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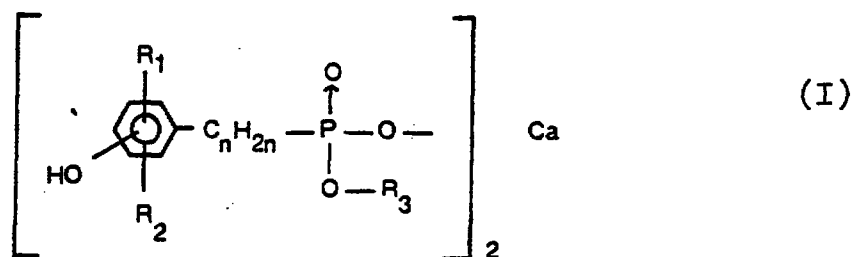
Stabilised polypropylene

The present invention relates to the use of calcium salts of phosphonic acids or half-esters thereof for stabilising polypropylene and to the polypropylene which has been stabilised by means of these calcium salts against the harmful influence of light and heat.

The use of metal salts of phosphonic acids or half-esters thereof for stabilising organic material is known from U.S. Patent Specification No. 3,310,575. The compounds described in that text possess the technical disadvantage that the substrate to be protected often has an objectionable intrinsic colour after these additives have been incorporated. Furthermore, it has been shown in Example 3 of German Offenlegungsschrift 2,517,226 that the activity, as stabilisers in low pressure polyethylene, of the calcium salts of phosphonic acids or half-esters thereof is inferior to that of the analogous compounds which are not in the form of salts.

It has now been found, not only that the calcium salts to be used in accordance with the invention impart no objectionable intrinsic colour to the polypropylene to be protected, but also that, in polypropylene, the activity of the calcium salts is superior to that of the analogous phosphonic acids or half-esters thereof which are not in the form of salts.

The invention relates, therefore, to polypropylene compositions containing at least one compound of the formula I



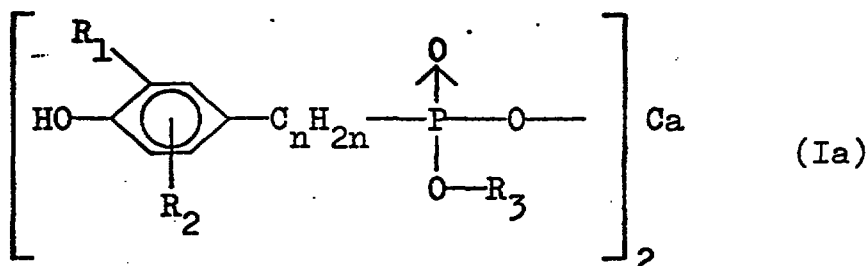
wherein n is 1, 2, 3 or 4 and R₁ is C₁-C₆ alkyl and R₂ is hydrogen or C₁-C₆ alkyl and R₃ denotes C₁-C₃₀ alkyl.

Examples of R₁ and R₂ as C₁-C₆ alkyl are methyl, ethyl, isopropyl, t-butyl, neopentyl, t-pentyl or isohexyl. Preferably, one of the radicals R₁ and R₂, and particularly preferably both of the radicals R₁ and R₂, is/are in the ortho-position in relation to the hydroxyl groups (sic). Compounds which have one or two t.-butyl groups in the ortho-position in relation to the hydroxyl group are of particular importance.

As C₁-C₃₀ alkyl, R₃ can denote, for example, methyl, ethyl, n-propyl, isopropyl, n-butyl, sec.-butyl, t.-butyl, n-pentyl, neopentyl, n-hexyl, n-octyl, t.-octyl, 2-ethylhexyl, n-decyl, n-dodecyl, n-tetradecyl, n-hexadecyl, n-octadecyl, n-eicosyl, n-docosyl or triacontyl. R₃ preferably denotes C₁-C₁₈ alkyl.

n can denote 1, 2, 3 or 4. Compounds having n = 1 or 2, and very particularly those having n = 1, are preferred.

