl or substituted aryl residue having from 6 to 12 carbon atoms; and when n is 2, R_3 is a divalent residue of an aliphatic or aromatic dicarbamoyl residue.

10 H) Compounds of the formula I wherein n is 1 or 2 and when n is 1, R_3 is a thiocarbamoyl residue having the formula:

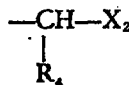


15 wherein R_1 is hydrogen or an alkyl residue having from 1 to 4 carbon atoms, and R_2 is hydrogen, an alkyl residue having from 1 to 20 carbon atoms, an alkenyl residue having from 3 to 20 carbon atoms, a cycloalkyl residue having from 5 to 12 carbon atoms or an aryl or substituted aryl residue having from 6 to 12 carbon atoms; and when n is 2, R_3 is a divalent residue of an aliphatic or aromatic dithiocarbamoyl residue.

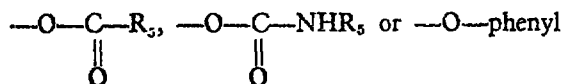
20 I) Compounds of formula I and their bicarbonate wherein n is 1, 2 or 3 R_1 is alkyl having from 1 to 18 carbon atoms, benzyl or alkenyl having 3 carbon atoms or a group of the formula:



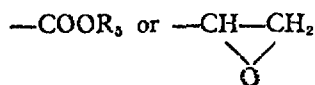
or



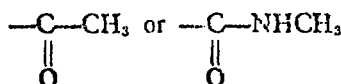
25 wherein R_4 is hydrogen, methyl or phenyl and X_1 is a group of the formula



and X_2 is a group of the formula



30 wherein R_3 is alkyl having 1 or 2 carbon atoms or phenyl or R_1 is a group of the formula



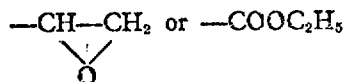
and

R_2 is hydrogen and

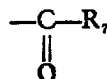
R_3 when n is 1 is alkyl having 3 to 18 carbon atoms, alkenyl having 3 carbon atoms, propargyl, benzyl, $-\text{CH}_2\text{CH}_2\text{CN}$ or a group of the formula



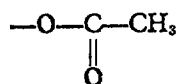
5 wherein X_2 is



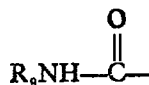
or of the formula



10 wherein R_7 is alkyl having 1 to 19 carbon atoms, $\text{CH}_3(\text{CH}_2)_{11}-\text{S}-\text{CH}_2-$, cycloalkyl having 6 to 10 carbon atoms, alkenyl having 2 to 17 carbon atoms, unsubstituted aralkyl having 7 to 13 carbon atoms, $\text{C}_6\text{H}_5-\text{CH}=\text{CH}-$, aralkyl substituted by hydroxy or butyl, unsubstituted aryl having 6 to 10 carbon atoms, aryl substituted by alkyl having 1 to 4 carbon atoms, $\text{CH}_3\text{O}-$, Cl , OH , or



15 or of the formula

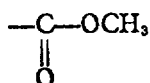


wherein R_8 is alkyl having 1 to 8 carbon atoms, alkenyl having 3 carbon atoms, cyclohexyl, unsubstituted aryl having 6 to 10 carbon atoms, aryl substituted by methyl or Cl or

20 R_3 when n is 2 is the group



wherein R is alkylene having 4 to 8 carbon atoms, $-\text{CH}_2\text{CH}_2-\text{S}-\text{CH}_2\text{CH}_2-$, vinylenic cyclohexylene, a divalent thiophen residue, unsubstituted phenylene or phenylene substituted by



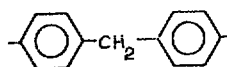
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or a group of the formula



wherein R^1 is hexylene, unsubstituted arylene having 6 to 10 carbon atoms, arylene substituted by methyl or R^1 is the group

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or a group of the formula $-\text{COCO}-$ or butylene, or R_3 when n is 3, is



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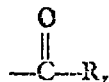
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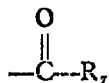
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J) Compounds of the formula I wherein n is 1, 2 or 4 and when n is 1, R₃ is an acyl group



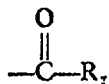
wherein R₇ is hydrogen, a substituted alkyl residue having from 1 to 20 carbon atoms, an alkenyl or alkynyl residue having from 2 to 20 carbon atoms, a cycloaliphatic residue having from 5 to 12 carbon atoms, an araliphatic residue having from 7 to 14 carbon atoms, or an heterocyclic residue, or R₃ represents a monovalent group obtained by removing a hydroxyl group from a sulphinic acid, a sulphonic acid, a phosphorus containing acid, sulphuric acid or a boric acid, or when n is 2, R₃ is a divalent residue of heterocyclic diacyl residue or a sulphinyl or sulphonyl residue or a divalent residue obtained by removing two hydroxyl groups from a disulphonic acid, a phosphorus containing acid, sulphuric acid, or a boric acid; or when n is 4, R₃ is a tetraacyl residue derived from an aliphatic tetracarboxylic acid.

K) Compounds of the formula I wherein n is 1, 2 and 4 and when n is 1, R₃ is an acyl group



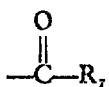
wherein R₇ is hydrogen, a cycloaliphatic residue having from 5 to 12 carbon atoms or a heterocyclic residue or R₃ represents a monovalent group obtained by removing a hydroxyl group from a sulphinic acid, a sulphonic acid, a phosphorus containing acid, sulphuric acid or a boric acid or when n is 2, R₃ is a divalent residue of a heterocyclic diacyl or a sulphinyl or sulphonyl residue or a divalent residue obtained by removing two hydroxyl groups from a disulphonic acid, a phosphorus containing acid or when n is 4, R₃ is a tetraacyl residue derived from an aliphatic tetracarboxylic acid.

L) Compounds of the formula I wherein n is 1, 2 or 4 and when n is 1, R₃ is an acyl group



wherein R₇ is hydrogen, a substituted alkyl residue having from 1 to 20 carbon atoms, an alkenyl or alkynyl residue having from 2 to 20 carbon atoms, a cycloaliphatic residue having from 5 to 12 carbon atoms, an araliphatic residue having from 7 to 14 carbon atoms, or an heterocyclic residue, or R₃ represents a monovalent group obtained by removing a hydroxyl group from a sulphinic acid, a sulphonic acid, a phosphorus containing acid, sulphuric acid or a boric acid, or when n is 2, R₃ is a divalent residue of heterocyclic diacyl residue or a sulphinyl or sulphonyl residue or a divalent residue obtained by removing two hydroxyl groups from a disulphonic acid, a phosphorus containing acid, sulphuric acid or a boric acid; or when n is 4, R₃ is a tetraacyl residue derived from an aliphatic tetracarboxylic acid.

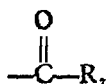
M) Compounds of the formula I wherein n is 1, 2 and 4 and when n is 1, R₃ is an acyl group



wherein R₇ is hydrogen, a cycloaliphatic residue having from 5 to 12 carbon atoms or a heterocyclic residue or R₃ represents a monovalent group obtained by removing a hydroxyl group from a sulphinic acid, a sulphonic acid, a phosphorus containing acid, sulphuric acid or a boric acid or when n is 2, R₃ is a divalent residue of a heterocyclic diacyl or a sulphinyl or sulphonyl

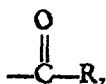
residue or a divalent residue obtained by removing two hydroxyl groups from a disulphonic acid, a phosphorus containing acid or when n is 4, R_3 is a tetraacyl residue derived from an aliphatic tetracarboxylic acid.

- 5 N) Compounds of the formula I wherein when n is 1, R_3 is an acyl group 5

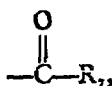


- 10 wherein R_7 is an unsubstituted aliphatic residue having from 1 to 20 carbon atoms or an aromatic residue having from 6 to 20 carbon atoms and when n is 2, R_3 is a divalent aliphatic or aromatic diacyl residue or the groups $-\text{CO}-$ or $-\text{COCO}-$ and 10
when n is 3, R_3 is a trivalent residue or and is an aliphatic or aromatic triacyl residue or a triacyl residue derived from *o*-phosphoric, *o*-phosphorous or *o*-boric acid and when n is 4, R_3 is a tetravalent residue of a tetraacyl residue derived from an aromatic tetracarboxylic acid or from *o*-silicic acid.

- 15 O) Compounds of the formula I wherein when n is 1, R_3 is an acyl group 15



- 20 wherein R_7 is an unsubstituted alkyl residue having from 1 to 20 carbon atoms or an aromatic residue having from 6 to 12 carbon atoms and when n is 2, R_3 is a divalent aliphatic or aromatic diacyl residue or the carbonyl group and 20
when n is 3, R_3 is a trivalent residue and is an aliphatic or aromatic triacyl residue or a triacyl residue derived from *o*-phosphoric, *o*-phosphorous or *o*-boric acid and when n is 4, R_3 is a tetravalent residue of a tetraacyl residue derived from an aromatic tetracarboxylic acid or from *o*-silicic acid; provided that when R_3 represents an acyl group 25

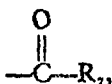


- 30 an aliphatic, aromatic or heterocyclic diacyl residue, the group $-\text{CO}-$ or $-\text{CO.CO}-$, an aliphatic or aromatic triacyl or tetraacyl residue, a triacyl residue derived from *o*-phosphonic, *o*-phosphorous or *o*-boric acid or a tetraacyl residue derived from *o*-silicic acid, the number of carbon atoms in the alkyl group designated by R_1 is from 5 to 20. The following groups P and Q are sub-groups of the compounds of formula Ia. 30

- 35 P) Compounds of the formula Ia wherein n_1 is 1 and R is hydrogen or a monovalent alicyclic residue having from 5 to 12 carbon atoms. 35

- 40 Q) Compounds of the formula Ia wherein when n_1 is 1, K is a monovalent aliphatic residue having from 1 to 20 carbon atoms or a monovalent aromatic residue having from 6 to 20 carbon atoms and when n_1 is 2, R is a divalent aliphatic residue having from 1 to 20 carbon atoms or a divalent aromatic residue having from 6 to 20 carbon atoms. 40

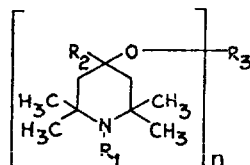
For groups B, F, I, J, K, L, M, N, O, P and Q the above definitions apply; provided that when R_3 represents an acyl group



- 45 an aliphatic, aromatic or heterocyclic diacyl residue, the group $-\text{CO}-$ or $-\text{CO.CO}-$, an aliphatic or aromatic triacyl or tetraacyl residue, a triacyl residue derived from *o*- 45

phosphonic, *o*-phosphorous or *o*-boric acid or a tetraacyl residue derived from *o*-silicic acid, the number of carbon atoms in the alkyl group designated by R_1 is from 5 to 20.

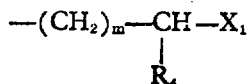
The following compounds of the formula I are also a group of compounds of the present invention.



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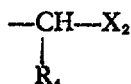
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wherein n is 1, 2, 3 or 4; R_1 is a monovalent residue and is an alkyl residue having from 1 to 20 carbon atoms, acycloalkyl residue having from 5 to 12 carbon atoms, an alkenyl or alkynyl residue having from 3 to 20 carbon atoms, an aralkyl residue having from 7 to 9 carbon atoms, or a residue having the formula:—

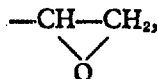


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or

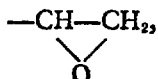


wherein m is 1, 2 or 3, R_4 is a hydrogen, or a methyl or phenyl residue, X_2 is halogen, cyano,

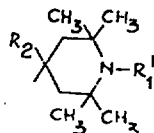


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---COR_5 , ---CO.OR_5 , ---CO.SR_5 , $\text{---CONR}_5\text{R}_6$ or $\text{---CS.NR}_5\text{R}_6$ and X_1 is hydroxyl, halogen, cyano,



---OR_5 , ---O.CO.R_5 , OCSR_5 , $\text{---O.CO.NR}_5\text{R}_6$, ---CO.R_5 , ---CO.OR_5 , ---CO.SR_5 , $\text{---CO.NR}_5\text{R}_6$, $\text{---CS.NR}_5\text{R}_6$, or ---SR_5 , wherein R_5 is an alkyl residue having from 1 to 20 carbon atoms, an alkenyl residue having from 2 to 20 carbon atoms, a cycloalkyl residue having from 5 to 12 carbon atoms, an aryl residue having from 6 to 11 carbon atoms or, when R_5 is joined to a nitrogen atom, also hydrogen, and R_6 is hydrogen or an alkyl residue having from 1 to 4 carbon atoms, or R_5 and R_6 together with the nitrogen atom to which they are bound form a 5- or 6-membered ring which contains no other heteroatom or contains one or more other heteroatoms or R_1 is an acyl group, an unsubstituted or N-substituted carbamoyl or thiocarbamoyl group; R_2 is an alkyl residue having from 1 to 4 carbon atoms, an alkenyl or alkynyl residue having 3 to 20, carbon atoms, a cycloalkyl residue having from 5 to 12 carbon atoms, an aryl residue having from 6 to 11 carbon atoms or an aralkyl residue having from 7 to 9 carbon atoms or also hydrogen; and when n is 1, R_3 is a monovalent radical having the same significance as R_1 , with the proviso that only one of R_1 and R_3 can represent an unsaturated acyl group or R_3 represents a monovalent group obtained by removing a hydroxyl group from a sulphinic acid, a sulphonic acid, a phosphorus containing acid, sulphuric acid or a boric acid, or R_3 is an aryl residue or a residue having the formula:—



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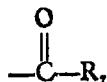
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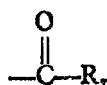
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wherein R_1' is hydrogen or R_1' has the same significance as R_1 ; provided that when R_3 represents an acyl group



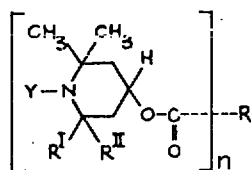
an aliphatic, aromatic or heterocyclic diacyl residue, the group $-\text{CO}-$ or $-\text{CO.CO}-$,
 5 an aliphatic or aromatic triacyl or tetraacyl residue, a triacyl residue derived from *o*-
 phosphonic, *o*-phosphorous or *o*-boric acid or a tetraacyl residue derived from *o*-silicic
 acid, the number of carbon atoms in the alkyl group designated by R_1 is from 5 to 20.

When n is 2, R_3 is a divalent residue and is an alkylene residue
 10 having from 1 to 20 carbon atoms, an alkenylene residue having from 3
 to 20 carbon atoms, an alkynylene residue having from 3 to 20 carbon
 atoms, an arylene residue having 6 to 14 carbon atoms, an aralkylene residue
 having from 8 to 14 carbon atoms or an aliphatic, aromatic or heterocyclic diacyl
 residue, an aliphatic or aromatic dicarbamoyl or dithiocarbamoyl, a carbonyl, sulphinyl
 15 or sulphonyl residue or a divalent residue obtained by removing two hydroxyl groups
 from a disulphonic acid, a phosphorus containing acid or a boric acid; when n is 3, R_3
 is a trivalent residue or an aliphatic or aromatic triacyl residue or a triacyl residue
 derived from *o*-phosphoric, *o*-phosphorous or *o*-boric acid or an alkanetriyl, an
 arenetriyl, or arenetriyltrialkylene group; and when n is 4, R_3 is a tetravalent residue
 20 and is a tetravalent aliphatic residue or tetraacyl residue derived from an aliphatic or
 aromatic tetracarboxylic acid or from *o*-silicic acid or an alkanetetrayl group; as well
 as partial ethers, esters and carbamoyloxy and thiocarbamoyloxy compounds related
 to the fully reacted compounds of formula I; provided that when R_3 represents an acyl
 group



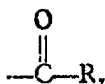
an aliphatic, aromatic or heterocyclic diacyl residue, the group $-\text{CO}-$ or $-\text{CO.CO}-$,
 25 an aliphatic or aromatic triacyl or tetraacyl residue, a triacyl residue derived from *o*-
 phosphonic, *o*-phosphorous or *o*-boric acid or a tetraacyl residue derived from *o*-silicic
 acid, the number of carbon atoms in the alkyl group designated by R_1 is from 5 to 20.

The following compounds of the formula II are also a group of compounds of the
 30 present invention.



II

and their salts, wherein R^{I} and R^{II} are the same or different and each is a straight or
 branched alkyl group, having from 1 to 4 carbon atoms, or R^{I} and R^{II} together with
 the carbon atom to which they are attached form a cycloalkyl residue having from 5
 35 to 12 carbon atoms; Y is an alkyl group having from 5 to 20 carbon atoms carbon
 atoms, alkenyl having from 2 to 20 carbon atoms or an aralkyl residue having from 7
 to 9 carbon atoms and n , is 1 or 2, when n is 1, R is hydrogen or a monovalent aliphatic
 residue having from 1 to 20, preferably 6 to 20 carbon atoms, a monovalent alicyclic
 residue having from 5 to 12 carbon atoms, or a monovalent aromatic residue having
 40 from 6 to 20 carbon atoms and when n is 2, R is a divalent aliphatic residue having
 from 1 to 20, preferably 4 to 20, carbon atoms, and is unsubstituted or substituted or
 interrupted by one or more, preferably one, sulphur atom, a divalent alicyclic residue
 having from 5 to 12 carbon atoms or a divalent aromatic residue having from 6 to 20
 carbon atoms; provided that when R represents an acyl group



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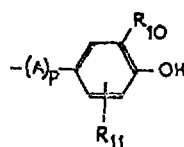
an aliphatic, aromatic or heterocyclic diacyl residue, the group $-\text{CO}-$ or $-\text{CO.CO}-$,

45

an aliphatic or aromatic triacyl or tetraacyl residue, a triacyl residue derived from *o*-phosphonic, *o*-phosphorous or *o*-boric acid or a tetraacyl residue derived from *o*-silicic acid, the number of carbon atoms in the alkyl group designated by R_1 is from 5 to 20.

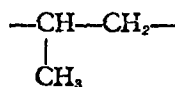
Subgroups of the compounds of formula II are

- 5 a) Compounds wherein n is 1 and R is a monovalent aromatic residue having the formula:



III

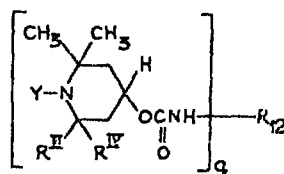
wherein R_{10} and R_{11} are the same or different and each is an alkyl group having from 1 to 6 carbon atoms, A is



or $-\text{CH}_2\text{CH}_2-$ and p is 0 or 1, or

- b) Compounds wherein R_{10} and R_{11} are methyl, isopropyl or *t*-butyl groups or
 c) Compounds wherein n is 2 and R is a methylene, 1,2-ethylene, 1,4-butylene, 1,8-*n*-octylene, 2,2,4-trimethyl-1,4-butylene, 1,10-*n*-decylene, 1,2-eicosylene, vinylene, propenylene, 1,2-, 1,3- or 1,4-cyclohexylene, cyclohexyl-3-ene, 1,2-, 1,3- or 1,4-phenylene, *p*-xylylene, 1,4- or 1,5-naphthylene, diphenylene or diphenylmethylenylene residue or the group $-\text{CH}_2\text{CH}_2\text{S}-\text{CH}_2\text{CH}_2-$ or R is absent.
 d) Compounds in the form of an inorganic or organic acid.
 e) Compounds wherein the salt is a phosphate, carbonate, sulphate, chloride, acetate, stearate, maleate, nitrate, tartrate, oxalate, benzoate or substituted carbamate.
 f) Compounds wherein R^I and R^{II} are methyl.

The following compounds of the formula IV are also compounds of the present invention:



IV

- 25 and its salts wherein R^{III} and R^{IV} are the same or different and each is a straight- or branched alkyl residue having from 1 to 12 carbon atoms or R^{III} and R^{IV} together with the carbon atom to which they are each attached form a cycloalkyl group having from 5 to 12 carbon atoms, Y is a straight- or branched alkyl residue having from 1 to 12 carbon atoms, an alkenyl residue having from 3 to 12 carbon atoms or an aralkyl residue having from 7 to 12 carbon atoms and R_{12} is hydrogen or a saturated or unsaturated hydrocarbyl or hydrocarbylene residue containing up to 20 carbon atoms optionally substituted, halogen or alkoxy having from 1 to 4 carbon atoms and q is 1 or 2.

Sub-groups of the compounds of formula IV are:

- a) Compounds wherein q is 1 and R_{12} is an aliphatic residue having from 1 to 20 carbon atoms, an alicyclic residue having from 5 to 12 carbon atoms or an aromatic residue having from 6 to 12 carbon atoms.
 b) Compounds wherein R_{12} is a methyl, ethyl, propyl, isopropyl, *n*-butyl, 2-ethylhexyl, dodecyl, octadecyl, allyl, oleyl, cyclohexyl, benzyl, phenyl, *o*-, *m*- or *p*-tolyl, 2,4- or 2,6-xylyl or a naphthyl residue.
 c) Compounds wherein q is 2 and R_{12} is an aliphatic residue having from 1 to 20 carbon atoms, an alicyclic residue having from 5 to 15 carbon atoms or an aromatic residue having from 6 to 15 carbon atoms.
 d) Compounds in the form of an inorganic or organic acid.

hexylene, 1,3- or 1,4-phenylene, 2,4-tolylene, 1,5-naphthylene or 4,4'-diphenyl-methylene residue.

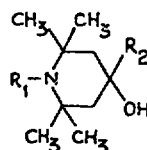
e) Compounds wherein Y_1 is methyl.

f) Compounds wherein R^I and R^{II} are methyl.

5 g) Compounds wherein the salt is a phosphate, carbonate, sulphate, chloride, acetate, carbonate, sulphate, chloride, acetate, stearate, maleate, citrate, tartrate, oxalate, benzoate or substituted carbamate.

h) Compounds wherein R^{III} and R^{IV} are methyl.

10 According to the present invention, there is also provided a first process in which a compound of formula I is produced, comprising reacting, in the presence of an acid-binding agent, a piperidinol having the formula:—



V

wherein R_1 and R_2 have their previous significance, with an acid halide having the formula:—

15 $R_3-(CO\ hal)_n$

VI

15

wherein R_3 and n have their previous significance and hal represents a halogen atom, preferably a chlorine atom.

Suitable acid binding agents are organic bases such as triethylamine; alternatively, an excess amount of the amine V can serve as the acid binding agent.

20 The reaction is conveniently carried out by heating the reactants together in a solvent such as cyclohexane, benzene or toluene which is inert under the reaction conditions. When the reaction is complete, the desired product is then separated by conventional techniques.

25 The present invention also provides a second process in which a compound of formula I is produced, comprising reacting, in the presence of a transesterification catalysts, a piperidinol compound of formula V, as hereinbefore defined, with an ester having the formula:—

$R_3-(CO_2R_{13})_n$

VII

30 wherein R_3 and n have their previous significance and R_{13} is an alkyl residue having from 1 to 4 carbon atoms, preferably 1 or 2 carbon atoms.

Examples of suitable transesterification catalysts are alkali metal amides such as lithium amide.

35 A third process according to this invention in which a compound of formula I is produced comprises reacting, in the presence of an esterification catalyst, a piperidinol compound of formula V, as hereinbefore defined, with an acid having the formula:—

$R_3\ (CO_2H)_n$

VIII

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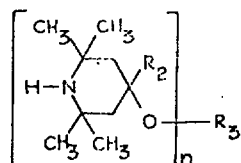
wherein R_3 and n have their previous significance.

Suitable examples of esterification catalysts are tetraalkyl titanates such as tetra-butyl titanate.

40 The second and third processes of the invention are conveniently effected by mixing the reactants together in the presence or absence of an inert solvent (for instance, benzene, toluene, xylene etc.) and agitating the reaction mixture until reaction is complete, as determined, for instance, by collecting the alcohol or water produced in the reaction, and stopping the reaction when the theoretical amount of alcohol or water, respectively, has been removed.

45 A fourth process in which a compound of formula I is produced comprises reacting a compound having the formula:—

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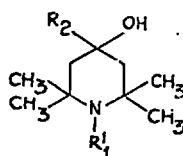
IX

wherein R_2 , R_3 and n have their previous significance, with a compound X capable of reaction with the compound IX and of introducing into it the group R_1 as hereinbefore defined.

