

PATENT SPECIFICATION

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(54) STABILIZING POLYOLEFINS BY MEANS OF AMIDOTHIOPHOSPHATE DIESTERS AND NOVEL AMIDOTHIOPHOSPHATE DIESTERS USEFUL FOR SUCH STABILIZATION

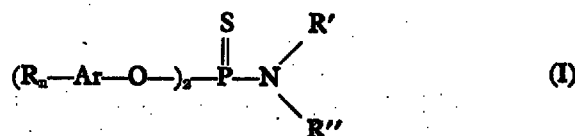
(71) We, AMERICAN CYANAMID COMPANY, a corporation organised and existing under the Laws of the State of Maine, United States of America, of Berdan Avenue, Township of Wayne, State of New Jersey, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to stabilizing polyolefins against the deteriorating effects of light by the use of certain amidothiophosphate diesters, alone or in combination with other stabilizers, especially a 2-hydroxy-4-alkoxybenzophenone, and to certain novel amidothiophosphate diester compounds useful for such stabilization.

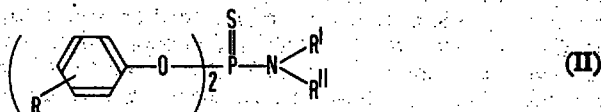
As is well known, polyolefins such as polypropylene and polyethylene tend to deteriorate from the effects of light, especially ultraviolet light. This deterioration generally manifests itself as a loss of tensile strength and loss of flexibility of the polymer.

In accordance with the present invention, we have found that certain O,O-bis-(aryl)amidothiophosphates, alone or in combination with other stabilizers especially a 2-hydroxy-4-alkoxybenzophenone, can retard or inhibit the deterioration due to light of polyolefin compositions, for example polyethylene and polypropylene compositions.

The O,O-bis(aryl)amidothiophosphates useful for the practice of the present invention are those having the formula:



wherein: R is hydrogen, alkyl of 1—12 carbons, or halogen; Ar is phenyl or naphthyl; n is 1 or 2; and R' and R'', which may be the same or different, are hydrogen, alkyl of 1—18 carbons, 2,2,6,6-tetramethyl-4-piperidyl, cycloalkyl of 5—6 carbons, or R' and R'' together with the nitrogen to which they are attached form a morpholino or piperidino ring. Within this class of compounds, those which are preferred since they give better light stability to polyolefins are the compounds of the formula:



wherein: R is hydrogen, alkyl of 1—12 carbons, or halogen; R' and R'', which may be the same or different, are hydrogen, cyclohexyl, or 2,2,6,6-tetramethyl-4-piperidyl. Especially preferred, since they give the best light stability to polyolefins, are the novel compounds of the formula:



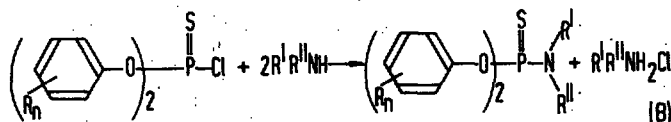
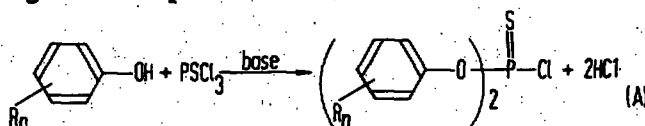
wherein: R is alkyl of 1—6 carbons or halogen; R' is cyclohexyl or 2,2,6,6-tetramethyl-4-piperidyl; and R'' is hydrogen or R'.

As a broad class, amidophosphates are known compounds as shown in such references as United States Patents 3,100,197; 3,309,317; and 3,531,550; British Patents 941,575 and 1,039,924; and Kosolapoff, "Organophosphorus Compounds" (1950) pages 278—324. Such broad class of amidophosphates may be represented by the formula:



wherein: Q, Q', and Q'' represent hydrogen or organic moieties, n is 1, 2, or 3, and X is oxygen or sulfur. We have found that only a very small segment of this broad class contains compounds useable alone or in combination with a 2-hydroxy-4-alkoxybenzophenone to stabilize polyolefins against deterioration by light. The compounds of this small segment, having the structural formulae (I), (II), or (III), *supra*, have certain structural features in common. First, the X of formula (IV) must be sulfur; compounds wherein the X is oxygen are greatly inferior or even inoperative as light stabilizers in polyolefins. Second, n of formula (IV) must be one; the diamides and triamides are inferior as light stabilizers in polyolefins. Third, the Q of formula (IV) should be aromatic and the Q' and Q'' should not be aromatic since compounds wherein Q is aliphatic and compounds wherein Q' or Q'' is aromatic are inferior for this purpose.