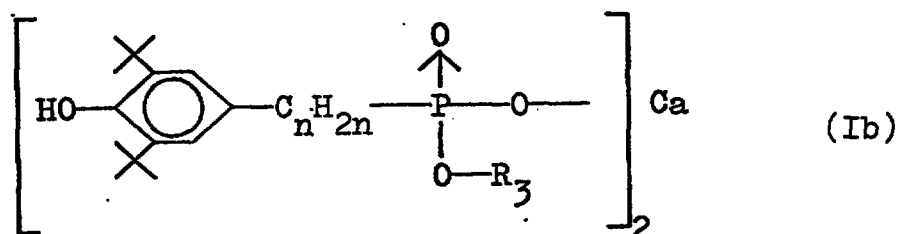
Compounds which correspond to the formula Ia



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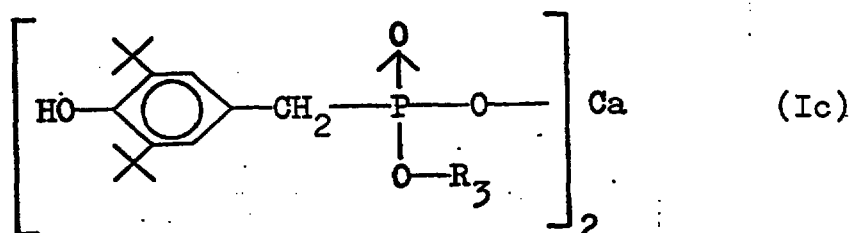
wherein n , R_1 , R_2 and R_3 have the meaning indicated above, should be singled out.

Compounds of the formula



wherein n and R_3 have the meaning indicated above, are preferred.

Particularly preferred compounds correspond to the formula



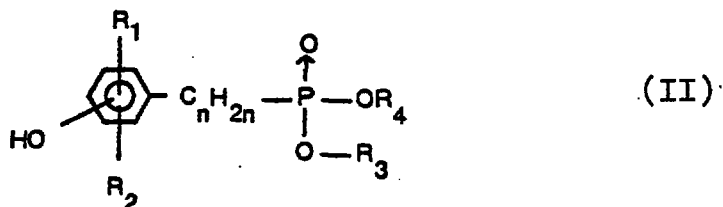
wherein R_3 has the definition indicated above.

The following may be mentioned as examples of compounds of the general formula I:

Calcium bis-[O-ethyl-(3,5-di-t.-butyl-4-hydroxybenzyl)-phosphonate], calcium bis-[O-n-butyl-(3,-di-t.-butyl-4-hydroxybenzyl)-phosphonate] (sic), calcium bis-[O-n-octyl-(3,5-di-t.-butyl-4-hydroxybenzyl)-phosphonate], calcium bis-[O-n-dodecyl-(3,5-di-t.-butyl-4-hydroxybenzyl)-phosphonate] (sic), calcium bis-[O-n-octadecyl-(3,5-di-t.-butyl-4-hydroxybenzyl)-phosphonate], calcium bis-[O-ethyl-β-(3,5-di-t.-butyl-4-hydroxyphenyl)-ethyl-phosphonate], calcium bis-[O-ethyl-β-(3-methyl-5-t.-butyl-4-hydroxyphenyl)-ethyl-phosphonate] and calcium bis-[O-ethyl-(3,5-di-isopropyl-4-hydroxybenzyl)-phosphonate] (sic).

The compounds of the formula I are prepared in a

known manner and they can be prepared in analogy with the methods described in U.S. Patent No. 3,310,575. Thus, for example, a phosphonic acid or a half-ester thereof of the formula II



wherein n, R₁, R₂ and R₃ have the meaning indicated and R₄ is hydrogen or sodium, is reacted with a calcium salt in water or in a water/alcohol mixture. If the half-ester of the free phosphonic acid is used as the starting material, a suitable calcium salt is calcium oxide, hydroxide or carbonate; if the corresponding sodium salt is used as the starting material, all calcium salts which are adequately soluble in water or mixtures thereof with alcohols, such as methanol, ethanol, isopropanol or butanol, are suitable. Examples of suitable calcium salts are calcium chloride, calcium bromide, calcium nitrate or calcium acetate. The compounds of the formula II are known. Their preparation is familiar to the expert and is carried out, for example, as described in Houben-Weyl 12 (1), 410.