For instance, compound X may be an alkylating, alkenylating alkynating or aralkylating agent such as the halides of these groups. Compound X may also be the aldehyde or ketone corresponding to the substituent R_1 , so that, when reacted with a compound of formula IX under Leuckart, Wallach or Eschweiler-Charles reaction conditions, compounds of formula I in which R_1 is methyl may be produced by reacting a compound of formula IX with formic acid and formaldehyde.

The starting-materials of formulae V, VI, VII, VIII, IX and X used in the processes of this invention can all be produced by methods well-known per se. The compound of formula V are described in our copending British Patent Application No. 48601/72(Serial No. 1,399,240) and those of formula IX are described generally in German Patent Specification No. 1,929,928.

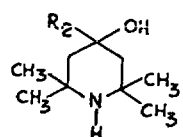
Compounds of the general formula I in which $n = 2, 3$ or 4 and R_3 represents a di-, tri- or tetra-valent radical derived from an alkyl, alkenyl, aryl or aralkyl radical may be prepared by reacting a compound of the formula:



XIII

wherein R_1' is hydrogen or R_1 , and R_2 has its previous significance, with a compound of the formula $R_3(X_1)_n$ wherein X_1 is a halogen atom and n is 2, 3 or 4. This reaction is preferably carried out by making the sodium salt of the piperidine compound and reacting this with the compound $R_3(X_1)_n$.

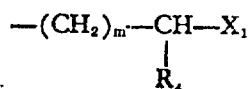
The substituents R_1 may be introduced before or after R_3 or in the case where R_1 and R_3 are identical may be introduced together by reacting a compound of the formula:



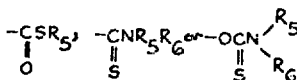
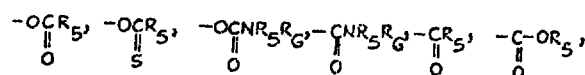
XI

with an alkylating, alkenylating, alkynylating, aralkylating, acylating agent or carbamoyloxyating agent, with an alkylating, alkenylating, alkynylating, aralkylating or acylating agent.

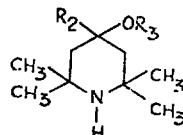
Compounds of formula I in which R_1 represents a residue of the formula:



in which R_4 is as defined above, m is 1 and X_1 represents $-CN$, $-OR_5$,

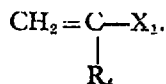


R_5 and R_6 being as defined above, may be produced by reacting a compound of the formula:



XII

wherein R_3 and R_2 are as defined above, with a compound having the formula

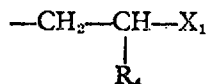


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Compounds of formula I wherein m is 1 and X_1 is $-\text{OH}$ may be prepared by reacting a compound of formula XII with ethylene oxide, propylene oxide or styrene oxide.

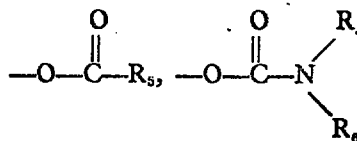
Compounds of formula I wherein R_1 is



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wherein X_1 is $-\text{OR}_5$,

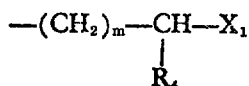


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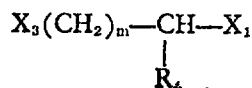
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or halogen may be prepared from the corresponding compounds wherein X_1 is $-\text{OH}$ by standard methods, such as alkylation, esterification, carbamoyloxylation or halogenation.

Compounds of formula I in which R_1 represents a residue of formula:—



wherein m , R_4 and X_1 are as hereinbefore defined may be prepared by reacting a compound of formula XII with the appropriate halogen compound having the formula:—

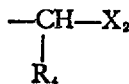


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wherein X_3 is a halogen atom.

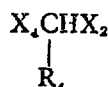
Compounds of formula I in which R_1 is the group of formula:—



wherein X_2 and R_4 are as defined above may be prepared by reacting a compound of the formula XII wherein R_2 is as defined above with a compound of the formula

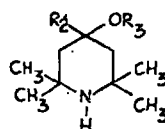
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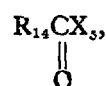
wherein X_4 is a halogen atom.

Compounds of the general formula I in which R_1 represents an acyl group may be prepared by reacting a compound of the formula:



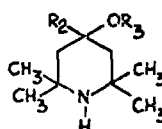
XII

wherein R_2 and R_3 are as defined above with an acyl halide of the formula



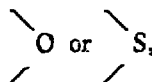
wherein X_3 is a halogen, and R_{14} is the remainder of the acyl group.

Compounds of the general formula I in which R_1 represents a carbamoyl or thio-carbamoyl group may be prepared by reacting a compound of the formula:



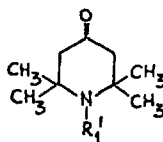
XII

R_2 and R_3 being as defined above with an isocyanate or thioisocyanate of the formula $R_{15}NCX^1$ in which X^1 is

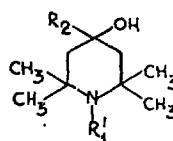


and R_{15} is the remainder of the isocyanate or thioisocyanate group.

Where R_2 in the general formula I is other than hydrogen it is preferred to introduce the appropriate group before or after the group R_1 is introduced, but before R_3 is introduced. The group R_2 may be introduced by reacting a ketone of the formula:

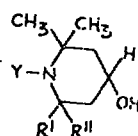


wherein R_1' is hydrogen or R_1 , with a Grignard reagent R_2MgX followed by hydrolysis to produce a compound of the formula:



All the reactions described above which result in the elimination of hydrogen halide between two reactants may be carried out in the presence of an acid acceptor.

Compounds of formula II as defined hereinbefore are produced by reacting, in the presence of an acid-binding agent, a piperidinol compound having the formula:—



XIV

wherein Y , R' and R'' are as defined hereinbefore with an acid halide having the formula:—



wherein R and n are as defined hereinbefore and hal. represents a halogen atom. The

acid binding agent can be an organic base or an excess amount of the amine reactant XIV and the reactants are for example heated together in a solvent inert under the reaction conditions.

5 The process can be performed in the presence of an esterification catalyst, such as an alkali metal amide, between a piperidinol compound having the formula XIV, with an ester having the formula:— 5



wherein R and n are as defined above and R_{16} is an alkyl group having from 1 to 4 carbon atoms, or with an acid having the formula:—

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wherein R and n are as defined above.

The catalyst for producing compounds of the formula II may be, for example, a tetraalkyl titanate.

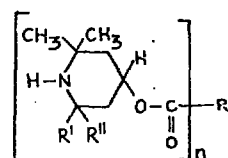
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The acetylation or esterification process for producing compounds of the formula II the reactants can also be fused, the mass is agitated until reaction is complete and the reaction is stopped when the reaction is complete. The completion of the reaction is determined for example by collecting, respectively, the alcohol or water produced in the reaction, and stopping the reaction when the theoretical amount of water or alcohol has been removed.

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Compounds of formula II are also produced by reacting an ester having the formula:— 20

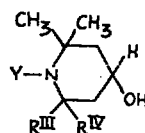


XV

wherein R, R', R'' and n are as defined above with a compound capable of reacting with the ester XV such as an alkylating or aralkylating agent or an aldehyde or ketone capable of introducing into it the group Y as defined above.

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Compounds having the formula IV as defined hereinbefore are produced by reacting a compound having the formula:— 25



XVII

wherein Y, R^{III} and R^{IV} are as defined hereinbefore with an isocyanate having the formula:

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wherein R_{12} and q are as defined hereinbefore. The reaction can be effected in a solvent inert under the reaction conditions and in the presence of a strong base.

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The present invention still further provides a composition comprising an organic material and a stabilising amount of a compound having the formula I, II or IV as hereinbefore defined.

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Compounds of formula I, II or IV, have been found to impart to polyolefines an exceptionally high degree of stability towards deterioration normally induced by the effects of ultra-violet radiation or exposure to heat. Moreover, this improved stability is achieved without affecting the colour properties of the treated polyolefine. The stabilisers of the invention provide effective light and/or heat stabilisation, especially for low- and high-density polyethylene and polypropylene and polystyrene as well as polymers of butene-1, pentene-1, 3-methyl-butene-1, hexene-1, 4-methylpentene-1, 4-methylhexene-1 and 4,4-dimethyl-pentene-1, and also co- and ter-polymers of olefines, particularly of ethylene or propylene.

40

45

Other organic materials susceptible to degradation by the effects of light and the 45

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properties of which are improved by the incorporation therein of a compound of formula I, II or IV, include natural and synthetic polymeric materials, for instance natural and synthetic rubbers, the latter including, for example, homo-, co- and ter-polymers of acrylonitrile, butadiene and styrene.

Specific synthetic polymers include polyvinyl chloride and vinyl chloride co-polymers, polyvinylidene chloride polyvinyl acetate as well as condensation polymers containing ether, ester (derived from carboxylic sulphonic or carbonic acids), amide or urethane groupings. These polymers can, for instance, form the basis of surface coating media such as paints and lacquers having an oil or resin, for instance an alkyd of poly-amide resin base.

The amount of the compound of formula I, II or IV, which is incorporated into the organic material in order to achieve maximum protection against degradation by light varies according to the properties of the organic material treated and according to the severity of the light radiation and to the length of exposure. However, for most purposes it is sufficient to use an amount of the compound of formula I, II or IV, within the range of from 0.01% to 5% by weight, more preferably within the range of from 0.1% to 2% by weight based on the weight of untreated organic material.

The compounds may be incorporated into the polymeric material by any of the known techniques for compounding additives with a polymer. For example, the compound and the polymer may be compounded in an internal mixer. Alternatively, the compound may be added as a solution or slurry in a suitable solvent or dispersant, for instance an inert organic solvent such as methanol, ethanol or acetone to powdered polymer and the whole mixed intimately in a mixer, and the solvent subsequently removed. As a further alternative the compound may be added to the polymer during the preparation of the latter, for instance at the latex stage of polymer production, to provide pre-stabilised polymer material.

Optionally, the composition of the invention may contain one or more further additives, especially those used in polymer e.g. polyolefine formulations, such as antioxidants e.g. of the phenol or amine type, U.V. absorbers and light protectants or stabilizers, phosphite stabilisers, peroxide decomposers, polyamide stabilisers, basic co-stabilisers, metal complexants/deactivators polyvinyl chloride stabilisers, nucleation agents, plasticizers, lubricants, emulsifiers, anti-slipping and antistatic agents, flame-protectants, pigments, dyes, fillers such as carbon black, asbestos, glass and other fibres, kaolin and talc.

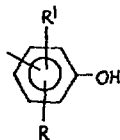
The present invention therefore includes binary, ternary and multi-component compositions containing the stabiliser of formula I, II or IV, together with one or more other functional additives for polymers.

Examples of suitable antioxidants are those of the hindered phenol type such as those selected from the following groups:—

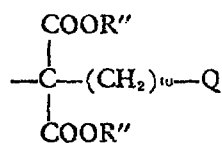
(1) Phenolic compounds having the general formula



wherein Q is



A₁ is —CR(COOR'')₂ or



R is hydrogen or alkyl of 1 to 6 carbon atoms,

R' is alkyl of 1 to 6 carbon atoms,

R'' is an alkyl group having from 6 to 24 carbon atoms, and

ω is O an integer from 1 to 4.

Illustrative examples of the compounds shown above are:

- 5 di-n-octadecyl- α -(3,5-di-t-butyl-4-hydroxy-benzyl)malonate,
 di-n-octadecyl- α -(3-t-butyl-4-hydroxy-5-methyl-benzyl)malonate which is disclosed in
 the Netherlands Patent Specification No. 6,711,199, and
 di-n-octadecyl- α,α' -bis-(3-t-butyl-4-hydroxy-5-methyl-benzyl)malonate which is dis-
 closed in the Netherlands Patent Specification No. 6,803,498. 5

(2) Phenolic compounds having the general formula



wherein Q is as hereinbefore defined and R''' represents hydrogen or one or two mono-
 valent residues derived from aliphatic hydrocarbons having from 1 to 30 carbon atoms.

10 Illustrative examples of the compounds shown above are:

2,6-di-t-butyl-*p*-cresol,
 2-methyl-4,6-di-t-butylphenol, and
 2,6-di-octadecyl-*p*-cresol.

(3) Phenolic compounds having the formula

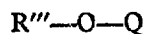


wherein Q and ω are as hereinbefore defined.

Illustrative examples of the compounds shown are:

2,2'-methylene-bis-(6-t-butyl-4-methylphenol),
 2,2'-methylene-bis-(6-t-butyl-4-ethylphenol),
 20 4,4'-butylidene-bis-(2,6-di-t-butylphenol),
 4,4'-(2-butylidene)-bis-(2-t-butyl-5-methylphenol),
 2,2'-methylene-bis-(3-t-butyl-5-ethylphenol),
 4,4'-methylene-bis-(3,5-di-t-butylphenol),
 4,4'-methylene-bis-(3-t-butyl-5-methylphenol), and
 25 2,2'-methylene-bis-(3-t-butyl-5-methylphenol). 25

(4) Phenolic compounds having the formula:

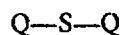


wherein Q is and R''' are as hereinafter defined.

Illustrative examples of such compounds are:

30 2,5-di-t-butylhydroquinone,
 2,6-di-t-butylhydroquinone, and
 2,5-di-t-butyl-4-hydroxyanisole. 30

(5) Phenolic compounds having the formula:

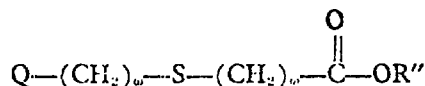


35 wherein Q is as hereinbefore defined. 35

Illustrative examples of such compounds are:

4,4'-thiobis-(2-t-butyl-5-methylphenol),
 4,4'-thiobis-(2-t-butyl-6-methylphenol),
 2,2'-thiobis-(6-t-butyl-4-methylphenol), and
 40 4,4'-thiobis-(2-methyl-5-t-butylphenol). 40

(6) Phenolic compounds having the formula:

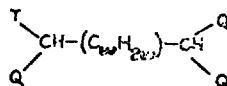


wherein Q, R'' and ω are as hereinbefore defined.

Illustrative examples of such compounds are:

octadecyl-(3,5-dimethyl-4-hydroxybenzylthio)-acetate, and dodecyl-(3,5-di-t-butyl-4-hydroxybenzylthio)-propionate.

(7) Phenolic compounds having the formula

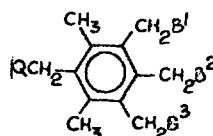


wherein T is hydrogen or Q, and Q and ω are as defined above.

Illustrative examples of such compounds are:

1,1,3-tris(3,5-dimethyl-4-hydroxyphenyl)-propane,
1,1,3-tris(5-t-butyl-4-hydroxy-2-methylphenyl)-butane, and
1,1,5,5-tetrakis-(3'-t-butyl-4'-hydroxy-6'-methylphenyl)-n-pentane.

(8) Phenolic compounds having the formula:

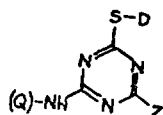


wherein B¹, B² and B³ are each independently hydrogen, methyl or Q, provided that when B¹ and B³ are Q then B² is hydrogen or methyl and when B² is Q then B¹ and B³ are each independently hydrogen or methyl; and Q is as hereinbefore defined.

Illustrative examples of such compounds are:

1,4-di(3,5-di-t-butyl-4-hydroxybenzyl)-2,3,5,6-tetramethylbenzene, and
1,3,5-tri(3,5-di-t-butyl-4-hydroxybenzyl)-2,4,6-trimethylbenzene.

(8) Phenolic compounds having the formula



wherein Z is NHQ, —S—D— or —O—Q

D is an alkyl group having from 4 to 18 carbon atoms or —(C_ωH_{2ω})—S—R''

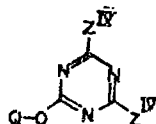
Q, R'' and ω are as hereinbefore defined.

Illustrative examples of such compounds are:

2,4-bis-(n-octylthio)-6-(3,5-di-t-butyl-4-hydroxyanilino)-1,3,5-triazine
6-(4-hydroxy-3-methyl-5-t-butylanilino)-2,4-bis-(n-octylthio)-1,3,5-triazine
6-(4-hydroxy-3,5-dimethylanilino)-2,4-bis-(n-octylthio)-1,3,5-triazine
6-(4-hydroxy-3,5-di-t-butylanilino)-4-(4-hydroxy-3,5-di-t-butylphenoxy)-2-(n-octylthio)-1,3,5-triazine, and
2,4-bis(4-hydroxy-3,5-di-t-butylanilino)-6-(n-octylthio)-1,3,5-triazine.

The above phenolic triazine stabilizers are more fully described in U.S. Patent Specification No. 3,255,191.

(10) Phenolic compounds having the formula:



wherein the Z^{IV} s, which may be the same or different, are $-O-Q$, $-S-D$ or $-S-(C_wH_{2w})-SD$;

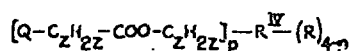
Q , D and w are as hereinbefore defined.

Illustrative examples of such compounds are:

- | | | |
|----|--|----|
| 5 | 2,4-bis-(3,5-di-t-butyl-4-hydroxyphenoxy)-6-(n-octylthio)-1,3,5-triazine, | 5 |
| | 2,4,6-tris-(4-hydroxy-3,5-di-t-butylphenoxy)-1,3,5-triazine, | |
| | 6-(4-hydroxy-3,5-di-t-butylphenoxy)-2,4-bis-(n-octylthioethylthio)-1,3,5-triazine, | |
| | 6-(4-hydroxy-3-methylphenoxy)-2,4-bis-(n-octylthio)-1,3,5-triazine, | |
| 10 | 6-(4-hydroxy-3-t-butylphenoxy)-2,4-bis-(n-octylthioethylthio)-1,3,5-triazine, | 10 |
| | 6-(4-hydroxy-3-methyl-5-t-butylphenoxy)-2,4-bis-(n-octylthio)-1,3,5-triazine, | |
| | 2,4-bis-(4-hydroxy-3-methyl-5-t-butylphenoxy)-6-(n-octylthio)-1,3,5-triazine, | |
| | 2,4,6-tris-(4-hydroxy-3-methyl-5-t-butylphenoxy)-1,3,5-triazine, | |
| | 6-(4-hydroxy-3,5-di-t-butylphenoxy)-2,4-bis-(n-octylthiopropylthio)-1,3,5-triazine, | |
| 15 | 6-(4-hydroxy-3,5-di-t-butylphenoxy)-2,4-bis-(n-dodecylthioethylthio)-1,3,5-triazine, | 15 |
| | 2,4-bis-(4-hydroxy-3,5-di-t-butylphenoxy)-6-butylthio-1,3,5-triazine, | |
| | 2,4-bis-(4-hydroxy-3,5-di-t-butylphenoxy)-6-(n-octadecylthio)-1,3,5-triazine, | |
| | 2,4-bis-(4-hydroxy-3,5-di-t-butylphenoxy)-6-(n-dodecylthio)-1,3,5-triazine, | |
| | 2,4-bis-(4-hydroxy-3,5-di-t-butylphenoxy)-6-(n-octylthiopropylthio)-1,3,5-triazine, | |
| 20 | 2,4-bis-(4-hydroxy-3,5-di-t-butylphenoxy)-6-(n-octylthioethylthio)-1,3,5-triazine, and | 20 |
| | 2,4-bis-(4-hydroxy-3,5-di-t-butylphenoxy)-6-(n-dodecylthioethylthio)-1,3,5-triazine. | |

The above phenolic triazine stabilizers are more fully described in U.S. Patent Specification No. 3,255,191.

(11) Phenolic compounds having the formula



- | | | |
|----|--|----|
| 25 | wherein p is an integer from 1 to 4 and R^{IV} is a tetravalent radical derived from an aliphatic hydrocarbon having from 1 to 30 carbon atoms, aliphatic mono- or diether having from 1 to 30 carbon atoms, aliphatic mono- or diether having from 1 to 30 carbon atoms and z is 0 or an integer from 1 to 6; Q and R as hereinbefore defined. Illustrative examples of such compounds are: | 25 |
|----|--|----|

- | | | |
|----|---|----|
| 30 | <i>Sub-class I</i> | 30 |
| | n-Octadecyl-3-(3,5-di-t-butyl-4-hydroxyphenyl)-propionate, | |
| | n-Octadecyl-2-(3,5-di-t-butyl-4-hydroxyphenyl)-acetate, | |
| | n-Octadecyl-3,5-di-t-butyl-4-hydroxybenzoate, | |
| 35 | n-Hexyl-3,5-di-t-butyl-4-hydroxybenzoate, | 35 |
| | n-Dodecyl-3,5-di-t-butyl-4-hydroxybenzoate, | |
| | Neo-dodecyl-3-(3,5-di-t-butyl-4-hydroxyphenyl)-propionate, | |
| | Dodecyl-β-(3,5-di-t-butyl-4-hydroxyphenyl)-propionate, | |
| | Ethyl-α-(4-hydroxy-3,5-di-t-butylphenyl)-isobutyrate, | |
| 40 | Octadecyl-α-(4-hydroxy-3,5-di-t-butylphenyl)-isobutyrate, and | 40 |
| | Octadecyl-α-(4-hydroxy-3,5-di-t-butylphenyl)-propionate. | |

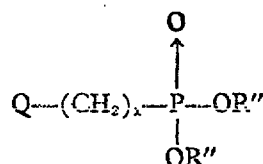
- | | | |
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| | <i>Sub-class II</i> | |
| | 2-(n-octylthio)ethyl 3,5-di-t-butyl-4-hydroxybenzoate, | |
| | 2-(n-octylthio)ethyl 3,5-di-t-butyl-4-hydroxyphenylacetate, | |
| 45 | 2-(n-octadecylthio)ethyl 3,5-di-t-butyl-4-hydroxyphenylacetate, | 45 |
| | 2-(n-octadecylthio)ethyl 3,5-di-t-butyl-4-hydroxybenzoate, and | |
| | 2-(n-octadecylthio)ethyl 3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate. | |

- | | | |
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| | <i>Sub-class III</i> | |
| | 1,2-propylene glycol bis-[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate], | |
| | Ethylene glycol bis-[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate], | |
| 50 | Neopentylglycol bis-[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate], | 50 |
| | Ethylene glycol bis-(3,5-di-t-butyl-4-hydroxyphenylacetate), | |
| | Glycerine-1-n-octadecanoate-2,3-bis-(3,5-di-t-butyl-4-hydroxyphenylacetate), | |
| | Pentaerythritol-tetrakis-[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate], | |
| | 1,1,1-trimethylol ethane-tris-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate, | |
| 55 | 1,2,3-butanetriol tris-[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate], | 55 |

2-stearoyloxyethyl 7-(3-methyl-5-*t*-butyl-4-hydroxyphenyl)heptanoate, and 1,6-*n*-hexanediol-bis[(3',5'-di-*t*-butyl-4-hydroxyphenyl)propionate].

The above phenolic ester stabilizers of sub-classes I, II and III are more fully described in British Patent Specifications Nos. 1,103,144, 1,105,699 and 1,001,098.

(12) Phenolic compounds having the formula

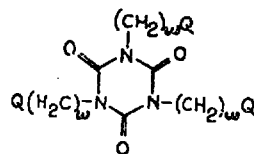


where x is 1 or 2; Q and R'' are as hereinbefore defined. Illustrative examples of such compounds are:

Di-*n*-octadecyl 3,5-di-*t*-butyl-4-hydroxybenzyl-phosphonate,
Di-*n*-octadecyl 3-*t*-butyl-4-hydroxy-5-methylbenzyl-phosphonate,
Di-*n*-octadecyl 2-(3,5-di-*t*-butyl-4-hydroxyphenyl)-ethanephosphonate,
Di-*n*-tetradecyl 3,5-di-*t*-butyl-4-hydroxybenzyl-phosphonate,
Di-*n*-hexydecyl 3,5-di-*t*-butyl-4-hydroxybenzyl-phosphonate, and
Di-*n*-docosyl-3,5-di-*t*-butyl-4-hydroxybenzyl-phosphonate.

The above di-(higher)alkyl phenolic phosphonates are more fully described in U.S. Patent Specification No. 3,281,505.

(13) Phenolic compounds having the formula



wherein w and Q are defined above. An illustrative example of such a compound is:

tris-(3,5-di-*t*-butyl-4-hydroxybenzyl) isocyanurate.

The above hydroxyphenylalkyl isocyanurates are more fully described in U.S. Patent Specification No. 3,531,483.

The above phenolic stabilizers are known and many are commercially available.

