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3,565,855

## PHOSPHORUS-CONTAINING ANTIOXIDANT IN POLYOLEFINS

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16 Claims

### ABSTRACT OF THE DISCLOSURE

Dihydrocarbylhydroxyphenyl aryl or alkyl phosphonites, phosphonates, phosphates, phosphites, phosphinates, phosphinites, phosphorothionates, phosphonothionates, and phosphinothionates are antioxidants. The effectiveness of these antioxidants is enhanced by use in combination with a dihydrocarbylthiodialkanoate such as dilaurylthiodipropionate (DLTDP). The stabilizers are especially useful in polypropylene.

This application is a division of application Ser. No. 612,317, filed Jan. 30, 1967.

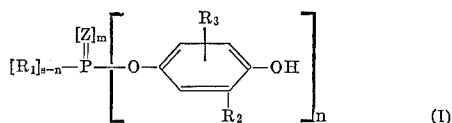
### BACKGROUND

This invention relates to the stabilization of organic material with phosphorus-containing antioxidants. In particular, this invention relates to the stabilization of organic material with phosphonites, phosphonates, phosphates, phosphites, phosphinites, phosphinates, phosphorothionates, phosphonothionates, and phosphinothionates containing dihydrocarbylhydroxyphenyl groups. The invention also relates to the use of these antioxidants in combination with a dihydrocarbylthiodialkanoate synergist.

Phosphorus-containing antioxidants for organic materials are known. For example, G. G. Knapp, in U.S. 3,155,704, issued Nov. 3, 1964, describes dialkyl(3,5-dialkyl-4-hydroxybenzyl)phosphonates that are useful as antioxidants. Also, trialkylphosphites and trialkarylphosphites have been disclosed as antioxidants.

### SUMMARY

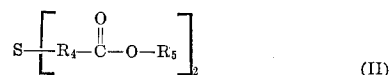
An object of this invention is to provide stable organic compositions. A further object is to provide polyolefin compositions of enhanced stability. These and other objects are fulfilled by furnishing an antioxidant having the formula:



wherein  $n$  is an integer from 1–2,  $m$  is an integer from 0–1,  $Z$  is selected from the group consisting of oxygen and sulfur,  $R_1$  is selected from the group consisting of alkyl radicals containing from 1–20 carbon atoms, alkoxy radicals containing from 1–20 carbon atoms, aryl radicals containing from 6–20 carbon atoms, and aralkyl radicals containing from 7–20 carbon atoms;  $R_2$  is selected from the group consisting of alpha-branched alkyl radicals containing from 3–20 carbon atoms, cycloalkyl radicals containing from 6–20 carbon atoms, and alpha-branched aralkyl radicals containing from 8–20 carbon atoms; and  $R_3$  is selected from the group consisting of alkyl radicals containing from 1–20 carbon atoms, cycloalkyl radicals containing from 6–20 carbon atoms, and aralkyl radicals containing from 7–20 carbon atoms. These antioxidants

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may be used alone to stabilize organic material or in combination with a synergist having the formula:



wherein  $R_4$  is a divalent hydrocarbon radical containing from about 1–6 carbon atoms, and  $R_5$  is selected from the group consisting of alkyl radicals containing from 6–20 carbon atoms, cycloalkyl radicals containing from 6–20 carbon atoms, aryl radicals containing from 6–20 carbon atoms, and aralkyl radicals containing from 7–20 carbon atoms.

Some examples of compounds of Formula I (employing the nomenclature recommended by the American Chemical Society publishers in the Chemical and Engineering News, vol. 30, p. 4515, Oct. 27, 1952) include:

di(2-methyl-5-tert-butyl-4-hydroxyphenyl) methyl phosphite  
di[2-ethyl-5-( $\alpha$ -methylbenzyl)-4-hydroxyphenyl] lauryl phosphite  
bis(3-methyl-5-cyclohexyl-4-hydroxyphenyl) eicosylphosphonite  
bis(2-methyl-5-sec-butyl-4-hydroxyphenyl) methylphosphonite  
bis(2-methyl-5-sec-eicosyl-4-hydroxyphenyl) eicosylphosphonite  
bis[3-methyl-5-( $\alpha$ , $\alpha$ -dimethylbenzyl)-4-hydroxyphenyl] cetylphosphonite  
bis(2-ethyl-5-tert-octyl-4-hydroxyphenyl) phenylphosphonite  
bis(3-methyl-5-cyclohexyl-4-hydroxyphenyl) (2,4-di-tert-butylphenyl) phosphonite  
bis(2-methyl-5-tert-butyl-4-hydroxyphenyl) hexyl phosphate  
bis[3-methyl-5-( $\alpha$ -methylbenzyl)-4-hydroxyphenyl] n-octadecyl phosphate  
bis(2,5-diisopropyl-4-hydroxyphenyl) phenylphosphonate  
bis(2-methyl-5-cyclohexyl-4-hydroxyphenyl) phenylphosphonate  
bis(3-methyl-5-tert-octyl-4-hydroxyphenyl) ethylphosphonate  
bis(2-sec-eicosyl-5-sec-butyl-4-hydroxyphenyl) laurylphosphonate  
bis[3-ethyl-5-( $\alpha$ , $\alpha$ -dimethylbenzyl)-4-hydroxyphenyl] eicosylphosphonate  
O,O-bis(2-methyl-5-tert-butyl-4-hydroxyphenyl) hexylphosphonothioate  
O,O-bis(2-methyl-5-cyclohexyl-4-hydroxyphenyl) phenylphosphonothioate  
O,O-bis[3-methyl-5-( $\alpha$ -methylbenzyl)-4-hydroxyphenyl] n-octadecylphosphonothioate  
O,O-bis(2,5-diisopropyl-4-hydroxyphenyl) phenylphosphonothioate  
O,O-bis(2-sec-eicosyl-5-tert-butyl-4-hydroxyphenyl) dodecylphosphonothioate  
O,O-bis[3-(4-tetradecylcyclohexyl)-5-cyclooctyl-4-hydroxyphenyl] octadecylphosphonothioate  
O,O-bis(3-methyl-5-tert-octyl-4-hydroxyphenyl) ethylphosphonothioate  
O,O-bis[3-ethyl-5-( $\alpha$ , $\alpha$ -dimethylbenzyl)-4-hydroxyphenyl] n-eicosylphosphonothioate  
bis(2-methyl-5-tert-butyl-4-hydroxyphenyl) hexyl phosphorothionate  
bis[3-methyl-5-( $\alpha$ -methylbenzyl)-4-hydroxyphenyl] n-octadecyl phosphorothionate  
2-methyl-5-tert-butyl-4-hydroxyphenyl diphenylphosphinate  
3,5-di-tert-butyl-4-hydroxyphenyl di-n-octadecylphosphinate