The compounds to be used in accordance with the invention are suitable for stabilising polypropylene. In principle, the latter can be in any desired form, such as moulding compositions, insulation for cables and the like. The calcium phosphonates are preferred and are particularly suitable, because of their good anti-oxidative and tinctorial properties, as additives for polypropylene fibres, filaments or films. However, the calcium phosphonates also display their good effectiveness in polypropylene copolymers obtained by

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copolymerisation of propylene with, for example, α -olefines, such as ethylene, 1-butene, 1-hexene or 1-octene. In these copolymers the propylene component is preferably more than 70%.

The calcium phosphonates are incorporated by means of customary methods, for example by dry mixing the polymer with at least one of the calcium phosphonates to be used in accordance with the invention and subsequently processing in a kneader, mixing roll or extruder. The said additives can also be applied to the polymer in the form of a solution or dispersion, the solvent being subsequently evaporated.

Preferably, 0.01 to 1% by weight, particularly preferably 0.05 to 0.2% by weight, of the additive, relative to the substrate to be protected, is incorporated.

The calcium phosphonates to be used in accordance with the invention can be used on their own or together with other conventional additives. If additive mixtures are employed, synergistic effects can occur. The following are examples of further additives which are suitable in this respect:

1. Phenolic antioxidants, such as:

- a) simple 2,6-dialkylphenols, for example 2,6-di-t.-butyl-4-methylphenol,
- b) bisphenols, for example 1,1,3-tris-(5-t.-butyl-4-hydroxy-2-methylphenyl)-butane or 4,4'-thiobis-(6-t.-butyl-3-methylphenol),
- c) hydroxybenzyl-aromatics, for example 1,3,5-tris-(3,5-di-t.-butyl-4-hydroxybenzyl) isocyanurate or 1,3,5-tri-(3,5-di-t.-butyl-4-hydrobenzyl)-2,4,6-methylbenzene (sic), and
- d) esters of β -(3,5-di-t.-butyl-4-hydroxyphenyl (sic) propionic acid with monohydric or polyhydric alcohols, such as, for example, octadecanol, thiodiethylene glycol or pentaerythritol.

2. UV absorbers and light stabilisers, such as:

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2-(2'-hydroxyphenyl)-benztriazoles, 2,4'-bis-(2'-hydroxyphenyl)-6-alkyl-s-triazines, 2-hydroxybenzophenones, 1,3-bis-2-(2'-hydroxybenzoyl)-benzenes, esters of optionally substituted benzoic acids, acrylates, nickel compounds, sterically hindered amines or oxalic acid diamides.

3. Metal deactivators, such as:

N,N'-bis-salicyloylhydrazine.

4. Phosphites, such as:

tri-(nonylphenyl) phosphite or tris-(2,4-di-tert-butylphenyl) phosphite.

5. Compounds which destroy peroxide, such as:

the esters of β -thiodipropionic acid.

6. Other additives, such as:

lubricants, emulsifiers, pigments, optical brighteners, flameproofing agents or antistatic agents.

Examples of further additives, together with which the stabilisers to be used according to the invention can be employed, are to be found on pages 18-24 of German Offenlegungsschrift 2,427,853.

The invention is described in greater detail in the examples which follow. In these, percentages (%) denote percentages by weight, calculated on the material to be stabilised.

Example 1

Preparation of calcium bis-[O-ethyl-(3,5-di-tert.-butyl-4-hydroxybenzyl)-phosphonate]

328 g (1 mol) of O-ethyl-4-hydroxy-3,5-di-tert.-butylbenzylphosphonic acid are suspended in 2.5 l of water and neutralised with 100 ml of 10N sodium hydroxide solution (pH 6.5). This gives a clear solution, into which a solution of 123 g (0.525 mol) of calcium nitrate tetrahydrate in 130 ml of water is added dropwise in the course of 45 minutes at room temperature. The precipitate which is deposited in a crystalline state is filtered off, washed with 500 ml of water and then dried for 14 hours at 70°C and under a pressure of 11 mm Hg.