The compounds of formula (IV), *supra*, can be prepared in several ways, one of which is described generically in United States Patent 3,531,550 (columns 3 and 4). To make the specific compounds of formulae (I), (II), or (III), *supra*, the appropriate phenol can be reacted with thiophosphoryl chloride in the presence of an HCl-acceptor i.e. a base to give an intermediate which can then be reacted with the appropriate amine to give the desired O,O-bis(aryl)amidothiophosphate, e.g. according to the following reaction sequence:



To make compounds of formulae (I), (II), or (III), *supra*, suitable monohydroxyphenols include phenol, methylphenols or cresols, ethylphenols, propylphenols, butylphenols, hexylphenols, octylphenols, nonylphenols, decylphenyls, dodecylphenols, dimethylphenols or xylenols, isopropylmethyl-phenol or thymol, di-tert.butyl-phenols, chlorophenols, methylchlorophenols, naphthols, methylnaphthols, ethylnaphthols, and chloronaphthols. Preferably, where the phenol has one substituent, such substituent is in the para position. Suitable amines include ammonia, methylamine, ethylamine, butylamines, hexylamines, octylamines, dodecylamines, octadecylamines, cyclopentylamine, cyclohexylamine, 4-amino-2,2,6,6-tetramethylpiperidine, morpholine, piperidine, dimethylamine, dibutylamines, dioctylamines, methylbutylamine, methylcyclohexylamine, and dicyclohexylamine.

The compounds of formulae (I), (II), and (III), *supra*, when incorporated alone in polyolefins are found to inhibit degradation due to exposure to light. This effect can usually be enhanced if a 2-hydroxy-4-alkoxybenzophenone, a 2-(2'-hydroxyphenyl)-benzotriazole, a nitroxide, a tetramethylpiperidine derivative, or a 3,5-ditert.butyl-4-hydroxybenzoate is also incorporated in the polyolefin. Illustrative of such enhancing

compounds are those mentioned in such prior art as United States Patents 3,189,615; 3,206,431; 3,230,194; 3,431,232; 3,431,233; 3,436,369; 3,448,074; 3,474,068; and 3,640,928. A stabilizer composition comprising, in combination, a 2-hydroxy-4-alkoxybenzophenone and an O,O-bis(aryl)amidothiophosphate of formula (I) forms one aspect of the present invention.

When used alone, or in combination with a 2-hydroxy-4-alkoxybenzophenone, the O,O-bis(aryl)amidothiophosphate is usually incorporated into the polyolefin at a concentration of 0.1 to 2% by weight, preferably at a concentration of 0.2 to 0.5% on the weight of the polyolefin. When used with a 2-hydroxy-4-alkoxybenzophenone enhancer, the ratio by weight of the O,O-bis(aryl)amidothiophosphate to the 2-hydroxy-4-alkoxybenzophenone is usually from 10/1 to 1/10, although a ratio of about 1/1 is normally preferred. Further enhancement is oftentimes obtained when the O,O-bis(aryl)amidothiophosphate or the combination thereof with the 2-hydroxy-4-alkoxybenzophenone is used with a phosphite, such as a cyclic phosphite as disclosed in United States Patent 3,205,250, especially distearylentaerythritol diphosphate; tris(p-nonylphenyl)phosphite; alkyl phosphites, such as dioctylphosphite and tridecylphosphite; alkyl aryl phosphites, such as phenyl didecyl phosphite; and aryl o-phenylene phosphites, such as phenyl or 4-methyl-2,6-di-t-butylphenyl o-phenylene phosphite. Other additives, such as processing antioxidants, secondary stabilizers such as dilauryl- or distearyl-thiodipropionate, pigments, dyes, flame retardants and lubricants, may also be included in the polyolefin for their usual purposes.