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- 2-methyl-5-( $\alpha$ -methylbenzyl)-4-hydroxyphenyl dibenzylphosphonate
- 3,5-di-tert-butyl-4-hydroxyphenyl diphenylphosphinothionate
- 3-methyl-5-tert-octyl-4-hydroxyphenyl dilaurylphosphinothionate
- 2-methyl-5-tert-butyl-4-hydroxyphenyl dibenzylphosphinothionate
- 3-methyl-5-tert-butyl-4-hydroxyphenyl diphenylphosphinite
- 3-methyl-5-cyclohexyl-4-hydroxyphenyl di-sec-eicosylphosphinite
- 2-methyl-5-( $\alpha$ -methylbenzyl)-4-hydroxyphenyl di-(3,5-di-tert-butylbenzyl)phosphinite

In a preferred embodiment,  $R_3$  in Formula I is bonded to the phenolic benzene ring at the position ortho to the phenolic hydroxyl group. Examples of these compounds are:

- di(3-methyl-5-tert-butyl-4-hydroxyphenyl) cetyl phosphite
- bis(3-ethyl-5-cyclohexyl-4-hydroxyphenyl) phenylphosphinite
- 3-methyl-5-( $\alpha$ -methylbenzyl)-4-hydroxyphenyl dilauryl phosphate
- O-(3-methyl-5-sec-butyl-4-hydroxyphenyl) dioctadecylphosphinothioate

In a more preferred embodiment,  $R_3$  in Formula I is bonded to the phenolic benzene ring at the position ortho to the phenolic hydroxyl radical and is selected from the same group as  $R_2$ ; that is,  $\alpha$ -branched alkyl radicals containing from 3-12 carbon atoms, cycloalkyl radicals containing from 6-20 carbon atoms, and  $\alpha$ -branched aralkyl radicals containing from 8-20 carbon atoms. Some examples of these are:

- 3,5-diisopropyl-4-hydroxyphenyl dioctadecyl phosphite
- 3,5-di( $\alpha$ -methylbenzyl)-4-hydroxyphenyl diphenylphosphinate
- bis(3,5-di-tert-butyl-4-hydroxyphenyl) hexyl phosphorothionate
- bis(3,5-dicyclohexyl-4-hydroxyphenyl) phenylphosphonate

In a highly preferred embodiment,  $R_3$  in Formula I is bonded to the phenolic benzene ring at the position ortho to the phenolic hydroxyl radical and both  $R_2$  and  $R_3$  are tert-butyl radicals. Examples of these highly preferred embodiments are:

- bis(3,5-di-tert-butyl-4-hydroxyphenyl) phenylphosphonite
- bis(3,5-di-tert-butyl-4-hydroxyphenyl) phenylphosphonate
- bis(3,5-di-tert-butyl-4-hydroxyphenyl) octadecyl phosphate
- 3,5-di-tert-butyl-4-hydroxyphenyl dilauryl phosphorothionate
- bis(3,5-di-tert-butyl-4-hydroxyphenyl) octadecyl phosphite
- 3,5-di-tert-butyl-4-hydroxyphenyl dioctadecyl phosphate

The compounds of this invention are readily prepared by methods known in the art. One such method is the reaction of the appropriate phosphonic, phosphite, phosphonous, or phosphinous halide with a hydroquinone. For example, the reaction of phenylphosphonous dichloride with 2,6-di-tert-butylhydroquinone yields bis(3,5-di-tert-butyl-4-hydroxyphenyl) phenylphosphonite. Likewise, the reaction of ethylphosphonous dichloride with 2-tert-butyl-5-methylhydroquinone yields bis(2-methyl-5-tert-butyl-4-hydroxyphenyl) ethylphosphonite. Still other compounds used in this invention wherein  $R_1$  is an alkoxy radical can be prepared from the corresponding alkylphosphoric chlorite. For example, the reaction of didodecylphosphorochlorodite with 2,6-di-tert-butylhydroquinone yields 3,5-

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di-tert-butyl-4-hydroxyphenyl didodecyl phosphite. The corresponding phosphates, phosphonates, phosphinates, phosphonothioates, phosphorothioates, and phosphinothioates can be prepared by using the appropriate oxygenated or thio phosphorous halide reactant. For example, the reaction of phenylphosphonic dichloride with 2,6-di-tert-butylhydroquinone yields bis(3,5-di-tert-butyl-4-hydroxyphenyl) phenylphosphonate. An especially useful method of preparing the thio analog is by the direct reaction of sulfur with the phosphite, phosphonite, or phosphinite. The following examples serve to illustrate the synthesis procedure. All parts are parts by weight unless otherwise specified.