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Calcium bis-[O-ethyl-(3,5-di-tert.-butyl-4-hydroxy-benzyl)-phosphonate] is obtained in this manner as colourless crystals.

Elementary analysis:

calculated:	C 58.75%	H 8.12%	P 8.92%	Ca 5.76%
found:	C 58.69%	H 8.20%	P 8.81%	Ca 5.43%

The same compound is also obtained by suspending 328 g (1 mol) of O-ethyl-4-hydroxy-3,5-di-tert.-butylbenzylphosphonic acid and 28 g (0.5 mol) of calcium oxide in 6 l of 50% strength aqueous ethanol and heating the mixture under reflux until a clear solution has been formed.

The resulting calcium salt of the acid mentioned is isolated by evaporating the solution to approx. 1/6 of its volume. In the course thereof, this salt separates out gradually as a crystalline precipitate, which is dried in the manner described above.

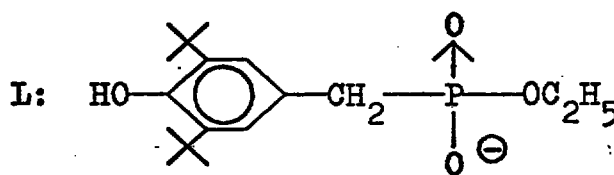
Example 2

1,000 parts of unstabilised polypropylene powder (melt index ~ 20) are mixed in a high-speed mixer with 1 part of calcium stearate and 2.5 parts of a delustering agent (rutile TiO_2) and also in each case with the additives listed in the following table, and are subsequently extruded at a maximum temperature of 220° and granulated. The resulting granules are spun into multifilaments on a laboratory extruder-spinning apparatus at a maximum temperature of 280°C and these multifilaments are stretched on a draw-twisting machine to give a final gauge of 130/37 denier and a residual elongation of 30%. Each of these multifilaments is then wound up in 4 parallel layers on a sheet of cardboard to form so-called yarn surfaces on which the yellowness index values (YI) are determined in accordance with ASTM 1925-70. (Smaller numbers denote better colours).

The results are listed in Table I:

Table I

Additives	YI
none	2.71
0.1% Ca(L)_2 0.2% Ca(L)_2	1.96 1.90
0.1% Ba(L)_2 0.2% Ba(L)_2	2.74 2.41
0.1% H(L) 0.2% H(L)	3.50 2.68
0.1% Ni(L)_2 0.2% Ni(L)_2	3.97 4.08
0.1% Zn(L)_2 0.2% Zn(L)_2	2.68 2.59

Example 3

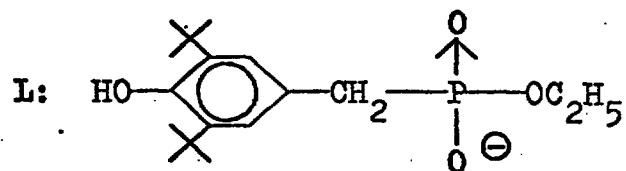
1,000 parts of unstabilised polypropylene powder (melt index ~ 20) are mixed in a high-speed mixer with 1 part of calcium stearate, 2.5 parts of a delustering agent (rutin (sic) TiO_2) and 6 parts of dilauryl thiodi-propionate and also in each case with the additives listed in the table and are subsequently extruded at a maximum temperature of 220°C and granulated. The multifilaments are prepared and the yellowness index values (YI) are determined as described in Example 2.