While any of the above mentioned antioxidants can be useful in combination with the ultraviolet light stabilizers of this invention, the preferred antioxidants consist of the hindered phenols in groups 1, 8, 9, 10, 11, 12 and 13 as mentioned above. The most preferred hindered phenols are those of groups 1, 9, 11, 12 and 13.

Further examples of antioxidants are those of the aminoaryl series for instance aniline and naphthylamine derivatives as well as their heterocyclic derivatives such as:—

phenyl-1-naphthylamine,
phenyl-2-naphthylamine,
N,N'-diphenyl-*p*-phenylenediamine,
N,N'-di-sec.butyl-*p*-phenylenediamine,
6-ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline,
6-dodecyl-2,2,4-trimethyl-1,2-dihydroquinoline,
mono- and di-octyliminodibenzyl, and
polymerised 2,2,4-trimethyl-1,2-dihydroquinoline.

Ultraviolet absorbers and light protectants include:

(a) 2-(2'-hydroxyphenyl)benzotriazoles, for instance 5'-methyl; 3',5'-di-*t*-butyl; 5'-*t*-butyl; 5-chloro-3',5-di-*t*-butyl; 5-chloro-3'-*t*-butyl-5'-methyl; 3'-sec.butyl-5'-tert.

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Some Examples will now be given. Parts and percentages are by weight unless otherwise stated.

Example 1.

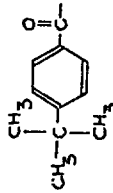
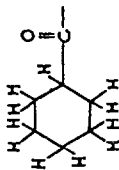
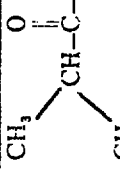
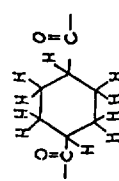
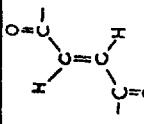
5 A mixture of 10.26 parts of 1,2,2,6,6-pentamethylpiperidin-4-ol, 6.06 parts of sebacic acid and 1.0 parts of tetra-n-butyl titanate in 100 parts of xylene was heated under reflux conditions for 60 hours. Removal of the xylene by distillation under reduced pressure gave an oily solid which was heated under reflux conditions with 0.5 parts of sodium carbonate and 0.5 parts of carbon in 25 parts of water for 1 hour. 5

10 Removal of the water by distillation under reduced pressure gave a black residue which was repeatedly extracted with ether. The combined ether extracts were dried and the ether removed by distillation under reduced pressure to give a yellow oil which was distilled under reduced pressure to give 5.0 parts of bis(1,2,2,6,6-pentamethyl-4-piperidiny!) sebacate as a colourless oil having a boiling point of 220—2°C at 0.2 mm of Hg and the following elemental analysis by weight: 10

15		<i>Found</i>	<i>Required (for C₃₀H₅₆N₂O₄)</i>	15
	Carbon	70.60%	70.82%	
	Hydrogen	11.00%	11.10%	
	Nitrogen	4.81%	5.51%	

20 Table I gives a list of esters prepared using the procedure of Example 1. In Table I the symbols referred to are those in Formula I. 20

TABLE 1
Analysis

Ex. sample No.	R ₁	R ₂	R ₃	m.p. or b.p. °C @ m.m.	Molecular Formula	Required (%)			Found (%)		
						C	H	N	C	H	N
2	CH ₃			88°C	C ₂₁ H ₂₃ NO ₂	76.09	10.03	4.23	76.36	9.90	3.99
3	CH ₂ =CH·CH ₂ -	H		130°C. at 0.05 m.m. Hg.	C ₁₉ H ₂₃ NO ₂	74.22	10.82	4.56	74.86	10.65	4.26
4	CH ₃	H		200°C at 0.1 m.m. Hg.	C ₂₀ H ₂₃ NO ₂	77.18	12.26	3.21	78.10	12.30	3.06
5	CH ₃	H		81- 3° at 0.05 m.m. Hg.	C ₁₄ H ₂₂ NO ₂	69.67	11.27	5.80	70.16	11.37	5.90
6	CH ₃	H		228- 30°C at 0.1 m.m. Hg.	C ₂₈ H ₃₅ N ₂ O ₄	70.25	10.53	5.85	70.26	10.44	5.38
7	CH ₃	H		91- 2°C	C ₂₄ H ₄₂ N ₂ O ₄	68.21	10.02	6.63	68.05	9.97	6.47

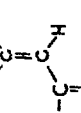
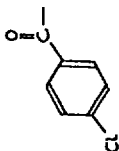
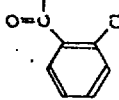
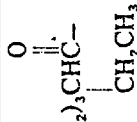
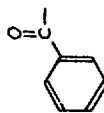
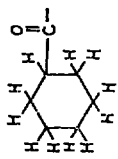
7	CH ₃	H		91- 2°C	C ₂₄ H ₄₂ N ₂ O ₄	68.71	10.02	0.63	0.00	0.00	0.00
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TABLE 1 (Continued) Analysis

Ex- ample No.	R ₁	R ₂ , R ₃	m.p. or b.p. °C@ m.m.	Molecular Formula	Required (%)				Found (%)			
					C	H	N		C	H	N	
8	CH ₃	H	210- 20°C at 0.4 m.m.	C ₂₈ H ₄₈ N ₂ O ₄ S	64.40	9.98	5.78	S=6.60	64.26	9.89	5.51	S=6.59
9	CH ₃	H	64- 5°C	C ₂₈ H ₄₈ N ₂ O ₄ S	68.99	10.69	6.19		69.53	10.62	6.02	
10	CH ₃	H	57°C.	C ₁₃ H ₁₇ NO ₂	75.71	9.03	4.65		75.50	8.97	4.71	
11	CH ₃	H	120°C. at 0.2 m.m. Hg	C ₁₈ H ₂₇ NO ₂	74.70	9.40	4.84		74.99	9.70	4.85	
12	CH ₃	H	148°C. at 0.4 m.m. Hg.	C ₁₈ H ₂₇ NO ₂	74.70	9.40	4.84		74.98	9.42	4.70	
13	CH ₃	H	51°C.	C ₁₈ H ₂₇ NO ₂	70.79	8.91	4.59		70.49	8.71	4.50	

TABLE I (Continued)

Ex- ample No.	R ₁	R ₂	R ₃	m.p. or b.p. °C. @ m.m.	Molecular Formula	Required (%)			Found (%)		
						C	H	N	C	H	N
14	CH ₃	H		147°C. at 0.9 m.m. Hg.	C ₁₇ H ₂₄ NO ₂ Cl	66.00	7.81	4.52	65.98	7.65	4.53
								Cl=11.44			Cl=11.56
15	CH ₃	H		152- 4°C. at 0.2 m.m. Hg.	C ₁₇ H ₂₄ NO ₂ Cl	66.00	7.81	4.52	65.89	7.65	4.53
								Cl=11.44			Cl=11.56
16	CH ₃	H		100°C. at 0.2 m.m. Hg.	C ₁₈ H ₂₂ NO ₂	72.68	11.68	4.71	72.53	11.96	4.50
17	CH ₃	H		65°C. at 0.4 m.m. Hg.	C ₁₃ H ₂₂ NO ₂	69.29	10.29	6.22	69.64	10.30	6.15
18	CH ₃	H		196°C. at 12 m.m. Hg.	C ₁₇ H ₂₂ NO ₂	74.14	9.15	5.09	74.35	9.23	5.13
19	CH ₃	H		180°C. at 0.5 m.m. Hg.	C ₁₇ H ₂₄ NO ₂	72.55	11.10	4.98	72.84	11.04	4.77

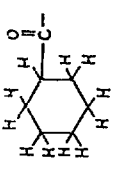
19	CH ₃	H		180°C. at 0.5 m.m. Hg.	C ₁₇ H ₃₁ NO ₂	72.55	11.10	4.98	72.84	11.04	4.77
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TABLE I (Continued)

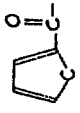
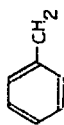
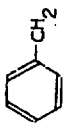
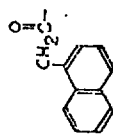
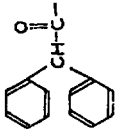
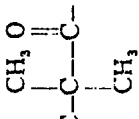
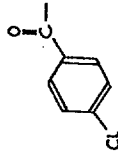
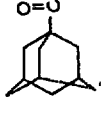
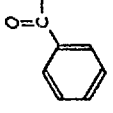
Ex- ample No.	R ₁	R ₂	R ₃	m.p. or b.p. °C. @ m.m.	Molecular Formula	Required (%)			Found (%)		
						C	H	N	C	H	N
20	CH ₃	H	CH ₃ (CH ₂) ₁₆ C=O	44°C.	C ₂₈ H ₅₅ NO ₂	76.83	12.66	3.20	76.71	12.35	3.22
21	CH ₃	H	CH ₃ (CH ₂) ₆ C=O	116–17°C at 0.2 m.m. Hg.	C ₁₈ H ₃₅ NO ₂	72.68	11.86	4.71	72.56	11.50	4.99
22	CH ₂ =CH·CH ₂ –	H		129–30°C at 0.05 m.m. Hg.	C ₁₇ H ₂₅ NO ₃	70.07	8.65	4.81	70.70	8.86	4.42
23	CH ₃	H	CH ₃ (CH ₂) ₁₈ C=O	41–2°C	C ₃₀ H ₅₉ NO ₂	77.36	12.77		75.84	12.25	
24		H	CH ₃ (CH ₂) ₃ CH=O CH ₂ CH ₃	183–5°C at 0.1 m.m. Hg.	C ₂₄ H ₃₉ NO ₂	77.16	10.52	3.75	77.43	10.39	3.54
25		H	CH ₃ (CH ₂) ₁₆ C=O	55–6°C	C ₃₄ H ₆₉ NO ₃	79.47	11.57	2.73	79.32	11.59	2.45
26	CH ₃	H		174–8°C at 0.1 m.m. Hg.	C ₂₂ H ₂₉ NO ₂	77.84	8.61	4.13	78.35	8.63	4.12

TABLE I (Continued) Analysis

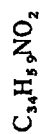
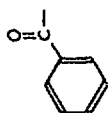
Ex- ample No.	R ₁	R ₂	R ₃	m.p. or b.p. °C. @ m.m.	Molecular Formula	Required (%)			Found (%)		
						C	H	N	C	H	N
27	CH ₃ (CH ₂) ₁₁ -	H	CH ₃ (CH ₂) ₆ -C(=O)-	190°C. at 0.05 m.m. Hg.	C ₂₂ H ₃₇ NO ₂	77.10	12.72	3.10	77.20	13.02	3.08
28	CH ₃	H		69- 70°C	C ₂₄ H ₃₁ NO ₂	78.87	8.55	3.83	79.38	8.80	3.69
29	CH ₃	H		90°C. at 0.1 m.m. Hg.	C ₁₅ H ₂₅ NO ₂	70.54	11.45	5.48	69.99	11.24	5.25
30	CH ₃ (CH ₂) ₁₁ -	H		56°C.	C ₂₃ H ₄₀ NO ₂ Cl	72.60	9.90	3.02	71.98	10.19	3.01
31	CH ₃	H	CH ₃ (CH ₂) ₁₁ -C(=O)-SCH ₂ -C(=O)-	200°C. at 0.2 m.m. Hg.	C ₂₄ H ₄₇ NO ₂ S	69.70	11.45	3.39	69.69	11.48	3.31
32	CH ₃	H		119°C.	C ₂₁ H ₃₃ NO ₂	75.63	10.58	4.20	75.94	10.30	3.93
33	CH ₃ (CH ₂) ₁₇ -	H		Purified by chromato- graphy	C ₃₄ H ₅₉ NO ₂	Molecular Weight=513 Found (From Mass Spectrometry=513)					

A solution of 17.10 parts of 1,2,2,6,6-pentamethylpiperidin-4-ol in 50 parts of dry benzene was stirred at 15—20°C whilst adding 6.0 parts of sebacyl chloride dropwise over 15 minutes. The mixture was stirred for a further 12 hours at room temperature after which the 1,2,2,6,6-pentamethylpiperidin-4-ol hydrochloride formed during the reaction was filtered off. The benzene was removed by distillation under reduced pressure to give a yellow oil, which was distilled under reduced pressure to give bis-(1,2,2,6,6-pentamethyl-4-piperidinyl) sebacate as a colourless oil having a boiling point of 218—20°C at 0.4 mm of Hg and the following elemental analysis by weight:

10		<i>Found</i>	<i>Required</i> (for $C_{10}H_{12}N_2O_2$)	10
	Carbon	70.99%	70.82%	
	Hydrogen	10.97%	11.10%	
	Nitrogen	5.26%	5.51%	

Table 2 gives a list of esters prepared using the procedure of Example 34.

Molecular Weight=513
Found(From Mass Spectrometry=513)

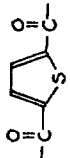
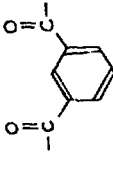
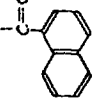
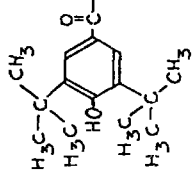
Purified by
chromato-
graphy

II

$$\text{CH}_3(\text{CH}_2)_{17}-$$

33

TABLE 2

Example No.	R ₁	R ₂	R ₃	m.p. or b.p. °C@ m.m.	Analysis						
					Molecular Formula	Required (%)			Found (%)		
						C	H	N	C	H	N
35	CH ₃	H		Purified by chromatography	C ₂₅ H ₄₂ N ₂ O ₄ S			5.86			5.64
36	CH ₃	H		118°C.	C ₂₂ H ₄₀ N ₂ O ₄	66.63	10.17	7.06	66.94	10.22	6.95
37	CH ₃	H		123°C.	C ₂₈ H ₄₄ N ₂ O ₄	70.15	9.38	5.93	70.75	9.68	5.69
38	CH ₃	H		75- 6°C.	C ₂₁ H ₂₇ NO ₂	77.50	8.36	4.30	77.78	8.45	4.06
39	CH ₃	H		138°C. at 12 m.m. Hg.	C ₁₂ H ₂₃ NO ₂	67.57	10.87	6.57	67.90	10.72	6.53
40	CH ₃	H		142°C.	C ₂₃ H ₄₁ NO ₃	74.40	10.24	3.47	74.80	9.99	3.43

Example 41.

5 A mixture of 17.10 parts of 1,2,2,6,6-pentamethylpiperidin-4-ol, 13.60 parts of methyl benzoate and 2.0 parts of lithium amide was heated at 160°C for six hours with removal of the methyl alcohol formed by distillation. Water pump vacuum was applied and heating continued for a further two hours; on cooling the residue was dissolved in chloroform and filtered to remove the lithium amide. The chloroform was removed by distillation under reduced pressure to give a yellow oil which was fractionally distilled under reduced pressure to yield 6.40 parts of 1,2,2,6,6-pentamethylpiperidinyl-4 benzoate having a boiling point of 126°C at 0.1 mm of Hg. and the following elemental analysis by weight:

	Found	Required (for $C_{17}H_{23}NO_2$)
Carbon	74.35%	74.14%
Hydrogen	9.23%	9.15%
Nitrogen	5.13%	5.09%

Example 42.

15 A mixture of 17.10 parts of 1,2,2,6,6-pentamethylpiperidin-4-ol, 14.60 parts of methyl- β -(3,5-di-*t*-butyl-4-hydroxyphenyl) propionate and 1.0 part of lithium amide was heated together to 130°C. Water pump vacuum was then applied to the reaction mixture whilst maintaining the temperature at 125—135°C for 3 hours. The temperature of the reaction mixture was then raised to 160°C and high vacuum (0.5—1 mm Hg) was applied for 1 hour. The reaction mixture cooled, dissolved in chloroform and filtered. Removal of the chloroform by distillation under reduced pressure gave a brown oil which, when triturated with ether, gave a white solid which was collected by filtration, washed well with ether and dried to give 16.0 parts of 1,2,2,6,6-pentamethylpiperidinyl-4- β -(3',5'-di-*t*-butyl-4'-hydroxyphenyl) propionate as its bicarbonate salt having a melting point of 210°—11°C., and the following elemental analysis by weight:

	Found	Required (for $C_{28}H_{41}NO_6$)
Carbon	68.90%	68.10%
Hydrogen	9.56%	9.60%
Nitrogen	2.91%	2.84%

Example 43.

35 15.0 parts of the product from Example 42 were dissolved in water and neutralised with sodium hydroxide solution. The aqueous solution was extracted with ether, the combined ether extracts were dried over anhydrous magnesium sulphate. The ether was removed by distillation under reduced pressure to give a white solid which was recrystallised from ethanol to give 9.30 parts of 1,2,2,6,6-pentamethylpiperidinyl-4- β -(3',5'-di-*t*-butyl-4'-hydroxyphenyl) propionate having a melting point of 124°—5°C and the following elemental analysis by weight:

	Found	Calculated (for $C_{27}H_{41}NO_3$)
Carbon	75.00%	75.30%
Hydrogen	10.50%	10.20%
Nitrogen	3.50%	3.30%

Example 44.

45 A mixture of 10.26 parts of 1,2,2,6,6-pentamethylpiperidin-4-ol, 5.04 parts of trimethyl trimesate and 0.20 parts of lithium amide in 100 parts of xylene was heated at 137°C for 7 hours. The methyl alcohol formed during the reaction being removed by distillation. The cooled reaction mixture was filtered to remove the lithium amide and the xylene solvent removed by distillation under reduced pressure. Purification of the residue by preparative thin layer chromatography yielded dimethyl (1,2,2,6,6-pentamethylpiperidinyl-4) trimesate having the following molecular weight:

Found (from mass spectrometry)	391
Required (for $C_{21}H_{29}NO_6$)	391

55 and methyl bis(1,2,2,6,6-pentamethylpiperidinyl-4) trimesate having the following molecular weight:

Found (from mass spectrometry)
Required (for $C_{30}H_{46}N_2O_4$)

530
530.

Example 45.

5 A mixture of 16.4 parts of 1,2,2,6,6-pentamethylpiperidin-4-ol, 6.27 parts of
methyl isocyanate and 0.5 parts of 1,4-diazabicyclo[2,2,2]octane was refluxed in 150
parts of dry benzene for 24 hours. Removal of the benzene solvent by distillation under
reduced pressure yielded an oily solid which was poured on to 200 parts of water and
allowed to stand for 24 hours. The solid formed was collected by filtration, dried and
crystallised from n-hexane to give 14.2 parts of 4-methylcarbamoyloxy-1,2,2,6,6-penta-
10 methylpiperidine having a melting point of 96—7°C. and the following elemental
analysis by weight:

	Found	Required (for $C_{12}H_{24}N_2O_2$)
Carbon	63.28%	63.12%
Hydrogen	10.70%	10.59%
15 Nitrogen	12.09%	12.27%

Table 3 gives a list of carbamoyloxy esters prepared using the procedure of
Example 45.

TABLE 3

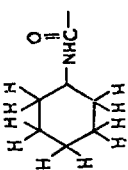
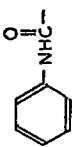
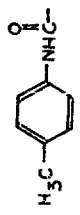
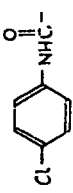
Example No.	R ₁	R ₂	R ₃	m.p. or b.p. °C. @ m.m.	Molecular Formula	Analysis					
						Required (%)			Found (%)		
						C	H	N	C	H	N
46	CH ₃	H	CH ₃ (CH ₂) ₅ NHC(=O)-	63°C.	C ₁₇ H ₂₅ N ₂ O ₂	68.41	11.48	9.39	68.17	11.32	9.16
47	CH ₃	H	CH ₃ (CH ₂) ₁₇ NHC(=O)-	56-7°C.	C ₂₅ H ₃₅ N ₂ O ₂	74.62	12.52	6.00	74.58	12.34	5.96
48	CH ₃	H	CH ₂ =CH.CH ₂ NHC(=O)-	62°C.	C ₁₄ H ₂₃ N ₂ O ₂	66.11	10.30	11.01	66.40	10.27	10.92
49	CH ₃	H		184-6°C. at 2 m.m. Hg.	C ₁₇ H ₂₅ N ₂ O ₂	68.88	10.88	9.45	68.98	10.84	9.43
50	CH ₃	H		109-10°C.	C ₁₇ H ₂₃ N ₂ O ₂	70.31	9.02	9.65	70.61	8.80	9.53
51	CH ₃	H		106-7°C.	C ₁₈ H ₂₅ N ₂ O ₂	71.02	9.27	9.20	71.42	9.41	9.02
52	CH ₃	H		121°C.	C ₁₇ H ₂₅ N ₂ O ₂ Cl	62.86	7.70	8.68	62.92	7.75	8.87

TABLE 3 (Continued)

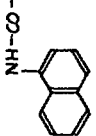
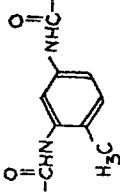
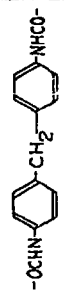
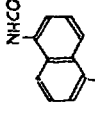
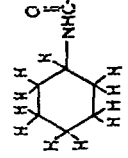
Example No.	R ₁	R ₂	R ₃	m.p. or b.p. °C. @ m.m.	Molecular Formula	Analysis					
						Required (%)			Found (%)		
						C	H	N	C	H	N
53	CH ₃	H		129°C.	C ₂₁ H ₁₈ N ₂ O ₂	74.08	8.29	8.23	74.37	8.07	8.41
54	CH ₃	H		101-4°C.	C ₂₃ H ₃₄ N ₄ O ₄	65.84	10.66	10.97	65.86	10.40	10.64
55	CH ₃	H		163-5°C	C ₂₉ H ₄₈ N ₄ O ₄	67.41	9.36	10.84	67.21	9.52	10.83
56	CH ₃	H		183°C.	C ₃₃ H ₅₂ N ₄ O ₄	70.91	8.84	9.45	70.64	8.79	9.24
57	CH ₃	H		178°C.	C ₃₂ H ₄₈ N ₄ O ₄	69.53	8.75	10.14	70.39	8.71	9.86
58	CH ₂ =CH.CH ₂ -	H		165°C. at 0.05 m.m. Hg.	C ₁₉ H ₃₄ N ₄ O ₄	70.76	10.63	8.69	70.64	10.80	9.04

TABLE 3 (Continued)

Example No.	R ₁	R ₂	R ₃	m.p. or b.p. °C. @ m.m.	Molecular Formula	Analysis					
						Required (%)			Found (%)		
						C	H	N	C	H	N
59	CH ₂ =CH·CH ₂ -	H									
60	CH ₃ CH ₂ CH ₂ -	H									
61		H									

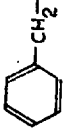
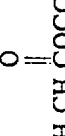
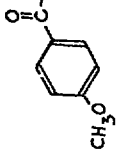
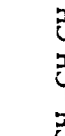
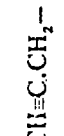
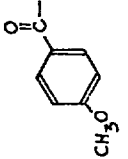
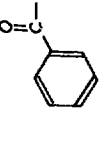
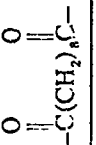
Example 62.

A mixture of 28.3 parts of 2,2,6,6-tetramethyl-4-piperidyl-n-octanoate and 8.55 parts of benzyl bromide was stirred and heated at 105°C for 72 hours. Ether was added to the cooled reaction mixture and the 2,2,6,6-tetramethyl-4-piperidyl-n-octanoate hydrobromide formed during the reaction was filtered off. The ether solvent was removed by distillation under reduced pressure and the residue distilled under reduced pressure to give 16.49 parts of 1-benzyl-2,2,6,6-tetramethyl-4-piperidyl-n-octanoate having a boiling point of 180°C at 0.1 mm of Hg and the following elemental analysis by weight:

	Found	Required (for C ₂₄ H ₃₉ NO ₂)
Carbon	77.46%	77.16%
Hydrogen	10.50%	10.52%
Nitrogen	3.86%	3.75%

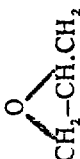
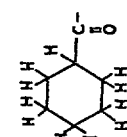
Table 4 gives a list of esters prepared using the procedure of Example 62.