#### EXAMPLE 1

In a reaction vessel equipped with stirrer, liquid addition means, thermometer, condenser, heating means, cooling means and provided with a nitrogen atmosphere place 21 parts of diethyl ether, 4.3 parts of 2,6-di-tert-butylhydroquinone and 1.96 parts of triethylamine. While stirring, add a solution of 1.73 parts of phenylphosphonous dichloride in 15 parts of ether over a period of 30 minutes at 10-20° C. Allow to stir an additional hour and then filter off the triethylamine hydrochloride which precipitates. The product is recovered by evaporating the filtrate and recrystallizing the residue from a solution containing 32 parts of methanol and 10 parts of water. Bis(3,5-di-tert-butyl-4-hydroxyphenyl) phenyl phosphonite is obtained as a white crystalline product.

#### EXAMPLE 2

To the reaction vessel of Example 1 add 71 parts of diethyl ether, 8.6 parts of 2,6-di-tert-butylhydroquinone and 3.9 parts of triethylamine. While stirring, add a solution of 3.78 parts of phenylphosphonic dichloride in 20 parts of diethyl ether over a period of 30 minutes at 10-20° C. Stir the mixture 2 hours at room temperature and then filter off the triethylamine hydrochloride precipitate. Wash the filtrate with water and dry over anhydrous sodium sulfate. Evaporate the ether and recrystallize the residue from 32 parts of methanol. The product is identified by infrared as bis(3,5-di-tert-butyl-4-hydroxyphenyl) phenylphosphonate.

The analogous thio compound can be prepared following the above procedure by the use of phenylphosphonothionic dichloride.

#### EXAMPLE 3

To the reaction vessel of Example 1 add 200 parts of isooctane, 53 parts of di-n-octadecylphosphorochlorodite and 10 parts of triethylamine. While stirring the mixture, at 20-30° C., add a solution of 22.2 parts of 2,6-di-tert-butylhydroquinone in 200 parts of isooctane. Heat the mixture to 50° C. and stir at this temperature for 4 hours. Filter and wash with the filtrate with water. Distill off the isooctane at 50° C. under vacuum and recrystallize the product, 3,5-di-tert-butyl-4-hydroxyphenyl di-n-octadecylphosphite, from ethanol.

#### EXAMPLE 4

To the reaction vessel of Example 1 add 1000 parts of isooctane and 360 parts of 2-tert-butyl-5-methylhydroquinone. Then, while stirring, add 117 parts of methylphosphonous dichloride dissolved in 300 parts of isooctane. Stir the mixture and heat to reflux. Stir at this temperature for one hour and then cool to 30° C. Wash twice with water. Distill off the isooctane to a temperature of 50° C. at 10 mm. and then recrystallize the residue from ethanol, obtaining bis(2-methyl-5-tert-butyl-4-hydroxyphenyl) methylphosphonite.

Other alkyl phosphonous dichlorides can be used in the above example yielding the corresponding alkyl phosphonite.

#### EXAMPLE 5

In the reaction vessel of Example 1 place 211 parts of phenylphosphonothioic dichloride and 1000 parts of

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hexane. Over a 30 minute period, while stirring, add 636 parts of 2,6-di( $\alpha$ -methylbenzyl)hydroquinone dissolved in 2500 parts of hexane. Heat to reflux and maintain at reflux for 4 hours. Cool and wash once with a 5 percent sodium carbonate solution and twice with water. Evaporate off the hexane, leaving as a residue, O,O-bis-[3,5-di( $\alpha$ -methylbenzyl)-4-hydroxyphenyl] phenylphosphonothioate.

In a similar manner, other phosphonothioic dichlorides and hydroquinones can be utilized in the above example to obtain a variety of compounds within the present invention.

#### EXAMPLE 6

In the reaction vessel of Example 1 place 548 parts of 2,6-dicyclohexylhydroquinone and 1000 parts of diethyleneglycol dimethyl ether. To this add 294 parts of lauryl phosphorodichloridethionate dissolved in 600 parts of diethyleneglycol dimethyl ether, while stirring at 50° C. Heat to 100° C. and stir one hour. Cool and add 1000 parts of water. Decant off the aqueous glycol ether layer and recrystallize the residue from ethanol to obtain di-(3,5-dicyclohexyl-4-hydroxyphenyl) lauryl phosphorothionate.

#### EXAMPLE 7

In the reaction vessel of Example 1 place 621 parts of dioctadecylphosphorochlorodate and 2000 parts of diethyleneglycol dimethyl ether. While stirring at 30-50° C., add 222 parts of 2,6-di-tert-butylhydroquinone over a one hour period. Heat to 75° C. and stir for an additional 2 hours. Cool to room temperature and add 1000 parts of water, causing the product, 3,5-di-tert-butyl-4-hydroxyphenyl dioctadecyl phosphate, to precipitate.

#### EXAMPLE 8

In the reaction vessel of Example 1 place 236.5 parts of diphenylphosphinic chloride and 1000 parts of isooctane. To this add, while stirring at 50° C., a solution of 274 parts of 2,6-dicyclohexylhydroquinone, 1000 parts of isooctane and 89 parts of triethylamine. The addition takes about one hour. Stir the mixture at 50-70° C. for an additional 4 hours. Cool to room temperature and filter to remove the triethylamine hydrochloride and wash the filtrate with water. Dry over anhydrous sodium sulfate and evaporate the isooctane under vacuum, leaving 3,5-dicyclohexyl-4-hydroxyphenyl diphenylphosphinate.

#### EXAMPLE 9

To the reaction vessel of Example 1 add 404.5 parts of dilaurylphosphinous chloride and 2000 parts of diethyleneglycol dimethyl ether. While stirring at 50° C., add, over a 30 minute period, 318 parts of 2,6-di( $\alpha$ -methylbenzyl)hydroquinone dissolved in 1000 parts of diethyleneglycol dimethyl ether. Heat to 100° C. and stir for 4 hours. Cool to room temperature and add 1500 parts of water, causing the product, 3,5-di( $\alpha$ -methylbenzyl)-4-hydroxyphenyl dilaurylphosphinite, to precipitate.