The results are listed in Table II:

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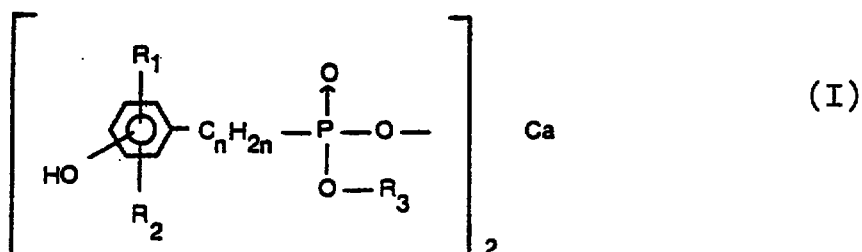
Table II

Additive	YI
none	2.16
0.2% Ca(L)_2	1.53
0.2% Ba(L)_2	2.17
0.2% H(L)	2.37
0.2% Ni(L)_2	5.00
0.2% Zn(L)_2	2.75



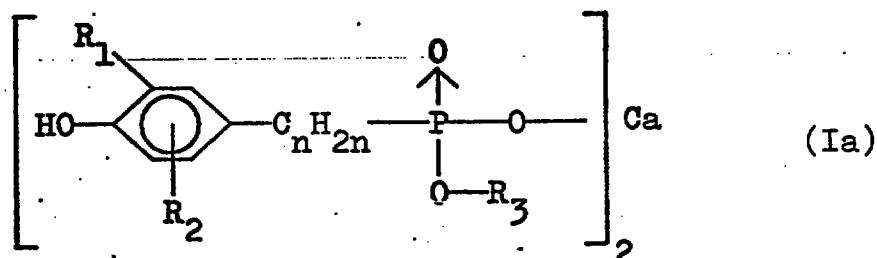
Patent Claims

1. Polypropylene compositions containing at least one compound of the formula I



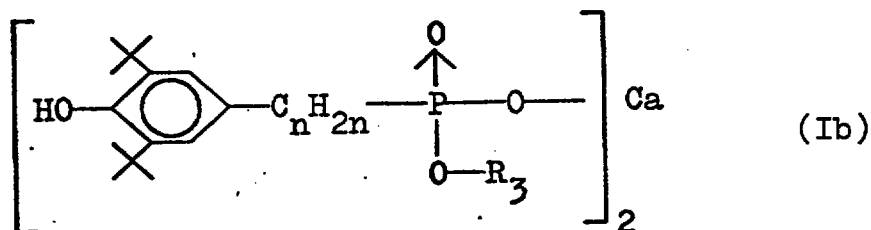
wherein n is 1, 2, 3 or 4 and R₁ is C₁-C₆ alkyl and R₂ is hydrogen or C₁-C₆ alkyl and R₃ denotes C₁-C₃₀ alkyl.

2. Polypropylene compositions according to claim 1, containing at least one compound of the formula



wherein n, R₁, R₂ and R₃ have the meaning indicated above.

3. Polypropylene compositions according to claim 1, containing at least one compound of the formula

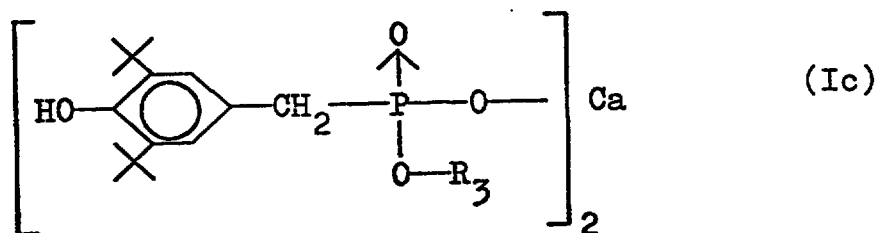


wherein n and R₃ have the meaning indicated above.

4. Polypropylene composition according to claim 1, containing at least one compound of the formula



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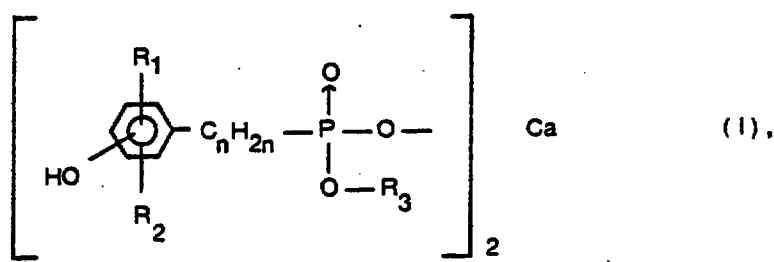
wherein R_3 has the meaning indicated above.