TABLE 4

Example No.	R ₁	R ₂	R ₃	m.p. or b.p. °C. @ m.m.	Molecular Formula	Analysis					
						Required (%)			Found (%)		
						C	H	N	C	H	N
63		H		98-9°C.	C ₄₂ H ₆₄ N ₂ O ₄	76.32	9.76	4.24	76.04	9.49	4.04
64		H		191-2°C. at 0.1 m.m. Hg.	C ₂₁ H ₃₁ NO ₅	66.82	8.28	3.71	66.81	8.52	3.84
65		H		142-4°C. at 0.2 m.m. Hg.	C ₂₁ H ₁₇ NO ₂	74.25	11.53	4.33	74.05	11.36	4.32
66		H		68-9°C.	C ₂₀ H ₂₇ NO ₃	72.92	8.26	4.25	72.82	8.28	4.55
67		H		150°C. at 0.05 m.m. fig.	C ₁₉ H ₂₇ NO ₂	75.71	9.03	4.65	75.58	9.25	4.45
68		H		250°C. at 0.5 m.m. Hg.	C ₃₄ H ₆₀ N ₂ O ₄	72.81	10.78	4.99	73.07	10.60	4.77

68	$\text{CH}_2=\text{CHCH}_2-$	$\text{H}-\text{C}(\text{CH}_2)_8\text{C}-$ $\parallel$ O	250°C. at 0.5 m.m. Hg.	$\text{C}_{11}\text{H}_{20}\text{N}_2\text{O}_4$	72.81	10.78	4.99	73.07	10.60	4.77
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TABLE 4 (Continued)

Example No.	R_1	R_2	R_3	m.p. or b.p. $^\circ\text{C. @ m.m.}$	Molecular Formula	Analysis					
						Required (%)			Found (%)		
						C	H	N	C	H	N
69		H		139-42°C. at 0.2 m.m. Hg.	$\text{C}_{13}\text{H}_{19}\text{NO}_3$	70.55	10.28	4.33	70.37	10.38	4.39

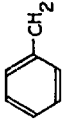
Example 70.

A mixture of 17.10 parts of 1,2,2,6,6-pentamethylpiperidin-4-ol and 3.50 parts of metallic sodium in 125 parts of toluene was heated under reflux conditions for 24 hours. The toluene solution was decanted off from the excess sodium and then refluxed for a further 24 hours with 36.60 parts of n-octadecyl bromide. The cooled solution was filtered to remove the sodium bromide which was formed during the reaction and the toluene solvent was removed by distillation under reduced pressure. Fractional distillation of the residue gave 4-octadecyloxy-1,2,2,6,6-pentamethylpiperidine having a boiling point of 184°C at 0.25 mm. of Hg and the following elemental analysis by weight:

	Found	Required (for $\text{C}_{28}\text{H}_{51}\text{NO}$)
Carbon	78.66%	79.36%
Hydrogen	13.77%	13.56%
Nitrogen	2.99%	3.31%

Table 5 gives a list of ethers prepared using the procedure of Example 70.

TABLE 5

Exampic No.	R ₁	R ₂	R ₃	m.p. or b.p. °C. @ m.m. Hg	Analysis						
					Molecular Formula	Required (%)			Found (%)		
						C	H	N	C	H	N
71	CH ₃	H	CH ₂ =CH·CH ₂ -								
72	CH ₃	H									
73	CH ₃	H	CH ₃ (CH ₂) ₁₁ -								
74	CH ₃	H	-(CH ₂) ₄ -	m.p. 62-63	C ₂₄ H ₄₈ N ₂ O ₂	72.74	12.09	7.07	73.00	11.94	6.85
75	CH ₃	H	CH ₃ CCH ₂ -	b.p. 0.3 mm. 73-74	C ₁₃ H ₂₃ NO	74.59	11.07	6.69	74.48	10.95	6.41
76	CH ₃	H	CH ₃ (CH ₂) ₅ -	b.p. 19 mm 123-124	C ₁₄ H ₂₈ NO	73.95	12.85	6.16	74.05	12.93	6.10

Example 77.

3.23 Parts of 1-allyl-2,2,6,6-tetramethyl-4-piperidyl n-octanoate in 50 parts of ethyl alcohol was hydrogenated at room temperature and 1 atmosphere pressure using 0.1 parts of 5% palladium on charcoal as the catalyst. The reaction mixture was filtered to remove the catalyst and the ethyl alcohol removed by distillation under reduced pressure to give 2.90 parts of 1-n-propyl-2,2,6,6-tetramethyl-4-piperidyl n-octanoate having a boiling point of 128°C at 0.05 mm of Hg and the following elemental analysis by weight:

10	Found	Required (for C ₂₀ H ₃₈ NO ₂)
	Carbon 73.50%	73.79%
	Hydrogen 12.26%	12.08%
	Nitrogen 4.31%	4.30%

Table 6 gives a list of compounds prepared using the procedure of Example 77.

TABLE 6

Example No.	R ₁	R ₂	R ₃	m.p. or b.p. °C. @ m.m.	Analysis						
					Molecular Formula	Required (%)			Found (%)		
						C	H	N	C	H	N
78	CH ₃ CH ₂ CH ₂ -	H	CH ₃ CH ₂ CH ₂ -								
79	CH ₃	H	CH ₃ CH ₂ CH ₂ -								

Example No.	R ₁	R ₂	R ₃	m.p. or b.p. °C. @ m.m.	Molecular Formula	Required (%)			Found (%)		
						C	H	N	C	H	N
78	CH ₃ CH ₂ CH ₂ -	H	CH ₃ CH ₂ CH ₂ -								
79	CH ₃	H	CH ₃ CH ₂ CH ₂ -								

Example 80.

a. A mixture of 2.83 parts of 2,2,6,6-pentamethyl-4-piperidiny1 n-octanoate and 1.50 parts by volume of liquid ethylene oxide was charged into a 50 ml autoclave previously cooled to -50°C. A pressure of 100 atmospheres of nitrogen was applied and the autoclave heated at 200°C, with stirring, for three hours. Fractional distillation of the cooled reaction mixture yielded 2.30 parts of 1-(2'-hydroxyethyl)-2,2,6,6-tetramethyl-4-piperidiny1 n-octanoate having a boiling point of 186—7°C at 0.25 mm of Hg and the following elemental analysis by weight:

	Found	Required (for C ₁₁ H ₂₃ NO ₃)
Carbon	69.93%	69.68%
Hydrogen	11.09%	11.39%
Nitrogen	4.37%	4.23%

b. A mixture of 11.32 parts of 2,2,6,6-tetramethyl-4-piperidiny1 n-octanoate and 2.50 parts of 2-bromoethanol was stirred at 100°C for 65 hours. Petroleum ether (bp 40—60°C) was added to the cooled reaction mixture and the 2,2,6,6-tetramethyl-piperidiny1 4-n-octanoate hydrobromide formed during the reaction was filtered off. The petroleum ether solvent was removed by distillation under reduced pressure and the residue distilled to yield 1-(2'-hydroxyethyl)-2,2,6,6-tetramethyl-4-piperidiny1 n-octanoate having a boiling point of 176°C at 0.2 mm of Hg. This sample was identical to that prepared under Example 80a.

Example 81.

A mixture of 11.45 parts of 4-phenylcarbamoyloxy-2,2,6,6-tetramethylpiperidine and 60 parts of styrene oxide in 60 parts of n-hexanol was heated under reflux conditions for 18 hours. The n-hexanol solvent and unreacted styrene oxide were removed by distillation under reduced pressure to yield a pale yellow crystalline solid. Purification by trituration with hot petroleum ether (b.p. 60—80°C) yielded 4-phenylcarbamoyloxy-1-[2'-hydroxy-2-phenylethyl]-2,2,6,6-tetramethylpiperidine having a melting point of 186—7°C with the following elemental analysis by weight:

	Found	Required (for C ₂₄ H ₃₂ N ₂ O ₃)
Carbon	72.51%	72.70%
Hydrogen	7.92%	8.13%
Nitrogen	6.91%	7.06%

Example 82.

A mixture of 5.61 parts of 2,2,6,6-tetramethyl-4-piperidin-n-octanoate and 5.0 parts of propylene oxide were charged to an autoclave. A pressure of 100 atmospheres nitrogen was applied. The mixture was heated at 200°C for 3 hours. Fractionation under reduced pressure gave a main fraction b.p. 160—183°C at 0.1 mm. which after passing down an alumina type H column eluting with chloroform yielded a pale yellow semi-solid 1-(2'-hydroxypropyl)-2,2,6,6-tetramethyl-4-piperidin-n-octanoate having the following elemental analysis by weight:

	Found	Required (for C ₂₀ H ₃₃ NO ₃)
Carbon	70.20%	70.34%
Hydrogen	11.45%	11.51%
Nitrogen	3.89%	4.10%

Example 83.

A mixture of 3.27 parts of the product from Example 80 a., 0.60 parts of acetic acid and 0.1 parts of tetra-n-butyl titanate in 40 parts of xylene was heated under reflux conditions for 24 hours. The xylene solvent was removed by distillation under reduced pressure and the residue fractionally distilled to give 1-(2'-acetoxyethyl)-2,2,6,6-tetramethyl-4-piperidiny1-n-octanoate having a boiling point of 190—2°C at 1 mm Hg and the following elemental analysis by weight:

	Found	Required (for C ₂₁ H ₃₃ NO ₄)
Carbon	68.17%	68.25%
Hydrogen	10.65%	10.64%
Nitrogen	3.36%	3.79%

Example 84.

A mixture of 3.27 parts of the product from Example 83, 0.63 parts of methyl isocyanate and 0.1 parts of 1,4-diazabicyclo[2,2,2] octane in 30 parts of dry benzene was heated under reflux conditions for 24 hours. The benzene solvent was removed by distillation under reduced pressure and the residue crystallised from aqueous ethyl alcohol to give 1-(2'-methylcarbamoyloxyethyl)-2,2,6,6-tetramethyl-4-piperidinyl-n-octanoate having a melting point of 61—3°C and the following elemental analysis by weight:

	Found	Required (for $C_{21}H_{35}N_2O_4$)
Carbon	65.72%	65.59%
Hydrogen	10.37%	10.48%
Nitrogen	7.11%	7.28%

Example 85.

A mixture of 3.0 parts of the product from Example 81, 0.90 parts of phenyl isocyanate and 0.1 parts of 1,4-diazabicyclo[2,2,2]octane in 25 parts of dry benzene was heated under reflux conditions for 24 hours. The benzene solvent was removed by distillation under reduced pressure and the residue crystallised from petroleum ether (b.p. 60—80°C) to give 4-phenylcarbamoyloxy-1-[2'-(phenylcarbamoyloxy)-2'-phenylethyl]-2,2,6,6-tetramethylpiperidine having a melting point of 173°C and the following elemental analysis by weight:

	Found	Required (for $C_{31}H_{37}N_3O_4$)
Carbon	72.65%	72.21%
Hydrogen	7.22%	7.23%
Nitrogen	7.97%	8.15%

Example 86.

A mixture of 3.14 parts of 2,2,6,6-tetramethylpiperidin-4-ol and 3.50 parts of acetic anhydride was heated on a steam bath for one hour. After this time 20 parts of water were added and heating continued for a further one hour. The solution was carefully neutralised with a saturated solution of sodium bi-carbonate and then ether extracted. The combined ether extracts were washed twice with 5% sodium bi-carbonate solution and twice with brine, the ether solution was then dried over anhydrous magnesium sulphate and the ether removed by distillation under reduced pressure to yield 1-acetyl-2,2,6,6-tetramethylpiperidinyl-4-acetate having a melting point of 33—4°C and the following elemental analysis by weight:

	Found	Required (for $C_{13}H_{23}NO_3$)
Carbon	64.51%	64.73%
Hydrogen	9.69%	9.54%
Nitrogen	5.67%	5.81%

Example 87.

A mixture of 15.70 parts of 2,2,6,6-tetramethylpiperidin-4-ol, 22.80 parts of methyl isocyanate and 0.5 parts of 1,4-diazabicyclo[2,2,2]octane in 100 parts of dry benzene was heated under reflux conditions for 24 hours. The benzene solvent was removed by distillation under reduced pressure and 150 parts of water added to the residue which was stood overnight at room temperature. The solid formed was collected by filtration and dried to yield 19.60 parts of a white crystalline solid having a melting point of 167—8°C. This solid was shown to contain 80% of 4-methylcarbamoyloxy-1-methylcarbamoyl-2,2,6,6-tetramethylpiperidine from microanalysis and nuclear magnetic resonance spectra.

Example 88.

a. 2.65 parts of acrylonitrile was added dropwise with stirring to a solution of 8.55 parts of 1,2,2,6,6-pentamethylpiperidin-4-ol and 0.30 parts of 40% potassium hydroxide solution in 80 parts of benzene. Stirring was continued at room temperature for 16 hours after which time the solution was washed with water, dried and the benzene solvent removed by distillation under reduced pressure. Fractional distillation of the residue, under reduced pressure gave 1.70 parts of 4-(2'-cyanoethoxy)-1,2,2,6,6-pentamethylpiperidine having a boiling point of 105—6°C at 0.1 mm of Hg and the following elemental analysis by weight:

	Found	Required (for $C_{13}H_{21}N_2O$)
Carbon	69.27%	69.60%
Hydrogen	10.69%	10.78%
Nitrogen	12.40%	12.49%

b. To 51 parts of 1,2,2,6,6-pentamethylpiperidin-4-ol a solution of metallic sodium in two parts of tert.butanol was added. 52.5 parts of acrylonitrile was dropped in with rapid stirring. After standing for two days at room temperature the mixture was heated to 80°C for two hours and distilled under reduced pressure yielding 4-(2'-cyanoethoxy) 1,2,2,6,6-pentamethylpiperidine with a boiling point of 172—4°C at 17 mm Hg. This sample was identical to that prepared under Example 88a.

Example 89.

A mixture of 13.0 parts of 4-dodecyloxy-2,2,6,6-tetramethylpiperidine and 3.42 parts of benzyl bromide was heated at 100°C for 48 hours. Petroleum ether (b.p. 40—60°C) was added to the cooled reaction mixture and the 4-dodecyloxy-2,2,6,6-tetramethylpiperidine hydrobromide formed during the reaction was filtered off. The petroleum ether solvent was removed by distillation under reduced pressure and the residue fractionally distilled to give 4-dodecyloxy-1-benzyl-2,2,6,6-tetramethylpiperidine having a boiling point of 200°C at 0.5 m.m. of Hg. and the following elemental analysis by weight:

	Found	Required (for $C_{28}H_{40}NO$)
Carbon	80.67%	80.90%
Hydrogen	11.82%	11.88%
Nitrogen	3.34%	3.37%

Example 90.

A mixture of 4-benzyloxy-2,2,6,6-tetramethylpiperidine and 1.67 parts of ethyl α -bromoacetate in 30 parts of ethyl alcohol was heated under reflux conditions for 115 hours. The ethyl alcohol solvent was removed by distillation under reduced pressure and the residue fractionally distilled to give 4-benzyloxy-1-ethoxycarbonylmethyl-2,2,6,6-tetramethylpiperidine having a boiling point of 145—6°C at 0.2 m.m. of Hg. and the following elemental analysis by weight:

	Found	Required (for $C_{26}H_{31}NO_3$)
Carbon	71.62%	72.04%
Hydrogen	8.90%	9.37%
Nitrogen	3.94%	4.20%

Example 91.

A mixture of 25.7 parts of 1,2,2,6,6-pentamethylpiperidin-4-ol and 3.09 parts of boric acid in 100 parts of toluene was heated under reflux conditions with azeotropic removal of water for 24 hours. The toluene solvent was removed by distillation under reduced pressure to give tris-(1,2,2,6,6-pentamethyl-4-piperidinyl)borate having a melting point of 83—9°C and the following elemental analysis by weight:

	Found	Required (for $C_{30}H_{45}N_3O_3B$)
Carbon	68.85%	69.05%
Hydrogen	11.68%	11.59%
Nitrogen	7.76%	8.06%

Example 92.

30 parts of 1,2,2,6,6-pentamethylpiperidin-4-ol were dissolved in 250 parts of benzene and 4 parts of sodium added. The solution was heated overnight at reflux temperature and then cooled. 38 parts of 2-phenoxyethanol tosylate were added dropwise and the solution heated at reflux for 5 hours. On cooling the precipitate was filtered off and the filtrate evaporated *in vacuo*. Treatment of the residue with dilute hydrochloric acid and then basification with dilute sodium hydroxide to a pH 10 was followed by extraction with ether. Evaporation afforded a pale yellow oil which was chromatographed on alumina to give 4-(2'-phenoxyethoxy)-1,2,2,6,6-pentamethylpiperidine as a colourless oil which gave the following elemental analysis by weight:

	Found	Required (for $C_{15}H_{29}NO_2$)
Carbon	72.49%	74.18%
Hydrogen	9.89%	10.03%
Nitrogen	4.91%	4.81%

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Example 93.

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A mixture of 9.87 parts of 4-allyloxy-2,2,6,6-tetramethylpiperidine and 3.03 parts of allyl bromide was heated at 90°C for 96 hours. Ether was added to the cooled reaction mixture and the 4-allyloxy-2,2,6,6-tetramethylpiperidine hydrobromide formed during the reaction was filtered off. The ether solvent was removed by distillation under reduced pressure and the residue purified by chromatography to give 4-allyloxy-1-allyl-2,2,6,6-tetramethylpiperidine.

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Examples 94—116.

Testing in polypropylene film

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38 parts of polypropylene were homogenised with 0.076 parts of n-octadecyl- β -(4'-hydroxy-3',5'-t-butylphenyl) propionate in a kneading machine over a period of 3 minutes at 200°C. 0.19 parts of the product of Example 13 was then added and homogenisation continued for another 7 minutes.

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This composition was compression moulded into films of 0.1 mm thickness at 260°C for 6 minutes and the films so obtained were then quenched in cold water.

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A section measuring 44 × 100 mm was separated from the 0.1 mm annealed polypropylene foil and exposed to light irradiation in a fadometer device consisting of a circular bank of 28 alternate sunlight and blacklight lamps. The sunlight lamps were 2 feet long, 20-watt fluorescent lamps characterised by a peak emission of 3,100 Angstrom units; the blacklight lamps were 2 feet long, 20-watt ultraviolet lamps characterised by a peak emission of 3,500 Angstrom units. The sample was rotated concentrically about the bank of lamps so that the radiation therefrom was uniformly distributed over the section under test.

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The exposed sample was examined periodically and portions of it tested for the percent/elongation at break, the time at which the sample reached 50% of the initial elongation at break was noted.

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Similar tests were carried out on polypropylene samples containing, respectively, no light stabiliser, 0.19 part of a known stabiliser 0.19 part of a stabiliser falling within the scope of German Patent Specification No. 1,929,928 and 0.19 part of the product of further Examples of the present invention. Correlation of the use Examples with the preparative Examples is shown in the Table.

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TABLE

Example	Additive	Factor
		Time to 50% of initial elongation at break (additive)
—	none	1.0
—	2/(2'-hydroxy-3',5'-di-t-butylphenyl)-5-chlorobenzotriazole	3.2
—	4-phenylcarbamoyloxy-2,2,6,6-tetramethylpiperidine	1.8
—	1,6-bis[4'-carbamoyloxy-2',2',6',6'-tetramethylpiperidine]hexane	2.4
—	2,2,6,6-tetramethylpiperidinyl-4 benzoate	2.6
—	bis(2,2,6,6-tetramethyl-4-piperidinyl) sebacate	4.7
94	1,2,2,6,6-pentamethylpiperidinyl-4 phenylacetate (Ex. 11)	5.2
95	bis(1,2,2,6,6-pentamethyl-4-piperidinyl) terephthalate (Ex. 37)	5.3
96	1,2,2,6,6-pentamethylpiperidinyl-4 (p-methoxybenzoate) (Ex. 13)	5.3
97	1,2,2,6,6-pentamethylpiperidinyl-4 (1'-naphthoate) (Ex. 38)	5.4
98	1,2,2,6,6-pentamethylpiperidinyl-4 octanoate (Ex. 21)	6.2
99	1,2,2,6,6-pentamethylpiperidinyl-4 isobutyrate (Ex. 5)	6.2
100	bis(1,2,2,6,6-pentamethyl-4-piperidinyl) sebacate (Ex. 1)	8.0

TABLE (Continued)

Example	Additive	Factor
		Time to 50% of initial elongation at break (additive)
101	2,4-bis(4'-carbamoxyloxy-1',2',6',6'-pentamethylpiperidine)toluene (Ex. 55)	5.2
102	4- <i>p</i> -tolylcarbamoxyloxy-1,2,2,6,6-pentamethylpiperidine (Ex. 51)	5.2
103	4-allylcarbamoxyloxy-1,2,2,6,6-pentamethylpiperidine (Ex. 48)	5.5
104	4-phenylcarbamoxyloxy-1,2,2,6,6-pentamethylpiperidine (Ex. 50)	5.6
105	4-methylcarbamoxyloxy-1,2,2,6,6-pentamethylpiperidine (Ex. 45)	5.8
106	1,6-bis-[4'-carbamoxyloxy-1',2',6',6'-pentamethylpiperidine]hexane (Ex. 54)	9.2
107	bis-(1-benzyl-2,2,6,6-tetramethyl-4-piperidyl)sebacate (Ex. 63)	5.0
108	1-ethoxycarbonylmethyl-2,2,6,6-tetramethylpiperidyl-4-(<i>p</i> -methoxy-benzoate)(Ex. 64)	5.1
109	1-benzyl-2,2,6,6-tetramethylpiperidyl-4-(2'-ethylhexanoate) (Ex. 24)	5.2
110	1-(<i>n</i> -dodecyl)-2,2,6,6-tetramethylpiperidyl-4-octanoate (Ex. 27)	5.2
111	1-(2'-hydroxyethyl)-2,2,6,6-tetramethylpiperidyl-4-octanoate (Ex. 80)	5.8
112	1-(<i>n</i> -propyl)-2,2,6,6-tetramethylpiperidyl-4-octanoate (Ex. 77)	6.0
113	4-(<i>n</i> -dodecyl)-1,2,2,6,6-pentamethylpiperidine (Ex. 73)	5.5
114	4-(2'-cyanoethoxy)-1,2,2,6,6-pentamethylpiperidine (Ex. 88)	>6.0
115	1,4-bis(1',2',2',6',6'-pentamethyl-4'-piperidinyloxy)butane (Ex. 74)	>6.0
116	Tris-(1,2,2,6,6-pentamethyl-4-piperidyl)borate (Ex. 91)	5.0

Examples 117 to 119.

The procedure described in Examples 94—116 was repeated except that 0.25% by weight of the light stabiliser under test was used, and, instead of polypropylene, a low-density polyethylene was employed as substrate.

The processing was conducted at 180°C and the compositions were compression-moulded into 1 mm. thick plaques at 150°C.

The plaques were stored at 20°C and were periodically examined visually for the first sign of exudation.

The results obtained are summarised in the following Table which also includes data relating to comparative experiments (known light stabilisers added).

TABLE

Example	Light stabiliser added	Time to exudation (days)
—	2,2,6,6-tetramethylpiperidiny-4-stearate	15
—	bis-(2,2,6,6-tetramethyl-4-piperidiny)sebacate	20
—	4-stearylcarbamoxyloxy-2,2,6,6-tetramethylpiperidine	13
117	1,2,2,6,6-pentamethylpiperidiny-4-stearate	>50
118	bis-(1,2,2,6,6-pentamethyl-4-piperidiny)sebacate	>50
119	4-stearylcarbamoxyloxy-1,2,2,6,6-pentamethylpiperidine	>50

Examples 120 to 122.

The procedure described in Examples 117 to 119 was repeated except that the compression moulding was carried out at 200°C and the substrate used was high-density polyethylene.

The results obtained are set out in the following Table, which also contains data relating to comparative experiments (using a known light stabiliser).

TABLE

Example	Light Stabiliser	Time to exudation (days)
—	2,2,6,6-tetramethylpiperidiny-4-stearate	40
120	1,2,2,6,6-pentamethylpiperidiny-4-stearate	>75
121	4-stearylcarbamoxyloxy-1,2,2,6,6-tetramethylpiperidine	>75
122	1-(n-dodecyl)-2,2,6,6-tetramethylpiperidiny-4-octanoate	>75

Examples 123 to 128.

100 Parts of crystal polystyrene pellets were dry blended with 0.25 part of 1,2,2,6,6-pentamethylpiperidiny-4-stearate, and the dry blend was homogenised by extrusion. The extrudate was chopped into pellets and the stabilised pellets so obtained were injection moulded to form plaques 2 mm. thick. These plaques were exposed for 3000 hours in a "Xenotest 150" exposure unit, and any yellowing of the plaques was measured by determining the yellowness factor by means of the following equation:—

$$\text{yellowness factor} = \frac{\Delta T_{(420)} - \Delta T_{(680)}}{T_{(560)}} \times 100$$

wherein the ΔT values represent the transmission loss of the sample at wavelengths of 420 nm. and 680 nm. respectively, after exposure in the Xenotest unit, and $T_{(560)}$ represents the transmission value of an unexposed sample at a wavelength of 560 nm. ("Xenotest" is a Trade Mark).