The compounds of this invention are useful as antioxidants in a wide variety of organic material normally susceptible to deterioration in the presence of oxygen. Thus, liquid hydrocarbon fuels such as gasoline, kerosene and fuel oil are found to possess increased storage stability when blended with a stabilizing quantity of an additive of this invention. Likewise, hydrocarbon fuels containing organometallic additives such as tetraethyllead, tetramethyllead, methyl cyclopentadienyl manganese tricarbonyl, cyclopentadienyl nickel nitrosyl, ferrocene and iron carbonyl have appreciably increased stability when treated with the additives of this invention. Furthermore, lubricating oils and functional fluids, both those derived from naturally occurring hydrocarbons and those synthetically prepared, have enhanced stability by the practice of this invention. The additives of this invention are useful in stabilizing antiknock fluids against oxidative degradation. For example, the stabilizing additives of this invention

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find utility in stabilizing a tetraethyllead antiknock fluid which contains ethylenedichloride and ethylenedibromide.

The additives of this invention are effective in stabilizing rubber against degradation caused by oxygen or ozone. As used in the description and claims, the term "rubber" is employed in a generic sense to define a high molecular weight plastic material which possesses high extensibility under load coupled with the property of forcibly retracting to approximately its original size and shape after the load is removed. Some examples are acrylic rubber, butadiene-styrene rubber (SBR), chloroprene, chlorosulfonated polyethylene, fluorocarbon rubbers, isobutylene-isoprene (IIR), isoprene, butadiene, nitrile-butadiene rubber, polyisobutylene rubber, polysulfide rubbers, silicone rubbers, urethanes, India rubber, reclaimed rubber balata rubber, gutta percha rubber, and the like. Both natural rubber and synthetic rubbers such as neoprene, SBR rubber, EPT rubber, GR-N rubber, chloroprene rubber, polyisoprene rubber, EPR rubber, and the like, are stabilized through the practice of this invention.

The compounds of this invention are also useful in protecting petroleum wax against degradation. The additives also find use in the stabilization of fats and oils of animal and vegetable origin which tend to become rancid during long periods of storage because of oxidative deterioration. Typical representatives of these edible fats and oils are linseed oil, cod liver oil, castor oil, soy bean oil, rapeseed oil, coconut oil, olive oil, palm oil, corn oil, sesame oil, peanut oil, babassu oil, butter, lard, beef tallow, and the like.

The compounds of this invention are superior antioxidants for high molecular weight polyolefins such as polyethylene, polypropylene (both high pressure and so-called Ziegler type), polybutene, polybutadiene (both cis and trans), and the like.

One of the features of the present stabilizers is that they do not cause discoloration when used in transparent, white, or light-colored organic materials such as white rubber or plastics such as polyethylene, polypropylene, and the like.

The amount of stabilizer used in the organic compositions of this invention is not critical, as long as a stabilizing quantity is present, and can vary from as little as 0.001 weight percent to about 5 weight percent. Generally, excellent results are obtained when from 0.1 to about 3 weight percent of the stabilizer is included in the organic compositions.

The following examples serve to illustrate the use of the stabilizers of the present invention in stabilizing some representative organic materials normally subject to deterioration in the presence of oxygen or ozone.

#### EXAMPLE 10

A rubber stock is prepared containing the following components:

| Component:            | Parts |
|-----------------------|-------|
| Pale crepe rubber     | 100   |
| Zinc oxide filler     | 50    |
| Titanium dioxide      | 25    |
| Stearic acid          | 2     |
| Ultramarine blue      | 0.12  |
| Sulfur                | 3.00  |
| Mercaptobenzothiazole | 1.00  |

To the above base formula is added one part by weight of bis(3,5-di-tert-butyl-4-hydroxyphenyl)phenylphosphonite and, following this, individual samples are cured for 20, 30, 45 and 60 minutes, respectively, at 274° C. After cure, all of these samples remain white in color and possess excellent tensile strength. Furthermore, they are resistant to degradation caused by either oxygen or ozone on aging.

## EXAMPLE 11

A synthetic rubber master batch comprising 100 parts of GR-S rubber having an average molecular weight of 60,000, 50 parts of mixed zinc propionate-stearate, 50 parts of carbon black, 5 parts of road tar, 2 parts of sulfur and 1.5 parts of mercaptobenzothiazole is prepared. To this is added 1.5 parts of di[2-ethyl-5-( $\alpha$ -methylbenzyl)-4-hydroxyphenyl]laurylphosphite. This composition is then cured for 60 minutes employing 45 p.s.i.g. steam pressure. The resulting synthetic rubber possesses resistance to oxygen and ozone induced degradation.

## EXAMPLE 12

A butadiene acrylonitrile copolymer is prepared from 68 percent 1,3-butadiene and 32 percent acrylonitrile. Two percent, based on the weight of the copolymer, of bis(3-methyl-5-cyclohexyl-4-hydroxyphenyl) eicosylphosphonite is added as an aqueous emulsion to the latex obtained from emulsion copolymerization of the butadiene and acrylonitrile monomers. The latex is coagulated with aluminum sulfate and the coagulum, after washing, is dried for 20 hours at 70° C. The synthetic copolymer so obtained is resistant to oxidative degradation.

## EXAMPLE 13

Three percent of bis(2-methyl-5-sec-butyl-4-hydroxyphenyl) methylphosphonite as an emulsion in sodium oleate is added to a rubber-like copolymer of 1,3-butadiene and styrene containing 25 percent styrene. The resulting synthetic elastomer possesses enhanced stability.