5. Polypropylene composition according to claim 1, characterised in that n is 1 or 2 in the formula I.
6. Polypropylene compositions according to claim 1, characterised in that they are copolymers of propylene with ethylene, 1-butene, 1-hexene or 1-octene.
7. Polypropylene compositions according to claim 1, characterised in that they are polypropylene filaments, fibres or films.
8. Polypropylene composition according to claim 1, characterised in that the compound of the formula I is calcium bis-[O-ethyl-(3,5-di-t.-butyl-4-hydroxybenzyl)-phosphonate].



Revendications (as printed)

1. Compositions à base de polypropylène qui contiennent au moins un composé répondant à la formule I



dans laquelle

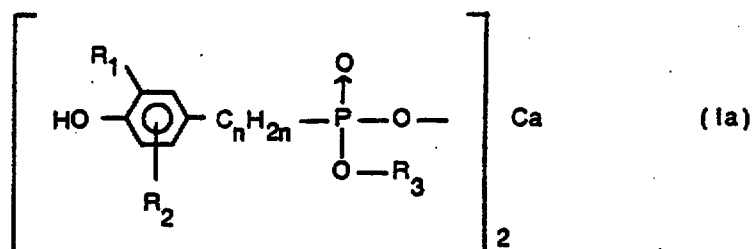
n est égal à 1, à 2, à 3 ou à 4;

R₁ représente un radical alkyle contenant de 1 à 6 atomes de carbone,

R₂ représente l'hydrogène ou un radical alkyle contenant de 1 à 6 atomes de carbone et

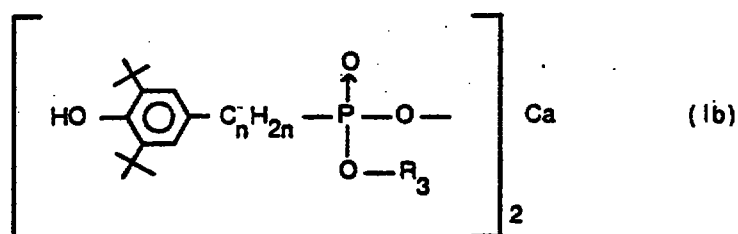
R₃ représente un radical alkyle contenant de 1 à 30 atomes de carbone.

2. Compositions à base de polypropylène selon la revendication 1, qui contiennent au moins un composé répondant à la formule



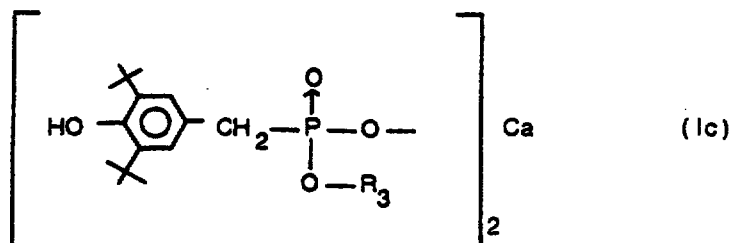
dans laquelle n, R₁, R₂ et R₃ ont les significations indiquées ci-dessus.

3. Compositions à base de polypropylène selon la revendication 1 qui contiennent au moins un composé répondant à la formule



dans laquelle n et R₃ ont les significations précédemment données.

4. Composition à base de polypropylène selon la revendication 1 qui contient au moins un composé répondant à la formule:



dans laquelle R₃ a la signification précédemment donnée.

5. Composition à base de polypropylène selon la revendication 1, caractérisée en ce que, dans la formule I, n est égal à 1 ou à 2.

6. Compositions à base de polypropylène selon la revendication 1, caractérisées en ce qu'il s'agit de copolymères du propylène avec l'éthylène, le butène-1, l'hexène-1 ou l'octène-1.

7. Compositions à base de polypropylène selon la revendication 1, caractérisées en ce qu'il s'agit de fils, de fibres ou de feuillets de polypropylène.