5 The results obtained, as well as the results relating to a control experiment and other compositions of this invention are recorded in the following Table. 5

TABLE

Example	Light stabiliser	Yellowing factor after 3000 hours
—	none	35.0
123	1,2,2,6,6-pentamethylpiperidiny-4-stearate	10.0
124	1-benzyl-2,2,6,6-tetramethylpiperidiny-4-(2'-ethylhexanoate)	9.8
125	1,2,2,6,6-pentamethylpiperidiny-4-(n-octanoate)	9.5
126	4-(2'-cyanoethoxy)-1,2,2,6,6-pentamethylpiperidine	8.0
127	4-stearylcarbamoyloxy-1,2,2,6,6-pentamethylpiperidine	7.5
128	bis-(1,2,2,6,6-pentamethyl-4-piperidiny)sebacate	6.6

Examples 129 to 132.

10 25 parts by weight of a polyester-based film-forming polyurethane were dissolved in 75 parts by weight of a 1:1 mixture (by volume) of dimethylformamide and acetone, and 1% by weight of 4-(2'-cyanoethoxy)-1,2,2,6,6-pentamethylpiperidine was added. 10

The clear and homogeneous solution was drawn out on a glass plate to a film of 400—500 μ thickness, which was then dried as follows:

15 at 50°C for 4 minutes
at 140°C for 6 minutes 15

The final thickness of the film was 80—100 μ .

20 The dried film samples were removed from the glass plate, mounted on white cardboard and exposed in a "Xenotest 450" exposure unit, one half of the exposed sample being covered to facilitate subsequent visual estimation of yellowing due to exposure. The sample was controlled and rated visually at intervals of 100 hours. 20

The data obtained are set out in the following Table which also includes data relating to a control experiment (no added light stabiliser) and to other experiments using stabilisers of this invention. 1% by weight of stabilizer is used in each Example.

TABLE

Example	Light Stabiliser	Time to onset of yellowing (hours)
—	none	<100
129	4-(2'-cyanoethoxy)-1,2,2,6,6-pentamethylpiperidine	200
130	1,2,2,6,6-pentamethylpiperidiny-4-octanoate	300
131	bis-(1,2,2,6,6-pentamethyl-4-piperidiny)sebacate	300
132	4-phenylcarbamoyloxy-1-n-propyl-2,2,6,6-tetramethyl-piperidine	400

Examples 133—135.

1000 Parts by weight of unstabilised polypropylene powder were thoroughly dry-blended with 1 part by weight of n-octadecyl- β -(4'-hydroxy-3',5'-di-t-butylphenyl) propionate and 2 parts by weight of 1,2,2,6,6-pentamethyl-4-piperidinyl-(3',5'-di-t-butyl-4'-hydroxy) benzoate. The dry-blend was extruded at cylinder temperatures of from 180° to 220°C, and the resulting strand was granulated. The stabilised formulation so obtained was melt-spun and stretched under the following conditions:

Extruder temperatures : 230/265/275°C.
 Melt temperature at the die : 270°C
 Spinning speed : 400 m./minute
 Stretching Ratio : 1:5
 Titer of Multifilament : 130/137 denier
 Tensile Strength : 6 g./denier

The multifilament obtained was mounted on a sample holder of a Xenotest 150 apparatus (Quarzlampen GmbH) using white cardboard as backing. In intervals of 200 hours of exposure time, 5 fibre samples are measured for their retained tensile strength. The data obtained are plotted against exposure time and the exposure time (T) to give 50% loss of original tensile strength is derived from the graph. This value is taken as the failure time.

The results obtained, as well as the results relating to a control experiment and other compositions of this invention are recorded in the following Table.

TABLE

Example No.	Light Stabiliser	Time (T) to 50% retained tensile strength	Factor $\frac{T_{\text{stabiliser}}}{T_{\text{control}}}$
none	none	430	1.0
	2-(2'-hydroxy-3",5"-di-t-butylphenyl)-5-chlorobenzotriazole	530	1.2
133	1,2,2,6,6-Pentamethyl-4-piperidinyl-(3',5'-di-t-butyl-4'-hydroxy benzoate)	1,400	3.3
134	1,2,2,6,6-Pentamethyl-4-piperidinyl- β -(3',5'-di-t-butyl-4'-hydroxyphenyl)-propionate	1,600	3.7
135	Bis(1,2,2,6,6-pentamethyl-4-piperidinyl) sebacate	2,600	6.0

Examples 136 to 144.

The procedure described in Examples 94 to 116 was repeated except that the annealed polypropylene specimens were exposed to light irradiation in a Xenotest 450 exposure unit rather than in the fadometer device.

The results obtained are summarised in the following Table which also includes data relating to a control experiment (no added light stabiliser) and a comparative experiment (a known light stabiliser added). The "time to failure" in the Table refers to the time to reach 50% of the elongation at break.

TABLE

Example	Light Stabiliser	Time to Failure (hours)
—	none (control)	800
—	2-(2'-hydroxy-3',5'-di-t-butylphenyl)-5-chlorobenzotriazole	1630
136	bis-(1,2,2,6,6-pentamethyl-4-piperidinyl)sebacate	>9000
137	1,2,2,6,6-pentamethylpiperidinyl-4-β-(3',5'-di-t-butyl-4'-hydroxyphenyl) propionate	10,000
138	1,2,2,6,6-pentamethylpiperidinyl-4-(3',5'-di-t-butyl-4'-hydroxy benzoate)	>8600
139	1,2,2,6,6-pentamethylpiperidinyl-4-octanoate	6500
140	4-phenylcarbamoyloxy-1,2,2,6,6-pentamethyl piperidine	>7000
141	4-methylcarbamoyloxy-1,2,2,6,6-pentamethyl-piperidine	6000
142	1,2,2,6,6-pentamethylpiperidinyl-4-cyclohexane-carboxylate	>6000
143	1,2,2,6,6-pentamethylpiperidinyl-4-stearate	>6000
144	1,2,2,6,6-pentamethylpiperidinyl-4-benzoate	>5000

Examples 145—150.

5 100 Parts by weight of nylon-6 pellets containing 1.8 parts by weight of TiO₂ were dry-blended with 0.5 part of 4-benzyloxy-1,2,2,6,6-pentamethylpiperidine. The resulting mixture was melt-spun directly into monofilaments of 20 denier. The monofilaments were mounted on white cardboard without tension and were exposed to light radiation in a Xenotest 450 exposure unit.

10 After 500, 1,000, 1,500 and 2000 hours of exposure time respectively, 5 fibre samples of each formulation and time interval were tested for tensile strength. The arithmetic mean percentage values of residual tensile strength were plotted as a function of exposure time. The failure points — time to 50% loss of original tensile strength — were obtained from these graphs.

TABLE

Example	Light Stabiliser	Time to 50% loss of original tensile strength (hours)
—	none (control)	475
145	4-benzyloxy-1,2,2,6,6-pentamethylpiperidine	1420
146	bis-(1,2,2,6,6-pentamethyl-4-piperidinyl) sebacate	1600
147	1,2,2,6,6-pentamethylpiperidinyl-4 octanoate	1450
148	1-phenylcarbamoyloxy-1,2,2,6,6-pentamethyl piperidine	1450
149	1,6-bis-[4'-carbamoyloxy-1',2',2',6',6'-pentamethylpiperidine]hexane	1500
150	1,4-bis-[1',2',2',2',6',6'-pentamethyl-4'-piperidinyl]oxybutane	1600



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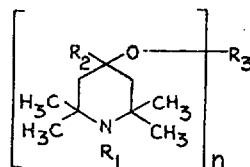
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WHAT WE CLAIM IS:—

1. A compound having the formula:—

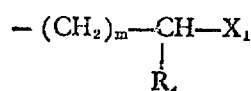


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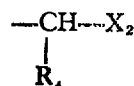
and their salts

5 wherein n is 1, 2, 3 or 4;

R_1 is a monovalent residue and is an alkyl residue having from 1 to 20 carbon atoms, an alkenyl or alkynyl residue having from 3 to 20 carbon atoms, an aralkyl residue having from 7 to 12 carbon atoms, or a residue having the formula:—



10 or

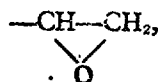


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wherein m is 1, 2 or 3,

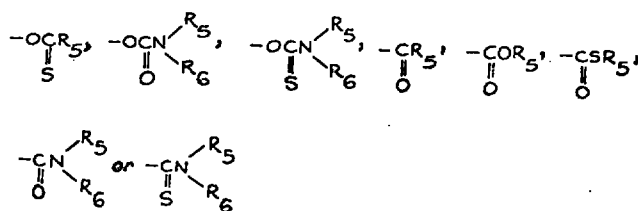
 R_4 is a hydrogen or a methyl or phenyl residue, X_2 is halogen, cyano,

15



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---COR_5 , ---CO.OR_5 , ---CO.SR_5 , or $\text{---CONR}_5\text{R}_6$ and X_1 is hydroxyl, halogen, cyano, ---OR_5 ,



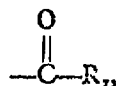
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wherein R_5 is an alkyl residue having from 1 to 20 carbon atoms, an alkenyl residue having from 2 to 20 carbon atoms, a cycloalkyl residue having from 5 to 12 carbon atoms, an aryl residue having from 6 to 11 carbon atoms or an aralkyl residue having 7—14 carbon atoms, or when R_5 is joined to a nitrogen atom, also hydrogen and R_6 is hydrogen or an alkyl residue having from 1 to 4 carbon atoms, or

20

R_5 and R_6 together with the nitrogen atom to which they are bound form a 5- or 6-membered ring which contains no other heteroatoms or contains one or more other heteroatoms, or

25

 R_1 is an acyl groupwherein R_7 is hydrogen, an unsubstituted alkyl or substituted alkyl residue having from



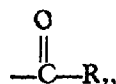
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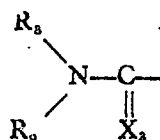
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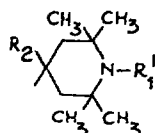
when R_5 is joined to a nitrogen atom, also hydrogen and R_6 is hydrogen or an alkyl residue having from 1 to 4 carbon atoms, or R_5 and R_6 together with the nitrogen atom to which they are bound form a 5- or 6-membered ring which contains no other heteroatoms or contains one or more other heteroatoms, or R_5 is an acyl group



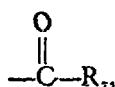
wherein R_7 is hydrogen, an unsubstituted alkyl or substituted alkyl residue having from 1 to 20 carbon atoms, an alkenyl or alkynyl residue having from 2 to 20 carbon atoms, a cycloaliphatic residue having from 5 to 12 carbon atoms, an araliphatic residue having from 7 to 14 carbon atoms, an aromatic residue having from 6 to 20 carbon atoms or an heterocyclic residue, or R_8 is a carbamoyl or thiocarbamoyl residue having the formula:—



wherein X_3 is —O— or —S—, R_8 is hydrogen or an alkyl residue having from 1 to 4 carbon atoms, and R_9 is hydrogen, an alkyl residue having from 1 to 20 carbon atoms, an alkenyl residue having from 3 to 20 carbon atoms, a cycloalkyl residue having from 5 to 12 carbon atoms; or R_3 represents a monovalent group obtained by removing a hydroxyl group from a sulphinic acid, a sulphonic acid, a phosphorus containing acid or sulphuric acid or a boric acid, or R_3 is an aryl residue or a residue having the formula:—



wherein R_1' is hydrogen or R_1' has the same significance as R_1 ; when n is 2, R_3 is a divalent residue and is an alkylene residue having from 1 to 20 carbon atoms, an alkenylene residue having from 2 to 20 carbon atoms, an alkynylene residue having from 2 to 20 carbon atoms, a cycloalkylidene residue having from 5 to 12 carbon atoms, an arylene residue having 6 to 14 carbon atoms, an aralkylene residue having from 8 to 14 carbon atoms or an aliphatic, aromatic or heterocyclic diacyl residue, the group —CO— or —CO.CO—, an aliphatic or aromatic dicarbamoyl or dithiocarbamoyl, sulphinyl or sulphonyl residue or a divalent residue obtained by removing two hydroxyl groups from a disulphonic acid, a phosphorus containing acid or sulphuric or a boric acid; when n is 3, R_3 is a trivalent residue and is an alkane-triyl, an arenetriyl or an arene-triyl-trialkylene residue, an aliphatic or aromatic triacyl residue or a triacyl residue derived from *o*-phosphoric, *o*-phosphorous or *o*-boric acid; and when n is 4, R_3 is a tetravalent residue and is an alkane-tetrayl residue or a tetraacyl residue derived from an aliphatic or aromatic tetracarboxylic acid or from *o*-silicic acid; provided that when R_3 represents an acyl group

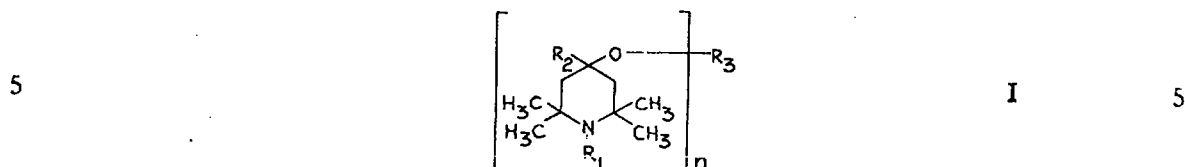


an aliphatic, aromatic or heterocyclic diacyl residue, the group —CO— or —CO.CO—, an aliphatic or aromatic triacyl or tetraacyl residue, a triacyl residue derived from *o*-phosphonic, *o*-phosphorous or *o*-boric acid or a tetraacyl residue derived from *o*-silicic



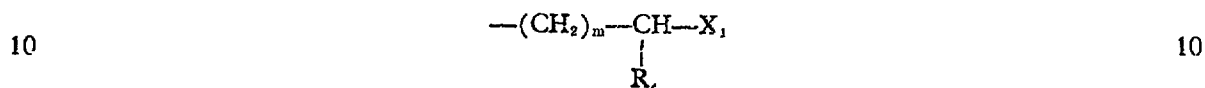
acid, the number of carbon atoms in the alkyl group designated by R_1 is from 5 to 20, as well as, when n is 2, 3 or 4, partial ethers, esters and carbamoyloxy and thio-carbamoyloxy compounds related to the fully reacted compounds of formula 1.

2. A compound as claimed in claim 1 having the formula:--

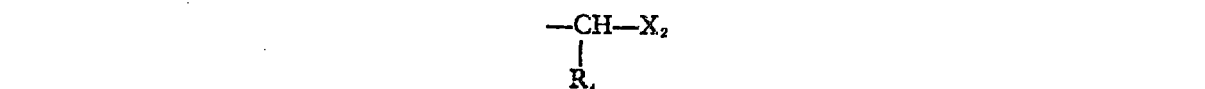


and their salts wherein n is 1, 2, 3 or 4;

R_1 is a monovalent residue and is an alkyl residue having from 1 to 20 carbon atoms, an alkenyl or alkynyl residue having from 3 to 20 carbon atoms, an aralkyl residue having from 7 to 9 carbon atoms, or a residue having the formula:--



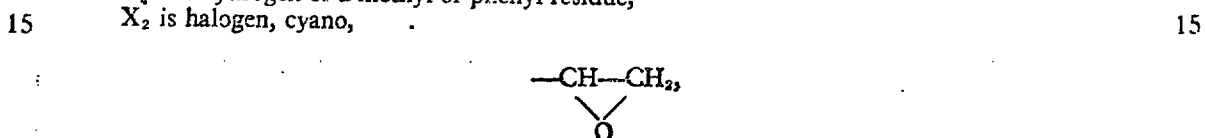
or



wherein m is 1, 2 or 3,

R_4 is a hydrogen or a methyl or phenyl residue,

X_2 is halogen, cyano,



—COR₅, —CO.OR₅, —CO.SR₅, or —CONR₅R₆ and

X_1 is hydroxyl, halogen, cyano, —OR₅, —O—CO.R₅, —OCSR₅, —O.CO.NR₅R₆,

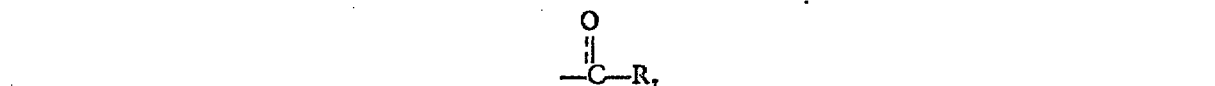
—CO.R₅, —CO.OR₅, —CO.SR₅, —CO.NR₅R₆ or —CS.NR₅R₆,

20 wherein R_5 is an alkyl residue having from 1 to 20 carbon atoms, an alkenyl residue having from 2 to 20 carbon atoms, a cycloalkyl residue having from 5 to 12 carbon atoms, an aryl residue having from 6 to 11 carbon atoms, or an aralkyl residue having from 6 to 11 carbon atoms, or an aralkyl residue having 7 to 11 carbon atoms, or, when

R_5 is joined to a nitrogen atom, also hydrogen and

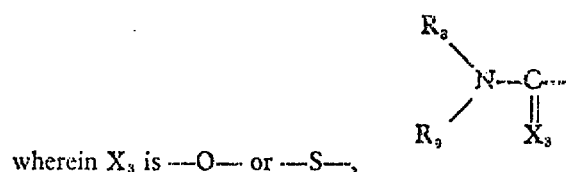
25 R_6 is hydrogen or an alkyl residue having from 1 to 4 carbon atoms, or

R_5 and R_6 together with the nitrogen atom to which they are bound form a 5- or 6-membered ring which contains no other heteroatom or contains one or more other heteroatoms or R_1 is an acyl group



30 wherein R_7 is an unsubstituted alkyl or substituted alkyl residue having from 1 to 20 carbon atoms, an alkenyl or alkynyl residue having from 2 to 20 carbon atoms, a cycloaliphatic residue having from 5 to 12 carbon atoms, an araliphatic residue having from 7 to 14 carbon atoms, an aromatic residue having from 6 to 12 carbon atoms or an heterocyclic residue, or

35 R_1 is a carbamoyl or thiocarbamoyl residue having the formula:

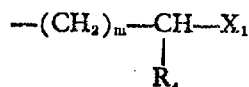




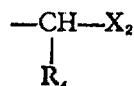
R_a is hydrogen or an alkyl residue having from 1 to 4 carbon atoms, and R_b is hydrogen, an alkyl residue having from 1 to 20 carbon atoms, an alkenyl residue having from 3 to 20 carbon atoms, a cycloalkyl residue having from 5 to 12 carbon atoms or an unsubstituted aryl or substituted aryl residue having from 6 to 12 carbon atoms;

R_2 is an alkyl residue having from 1 to 4 carbon atoms, an alkenyl or alkynyl residue having from 3 to 20 carbon atoms, a cycloalkyl residue having from 5 to 12 carbon atoms, an aryl residue having from 6 to 10 carbon atoms or an aralkyl residue having from 7 to 9 carbon atoms or hydrogen; and

when n is 1, R_3 is a monovalent radical and is an alkyl residue having from 1 to 20 carbon atoms, a cycloalkyl residue having from 5 to 12 carbon atoms, an alkenyl or alkynyl residue having from 3 to 20 carbon atoms, an aralkyl residue having from 7 to 9 carbon atoms, or a residue having the formula:—



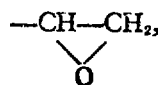
or



wherein m is 1, 2 or 3,

R_4 is a hydrogen or a methyl or phenyl residue,

X_2 is halogen, cyano,



—COR₅, —CO.OP₃, —CO—SR₅ or —CONR₅R₆ and

X_1 is hydroxyl, halogen, cyano, —OR₅, —C—CO.R₅, —OCSR₅, —O.CO.NR₅R₆, —CO.R₅, —CO.OR₅, —CO.SR₅, —CO.NR₅R₆ or —CS.NR₅R₆,

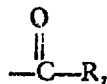
wherein R_5 is an alkyl residue having from 1 to 20 carbon atoms, an alkenyl residue having from 2 to 20 carbon atoms, a cycloalkyl residue having from 5 to 12 carbon atoms, an aryl residue having from 6 to 11 carbon atoms, or an aralkyl residue having from 7 to 11 carbon atoms, or,

when R_5 is joined to a nitrogen atom, also hydrogen and

R_6 is hydrogen or an alkyl residue having from 1 to 4 carbon atoms, or

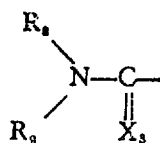
R_5 and R_6 together with the nitrogen atom to which they are bound form a 5- or 6-membered ring which contains no other heteroatoms or contains one or more heteroatoms or

R_3 is an acyl group



wherein R_7 is an unsubstituted alkyl or substituted alkyl residue having from 1 to 20 carbon atoms, an alkenyl or alkynyl residue having from 2 to 20 carbon atoms, a cycloaliphatic residue having from 5 to 12 carbon atoms, an araliphatic residue having from 7 to 14 carbon atoms, an aromatic residue having from 6 to 12 carbon atoms or an heterocyclic residue, or

R_3 is a carbamoyl or thiocarbamoyl residue having the formula:



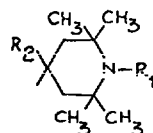
wherein X_3 is —O— or —S—,

R_8 is hydrogen or an alkyl residue having from 1 to 4 carbon atoms, and

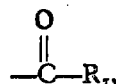


R_2 is hydrogen, an alkyl residue having from 1 to 20 carbon atoms, an alkenyl residue having from 3 to 20 carbon atoms, a cycloalkyl residue having from 5 to 12 carbon atoms or an unsubstituted aryl or substituted aryl residue having from 6 to 12 carbon atoms;

- 5 with the proviso that only one of R_1 and R_2 can represent an unsaturated acyl group or R_1 represents a monovalent group obtained by removing a hydroxyl group from a sulphonic acid, a sulphonic acid, a phosphorus containing acid or sulphuric or a boric acid R_2 is an aryl residue or a residue having the formula:



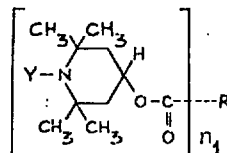
- 10 wherein R_1' is hydrogen or R_1' has the same significance as R_1 ;
when n is 2, R_n is a divalent residue and is an alkylene residue having from 1 to 20 carbon atoms, an alkenylene residue having from 3 to 20 carbon atoms, an alkynylene residue having from 3 to 20 carbon atoms, an arylene residue having from 6 to 14 carbon atoms, an aralkylene residue having from 8 to 14 carbon atoms
15 or an aliphatic, aromatic or heterocyclic diacyl residue, an aliphatic or aromatic dicarbonyl or dithiocarbonyl, a carbonyl, sulphinyl or sulphonyl residue or a divalent residue obtained by removing two hydroxyl groups from a disulphonic acid, a phosphorus containing acid or sulphuric or a boric acid;
20 when n is 3, R_n is a trivalent residue and is an aliphatic or aromatic triacyl residue or a triacyl residue derived from *o*-phosphoric, *o*-phosphorous or *o*-boric acid or an alkanetriyl, an arenetriyl, or arenetriyltrialkylene group; and
when n is 4, R_n is a tetravalent residue and is a tetraacyl residue derived from an aliphatic or aromatic tetracarboxylic acid or from *o*-silicic acid or an alkanetetrayl group;
25 provided that when R_2 represents an acyl group



- an aliphatic, aromatic or heterocyclic diacyl residue, the group $-\text{CO}-$ or $-\text{CO}\cdot\text{CO}-$,
an aliphatic or aromatic triacyl or tetraacyl residue, a triacyl residue derived from *o*-phosphonic, *o*-phosphorous or *o*-boric acid or a tetraacyl residue derived from *o*-silicic
30 acid, the number of carbon atoms in the alkyl group designated by R_1 is from 5 to 20.
as well as partial ethers, esters and carbamoyloxy and thiocarbamoyloxy compounds related to the fully reacted compounds of formula 1.