## EXAMPLE 14

To a master batch of GR-N synthetic rubber containing 100 parts of GR-N rubber, 5 parts of zinc stearate, 50 parts of carbon black, 5 parts of road tar, 2 parts of sulfur and 2 parts of mercaptobenzothiazole is added 5 percent, based on weight, of bis(3-methyl-5-cyclohexyl-4-hydroxyphenyl) (2,4-di-tert-butylphenyl) phosphonite. After curing, a synthetic rubber is obtained of improved oxidative stability.

## EXAMPLE 15

To a master batch of polyethylene having an average molecular weight of 1,000,000, a tensile strength of 6,700 p.s.i., a Shore D hardness of 74 and a softening temperature under low load of 150° C. is added 5 percent of bis(3,5-di-tert-butyl-4-hydroxyphenyl) phenylphosphonate. The resulting polyethylene possesses stability against oxidative degradation and shows no tendency to yellow after extensive aging.

## EXAMPLE 16

A linear polyethylene having a high degree of crystallinity (93 percent), and less than one branched chain per 100 carbon atoms, a density of about 0.96 grams per ml. and which has about 1.5 double bonds per 100 carbon atoms, is mixed with 0.005 weight percent of bis[3-methyl-5-( $\alpha$ -methylbenzyl)-4-hydroxyphenyl] n-octadecyl phosphate. The resulting polyethylene is found to possess stability against oxidative degradation.

## EXAMPLE 17

To 100 parts of an ethylenepropylene terpolymer is added bis(2,5-diisopropyl-4-hydroxyphenyl) phenylphosphonate, resulting in an ethylenepropylene terpolymer of enhanced stability.

## EXAMPLE 18

To 100 parts of an ethylenepropylene rubber is added 2 parts of bis(3-methyl-5-tert-octyl-4-hydroxyphenyl) ethylphosphonate, resulting in an EPR rubber stock of improved stability.

## EXAMPLE 19

After the polymerization of polypropylene in a hexane solvent employing a Ziegler catalyst, the catalyst is neutralized with water and bis(3,5-di-tert-butyl-4-hydroxy-

phenyl)octadecyl phosphate is added to the mixture in quantities such that, after evaporation of the solvent, a Ziegler polypropylene is obtained containing 2 percent of bis(3,5-di-tert-butyl-4-hydroxyphenyl) octadecyl phosphate. This polypropylene is found to possess excellent stability against degradation caused by oxygen or ozone. Furthermore, this polypropylene is found to resist degradation at elevated temperatures, even in the presence of oxygen. During this high temperature aging the Ziegler polypropylene shows no tendency to discolor.

## EXAMPLE 20

To 1,000 parts of a gasoline containing 26.6 percent aromatics, 20.8 percent olefins, 52.6 percent saturates and having an API gravity of 62.1 is added 10 parts of 0,0-bis(2-methyl-5-tert-butyl-4-hydroxyphenyl) hexylphosphonothioate. The resulting gasoline is stable.

## EXAMPLE 21

To 10,000 parts of gasoline containing 8.6 percent aromatics, 7.9 percent olefins, 83.5 percent saturates and having an API gravity of 68.5 is added 200 parts of 0,0-bis(2-methyl-5-cyclohexyl-4-hydroxyphenyl) phenylphosphonothioate. The resulting gasoline is stable against oxidative degradation.

## EXAMPLE 22

To 10,000 parts of a gasoline containing 20.0 percent aromatics, 41.2 percent olefins, 38.8 percent saturates and containing additionally 1.5 grams of manganese per gallon as methyl cyclopentadienyl manganese tricarbonyl is added 300 parts of 0,0-bis[3-methyl-5-( $\alpha$ -methylbenzyl)-4-hydroxyphenyl] n-octadecylphosphonothioate. The resulting gasoline containing a manganese antiknock was resistant to oxidative degradation.

## EXAMPLE 23

To 10,000 parts of a gasoline containing 20.5 percent aromatics, 32.9 percent olefins and 46.6 percent saturates and containing 2.39 grams per gallon of tetraethyllead and one theory of chlorine as ethylenedichloride and 0.5 theory of bromine as ethylenedibromide is added 500 parts of 0,0-bis(2,5-diisopropyl-4-hydroxyphenyl) phenylphosphonothioate. The resulting gasoline containing a lead antiknock and halogen scavenger is resistant to oxidative degradation. Not only this, but it is also found when used to give prolonged spark plug life due to the presence of the phosphorus-containing antioxidant.

## EXAMPLE 24

To 10,000 parts of gasoline containing 38.1 percent aromatics, 7.3 percent olefins and 54.6 percent saturates and which contains 3.17 grams per gallon of lead as tetramethyllead, one theory of chlorine as ethylenedichloride, 0.5 theory of bromine as ethylenedibromide and 0.2 theory of phosphorus as tris( $\beta$ -chloroisopropyl) thionophosphate is added 50 parts of 0,0-bis(2-sec-eicosyl-5-tert-butyl-4-hydroxyphenyl) dodecylphosphonothioate. The resulting gasoline is resistant to degradation and gives prolonged spark plug life on use.

## EXAMPLE 25

An antiknock fluid composition is prepared by mixing together 61.5 parts of tetraethyllead, 17.9 parts of ethylenedibromide, 18.8 parts of ethylenedichloride and 1.3 parts of 0,0-bis(3-methyl-5-tert-octyl-4-hydroxyphenyl) ethylphosphonothioate, resulting in a stable antiknock fluid composition.

## EXAMPLE 26

To 1,000 parts of a commercial diesel fuel having a cetane number of 42, is added 5 parts of amyl nitrate and 4 parts of 0,0-bis[3-ethyl-5-( $\alpha,\alpha$ -dimethylbenzyl)-4-hydroxyphenyl] n-eicosylphosphonothioate, resulting in

a diesel fuel of high resistance to oxidative deterioration which does not form gum or sludge on storage.