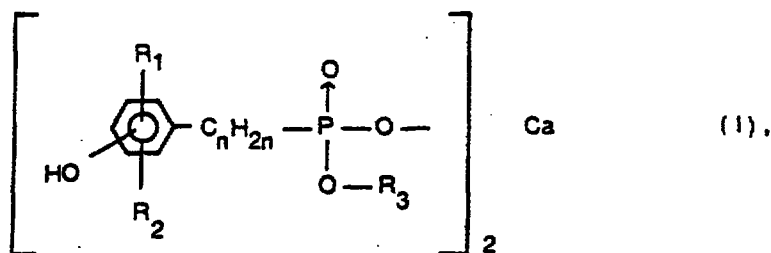
8. Composition à base de polypropylène selon la revendication 1, caractérisée en ce que le composé de formule I est le bis-[O-éthyl-(di-tert-butyl-3,5-hydroxy-4-benzyl)-phosphonate] de calcium.



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Claims (as printed)

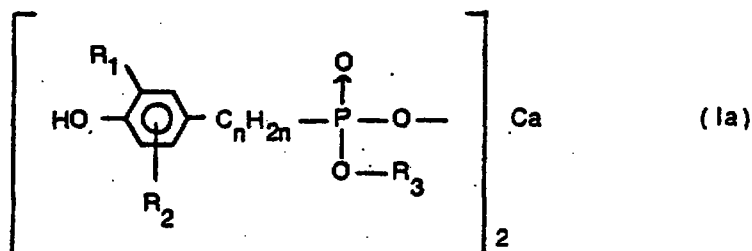
1. A polypropylene composition containing at least one compound of the formula I



wherein

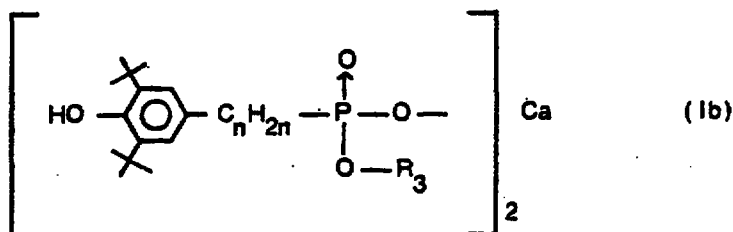
- n is 1, 2, 3 or 4,
 R_1 is C_1 — C_8 -alkyl,
 R_2 is hydrogen or C_1 — C_8 -alkyl, and
 R_3 is C_1 — C_{30} -alkyl.

2. A polypropylene composition according to Claim 1 containing at least one compound of the formula



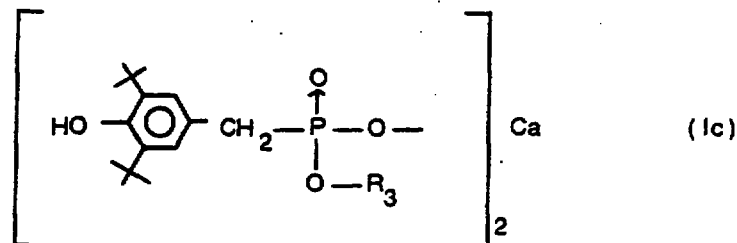
wherein n , R_1 , R_2 and R_3 have the meanings defined above.

3. A polypropylene composition according to Claim 1 containing at least one compound of the formula



wherein n and R_3 have the meanings defined above.

4. A polypropylene composition according to Claim 1 containing at least one compound of the formula



wherein R_3 has the meaning defined above.

5. A polypropylene composition according to Claim 1, wherein n is 1 or 2 in the formula I.
 6. A polypropylene composition according to Claim 1, wherein a copolymer of propylene with ethylene, 1-butene, 1-hexene or 1-octene is used.
 7. A polypropylene composition according to Claim 1, which is in the form of polypropylene filaments, fibres or films.
 8. A polypropylene composition according to Claim 1, wherein the compound of the formula I is calcium-bis-[O-ethyl-(3,5-di-t-butyl-4-hydroxybenzyl)-phosphonate].