3. A compound as claimed in claim 2 wherein R_2 is hydrogen, methyl, ethyl, i-propyl, n-propyl, n-butyl, n-pentyl, n-octyl, n-decyl, n-dodecyl, n-octadecyl, n-eicosyl, allyl, methallyl, undecenyl, cyclopentyl, cyclohexyl, methylcyclohexyl, cyclododecyl, 1- or 2-perhydronaphthyl, adamantyl, benzyl, β -phenylethyl, 1- or 2-naphthylmethyl, phenyl, *o*-, *m*- or *p*-tolyl, 2,4- or 2,6-xylyl or α - or β -naphthyl.

4. Compounds as claimed in claim 1 having the formula:



Ia

- 40 and their salts,
wherein Y is an alkyl group having from 5 to 20 carbon atoms, alkenyl having from 3 to 20 carbon atoms or an aralkyl residue having from 7 to 9 carbon atoms, and n_1 is 1 or 2;
when n_1 is 1, R is hydrogen or a monovalent aliphatic residue having from 1 to 20 carbon atoms, a monovalent alicyclic residue having from 5 to 12 carbon atoms, or a monovalent aromatic residue having from 6 to 20 carbon atoms; and
45 when n_1 is 2, R is a divalent aliphatic residue having from 1 to 20 carbon atoms, or a divalent alicyclic residue having from 5 to 12 carbon atoms, a divalent aromatic residue having from 6 to 14 carbon atoms.



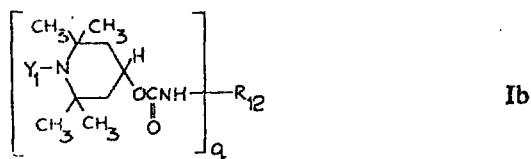
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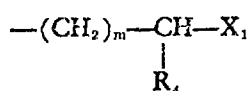
5. A compound as claimed in claim 1 having the formula:



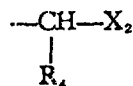
and its salts

wherein Y_1 is an alkyl residue having from 1 to 12 carbon atoms, an alkenyl residue having from 3 to 12 carbon atoms or an aralkyl residue having from 7 to 12 carbon atoms and

R_{12} is hydrogen or an alkyl or alkylene residue containing up to 20 carbon atoms, a substituted alkyl having the formula



or



wherein m is 1, 2 or 3,

R_4 is hydrogen or methyl,

X_1 is halogen or methoxy and

X_2 is halogen or

R_{12} is an alkenyl or alkenylene having up to 20 carbon atoms, a cycloalkyl or cycloalkylidene having 5 to 12 carbon atoms, an aryl or arylene having 6 to 12 carbon atoms and

q is 1 or 2.

6. A compound as claimed in claim 5

wherein when q is 1, R_{12} is hydrogen or an alkyl residue having 1 to 20 carbon atoms, or a cycloalkyl residue having 5 to 12 carbon atoms or an aromatic residue having 6 to 12 carbon atoms or

when q is 2, R_{12} is an alkylene residue having up to 20 carbon atoms, or an alicyclic residue having 5 to 15 carbon atoms or an aromatic residue having 6 to 12 carbon atoms.

7. A compound as claimed in claim 5 wherein

when n is 1, R_{12} is hydrogen, methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, secbutyl, *t*-butyl, *n*-pentyl, 2-ethylpropyl, 2-methylbutyl, *n*-hexyl, 2-methylpentyl, *n*-heptyl, 2-ethylpentyl, *n*-octyl, 2-ethylhexyl, 2,2,4-trimethylpentyl, *n*-decyl, *n*-dodecyl, *n*-tetradecyl, *n*-octadecyl, eicosyl, mesityl, allyl, oleyl, cyclopentyl, cyclohexyl, methylcyclohexyl, *t*-butylcyclohexyl, *t*-octylcyclohexyl, cyclododecyl, 1- and 2-perhydronaphthyl, adamantyl, cyclopentylmethyl, cyclohexylmethyl, β -cyclohexylethyl, benzyl, β -phenylethyl, 1- and 2-naphthylmethyl, β -[1- and 2-naphthyl]ethyl, phenyl, *o*-, *m*- and *p*-tolyl, 2,4- and 2,6-xylol, *p*-chlorophenyl, 3-chloro-*p*-tolyl, *o*-ethylphenyl, *p*-*t*-butylphenyl, 2,3- and 2,5-di-chlorophenyl, α - and β -naphthyl, and

when q is 2, R_{12} is methylene, 1,2-ethylene, 1,4-*n*-butylene, 1,6-*n*-hexylene, 1,8-*n*-octylene, 2,4,4-trimethyl-1,6-hexylene, 1,10-*n*-decylene, 1,2-eicosylene, 1,2-eicosenylene, 1,3- and 1,4-cyclohexylene, 1,3- and 1,4-phenylene, 2,4-tolylene, 1,5-naphthylene, 4,4'-diphenylene, 4,4'-diphenylmethylene, 3,3'-dimethyl-4,4'-diphenylene, 3,3'-dimethyl-4,4'-diphenylmethylene.

8. A compound according to claim 1 wherein R_1 is an alkyl residue having from 1 to 20 carbon atoms.

9. A compound according to claim 1 wherein R_1 is an alkyl residue having from 1 to 12 carbon atoms.

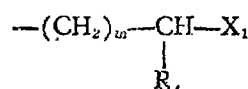
10. A compound according to claim 1 wherein R_1 is an alkenyl residue having from 3 to 20 carbon atoms.

11. A compound according to claim 1 wherein R_1 is an alkynyl residue having from 3 to 20 carbon atoms.

12. A compound according to claim 1 wherein R_1 is an aralkyl residue having from 7 to 12 carbon atoms.



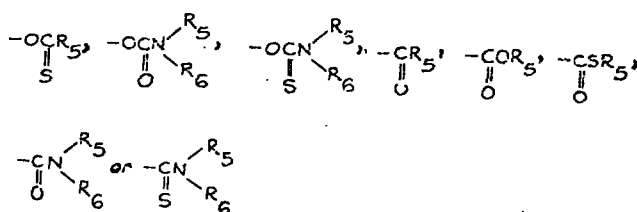
13. A compound according to claim 1 wherein R_1 is a residue having the formula:



wherein m is 1, 2 or 3,

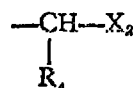
R_4 is a hydrogen, or a methyl or phenyl residue,

X_1 is hydroxyl, halogen, cyano, ---OR_5 ,



wherein R_5 is an alkyl residue having from 1 to 20 carbon atoms, an alkenyl residue having from 2 to 20 carbon atoms, a cycloalkyl residue having from 5 to 12 carbon atoms, an aryl residue having from 6 to 11 carbon atoms, or an aralkyl residue having from 7 to 14 carbon atoms, or, when R_5 is joined to a nitrogen atom, also hydrogen and R_6 is hydrogen or an alkyl residue having from 1 to 4 carbon atoms, or R_5 and R_6 together with the nitrogen atom to which they are bound form a 5- or 6-membered ring which contains no other heteroatoms or contains one or more other heteroatoms.

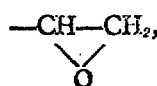
14. A compound according to claim 1 wherein R_1 is a residue having the formula:



wherein m is 1, 2 or 3,

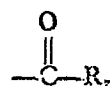
R_4 is a hydrogen, or a methyl or phenyl residue,

X_2 is halogen, cyano,



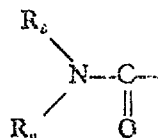
---COR_5 , ---CO.OR_5 , ---CO.SR_5 or $\text{---CONR}_5\text{R}_6$ wherein R_5 is an alkyl residue having from 1 to 20 carbon atoms, an alkenyl residue having from 2 to 20 carbon atoms, a cycloalkyl residue having from 5 to 12 carbon atoms, an aryl residue having from 6 to 11 carbon atoms, or an aralkyl residue having from 7 to 14 carbon atoms, or, when R_5 is joined to a nitrogen atom, also hydrogen, and R_6 is hydrogen or an alkyl residue having from 1 to 4 carbon atoms, or R_5 and R_6 together with the nitrogen atom to which they are bound form a 5- or 6-membered ring which contains no other heteroatoms or contains one or more other heteroatoms.

15. A compound according to claim 1 wherein R_1 is an acyl group



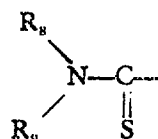
wherein R_7 is hydrogen, an unsubstituted alkyl or substituted alkyl residue having from 1 to 20 carbon atoms, an alkenyl or alkynyl residue having from 2 to 20 carbon atoms, a cycloaliphatic residue having from 5 to 12 carbon atoms, an araliphatic residue having from 7 to 14 carbon atoms, an aromatic residue having from 6 to 20 carbon atoms or an heterocyclic residue.

16. A compound according to claim 1 wherein R_1 is a carbamoyl residue having the formula:



wherein R_8 is hydrogen or an alkyl residue having from 1 to 4 carbon atoms, and R_9 is hydrogen, an alkyl residue having from 1 to 20 carbon atoms, an alkenyl residue having from 3 to 20 carbon atoms, a cycloalkyl residue having from 5 to 12 carbon atoms or an unsubstituted aryl or substituted aryl residue having from 6 to 12 carbon atoms.

17. A compound according to claim 1 wherein R_1 is a thiocarbamoyl residue having the formula:



wherein R_8 is hydrogen or an alkyl residue having from 1 to 4 carbon atoms, and R_9 is hydrogen, an alkyl residue having from 1 to 20 carbon atoms, an alkenyl residue having from 3 to 20 carbon atoms, a cycloalkyl residue having from 5 to 12 carbon atoms or an unsubstituted aryl or substituted aryl residue having from 6 to 12 carbon atoms.

18. A compound according to claim 2 wherein R_1 is an alkyl residue having from 1 to 20 carbon atoms.

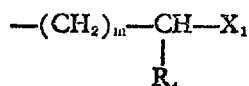
19. A compound according to claim 2 wherein R_1 is an alkyl residue having from 1 to 12 carbon atoms.

20. A compound according to claim 2 wherein R_1 is an alkenyl residue having from 3 to 20 carbon atoms.

21. A compound according to claim 2 wherein R_1 is an alkynyl residue having from 3 to 20 carbon atoms.

22. A compound according to claim 2 wherein R_1 is an aralkyl residue having from 7 to 9 carbon atoms.

23. A compound according to claim 2 wherein R_1 is a residue having the formula



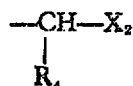
wherein m is 1, 2 or 3,

R_4 is a hydrogen, or a methyl or phenyl residue, and

X_1 is hydroxyl, halogen, cyano, $-OR_5$, $-O-CO-R_5$, $-OCSR_5$, $-O.CO.NR_5R_6$, $-CO.R_5$, $-CO.OR_5$, $-CO.SR_5$, $-CO.NR_5R_6$ or $-CS.NR_5R_6$,

wherein R_5 is an alkyl residue having from 1 to 20 carbon atoms, an alkenyl residue having from 2 to 20 carbon atoms, a cycloalkyl residue having from 5 to 12 carbon atoms, an aryl residue having from 6 to 11 carbon atoms, or an aralkyl residue having from 7 to 11 carbon atoms, or, when R_5 is joined to a nitrogen atom, also hydrogen and R_6 is hydrogen or an alkyl residue having from 1 to 4 carbon atoms, or R_5 and R_6 together with the nitrogen atom to which they are bound form a 5- or 6-membered ring which contains no other heteroatoms or contains one or more other heteroatoms.

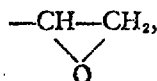
24. A compound according to claim 2 wherein R_1 is a residue having the formula



wherein m is 1, 2 or 3,

R_4 is a hydrogen, or a methyl, or phenyl residue,

X_2 is halogen, cyano,

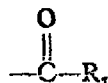


$-COR_5$, $-CO.OR_5$, $-CO.SR_5$ or $-CONR_5R_6$



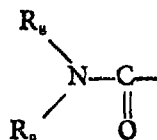
- wherein R_5 is an alkyl residue having from 1 to 20 carbon atoms, an alkenyl residue having from 2 to 20 carbon atoms, a cycloalkyl residue having from 5 to 12 carbon atoms, an aryl residue having from 6 to 11 carbon atoms, or an aralkyl residue having from 7 to 11 carbon atoms, or, when R_5 is joined to a nitrogen atom, also hydrogen and R_6 is hydrogen or an alkyl residue having from 1 to 4 carbon atoms, or R_5 and R_6 together with the nitrogen atom to which they are bound form a 5- or 6-membered ring which contains no other heteroatoms or contains one or more other heteroatoms.

25. A compound according to claim 2 wherein R_1 is an acyl group



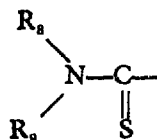
- wherein R_7 is an alkyl or substituted alkyl residue having from 1 to 20 carbon atoms, an alkenyl or alkynyl residue having from 2 to 20 carbon atoms, a cycloaliphatic residue having from 5 to 12 carbon atoms, an araliphatic residue having from 7 to 14 carbon atoms, an aromatic residue having from 6 to 12 carbon atoms or an heterocyclic residue.

26. A compound according to claim 2 wherein R_1 is a carbamoyl residue having the formula:



- wherein R_8 is hydrogen or an alkyl residue having from 1 to 4 carbon atoms, and R_9 is hydrogen, an alkyl residue having from 1 to 20 carbon atoms, an alkenyl residue having from 3 to 20 carbon atoms, a cycloalkyl residue having from 5 to 12 carbon atoms or an aryl or substituted aryl residue having from 6 to 12 carbon atoms.

27. A compound according to claim 2 wherein R_1 is a thiocarbamoyl residue having the formula:



- wherein R_8 is hydrogen or an alkyl residue having from 1 to 4 carbon atoms, and R_9 is hydrogen, an alkyl residue having from 1 to 20 carbon atoms, an alkenyl residue having from 3 to 20 carbon atoms, a cycloalkyl residue having from 5 to 12 carbon atoms or an aryl or substituted aryl residue having from 6 to 12 carbon atoms.

28. A compound according to claim 4 wherein Y is an alkyl group having from 5 to 20 carbon atoms.

29. A compound according to claim 4 wherein Y is an alkenyl having from 3 to 20 carbon atoms.

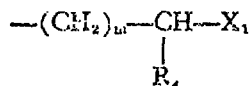
30. A compound according to claim 4 wherein Y is an aralkyl residue having from 7 to 9 carbon atoms.

31. A compound according to claim 5 wherein Y_1 is an alkyl residue having from 1 to 12 carbon atoms.

32. A compound according to claim 5 wherein Y_1 is an alkenyl residue having from 3 to 12 carbon atoms.

33. A compound according to claim 5 wherein Y_1 is an aralkyl residue having from 7 to 12 carbon atoms.

34. A compound according to claim 1 wherein when n is 1, R_3 is a monovalent residue and is an alkyl residue having from 1 to 20 carbon atoms, a cycloalkyl residue having from 5 to 12 carbon atoms, an alkenyl or alkynyl residue having from 3 to 20 carbon atoms, an aralkyl residue having from 7 to 12 carbon atoms, or a residue having the formula:



or



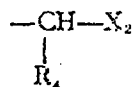


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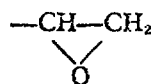
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wherein m is 1, 2 or 3,
 R_4 is a hydrogen, or a methyl or phenyl residue,
 X_2 is halogen, cyano,

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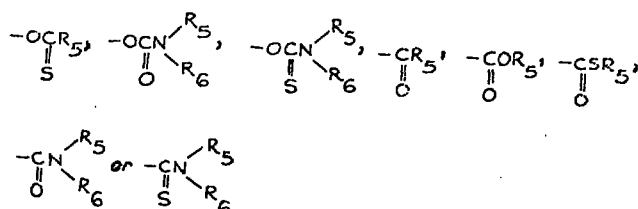
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$-\text{COR}_5$, $-\text{CO}_2\text{OR}_5$, $-\text{CO}_2\text{SR}_5$ or $-\text{CONR}_5\text{R}_6$ and
 X_1 is hydroxyl, halogen, cyano, $-\text{OR}_5$,



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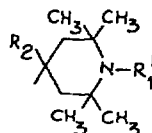
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wherein R_5 is an alkyl residue having from 1 to 20 carbon atoms, an alkenyl residue having from 2 to 20 carbon atoms, a cycloalkyl residue having from 5 to 12 carbon atoms, an aryl residue having from 6 to 11 carbon atoms, or an aralkyl residue having from 7 to 14 carbon atoms or, when R_5 is joined to a nitrogen atom, also hydrogen and R_6 is hydrogen or an alkyl residue having from 1 to 4 carbon atoms, or R_5 and R_6 together with the nitrogen atom to which they are bound form a 5- or 6-membered ring which contains no other heteroatoms or contains one or more heteroatoms or R_6 is an aryl residue or a residue having the formula:

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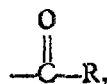
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wherein R_1' is hydrogen or R_1' has the same significance as R_1 of claim 1;
 when n is 2, R_3 is a divalent residue and is an alkylene residue having up to 20 carbon atoms, an alkenylene residue having from 2 to 20 carbon atoms, an alkynylene residue having from 2 to 20 carbon atoms, a cycloalkylidene residue having from 5 to 12 carbon atoms, an arylene residue having from 6 to 14 carbon atoms, an aralkylene residue having from 8 to 14 carbon atoms;
 when n is 3, R_3 is a trivalent residue and is an alkanetriyl, an arenetriyl or an arenetriyl-trialkylene residue, and
 when n is 4, R_3 is a tetravalent residue and is an alkanetetrayl residue.

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35. A compound according to claim 1 wherein
 when n is 1, R_3 is an acyl group



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wherein R_3 is hydrogen, an unsubstituted alkyl or substituted alkyl residue having from 1 to 20 carbon atoms, an alkenyl or alkynyl residue having from 2 to 20 carbon atoms, a cycloaliphatic residue having from 5 to 12 carbon atoms, an araliphatic residue having from 7 to 14 carbon atoms, an aromatic residue having from 6 to 20 carbon atoms or an heterocyclic residue,

35

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or R_3 represents a monovalent group obtained by removing a hydroxyl group from a sulphinic acid, a sulphonic acid, a phosphorus containing acid or sulphuric or a boric acid,
 when n is 2, R_3 is an divalent residue of an aliphatic, aromatic or heterocyclic

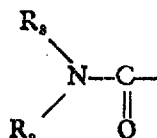


diacyl, the group —CO— or —CO.CO— , a sulphonyl or sulphonyl residue or a divalent residue obtained by removing two hydroxyl groups from a disulphonic acid, a phosphorus containing acid or sulphuric or a boric acid;

when n is 3, R_3 is a trivalent residue of an aliphatic or aromatic triacyl residue or a triacyl residue derived from *o*-phosphoric, *o*-phosphorous or *o*-boric acid;

when n is 4, R_3 is a tetravalent residue of a tetraacyl residue derived from an aliphatic or aromatic tetracarboxylic acid or from *o*-silicic acid.

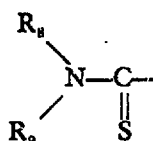
36. A compound according to claim 1 wherein n is 1 or 2 and when n is 1, R_3 is a carbamoyl residue having the formula:



wherein R_3 is hydrogen or an alkyl residue having from 1 to 4 carbon atoms, and R_4 is hydrogen, an alkyl residue having from 1 to 20 carbon atoms, an alkenyl residue having from 3 to 20 carbon atoms, a cycloalkyl residue having from 5 to 12 carbon atoms or an unsubstituted aryl or substituted aryl residue having from 6 to 12 carbon atoms; and

when n is 2, R_3 is a divalent aliphatic or aromatic dicarbamoyl residue.

37. A compound according to claim 1 wherein n is 1 or 2 and when n is 1, R_3 is a thiocarbamoyl residue having the formula:

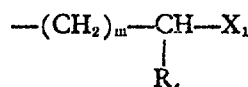


wherein R_3 is hydrogen or an alkyl residue having from 1 to 4 carbon atoms, and R_4 is hydrogen, an alkyl residue having from 1 to 20 carbon atoms, an alkenyl residue having from 3 to 20 carbon atoms, a cycloalkyl residue having from 5 to 12 carbon atoms or an unsubstituted aryl or substituted aryl residue having from 6 to 12 carbon atoms; and

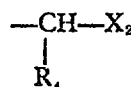
when n is 2, R_3 is a divalent aliphatic or aromatic dithiocarbamoyl residue.

38. A compound according to claim 2 wherein

when n is 1, R_3 is a monovalent residue and is an alkyl residue having from 1 to 20 carbon atoms, a cycloalkyl residue having from 5 to 12 carbon atoms, an alkenyl or alkynyl residue having from 3 to 20 carbon atoms, an aralkyl residue having from 7 to 9 carbon atoms, or a residue having the formula:



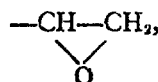
or



wherein m is 1, 2 or 3,

R_4 is a hydrogen, or a methyl or phenyl residue,

X_2 is halogen, cyano,

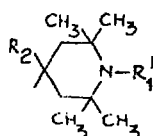


—COR_5 , —CO.OR_5 , —CO.SR_5 , or —CONR_5R_6 and

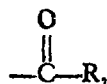
X_1 is hydroxyl, halogen, cyano, —OR_5 , —O—CO.R_5 , —OCSR_5 , —O.CO.NR_5R_6 , —CO.R_5 , —CO.OR_5 , —CO.SR_5 , —CO.NR_5R_6 , or —CS.NR_5R_6 ,

wherein R_5 is an alkyl residue having from 1 to 20 carbon atoms, an alkenyl residue

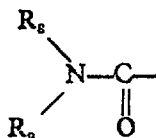
- 5 having from 2 to 20 carbon atoms, a cycloalkyl residue having from 5 to 12 carbon atoms, an aryl residue having from 6 to 11 carbon atoms or an aralkyl residue having from 7 to 11 carbon atoms, or, when R_3 is joined to a nitrogen atom, also hydrogen and R_6 is hydrogen or an alkyl residue having from 1 to 4 carbon atoms, or R_3 and R_6 together with the nitrogen atom to which they are bound form a 5- or 6-membered ring which contains no other heteroatoms or contains one or more other heteroatoms or R_3 is an aryl residue or a residue having the formula:



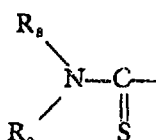
- 10 wherein R_1' is hydrogen or R_1' has the same significance as R_1 of claim 2;
 10 when n is 2, R_3 is a divalent residue and is an alkylene residue having up to 20 carbon atoms, an alkenylene residue having from 3 to 20 carbon atoms, an alkynylene residue having from 3 to 20 carbon atoms, an arylene residue having from 6 to 14 carbon atoms, an aralkylene residue having from 8 to 14 carbon atoms;
 15 when n is 3, R_3 is a trivalent residue of an alkanetriyl, an arenetriyl, or arenetriyl-trialkylene group; and
 15 when n is 4, R_3 is a tetravalent residue of an alkanetetrayl group.
 39. A compound according to claim 2 wherein
 when n is 1, R_3 is an acyl group



- 20 wherein R_1 is an alkyl or substituted alkyl residue having from 1 to 20 carbon atoms, an alkenyl or alkynyl residue having from 2 to 20 carbon atoms, a cycloaliphatic residue having from 5 to 12 carbon atoms, an araliphatic residue having from 7 to 14 carbon atoms, an aromatic residue having from 6 to 12 carbon atoms or an heterocyclic residue with the proviso that only one of R_1 and R_3 can represent an unsaturated acyl group or
 25 R_3 represents a monovalent group obtained by removing a hydroxyl group from a sulphinic acid, a sulphonic acid, a phosphorus containing acid or sulphuric or a boric acid;
 25 when n is 2, R_3 is a divalent residue of an aliphatic, aromatic or heterocyclic diacyl residue, a carbonyl, sulphinyl or sulphonyl residue or a divalent residue obtained by removing two hydroxyl groups from a disulphonic acid, a phosphorus containing acid or sulphuric or a boric acid;
 30 when n is 3, R_3 is a trivalent residue of an aliphatic or aromatic triacyl residue or a triacyl residue derived from *o*-phosphoric, *o*-phosphorous or *o*-boric acid and
 30 when n is 4, R_3 is a tetravalent residue of a tetraacyl residue derived from an aliphatic or aromatic tetracarboxylic acid or from *o*-silicic acid.
 35 40. A compound according to claim 2 wherein n is 1 or 2 and when n is 1, R_3 is a carbamoyl residue having the formula:



- 35 wherein R_6 is hydrogen or an alkyl residue having from 1 to 4 carbon atoms, and R_9 is hydrogen, an alkyl residue having from 1 to 20 carbon atoms, an alkenyl residue having from 3 to 20 carbon atoms, a cycloalkyl residue having from 5 to 12 carbon atoms or an aryl or substituted aryl residue having from 6 to 12 carbon atoms; and
 40 when n is 2, R_3 is a divalent residue of an aliphatic or aromatic dicarbamoyl residue.
 41. A compound according to claim 2 wherein n is 1 or 2 and when n is 1, R_3 is a thiocarbamoyl residue having the formula:

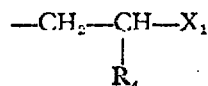




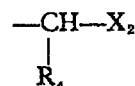
wherein R_8 is hydrogen or an alkyl residue having from 1 to 4 carbon atoms, and R_9 is hydrogen, an alkyl residue having from 1 to 20 carbon atoms, an alkenyl residue having from 3 to 20 carbon atoms, a cycloalkyl residue having from 5 to 12 carbon atoms or an aryl or substituted aryl residue having from 6 to 12 carbon atoms; and when n is 2, R_3 is a divalent residue of an aliphatic or aromatic dithiocarbamoyl residue.