#### EXAMPLE 27

To 1,000 parts of a solvent-refined neutral oil (95 viscosity index and 200 SUS at 100° F.) containing 6 percent of a commercial methacrylate type VI improver is added 5 percent of bis[3-methyl-5-( $\alpha$ -methylbenzyl)-4-hydroxyphenyl] n-octadecyl phosphorothioate, resulting in a stable lubricating oil.

#### EXAMPLE 28

To a solvent-refined crankcase lubricating oil having a viscosity index of 95 and a SAE viscosity of 10 is added 0.1 percent of 3,5-di-tert-butyl-4-hydroxyphenyl dilauryl phosphorothionate. The resulting oil was stable against oxidative degradation.

#### EXAMPLE 29

To 100,000 parts of a petroleum hydrocarbon oil having a gravity of 30.3° API at 60° F., viscosity of 178.8 SUS at 100° F., a viscosity index of 154.2, and containing 1,000 parts of the reaction product of an alkenyl succinic anhydride where the alkenyl group has a molecular weight of 1,000, with a tetraethylene pentamine, is added 200 parts of 3,5-di-tert-butyl-4-hydroxyphenyl di-n-octadecylphosphinate. The resulting lubricating oil possesses excellent dispersancy and is resistant to oxidative degradation.

#### EXAMPLE 30

To 100,000 parts of a commercially available pentaerythritol ester having a viscosity at 100° F. of 22.4 centistokes and known under the tradename of "Hercoflex 600" is added 400 parts of 3-methyl-5-tert-butyl-4-hydroxyphenyl diphenylphosphinite. The resulting synthetic lubricating oil possesses improved resistance against oxidative deterioration.

#### EXAMPLE 31

To 100,000 parts of dioctyl sebacate having a viscosity at 210° F. of 36.7 SUS, a viscosity index of 159, and a molecular weight of 427, is added 250 parts of 3,5-diisopropyl-4-hydroxyphenyl dioctadecyl phosphite, resulting in a synthetic diester lubricating oil having improved resistance to oxidative degradation.

#### EXAMPLE 32

To 1,000 parts of a commercial coconut oil is added 5 parts of 3-methyl-5-tert-octyl-4-hydroxyphenyl dilaurylphosphinothionate, resulting in a vegetable oil with good aging characteristics.

#### EXAMPLE 33

To 100,000 parts of lard is added 100 parts of 2-methyl-5-tert-butyl-4-hydroxyphenyl dibenzylphosphinothionate, resulting in a lard having resistance to rancidity.

The stabilizing additives of this invention are eminently useful as stabilizers in polyolefins such as polyethylene, polypropylene, and the like. In this use they function as antioxidants, antiozonants, and also as thermal stabilizers. They are extremely long lasting and highly resistant to the formation of color.

In order to demonstrate their superior stabilization effect tests were conducted using a commercial polypropylene. These test are known as "Oven Aging Tests" and are recognized in the plastic industry as an accurate guide to oxidative stability. In these tests small specimens of polypropylene are prepared containing the test stabilizer. These test specimens are placed in an air circulating oven maintained at 150° C. Five replicates are made of each polypropylene-stabilizer composition and the test criteria is the time and hours until three of the five replicates show signs of deterioration. Deterioration

is evidenced by cracking, discoloration or any visual appearance of change in the specimen.

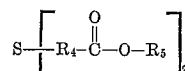
Test specimens are prepared by mixing the test stabilizers with polypropylene powder for 3 minutes in a Waring Blendor. The mixture is then molded into a 6" x 6" sheet with a thickness of 0.025". This is accomplished in a molding press at 400° F. under 5,000 p.s.i. pressure. Each sheet is then cut into 1/2" x 1" test specimens in order to obtain the five replicate samples. These samples are then subjected to the Oven Aging Tests.

In order to compare the stabilizing additives of this invention tests were carried out employing several commercially accepted stabilizers along with stabilizers of the present invention. The results obtained are shown in the following table.

| Additive                                                   | Conc.,<br>wt.<br>percent | Hours to<br>failure |
|------------------------------------------------------------|--------------------------|---------------------|
| None                                                       |                          | 2.5                 |
| 2,6-di-tert-butyl-4-methylphenol                           | 0.3                      | 16                  |
| 2,2'-methylenebis(4-methyl-6-tert-butylphenol)             | 0.3                      | 112                 |
| 4,4'-thiobis(2-tert-butyl-5-methylphenol)                  | 0.3                      | 90                  |
| Bis(3,5-di-tert-butyl-4-hydroxy-phenyl) phenylphosphonite  | 0.3                      | 600                 |
| Bis(3,5-di-tert-butyl-4-hydroxy-phenyl) phenylphosphonate  | 0.3                      | 760                 |
| Bis(3,5-di-tert-butyl-4-hydroxy-phenyl) octadecylphosphate | 0.3                      | 1,408               |

As the above table shows, the additive of the present invention increased the oven life of the polypropylene about 250 times that obtained without any additive, and about 5 to 14 times as much as the life obtained with two commercially accepted antioxidants. Thus, it can be seen that the additives of the present invention are vastly superior to stabilizers available in the prior art.

The effectiveness of the present stabilizers can be enhanced still further by employing synergistic mixtures of the stabilizers of this invention. The preferred synergists are those having the formula:



wherein R<sub>4</sub> is a divalent hydrocarbon radical containing from about 1-6 carbon atoms, R<sub>5</sub> is selected from the group consisting of alkyl radicals containing from about 6-20 carbon atoms, aryl radicals containing from 6-20 carbon atoms, aralkyl radicals containing from 7-20 carbon atoms and cycloalkyl radicals containing from 6-20 carbon atoms. In the preferred synergist R<sub>4</sub> is a divalent hydrocarbon radical containing 1-3 carbon atoms and R<sub>5</sub> is an alkyl radical containing from 10-18 carbon atoms. The most preferred synergists are dilaurylthiodipropionate and distearylthiodipropionate.