The invention extends to a shaped article formed from a polyolefin composition having incorporated therein an O,O-bis(aryl)amidothiophosphate of formula I above.

The following examples illustrate the invention.

Example 1

Preparation of O,O-bis(p-tert.butylphenyl)-N-cyclohexylamidothiophosphate

To a solution of cyclohexylamine (20 grams, 0.2 mole) in 10 milliliters of dimethylformamide and 50 milliliters of benzene at 50–60°C. was added dropwise, with stirring, a solution of O,O-bis(p-tert.butylphenyl)chlorothiophosphate (20 grams, 0.05 mole) in 100 milliliters of benzene. The mixture was refluxed for eight hours, cooled, and filtered. The filtrate was evaporated under reduced pressure, and the oil that remained was triturated with cold methanol. The solid which formed was filtered and recrystallized twice from methanol to give 17.6 grams of product, m.p. 107–190°C.

Example 2

Testing in Polypropylene

The compound of Example 1 (0.5% by weight) was dry blended with a mastermix of unstabilized polypropylene ("Profax" 6401—"Profax" is a registered Trade Mark) and 0.2% by weight of a processing antioxidant viz 2,4,6-tritert.butylphenol. The blend was milled for five minutes at 350–370°F. and the milled sample was compression molded into a film 4–5 mils thick at 400°F. The compression molded film, and a control film identically prepared except without the compound of Example 1, were exposed in a "Xenon" (registered Trade Mark) Weather-O-Meter (Atlas) until they failed. The samples were considered as having failed when the carbonyl content in the infrared spectrum reached 0.1%, a generally accepted point of film embrittlement. The test sample lasted 1625 hours.

Example 3

In the manner of Example 1, using the appropriate amines and appropriate O,O-bis(phenyl)chlorothiophosphates, additional compounds were prepared and tested as in Example 2. The compounds and the test results are described below.

Example 3—dicyclohexylamine reacted with O,O-bis(p-tert.butylphenyl)chlorothiophosphate to yield O,O-bis(p-tert.butylphenyl)-N,N-dicyclohexylamidothiophosphate, m.p. 208–212°C. which, in polypropylene test sample, lasted 1125 hours.

Example 4—cyclohexylamine reacted with O,O-bis(p-methylphenyl)chlorothiophosphate to yield O,O-bis(p-methylphenyl)-N-cyclohexylamidothiophosphate, a liquid, which, on testing, lasted 925 hours.

Example 5—cyclohexylamine reacted with O,O-bis(p-chlorophenyl)chlorothiophosphate to yield O,O-bis(p-chlorophenyl)-N-cyclohexylamidothiophosphate, m.p. 65–67°C. which, on testing, lasted 1225 hours.

Example 6—cyclohexylamine reacted with O,O-bis(p-tert.octylphenyl)chlorothiophosphate to yield O,O-bis(p-tert.octylphenyl)-N-cyclohexylamidothiophosphate, m.p. 80–82°C. which, on testing, lasted 725 hours.

Example 7—cyclohexylamine reacted with O,O-bis(2,4-di-tert.butylphenyl)chlorothiophosphate to yield O,O-bis(2,4-di-tert.butylphenyl)-N-cyclohexylamidothiophosphate, m.p. 167—168°C. which, on testing, lasted 974 hours.

Example 8—cyclohexylamine reacted with O,O-bis(phenyl)chlorothiophosphate to yield O,O-bis(phenyl)-N-cyclohexylamidothiophosphate, m.p. 76—77°C. which, on testing, lasted 1035 hours.

Example 9—4-amino-2,2,6,6-tetramethylpiperidine reacted with O,O-bis(p-tert.butylphenyl)chlorothiophosphate to yield O,O-bis(p-tert.butylphenyl)-N-(2,2,6,6-tetramethyl-4-piperidyl)amidothiophosphate, m.p. 131—133°C. which, on testing, lasted 1225 hours.