42. A compound of formula I and its bicarbonate according to claim 1 wherein n is 1, 2 or 3

R_1 is alkyl having from 1 to 18 carbon atoms, benzyl or alkenyl having 3 carbon atoms or a group of the formula

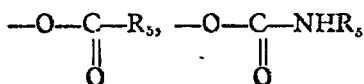


or



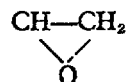
wherein

R_4 is hydrogen, methyl or phenyl and X_1 is a group of the formula



or $-O-$ phenyl and

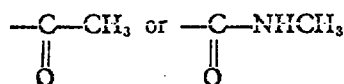
X_2 is a group of the formula $-COOR_6$ or



wherein

R_5 is alkyl having 1 or 2 carbon atoms or phenyl or

R_6 is a group of the formula



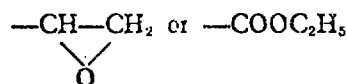
and

R_2 is hydrogen and

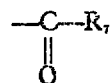
R_3 when n is 1 is alkyl having 3 to 18 carbon atoms, alkenyl having 3 carbon atoms, propargyl, benzyl, $-CH_2CH_2CN$ or a group of the formula



wherein X_2 is



or of the formula



wherein R_7 is alkyl having 1 to 19 carbon atoms, $CH_3(CH_2)_{11}-S-CH_2-$, cycloalkyl having 6 to 10 carbon atoms, alkenyl having 2 to 17 carbon atoms, unsubstituted aralkyl having 7 to 13 carbon atoms, $C_6H_5-CH-CH-$, aralkyl substituted by hydroxy or



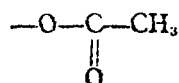
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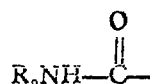
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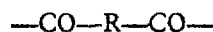
butyl, unsubstituted aryl having 6 to 10 carbon atoms, aryl substituted by alkyl having 1 to 4 carbon atoms, $\text{CH}_3\text{O}-$, Cl , OH , or



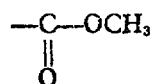
or of the formula



wherein R_n is alkyl having 1 to 8 carbon atoms, alkenyl having 3 carbon atoms, cyclohexyl, unsubstituted aryl having 6 to 10 carbon atoms, aryl substituted by methyl or Cl or R_3 when n is 2, is the group



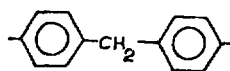
wherein R is alkylene having 4 to 8 carbon atoms, $\text{—CH}_2\text{CH}_2\text{—S—CH}_2\text{CH}_2\text{—}$, vinylene, cyclohexylene, a divalent thiophen residue, unsubstituted phenylene or phenylene substituted by



or a group of the formula



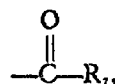
wherein R^1 is hexylene, unsubstituted arylene having 6 to 10 carbon atoms, arylene substituted by methyl or R^1 is the group



or a group of the formula —COCO— or butylene, or R_3 when n is 3 is



provided that when R_3 represents an acyl group



an aliphatic, aromatic or heterocyclic diacyl residue, the group —CO— or —CO.CO— , an aliphatic or aromatic triacyl or tetraacyl residue, a triacyl residue derived from *o*-phosphonic, *o*-phosphorous or *o*-boric acid or a tetraacyl residue derived from *o*-silicic acid, the number of carbon atoms in the alkyl group designated by R_1 is from 5 to 20.

43. A compound as claimed in claim 1 wherein n is 1 and R_1 and/or R_3 is an alkyl residue containing from 1 to 18 carbon atoms.

44. A compound as claimed in claim 1 wherein n is 1 and R_1 and/or R_2 is methyl.

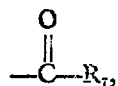
45. A compound as claimed in claim 43 wherein R_1 and/or R_3 is an alkenyl residue containing from 3 to 12 carbon atoms.

46. A compound as claimed in claim 1 wherein n is 1 and R_1 and/or R_3 is an allyl or methallyl residue.

47. A compound as claimed in claim 1 wherein n is 1 and R_1 and/or R_3 is a propargyl or methylpropargyl residue.

48. A compound as claimed in claim 1 wherein n is 1 and R_1 and/or R_3 is a benzyl, β -phenethyl, α -methylbenzyl, α,α -dimethylbenzyl, α -naphthylmethyl and p -methyl- α -methylbenzyl residues; provided that when R_3 represents an acyl group

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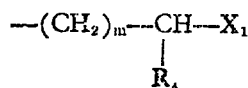
5

an aliphatic, aromatic or heterocyclic diacyl residue, the group $-\text{CO}-$ or $-\text{CO.CO}-$, an aliphatic or aromatic triacyl or tetraacyl residue, a triacyl residue derived from o -phosphonic, o -phosphorous or o -boric acid or a tetraacyl residue derived from o -silicic acid, the number of carbon atoms in the alkyl group designated by R_1 is from 5 to 20.

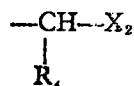
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49. A compound as claimed in claim 1 wherein n is 1 and R_1 and/or R_3 has the formula:

10



or

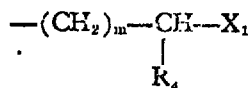


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wherein X_1 and X_2 are as defined in claim 1, R_4 is hydrogen and m is 1.

15

50. A compound as claimed in claim 49, wherein n is 1 and R_1 and/or R_3 has the formula:



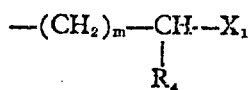
20

wherein R_4 and m have their previous significance and X_1 is an hydroxyl residue.

20

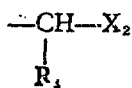
51. A compound as claimed in claim 50 wherein R_1 and/or R_3 is 2-hydroxyethyl, 2-hydroxypropyl or 2-hydroxy-2-phenylethyl.

52. A compound as claimed in claim 1 wherein n is 1 and R_1 and/or R_3 has the formula:



25

or



25

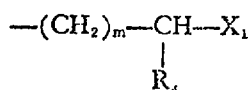
wherein R_4 and m are as defined in claim 1 and X_1 and/or X_2 are halogen atoms, cyano groups or X_2 is a 1,2-epoxy group.

30

53. A compound as claimed in claim 52, wherein R_1 and/or R_3 is a 2-chloroethyl, 2-chloropropyl or 2-chloro-2-phenylethyl residue, a 2-cyanoethyl group or a 2,3-epoxy-n-propyl group.

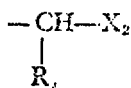
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54. A compound as claimed in claim 1 wherein n is 1 and R_1 and/or R_3 has the formula:



35

or



35



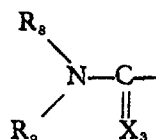
wherein R_1 and m are as defined in claim 1 and X_1 is $-\text{OR}_3$, $-\text{OCOR}_3$, $-\text{OCSR}_3$, $-\text{OCONR}_3$, R_3 or X_1 and/or X_2 is $-\text{COR}_3$, $-\text{COOR}_3$, $-\text{COSR}_3$, $-\text{CONR}_3$, R_3 or X_1 is $-\text{CSNR}_3$, wherein R_3 is an alkyl group having from 1 to 12 carbon atoms, an alkenyl group having from 2 to 4 carbon atoms, a cycloalkyl group having 6 carbon atoms, an aryl residue containing 6 or 7 carbon atoms or an aralkyl residue having 7 or 8 carbon atoms.

55. A compound as claimed in claim 1 wherein n is 1 and R_1 and/or R_3 is an acyl group having the formula $-\text{COR}_7$ wherein R_7 is an alkyl, substituted alkyl, alkenyl, alkynyl, cycloaliphatic, araliphatic, aromatic or heterocyclic residue.

56. A compound as claimed in claim 55 wherein R_7 is a methyl, ethyl, propyl, butyl, hexyl, n -octyl, 2-ethylhexyl, n -decyl, n -undecyl, n -tridecyl, n -tetradecyl, n -hexadecyl, n -heptadecyl, eicosyl, chloroethyl, chlorohexyl, methylthioethyl, ethylthioethyl, octylthioethyl or dodecylthioethyl residue.

57. A compound as claimed in claim 55 wherein R_7 is an alkenyl residue having from 2 to 6 carbon atoms, an alkynyl residue having from 2 to 6 carbon atoms, a cycloaliphatic residue having 5 or 6 carbon atoms, an araliphatic residue having 7 to 9 carbon atoms, a phenyl, tolyl, or p -tert.-butylphenyl or naphthyl residue, or a furan or thiophene residue.

58. A compound as claimed in claim 1 wherein n is 1 and R_1 and/or R_3 is a carbamoyl or thiocarbamoyl residue having the formula:



wherein X_3 is $-\text{O}-$ or $-\text{S}-$, R_8 is hydrogen or an alkyl residue having from 1 to 4 carbon atoms and R_9 is hydrogen, an alkyl residue having from 1 to 20 carbon atoms, an alkenyl residue having from 3 to 20 carbon atoms, a cycloalkyl residue having from 5 to 12 carbon atoms or an aryl or substituted aryl residue having from 6 to 12 carbon atoms.

59. A compound as claimed in claim 1 wherein n is 1 and R_3 is a phenyl residue.

60. A compound as claimed in claim 1 wherein n is 2 and R_3 is an alkylene residue having from 2 to 6 carbon atoms, an alkenylene residue having 3 or 4 carbon atoms, an alkynylene residue having 4 carbon atoms or a cycloalkylidene residue containing 7 or 8 carbon atoms.

61. A compound as claimed in claim 1 wherein n is 2 and R_3 is a 1,3-phenylene or a 4,4'-diphenylene residue.

62. A compound as claimed in claim 1 wherein n is 2 and R_3 is a diacyl residue derived from an aliphatic dicarboxylic acid having from 2 to 20 carbon atoms.

63. A compound as claimed in claim 1 wherein n is 2 and R_3 is a diacyl residue derived from phthalic, isophthalic or terephthalic acid.

64. A compound as claimed in claim 63 wherein the acid is ring-substituted by halogen, an alkyl or alkoxy group each having from 1 to 20 carbon atoms, a hydroxy or tertiary amino group.

65. A compound as claimed in claim 1 wherein n is 2 and R_3 is a diacyl residue derived from 2,5-thiophene dicarboxylic acid or 2,5-furandicarboxylic acid.

66. A compound as claimed in claim 1 wherein n is 3 and R_3 is a triacyl group derived from nitrilotriacetic acid, tricarballic acid, benzenetricarboxylic acid, o -phosphorous acid, o -boric acid or benzene-1,3,5-trisulphonic acid.

67. A compound as claimed in claim 1 wherein n is 4 and R_3 is a tetraacyl group derived from ethylene diamine tetracarboxylic acid, a tetracarboxylic acid described in British Patent Specification No. 1,080,335, 1,2,4,5-benzene tetracarboxylic acid or o -silicic acid.

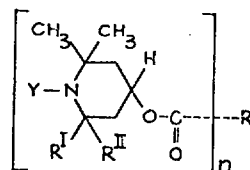
68. A compound as claimed in claim 1 wherein n is 4, R_3 is an acyl residue and R_1 is an alkyl, alkenyl or substituted alkyl group.

69. A compound as claimed in claim 1 in the form of its salt of an inorganic acid.

70. A compound as claimed in claim 69 wherein the salt is a phosphate, carbonate, sulphate, chloride, acetate, stearate, malate, citrate, tartrate, oxalate, benzoate or substituted carbonate.



71. Compounds having the formula:



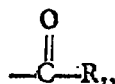
II

and their salts, wherein R^I and R^{II} are the same or different and each is a straight or branched alkyl group, having from 1 to 4 carbon atoms, or R^I and R^{II} , together with the carbon atom to which they are attached form a cycloalkyl residue having from 5 to 12 carbon atoms; Y is an alkyl group, having from 5 to 20 carbon atoms, alkenyl having from 2 to 20 carbon atoms or an aralkyl residue having from 7 to 9 carbon atoms, and n is 1 or 2;

when n is 1, R is hydrogen or a monovalent aliphatic residue having from 1 to 20 carbon atoms, a monovalent alicyclic residue having from 5 to 12 carbon atoms, or a monovalent aromatic residue having from 6 to 20 carbon atoms;

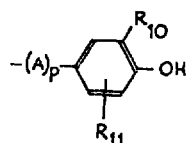
and when n is 2, R is a divalent aliphatic residue having from 1 to 20 carbon atoms, and is unsubstituted or substituted or interrupted by one or more sulphur atom, a divalent alicyclic residue having from 5 to 12 carbon atoms, or a divalent aromatic residue having from 6 to 20 carbon atoms;

provided that when R represents an acyl group



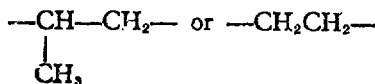
an aliphatic, aromatic or heterocyclic diacyl residue, the group $-\text{CO}-$ or $-\text{CO.CO}-$, an aliphatic or aromatic triacyl or tetraacyl residue, a triacyl residue derived from *o*-phosphoric, *o*-phosphorous or *o*-boic acid or a tetraacyl residue derived from *o*-silicic acid, the number of carbon atoms in the alkyl group designated by R , is from 5 to 20.

72. A compound as claimed in claim 71 wherein n is 1 and R is a monovalent aromatic residue having the formula:



III

wherein R_{10} and R_{11} are the same or different and each is an alkyl group having from 1 to 6 carbon atoms, A is



and p is 0 or 1.

73. A compound as claimed in claim 72 wherein R_{10} and R_{11} are methyl, isopropyl or t-butyl groups.

74. A compound as claimed in claim 71 wherein n is 2 and R is a methylene, 1,2-ethylene, 1,4-butylene, 1,8-n-octylene, 2,2,4-trimethyl-1, 4-butylene, 1,10-n-decylene, 1,2-cicosylene, vinylene, propenylene, 1,2-, 1,3- or 1,4-cyclohexylene, cyclohexyl-3-ene, 1,2-, 1,3- or 1,4-phenylene, *p*-xylylene, 1,4- or 1,5-naphthylene, diphenylene or diphenylmethylene residue or the group $-\text{CH}_2\text{CH}_2\text{S CH}_2\text{CH}_2-$ or R is absent.

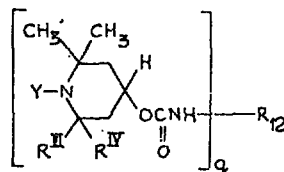
75. A compound as claimed in claim 71 in the form of its salt of an inorganic or organic acid.

76. A compound as claimed in claim 76 wherein the salt is a phosphate, carbonate, sulphate, chloride, acetate, stearate, maleate, nitrate, tartrate, oxalate, benzoate or substituted carbamate.

77. A compound of formula II as defined in claim 71 wherein R^I and R^{II} are methyl.

78. A compound having the formula:





IV

and its salts wherein R^{III} and R^{IV} are the same or different and each is a straight or branched alkyl residue having from 1 to 12 carbon atoms or R^{III} and R^{IV} together with the carbon atom to which they are each attached form a cycloalkyl group having from 5 to 12 carbon atoms, Y is a straight- or branched alkyl residue having from 5 to 12 carbon atoms, an alkenyl residue having from 3 to 12 carbon atoms or an aralkyl residue having from 7 to 12 carbon atoms and R_{12} is hydrogen or a saturated or unsaturated hydrocarbyl or hydrocarbylene residue containing up to 20 carbon atoms optionally substituted, halogen or alkoxy having from 1 to 4 carbon atoms and q is 1 or 2.

79. A compound as claimed in claim 78, wherein q is 1 and R_{12} is an aliphatic residue having from 1 to 20 carbon atoms, an alicyclic residue having from 5 to 12 carbon atoms or an aromatic residue having from 6 to 12 carbon atoms.

80. A compound as claimed in claim 79 wherein R_{12} is a methyl, ethyl, propyl, isopropyl, n-butyl, 2-ethylhexyl, dodecyl, octadecyl, allyl, oleyl, cyclohexyl, benzyl, phenyl, o-, m- or p-tolyl, 2,4- or 2,6-xylol or a naphthyl residue.

81. A compound as claimed in claim 78 wherein q is 2 and R_{12} is an aliphatic residue having from 1 to 20 carbon atoms, an alicyclic residue having from 5 to 15 carbon atoms or an aromatic residue having from 6 to 15 carbon atoms.

82. A compound as claimed in claim 79 wherein R_{12} is a 1,2-ethylene, 1,6-hexylene, 2,4,4-trimethyl-1,6-hexylene, 1,3- or 1,4-phenylene, 2,4-tolylene, 1,5-naphthylene or 4,4'-diphenylmethylen residue.

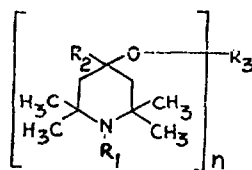
83. A compound as claimed in claim 78 wherein Y is methyl.

84. A compound as claimed in claim 78 in the form of its salt of an inorganic or organic acid.

85. A compound as claimed in claim 84 wherein the salt is a phosphate, carbonate, sulphate, chloride, acetate, stearate, malate, citrate, tartrate, oxalate, benzoate or substituted carbamate.

86. A compound of formula IV as defined in claim 78 wherein R^{III} and R^{IV} are methyl.

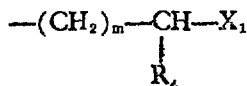
87. A compound having the formula:



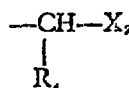
I

wherein n is 1, 2, 3 or 4;

R_1 is a monovalent residue and is an alkyl residue having from 1 to 20 carbon atoms, a cycloalkyl residue having 5 to 12 carbon atoms, an alkenyl or alkynyl residue having from 3 to 20 carbon atoms, an aralkyl residue having from 7 to 9 carbon atoms, or a residue having the formula:



or

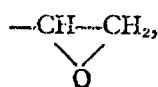


wherein m is 1, 2 or 3,

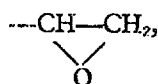
R_4 is a hydrogen, or a methyl or phenyl residue,

X_2 is halogen, cyano,

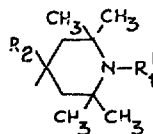




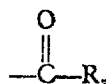
---COR₅, ---CO.OR₅, ---CO.SR₅, ---CONR₅R₆ or ---CS.NR₅R₆ and X₁ is hydroxyl, halogen, cyano,



- 5 ---OR₅, ---O---CO.R₅, OCSR₅, ---O.CO.NR₅R₆, ---CO.R₅, ---CO.OR₅, ---CO.SR₅,
 10 ---CO.NR₅R₆, ---CS.NR₅R₆ or ---SR₅, wherein R₅ is an alkyl residue having from 1 to 20 carbon atoms, an alkenyl residue having from 2 to 20 carbon atoms, a cycloalkyl residue having from 5 to 12 carbon atoms, an aryl residue having from 6 to 11 carbon atoms or, when R₅ is joined to a nitrogen atom, also hydrogen and R₅ is hydrogen or an alkyl residue having from 1 to 4 carbon atoms, or R₅ and R₆ together with the nitrogen atom to which they are bound form a 5- or 6-membered ring which contains no other heteroatoms or contains one or more other heteroatoms or R₁ is an acyl group, an unsubstituted or N-substituted carbamoyl or thiocarbamoyl group;
 15 R₂ is an alkyl residue having from 1 to 4 carbon atoms, an alkenyl or alkynyl residue having 3 to 20 carbon atoms, a cycloalkyl residue having from 5 to 12 carbon atoms, an aryl residue having from 6 to 11 carbon atoms or an aralkyl residue having from 7 to 9 carbon atoms or also hydrogen;
 20 and when n is 1, R₃ is a monovalent radical having the same significance as R₁, with the proviso that only one of R₁ and R₃ can represent an unsaturated acyl group or R₃ represents a monovalent group obtained by removing a hydroxyl group from a sulphinic acid, a sulphonic acid, a phosphorus containing acid or sulphuric or a boric acid, or R₃ is an aryl residue or a residue having the formula:



- wherein R₁' is hydrogen or R₁' has the same significance as R₁;
 25 when n is 2, R₃ is a divalent residue and is an alkylene residue having from 1 to 20 carbon atoms an alkenylene residue having from 3 to 20 carbon atoms, an alkynylene residue having from 3 to 20 carbon atoms, an arylene residue having 6 to 14 carbon atoms, an aralkylene residue having from 8 to 14 carbon atoms or an aliphatic, aromatic or heterocyclic diacyl residue, an aliphatic or aromatic dicarbamoyl or dithiocarbamoyl, a carbonyl, sulphinyl or sulphonyl residue or a divalent residue obtained by removing two hydroxyl groups from a disulphonic acid, a phosphorus containing acid or sulphuric or a boric acid;
 30 when n is 3, R₃ is a trivalent residue or an aliphatic or aromatic triacyl residue or a triacyl residue derived from o-phosphoric, o-phosphorous or o-boric acid or an alkanetriyl, an arenetriyl, or arenetriyltrialkylene group;
 35 and when n is 4, R₃ is a tetravalent residue and is a tetravalent aliphatic residue or tetraacyl residue derived from an aliphatic or aromatic tetracarboxylic acid or from o-silicic acid or an alkanetetrayl group;
 provided that when R₃ represents an acyl group



- 40 an aliphatic, aromatic or heterocyclic diacyl residue, the group ---CO--- or ---CO.CO---, an aliphatic or aromatic triacyl or tetraacyl residue, a triacyl residue derived from o-phosphoric, o-phosphorous or o-boric acid or a tetraacyl residue derived from o-silicic acid, the number of carbon atoms in the alkyl group designated by R₁ is from 5 to 20, as well as partial ethers esters and carbamoyloxy and thiocarbamoyloxy compounds related to the fully reacted compounds of formula I.
 45

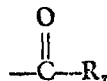
88. A compound according to claim 1 wherein R₁ is alkyl having 5 to 20 carbon atoms.
 89. A compound according to claim 2 wherein R₁ is alkyl having 5 to 20 carbon atoms.
 50



90. A compound according to claim 5 wherein Y_1 is alkyl having 5 to 12 carbon atoms.

91. A compound according to claim 5 wherein Y_1 is alkyl having 1 to 4 carbon atoms.

5 92. A compound according to claim 1 wherein n is 1, 2 or 4 and when n is 1, R_3 is an acyl group 5

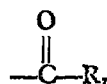


wherein R_1 is hydrogen, a substituted alkyl residue having from 1 to 20 carbon atoms, an alkenyl or alkynyl residue having from 2 to 20 carbon atoms, a cycloaliphatic residue having from 5 to 12 carbon atoms, an araliphatic residue having from 7 to 14 carbon atoms or an heterocyclic residue,

10 or R_1 represents a monovalent group obtained by removing a hydroxyl group from a sulphinic acid, a sulphonic acid, a phosphorus containing acid or sulphuric or a boric acid, or

15 when n is 2, R_3 is an divalent residue of heterocyclic diacyl residue or a sulphinyl or sulphonyl residue or a divalent residue obtained by removing two hydroxyl groups from a disulphonic acid, a phosphorus containing acid or sulphuric or a boric acid; when n is 4, R_3 is a tetraacyl residue derived from an aliphatic tetracarboxylic acid.

20 93. A compound according to claim 1 wherein n is 1, 2 and 4 and when n is 1, R_3 is an acyl group 20

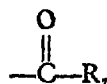


wherein R_1 is hydrogen, a cycloaliphatic residue having from 5 to 12 carbon atoms or a heterocyclic residue or R_3 represents a monovalent group obtained by removing a hydroxyl group from a sulphinic acid, a sulphonic acid, a phosphorus containing acid or sulphuric or a boric acid or

25 when n is 2, R_3 is a divalent residue of a heterocyclic diacyl or a sulphinyl or sulphonyl residue or a divalent residue obtained by removing two hydroxyl groups from a disulphonic acid, a phosphorus containing acid or

30 when n is 4, R_3 is a tetraacyl residue derived from an aliphatic tetracarboxylic acid.