The ratio of synergist to stabilizing compound should be adjusted to give the desired protection at the least cost. Mixtures containing from 1 percent synergist and 99 percent stabilizer to those containing 99 percent synergist and 1 percent stabilizer can be employed. Best results are usually obtained with stabilizing mixtures containing from 50 to 66 percent synergist and from 34 to 50 percent stabilizing compound.

The synergists can be employed to obtain increased stability using the same concentration of stabilizer or they can be employed to obtain the same stability with less of the stabilizer. Synergists are especially useful in this latter application. Thus, although dilaurylthiodipropionate (DLTDP) is only moderately effective by itself in stabilizing polypropylene, when used with a compound of the present invention a synergist interaction occurs, resulting in a degree of stability totally unexpected from the amount of stabilizers employed. This effect is shown in the following data obtained using the previously-described Oven Aging Test.

| Sample No. |                                                                                          | Conc., wt. percent | Hours to failure |
|------------|------------------------------------------------------------------------------------------|--------------------|------------------|
| 1          | None                                                                                     |                    | 2.5              |
| 2          | DLTDP                                                                                    | 0.3                | 288              |
| 3          | Bis(3,5-di-tert-butyl-4-hydroxyphenyl)-phenyl-phosphonite                                | 0.3                | 600              |
| 4          | Bis(3,5-di-tert-butyl-4-hydroxyphenyl)-phenyl-phosphonite—plus dilaurylthiodipropionate  | 0.1, 0.2           | 744              |
| 5          | Bis(3,5-di-tert-butyl-4-hydroxyphenyl)-phenyl-phosphonate                                | 0.3                | 760              |
| 6          | Bis(3,5-di-tert-butyl-4-hydroxyphenyl)-phenyl-phosphonate—plus dilaurylthiodipropionate  | 0.1, 0.2           | 928              |
| 7          | Bis(3,5-di-tert-butyl-4-hydroxyphenyl) octadecyl phosphate                               | 0.3                | 1,408            |
| 8          | Bis(3,5-di-tert-butyl-4-hydroxyphenyl) octadecyl phosphate—plus dilaurylthiodipropionate | 0.1, 0.2           | 1,504            |

Despite the fact that Samples 4, 6 and 8 containing the synergist contained only one-third as much stabilizer as did Samples 3, 5 and 7, it can be seen that they exhibited an even longer oven aging life. This can only be attributed to a synergistic interaction between DLTDP and the stabilizer, because DLTDP alone, even at 0.3 weight percent (Sample 2), only gave an oven life of 288 hours.

The amount of synergist included in the organic compositions should be enough to provide a synergistic response with the antioxidant used. In general, good results can be obtained with from about 0.01 to 5 weight percent synergist. In most cases, it is preferred to use from about 0.1 to 3 weight percent synergist in the organic compositions.

Following are some examples of the synergistic stabilizing compositions of the present invention.

33%—di[2-ethyl-5-( $\alpha$ -methylbenzyl)-4-hydroxyphenyl] lauryl phosphite  
 67%—dilaurylthiodipropionate  
 50%—bis(2-methyl-5-sec-butyl-4-hydroxyphenyl) methylphosphonite  
 50%—dihexylthiodiacetate  
 1%—bis[3-methyl-5-( $\alpha$ -methylbenzyl)-4-hydroxyphenyl] n-octadecyl phosphate  
 99%—diheptylthiodivalerate  
 99%—O,O-bis(2-methyl-5-cyclohexyl-4-hydroxyphenyl) phenylphosphonothioate  
 1%—di-n-octyl-thiodipropionate  
 75%—bis[3-methyl-5-( $\alpha$ -methylbenzyl)-4-hydroxyphenyl] n-octadecyl phosphorothionate  
 25%—didecylthiodiacetate  
 25%—3,5-di-tert-butyl-4-hydroxyphenyl di-n-octadecylphosphinate  
 75%—diundecylthiodibutyrate  
 25%—3-methyl-5-tert-octyl-4-hydroxyphenyl dilaurylphosphinothionate  
 75%—dioctadecylthiodipropionate  
 80%—3-methyl-5-tert-butyl-4-hydroxyphenyl diphenylphosphinite  
 20%—dinonadecylthiodibutyrate  
 60%—3,5-diisopropyl-4-hydroxyphenyl dioctadecyl phosphite  
 40%—dieicosylthiodipropionate  
 10%—bis(3,5-di-tert-butyl-4-hydroxyphenyl) phenylphosphonite  
 90%—dilaurylthiodipropionate  
 90%—bis(3,5-di-tert-butyl-4-hydroxyphenyl) phenylphosphonate  
 10%—dilaurylthiodipropionate  
 30%—bis(3,5-di-tert-butyl-4-hydroxyphenyl) octadecylphosphate  
 70%—distearylthiodipropionate

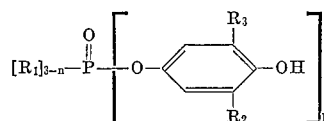
The above synergistic stabilizer compositions are beneficially employed in any of the previously-described organic materials normally susceptible to deterioration due to the effect of oxygen or ozone. In Examples 10 through 33, each of the above synergistic compositions can be substituted for the stabilizing compound of the present in-

vention now shown, resulting in an organic composition of increased resistance to degradation from the effects of oxygen or ozone.

Having fully described new compositions of matter eminently useful in stabilizing organic materials and having further described synergistic combinations of these stabilizers with sulfur compounds and further shown use of these combinations in stabilizing organic material, it is intended that this invention should be limited only within the spirit and scope of the following claims.