Example 10—morpholine reacted with O,O-bis(p-tert.butylphenyl)chlorothiophosphate to yield O,O-bis(p-tert.butylphenyl)-N-oxydiethylenamidothiophosphate, m.p. 110—112°C. which, on testing, lasted 975 hours.

Example 11—ammonia reacted with O,O-bis(p-tert.butylphenyl)chlorothiophosphate to yield O,O-bis(p-tert.butylphenyl)amidothiophosphate, m.p. 128—129°C. which, on testing, lasted 1025 hours.

Example 12—di-n-butylamine reacted with O,O-bis(p-tert.butylphenyl)chlorothiophosphate to yield O,O-bis(p-tert.butylphenyl)-N,N-di-n-butylamidothiophosphate, a liquid, which, on testing lasted 725 hours.

Examples 13—n-butylamine reacted with O,O-bis(p-tert.butylphenyl)chlorothiophosphate to yield O,O-bis(p-tert.butylphenyl)-N-n-butylamidothiophosphate, m.p. 78—80°C. which, on testing, lasted 975 hours.

Example 14—tert.butylamine reacted with O,O-bis(p-tert.butylphenyl)chlorothiophosphate to yield O,O-bis(p-tert.butylphenyl)-N-tert.butylamidothiophosphate, m.p. 75—77°C. which, on testing, lasted 875 hours.

Example 15—n-octylamine reacted with O,O-bis(p-tert.butylphenyl)chlorothiophosphate to yield O,O-bis(p-tert.butylphenyl)-N-n-octylamidothiophosphate, m.p. 33—37°C. which, on testing, lasted 875 hours.

Example 16

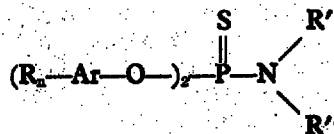
Following the procedure of Example 2, films were prepared containing 0.25% for the compound of one of the foregoing examples in combination with 0.25% 2-hydroxy-4-octyloxybenzophenone (Cyasorb) UV-531) and tested with the results shown in the following table.

Compound of Example	Hours to Failure
1	2200
3	3000
7	2200
8	2100
10	2100
13	2000
15	2200

For comparison, a control (without either additive) only lasted 500 hours, and a film containing 0.5% of the 2-hydroxy-4-octyloxybenzophenone without any amidothiophosphate only lasted 1700 hours.

WHAT WE CLAIM IS:—

1. A polyolefin composition stabilized against the deteriorating effects of light by having incorporated therein a stabilizer of the formula:



wherein: R is hydrogen, alkyl of 1—12 carbons, or halogen; Ar is phenyl or naphthyl; n is 1 or 2; and R' and R'' are hydrogen, alkyl of 1—18 carbons, 2,2,6,6-tetramethyl-4-piperidyl, cycloalkyl of 5—6 carbons, or R' and R'', together with the nitrogen to which they are attached form a morpholino or piperidino ring.

2. A composition as defined in Claim 1, wherein the stabilizer has the formula:



Example 7—cyclohexylamine reacted with O,O-bis(2,4-di-tert.butylphenyl)chlorothiophosphate to yield O,O-bis(2,4-di-tert.butylphenyl)-N-cyclohexylamidothiophosphate, m.p. 167—168°C. which, on testing, lasted 974 hours.

Example 8—cyclohexylamine reacted with O,O-bis(phenyl)chlorothiophosphate to yield O,O-bis(phenyl)-N-cyclohexylamidothiophosphate, m.p. 76—77°C. which, on testing, lasted 1035 hours.

Example 9—4-amino-2,2,6,6-tetramethylpiperidine reacted with O,O-bis(p-tert.butylphenyl)chlorothiophosphate to yield O,O-bis(p-tert.butylphenyl)-N-(2,2,6,6-tetramethyl-4-piperidyl)amidothiophosphate, m.p. 131—133°C. which, on testing, lasted 1225 hours.

Example 10—morpholine reacted with O,O-bis(p-tert.butylphenyl)chlorothiophosphate to yield O,O-bis(p-tert.butylphenyl)-N-oxydiethyleneamidothiophosphate, m.p. 110—112°C. which, on testing, lasted 975 hours.