94. A compound according to claim 2 wherein n is 1, 2 or 4 and when n is 1, R_3 is an acyl group 30

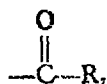


wherein R_1 is hydrogen, a substituted alkyl residue having from 1 to 20 carbon atoms, an alkenyl or alkynyl residue having from 2 to 20 carbon atoms, a cycloaliphatic residue having from 5 to 12 carbon atoms, an araliphatic residue having from 7 to 14 carbon atoms or an heterocyclic residue,

35 or R_1 represents a monovalent group obtained by removing a hydroxyl group from a sulphinic acid, a sulphonic acid, a phosphorus containing acid or sulphuric or a boric acid, or

40 when n is 2, R_3 is an divalent residue of heterocyclic diacyl residue or a sulphinyl or sulphonyl residue or a divalent residue obtained by removing two hydroxyl groups from a disulphonic acid, a phosphorus containing acid or sulphuric or a boric acid; and when n is 4, R_3 is a tetraacyl residue derived from an aliphatic tetracarboxylic acid.

45 95. A compound according to claim 2 wherein n is 1, 2 and 4 and when n is 1, R_3 is an acyl group 45



wherein R_1 is hydrogen, a cycloaliphatic residue having from 5 to 12 carbon atoms or a heterocyclic residue or R_3 represents a monovalent group obtained by removing a



hydroxyl group from a sulphinic acid, a sulphonic acid, a phosphorus containing acid or sulphuric or a boric acid or

when n is 2, R_3 is a divalent residue of a heterocyclic diacyl or a sulphinyl or sulphenyl residue or a divalent residue obtained by removing two hydroxyl groups from a disulphonic acid, a phosphorus containing acid or

when n is 4, R_3 is a tetraacyl residue derived from an aliphatic tetracarboxylic acid.

96. A compound as claimed in claim 4, wherein n is 1 and R is hydrogen or a monovalent alicyclic residue having from 5 to 12 carbon atoms.

97. A compound according to claim 1 wherein when n is 1, R_3 is an acyl group



wherein R_7 is an unsubstituted aliphatic residue having from 1 to 20 carbon atoms or an aromatic residue having from 6 to 20 carbon atoms and

when n is 2, R_3 is a divalent aliphatic or aromatic diacyl residue or the groups $-\text{CO}-$ or $-\text{COCO}-$ and

when n is 3, R_3 is a trivalent residue and is an aliphatic or aromatic triacyl residue or a triacyl residue derived from *o*-phosphoric, *o*-phosphorous or *o*-boric acid and

when n is 4, R_3 is a tetravalent residue of a tetraacyl residue derived from an aromatic tetracarboxylic acid or from *o*-silicic acid.

98. A compounds according to claim 2 wherein when n is 1, R_3 is an acyl group



wherein R_7 is an unsubstituted alkyl residue having from 1 to 20 carbon atoms or an aromatic residue having from 6 to 12 carbon atoms and

when n is 2, R_3 is a divalent aliphatic or aromatic diacyl residue or the carbonyl group and

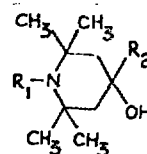
when n is 3, R_3 is a trivalent residue and is an aliphatic or aromatic triacyl residue or a triacyl residue derived from *o*-phosphoric, *o*-phosphorous or *o*-boric acid and

when n is 4, R_3 is a tetravalent residue derived from an aromatic tetracarboxylic acid or from *o*-silicic acid.

99. A compound as claimed in claim 4, wherein when n is 1, R is a monovalent aliphatic residue having from 1 to 20 carbon atoms or a monovalent aromatic residue having from 6 to 20 carbon atoms and

when n is 2, R is a divalent aliphatic residue having from 1 to 20 carbon atoms or a divalent aromatic residue having from 6 to 20 carbon atoms.

100. A process of producing a compound having the formula 1 as defined in claim 1 comprising reacting, in the presence of an acid-binding agent, a piperidinol having the formula:



V

wherein R_1 and R_2 are as defined in claim 1, with an acid halide having the formula:



VI

wherein R_3 and n are as defined in claim 1 and hal represents a halogen atom.

101. A process as claimed in claim 100 wherein the acid-binding agent is an organic base or an excess amount of the amine of formula V as defined in claim 100.

102. A process as claimed in claim 100 wherein the reaction is effected in a solvent which is inert under the reaction conditions.

103. A process of producing a compound of formula I comprising reacting, in the presence of a transesterification catalyst, a piperidinol compound of formula V as defined in claim 100, with an ester having the formula:

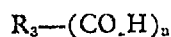


VII

wherein R_3 and n are as defined in claim 1 and R_{13} is an alkyl residue having from 1 to 4 carbon atoms.

104. A process as claimed in claim 103 wherein the catalyst is an alkali metal amide.

5 105. A process of producing a compound of formula I as defined in claim 1 comprising reacting, in the presence of an esterification catalyst, a piperidinol compound of formula V as defined in claim 100, with an acid having the formula:



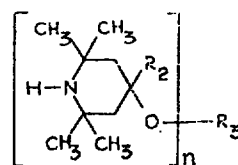
wherein R_3 and n are as defined in claim 1.

10 106. A process as claimed in claim 105 wherein the catalyst is a tetraalkyl titanate.

107. A process as claimed in claim 103 wherein the reactants are mixed and the mass is agitated until reaction is complete in the presence or absence of an inert solvent.

15 108. A process as claimed in any of claims 103 to 107 wherein the completion of the reaction is determined by collecting respectively the alcohol or water produced in the reaction and stopping the reaction when the theoretical amount of water or alcohol has been removed.

109. A process of producing a compound of formula I comprising reacting a compound having the formula:

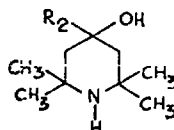


IX

wherein R_2 , R_3 and n are as defined in claim 1 with a compound capable of reacting with the compound of formula IX and of introducing into it the group R_1 as defined in claim 1.

25 110. A process as claimed in claim 109 wherein said compound capable of reacting with the compound of formula IX is an alkylating, alkenylating, alkynylating or aralkylating agent or an aldehyde or ketone corresponding to the substituent R_1 .

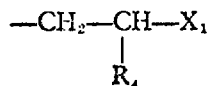
111. A process as claimed in claim 109 wherein R_1 and R_3 are identical, and are introduced by reacting a compound having the formula:



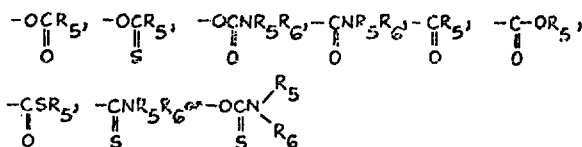
XI

30 with the corresponding alkylating, alkenylating, alkynylating, aralkylating, acylating agent or carbamoyloxylating agent.

112. A process of producing a compound of formula I in which R_1 represents a residue having the formula:

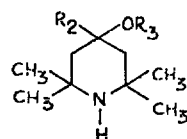


35 wherein R_4 is as defined in claim 1 and X_1 is $-CN$, $-OR_5$,



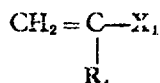
wherein R_5 and R_6 are as defined in claim 1, comprising reacting a compound having the formula:





XII

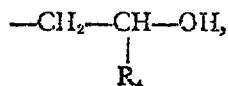
wherein R_3 and R_2 are as defined in claim 1, with a compound having the formula



wherein X_1 and R_4 are as defined in this claim.

5

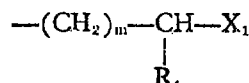
113. A process of producing a compound of formula I in which R_1 represents a residue having the formula



wherein R_4 is as defined in claim 1, comprising reacting a compound XII as defined in claim 112 with ethylene oxide, propylene oxide or styrene oxide.

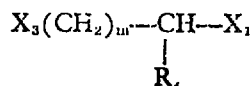
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114. A process of producing a compound of formula I in which R_1 represents a residue having the formula:



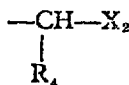
wherein m , R_4 and X_1 are as defined in claim 1, comprising reacting a compound having the formula XII as defined in claim 112, with the corresponding halogen compound having the formula:

15



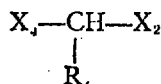
wherein X_3 is a halogen atom.

115. A process of producing a compound of formula I in which R_1 represents the group



20

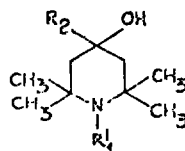
wherein X_2 and R_4 are as defined in claim 1, comprising reacting a compound having the formula XII as defined in claim 112 with a compound having the formula:



wherein X_4 is a halogen atom.

25

116. A process of producing a compound of formula 1 in which n is 2, 3 or 4 and R_3 represents a di-, tri- or tetra-valent radical derived from an alkyl, alkenyl, alkynyl, aryl or aralkyl radical, comprises reacting a compound having the formula:



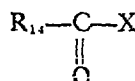
XIII



wherein R_1' is hydrogen or R_1 , and R_2 is as defined in claim 1, with a compound having the formula $R_3(X_4)_n$ wherein R_3 and n have the meanings given in this claim and X_4 is a halogen atom.

117. A process as claimed in claim 116 wherein the sodium salt of the compound of formula XIII is reacted with the compound $R_3(X_4)_n$.

118. A process of producing a compound having the formula I in which R_1 represents an acyl group, comprises reacting a compound having the formula XII as defined in claim 112 with an acyl halide having the formula

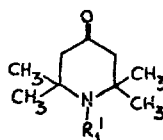


wherein X_5 is a halogen atom and R_1 is the remainder of the acyl group.

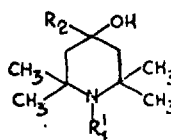
119. A process of producing a compound of formula I in which R_1 represents a carbamoyl or thiocarbamoyl group, comprising reacting a compound having the formula XII as defined in claim 113, with an isocyanate or isothiocyanate having the formula $R_{10}NCX'$ wherein X' is $-O-$ or $-S-$ and R_{10} is the remainder of the isocyanate or thioisocyanate group.

120. A process as claimed in claim 100 wherein R_2 is not hydrogen and is introduced before or after the group R_1 is introduced but before the group R_3 is introduced.

121. A process as claimed in claim 120 wherein the group R_2 is introduced by reacting a ketone having the formula:

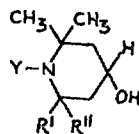


wherein R_1' is hydrogen or R_1 , with a Grignard reagent R_2MgX and then hydrolysing the reaction product to produce a compound having the formula:



122. A process as claimed in claim 112 wherein the reaction is effected in the presence of an acid acceptor.

123. A process of producing a compound of formula II as defined in claim 71, comprising reacting, in the presence of an acid-binding agent, a piperidinol compound having the formula:



XIV

wherein Y , R' and R'' are as defined in claim 71, with an acid halide having the formula:



wherein R and n are as defined in claim 71 and hal represents a halogen atom.

124. A process as claimed in claim 123 wherein the acid binding agent is an organic base or an excess amount of the amine reactant XIV as defined in claim 124.

125. A process as claimed in claim 123 wherein the reactants are heated together in a solvent inert under the reaction conditions.

126. A process of producing a compound of formula II as defined in claim 71, comprising reacting, in the presence of an esterification catalyst, a piperidinol compound having the formula XIV as defined in Claim 123, with an ester having the formula:





wherein R and n are as defined in claim 71 and R₁₂ is an alkyl group having from 1 to 4 carbon atoms.

127. A process as claimed in claim 126 wherein the catalyst is an alkali metal amide.

5 128. A process of producing a compound of formula II as defined in claim 71 comprising reacting, in the presence of an esterification catalyst, a piperidinol compound having the formula XIV as defined in claim 123, with an acid having the formula:



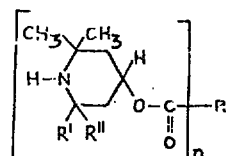
wherein R and n are as defined in claim 71.

10 129. A process as claimed in claim 128 wherein the catalyst is a tetraalkyl titanate.

130. A process as claimed in claim 126 wherein the reactants are fused and the mass is agitated until reaction is complete.

15 131. A process as claimed in any of claims 123 to 130 wherein the completion of the reaction is determined by collecting, respectively, the alcohol or water produced in the reaction, and stopping the reaction when the theoretical amount of water or alcohol has been removed.

132. A process of producing a compound of formula II as defined in claim 71 comprising reacting an ester having the formula:

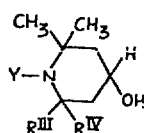


XV

wherein R, R', R'' and n are as defined in claim 71 with a compound capable of reacting with the ester XV and of introducing into it the group Y as defined in claim 71.

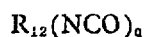
25 133. A process as claimed in claim 132 wherein the compound capable of reacting with the ester XV is an alkylating or aralkylating agent or an aldehyde or ketone capable of reacting to provide the substituent Y.

134. A process of producing a compound having the formula IV as defined in claim 78 comprising reacting a compound having the formula:



XVII

30 wherein Y is as defined in claim 78, with an isocyanate having the formula:



wherein R₁₂ and q are as defined in claim 78.

135. A process as claimed in claim 134 wherein the reaction is effected in a solvent inert under the reaction conditions and in the presence of a strong base.

35 136. A process according to claim 100 for producing compounds of claims 2 to 70 or 88 to 99.

137. A process according to claim 103 for producing compounds of claims 2 to 70 or 88 to 99.

40 138. A process according to claim 105 for producing compounds of claims 2 to 70 or 88 to 99.

139. A process according to claim 109 for producing compounds of claims 2 to 70 or 85 to 99.

140. A process according to claim 112 for producing compounds of claims 2 to 70.

141. A process according to claim 113 for producing compounds of claims 2 to 70.

45 142. A process according to claim 114 for producing compounds of claims 2 to 70.

143. A process according to claim 115 for producing compounds of claims 2 to 70.

144. A process according to claim 116 for producing compounds of claims 2 to 70.

145. A process according to claim 118 for producing compounds of claims 2 to 70.



88	89	1,399,239	89
1 to		146. A process according to claim 119 for producing compounds of claims 2 to 70.	
total		147. A process according to claim 123 for producing compounds of claims 72 to 77.	
71	5	148. A process according to claim 126 for producing compounds of claims 72 to 77.	5
and		149. A process according to claim 128 for producing compounds of claims 72 to 77.	
71	5	150. A process according to claim 133 for producing compounds of claims 72 to 77.	5
and		151. A process according to claim 135 for producing compounds of claims 79 to 86.	
71		152. A process according to claim 100 for producing compounds of claim 87.	
71		153. A process according to claim 103 for producing compounds of claim 87.	
71		154. A process according to claim 105 for producing compounds of claim 87.	
71	10	155. A process according to claim 109 for producing compounds of claim 87.	10
71		156. A process according to claim 112 for producing compounds of claim 87.	
71	10	157. A process according to claim 113 for producing compounds of claim 87.	10
71		158. A process according to claim 114 for producing compounds of claim 87.	
71	15	159. A process according to claim 115 for producing compounds of claim 87.	15
71		160. A process according to claim 116 for producing compounds of claim 87.	
71	15	161. A process according to claim 118 for producing compounds of claim 87.	15
71		162. A process according to claim 119 for producing compounds of claim 87.	
71	20	163. A composition comprising an organic material and a stabilising amount of a compound of formula I as defined in claim 1.	20
71		164. A composition as claimed in claim 163 wherein the organic material is a polyolefine.	
71	20	165. A composition as claimed in claim 164 wherein the polyolefine is low- or high-density polyethylene or polypropylene or polystyrene.	20
71		166. A composition as claimed in claim 164 wherein the polyolefine is a polymer of butene-1, pentene-1, 3-methylbutene-1, hexene-1, 4-methylpentene-1, 4-methylhexene-1, 4,4-dimethylpentene-1 or co- or ter-polymers of ethylene or propylene.	
71	25	167. A composition as claimed in claim 164 wherein the organic material is a natural or synthetic polymeric material.	25
71		168. A composition as claimed in claim 167 wherein the polymeric material is a natural or synthetic rubber.	
71	30	169. A composition as claimed in claim 168 wherein the synthetic rubber is a mono-, co- or ter-polymer of acrylonitrile, butadiene and styrene.	30
71		170. A composition as claimed in claim 167 wherein polymeric material is polyvinyl chloride, polyvinylidene chloride, vinyl chloride copolymers, polyvinyl acetate or a condensation polymer containing ether, ester (derived from carboxylic sulphonic or carbonic acids), amide or urethane groupings.	
71	35	171. A composition as claimed in claim 163 wherein the amount of the compound of formula I is within the range of from 0.01% to 5% by weight based on the weight of untreated organic materials.	35
71		172. A composition as claimed in claim 171 wherein the amount of the compound of formula I is within the range of from 0.1% to 2% by weight based on the weight of untreated organic material.	
71	40	173. A composition as claimed in claim 163 wherein one or more further additives used in polymer formulations are present.	40
71		174. A composition as claimed in claim 173 wherein the further additives are antioxidants of the phenol or amine type, U.V. absorbers and light protectants, phosphite stabilisers, peroxide decomposers, polyamide stabilisers, basic co-stabilisers, polyvinyl chloride stabilisers, lubricants, emulsifiers, anti-static agents, flame-protectants, pigments, carbon black, asbestos, glass fibres, kaolin and talc.	
71	45	175. A composition comprising an organic material and a stabilizing amount of a compound having the formula II as defined in claim 71.	45
71		176. A composition as claimed in claim 175 wherein the organic material is a polyolefine.	
71	50	177. A composition as claimed in claim 176 wherein the polyolefine is a low- or high-density polyethylene or polypropylene or polystyrene.	50
71		178. A composition as claimed in claim 176 wherein the polyolefine is a polymer of butene-1, pentene-1, 3-methylbutene-1, hexene-1, 4,4-dimethylpentene-1, or co- or terpolymers of ethylene or propylene.	
71	55	179. A composition as claimed in claim 175 wherein the organic material is a natural or synthetic polymeric material.	55
71		180. A composition as claimed in claim 179 wherein the polymeric material is a natural or synthetic rubber.	
71	60	181. A composition as claimed in claim 180 wherein the synthetic rubber is a homo-, co- or ter-polymer of acrylonitrile, butadiene and styrene.	60
71		182. A composition as claimed in claim 179 wherein the polymeric material is	
71	65		65

- polyvinyl chloride, a vinyl chloride co-polymer, polyvinyl acetate, or a condensation polymer containing ether, ester (derived from carboxylic, sulphonic or carbonic acids), amide or urethane groupings.
- 5 183. A composition as claimed in claim 175 wherein the amount of the compound of formula II is within the range of from 0.01% to 5% by weight based on the weight of untreated organic material. 5
184. A composition as claimed in claim 183 wherein the amount of the compound of formula II is within the range of from 0.1% to 2% by weight based on the weight of untreated organic material.
- 10 185. A composition as claimed in claim 175 wherein further additives used in polyolefine formulations are present. 10
186. A composition as claimed in claim 185 wherein the further additives are anti-oxidants, further light stabilisers, metal complexants/deactivators, pigments, antislipping or anti-static agents, fillers, dyes, or glass or other fibres.
- 15 187. A composition comprising an organic material and, as stabiliser, a stabilizing proportion of a compound of formula IV as defined in claim 78. 15
188. A composition as claimed in claim 187 wherein the organic material is a polyolefine.
- 20 189. A composition as claimed in claim 188 wherein the polyolefine is a low- or high-density polyethylene or polypropylene or polystyrene. 20
190. A composition as claimed in claim 188 wherein the polyolefine is a polymer of butene-1, pentene-1, 3-methylbutene-1, hexene-1, 4-methylpentene-1, 4-methylhexene-1, 4,4-dimethylpentene-1, or co- or ter-polymers of ethylene or propylene.
- 25 191. A composition as claimed in claim 187 wherein the organic material is a natural or synthetic polymeric material. 25
192. A composition as claimed in claim 191 wherein the polymeric material is a natural or synthetic rubber.
- 30 193. A composition as claimed in claim 192 wherein the synthetic rubber is a homo-, co- or ter-polymer of acrylonitrile, butadiene and styrene. 30
194. A composition as claimed in claim 191 wherein the polymeric material is polyvinyl chloride, a vinyl chloride co-polymer, polyvinyl acetate, or a condensation polymer containing ether, ester (derived from carboxylic, sulphonic or carbonic acids) amide or urethane groupings.
- 35 195. A composition as claimed in claim 187 wherein the amount of the compound of formula IV is within the range of from 0.01% to 5% by weight based on the weight of untreated organic material. 35
196. A composition as claimed in claim 195 wherein the amount of the compound of formula IV is within the range of from 0.1% to 2% by weight based on the weight of untreated organic material.
- 40 197. A composition as claimed in claim 187 wherein further additives used in polyolefine formulations are present. 40
198. A composition as claimed in claim 197 wherein the further additives are anti-oxidants, further light stabilisers, metal complexants/deactivators, pigments, antislipping and anti-static agents, fillers, dyes, or glass or other fibres.
- 45 199. A composition according to claim 163 wherein the compound is a compound of claims 2 to 70 or 88 to 99. 45
200. A composition according to claim 175 wherein the compound is a compound of claims 72 to 77.
- 50 201. A composition according to claim 187 wherein the compound is a compound of claims 79 to 86. 50
202. A composition comprising an organic material and as stabilizer a stabilizing proportion of a compound of claim 87.
203. The process for stabilizing organic material which comprises adding thereto a compound of claim 1.
- 55 204. The process according to claim 203 which comprises adding to the organic material a compound of claims 2 to 70 or 88 to 99. 55
205. The process for stabilizing organic material which comprises adding thereto a compound of claim 71.
206. The process according to claim 217 which comprises adding to the organic material a compound of claims 72 to 77.
- 60 207. The process for stabilizing organic material which comprises adding thereto a compound of claim 78. 60
208. The process according to claim 219 which comprises adding to the organic material a compound of claims 79 to 86.



209. The process for stabilizing organic material which comprises adding thereto a compound of claim 87.

210. A compound according to claim 1 which is 1,2,2,6,6-pentamethylpiperidinyl-4 octanoate.

211. A compound according to claim 1 which is 1,2,2,6,6-pentamethylpiperidinyl-4 stearate.

212. A compound according to claim 1 which is bis-(1,2,2,6,6-pentamethyl-4-piperidinyl) sebacate.

213. A compound according to claim 1 which is 1,6-bis-(4'-carbamoyloxy-1',2',2',6',6'-pentamethylpiperidine)-hexane.

214. A compound according to claim 1 which is 4-stearylcarbamoyloxy-1,2,2,6,6-pentamethylpiperidine.

215. A compound of formula I as claimed in Claim 1 substantially as described with reference to any of Examples 2 to 17, 22 to 33, 35 to 38, 41, 44, 51, 58, 62 to 67, 76, 77, 80 and 86 to 88.

216. A compound of formula II as claimed in Claim 71 substantially as described with reference to any of Examples 1, 18 to 21, 34, 39, 40, 42 or 43.

217. A compound of formula IV as claimed in Claim 78 substantially as described with reference to any of Examples 45 to 50 or 52 to 57.

218. A process of producing a compound of formula I as claimed in Claim 1 substantially as described in any of Examples 2 to 17, 22 to 23, 35 to 38, 41, 44, 51, 58, 62 to 67, 76, 77, 80, 86 to 88.

219. A process of producing a compound of formula II as claimed in Claim 71 substantially as described with reference to any of Examples 1, 18 to 21, 34, 39, 40, 42 or 43.

220. A process of producing a compound of formula IV as claimed in Claim 134 substantially as described in any of Examples 45 to 50 or 52 to 57.

221. A composition as claimed in Claim 175 substantially as described with reference to Example 100.

222. A composition as claimed in Claim 187 substantially as described with reference to any of Examples 101 or 104 to 106.

223. A compound of formula I as claimed in Claim 1 substantially as described with reference to any of Examples 59 to 61, 68, 69 to 75, 78, 79, 81 to 85 or 89 to 93.

224. A process of producing a compound of formula I as claimed in Claim 1 substantially as described with reference to any of Examples 59 to 61, 68, 69 to 75, 78, 79, 81 to 85 or 89 to 93.

225. A composition as claimed in Claim 163 substantially as described with reference to any of Examples 94 to 99, 102, 103 or 107 to 150.

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