What is claimed is:

1. Organic material normally subject to oxidative deterioration selected from the group consisting of natural and synthetic rubbers and polymers of alpha mono-olefins containing a stabilizing amount of an antioxidant having the formula:



wherein  $n$  is an integer from 1–2,  $R_1$  is selected from the group consisting of alkyl radicals containing from 1–20 carbon atoms, alkoxy radicals containing from 1–20 carbon atoms, aryl radicals containing from 6–20 carbon atoms, and aralkyl radicals containing from 7–20 carbon atoms;  $R_2$  is selected from the group consisting of alpha-branched alkyl radicals containing from 3–20 carbon atoms, cycloalkyl radicals containing from 6–20 carbon atoms, and alpha-branched aralkyl radicals containing from 8–20 carbon atoms; and  $R_3$  is selected from the group consisting of alkyl radicals containing from 1–20 carbon atoms, cycloalkyl radicals containing from 6–20 carbon atoms, and aralkyl radicals containing from 7–20 carbon atoms.

2. A composition of claim 1 wherein said organic material is derived from the polymerization of an olefin containing from 2–5 carbon atoms.

3. A composition for claim 2 wherein said organic material is polypropylene.

4. The composition of claim 3 wherein said antioxidant is O,O-bis(3,5 - di-tert-butyl - 4-hydroxyphenyl) phenyl phosphonite.

5. The composition of claim 3 wherein said antioxidant is O,O-bis(3,5 - di-tert-butyl - 4-hydroxyphenyl) phenyl phosphonate.

6. A composition of claim 1 wherein  $n$  is an integer from 1–20,  $R_1$  is an alkoxy group containing from 6–20 carbon atoms,  $R_2$  is the tert-butyl radical, and  $R_3$  is the tert-butyl radical.

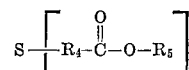
7. An organic composition of claim 6 wherein said organic material is derived from the polymerization of an olefin containing from 2–5 carbon atoms.

8. A composition of claim 7 wherein said organic material is polypropylene.

9. The composition of claim 8 wherein said antioxidant is bis-octadecyl 3,5 - di-tert-butyl - 4-hydroxyphenyl phosphate.

10. The composition of claim 8 wherein said antioxidant is bis-(3,5-di-tert-butyl-4-hydroxyphenyl) octadecyl phosphate.

11. An organic composition of claim 1 containing a synergistic amount of a synergist having the formula:



wherein  $R_4$  is a divalent hydrocarbon radical containing from about 1–6 carbon atoms, and  $R_5$  is selected from the group consisting of alkyl radicals containing from 6–20 carbon atoms, cycloalkyl radicals containing from 6–20 carbon atoms, aryl radicals containing from 6–20 carbon atoms, and aralkyl radicals containing from 7–20 carbon atoms.

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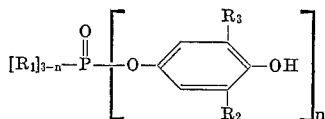
12. An organic composition of claim 11 wherein said synergist is dilaurylthiodipropionate.

13. An organic composition of claim 7 containing a synergistic amount of dilaurylthiodipropionate.

14. An organic composition of claim 13 wherein said organic material is polypropylene.

15. The organic composition of claim 14 wherein said antioxidant is bis-(3,5 - di-tert-butyl-4-hydroxyphenyl) octadecyl phosphate.

16. A polyolefin composition normally subject to oxidative deterioration containing a stabilizing amount of an antioxidant having the formula:



wherein  $n$  is an integer from 1-2,  $R_1$  is selected from the group consisting of alkyl radicals containing from 1-20 carbon atoms, alkoxy radicals containing from 1-20 carbon atoms, aryl radicals containing from 6-20 carbon atoms, and aralkyl radicals containing from 7-20 carbon atoms;  $R_2$  is selected from the group consisting of alpha-

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branched alkyl radicals containing from 3-20 carbon atoms, cycloalkyl radicals containing from 6-20 carbon atoms, and alpha-branched aralkyl radicals containing from 8-20 carbon atoms; and  $R_3$  is selected from the group consisting of alkyl radicals containing from 1-20 carbon atoms, cycloalkyl radicals containing from 6-20 carbon atoms, and aralkyl radicals containing from 7-20 carbon atoms.

## References Cited

## UNITED STATES PATENTS

|           |         |            |           |
|-----------|---------|------------|-----------|
| 3,245,949 | 4/1966  | Murdock    | 260—45.95 |
| 3,261,804 | 7/1966  | Graham     | 260—45.7P |
| 3,406,146 | 10/1968 | Ley et al. | 260—45.95 |
| 3,412,064 | 11/1968 | Brindell   | 260—45.95 |
| 3,467,735 | 9/1969  | Hunter     | 260—45.95 |
| 3,467,737 | 9/1969  | Brindell   | 260—45.95 |

HOSEA E. TAYLOR, Primary Examiner

U.S. Cl. X.R.

44—76, 78; 99—163; 252—46.6, 54, 404; 260—45.95, 398.5, 666.5, 953

UNITED STATES PATENT OFFICE  
CERTIFICATE OF CORRECTION

Patent No. 3,565,855 Dated February 23, 1971

Inventor(s) Bernard R. Meltsner

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, in Formula (I), that portion of the formula readin

$\boxed{R_1}_{s-n}$  should read  $\boxed{R_1}_{s-n}$

Column 3, line 63, "phosphite" should read -- phosphinic;  
lines 73-74, "alkylphosphoric chlorite" should read --  
alkylphosphoro chlorodite --. Column 5, line 17, "phosphoro  
dichloridethionate" should read -- phosphorodichloridothiona  
Column 12, Claim 6, line 49, "1-20" should read -- 1-2 --;  
Claim 6, line 51, "ardical" should read -- radical --.

Signed and sealed this 29th day of June 1971.

(SEAL)  
Attest:

EDWARD M. FLETCHER, JR.  
Attesting Officer

WILLIAM E. SCHUYLER, JR.  
Commissioner of Patents

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