Example 11—ammonia reacted with O,O-bis(p-tert.butylphenyl)chlorothiophosphate to yield O,O-bis(p-tert.butylphenyl)amidothiophosphate, m.p. 128—129°C. which, on testing, lasted 1025 hours.

Example 12—di-n-butylamine reacted with O,O-bis(p-tert.butylphenyl)chlorothiophosphate to yield O,O-bis(p-tert.butylphenyl)-N,N-di-n-butylamidothiophosphate, a liquid, which, on testing lasted 725 hours.

Examples 13—n-butylamine reacted with O,O-bis(p-tert.butylphenyl)chlorothiophosphate to yield O,O-bis(p-tert.butylphenyl)-N-n-butylamidothiophosphate, m.p. 78—80°C. which, on testing, lasted 975 hours.

Example 14—tert.butylamine reacted with O,O-bis(p-tert.butylphenyl)chlorothiophosphate to yield O,O-bis(p-tert.butylphenyl)-N-tert.butylamidothiophosphate, m.p. 75—77°C. which, on testing, lasted 875 hours.

Example 15—n-octylamine reacted with O,O-bis(p-tert.butylphenyl)chlorothiophosphate to yield O,O-bis(p-tert.butylphenyl)-N-n-octylamidothiophosphate, m.p. 33—37°C. which, on testing, lasted 875 hours.

Example 16

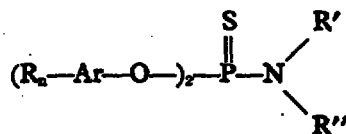
Following the procedure of Example 2, films were prepared containing 0.25% for the compound of one of the foregoing examples in combination with 0.25% 2-hydroxy-4-octyloxybenzophenone (Cyasorb) UV-531 and tested with the results shown in the following table.

Compound of Example	Hours to Failure
1	2200
3	3000
7	2200
8	2100
10	2100
13	2000
15	2200

For comparison, a control (without either additive) only lasted 500 hours, and a film containing 0.5% of the 2-hydroxy-4-octyloxybenzophenone without any amidothiophosphate only lasted 1700 hours.

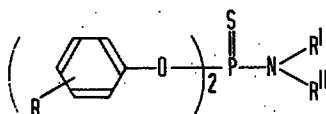
WHAT WE CLAIM IS:—

1. A polyolefin composition stabilized against the deteriorating effects of light by having incorporated therein a stabilizer of the formula:



wherein: R is hydrogen, alkyl of 1—12 carbons, or halogen; Ar is phenyl or naphthyl; n is 1 or 2; and R' and R'' are hydrogen, alkyl of 1—18 carbons, 2,2,6,6-tetramethyl-4-piperidyl, cycloalkyl of 5—6 carbons, or R' and R'', together with the nitrogen to which they are attached form a morpholino or piperidino ring.

2. A composition as defined in Claim 1, wherein the stabilizer has the formula:



wherein: R is hydrogen, alkyl of 1—12 carbons, or halogen; and R' and R'' are hydrogen, 2,2,6,6-tetramethyl-4-piperidyl, or cyclohexyl.

3. A composition as defined in Claim 2, wherein: R is a para-substituent and is alkyl of 1—6 carbons, or halogen; R' is cyclohexyl or 2,2,6,6-tetramethyl-4-piperidyl; and R'' is hydrogen or R'.

4. A composition as defined in Claim 3, wherein the stabilizer is O,O-bis(p-tert-butylphenyl)-N,N-di-cyclohexylamidothiophosphate.

5. A composition as defined in Claim 3, wherein the stabilizer is O,O-bis(p-tert-butylphenyl)-N-cyclohexylamidothiophosphate.

6. A composition as defined in Claim 3, wherein the stabilizer is O,O-bis(p-chlorophenyl)-N-cyclohexylamidothiophosphate.

7. A composition as defined in Claim 3, wherein the stabilizer is O,O-bis(p-methylphenyl)-N-cyclohexylamidothiophosphate.

8. A composition as defined in Claim 2, wherein the stabilizer is O,O-bis(phenyl)-N-cyclohexylamidothiophosphate.

9. A composition as defined in any preceding claim and containing from 0.1 to 2% by weight of said stabilizer, based on the weight of polyolefin.

10. A composition as defined in Claim 9 and containing from 0.2 to 0.5% by weight of said stabilizer, based on the weight of polyolefin.

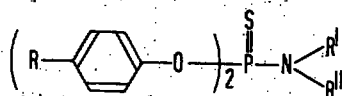
11. A composition as defined in any preceding claim, wherein said polyolefin is polypropylene or polyethylene.

12. A composition as defined in any preceding claim and also having incorporated therein a 2-hydroxy-4-alkoxybenzophenone.

13. A composition as defined in Claim 12, wherein said 2-hydroxy-4-alkoxybenzophenone is 2-hydroxy-4-octyloxybenzophenone.

14. A composition as defined in Claim 12 or Claim 13, wherein the ratio by weight of the 2-hydroxy-4-alkoxybenzophenone to said stabilizer is from 10:1—1:10.

15. A compound having the formula:



wherein: R is alkyl of 1—6 carbons, or halogen; R' is cyclohexyl or 2,2,6,6-tetramethyl-4-piperidyl; and R'' is hydrogen or R'.

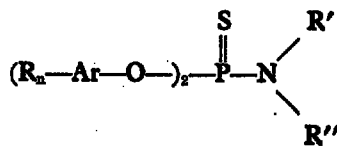
16. A compound as defined in Claim 15, wherein R is tert-butyl and R' is cyclohexyl, and R'' is hydrogen or cyclohexyl.

17. A compound as defined in Claim 15, wherein R is chlorine, methyl, or tert-butyl, R' is cyclohexyl, and R'' is hydrogen.

18. A compound as defined in Claim 15 which is O,O-bis(p-tert-butylphenyl)-N-(2,2,6,6-tetramethyl-4-piperidyl)amidothiophosphate.

19. A compound as defined in Claim 15 which is O,O-bis(p-tert-butylphenyl)-N-cyclohexylamidothiophosphate.

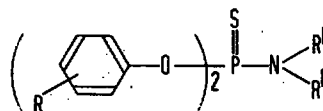
20. A stabilizer composition useful for stabilizing polyolefins against the deteriorating effects of light, comprising, in combination, a 2-hydroxy-4-alkoxybenzophenone and a compound of the formula:



wherein: R is hydrogen, alkyl of 1—12 carbons, or halogen; Ar is phenyl or naphthyl; n is 1 or 2; and R' and R'' are hydrogen, alkyl of 1—18 carbons, 2,2,6,6-tetramethyl-4-piperidyl, cycloalkyl of 5—6 carbons, or R' and R'', together with the nitrogen to which they are attached form a morpholino or piperidino ring.

21. A stabilizer composition as defined in Claim 20, wherein said compound has the formula:





wherein R is hydrogen, alkyl of 1—12 carbons, or halogen; and R' and R'' are hydrogen, 2,2,6,6-tetramethyl-4-piperidyl, or cyclohexyl.

22. A stabilizer composition as defined in Claim 21 wherein: R is a para substituent and is alkyl of 1—6 carbons or halogen; R' is cyclohexyl or 2,2,6,6-tetramethyl-4-piperidyl; and R'' is hydrogen or R'.

23. A stabilizer composition as defined in Claim 22, wherein said compound is O,O-bis(p-tert.butylphenyl)-N-cyclohexylamidothiophosphate or O,O-bis(p-tert.butylphenyl)-N,N-dicyclohexylamidothiophosphate.

24. A stabilizer composition as defined in any one of Claims 20—23, wherein said 2-hydroxy-4-alkoxybenzophenone is 2-hydroxy-4-octyloxybenzophenone.

25. A stabilizer composition as defined in any one of Claims 20—24, wherein the ratio by weight of said 2-hydroxy-4-alkoxybenzophenone to said compound is from 10/1 to 1/10.

26. A compound as defined in Claim 15 and substantially as described in any one of Examples 1 and 3 to 6 herein.

27. A polyolefin composition as defined in Claim 1 and substantially as described in any one of Examples 2 to 16 herein.

28. A shaped article formed from a polyolefin composition as defined in any one of Claims 1—14 or Claim 27.

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