

LIQUID NEO-DIOL PHOSPHITES AS POLYMER STABILIZERS

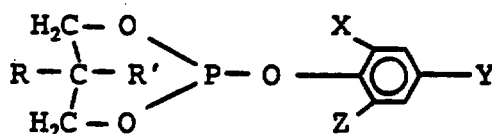
BACKGROUND OF THE INVENTION

Field of the Invention

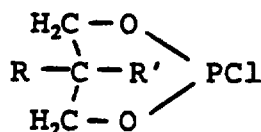
The present invention relates to phosphites, and more particularly related to liquid neoalkyl phenyl phosphites.

Description of the Related Art

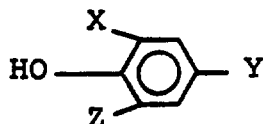
5 Neoalkyl phenyl phosphites are known, see Dever et al U.S. Patent 3,714,302 which is incorporated herein by reference. Dever et al teaches neoalkyl phenyl phosphites of the formula:



10 wherein R and R' are independently lower alkyl groups and X, Y and Z are independently selected from the group consisting of -H and alkyl groups of from 1 to 5 carbon atoms, providing that the sum of the carbon atoms in X, Y and Z does not
 15 exceed 5, may be simply and economically produced by the reaction of a neoglycol with PCl_3 in the absence of a catalyst, HCl acceptor and solvent to produce a crude product of the formula:



wherein R and R' are defined above, followed by reaction with phenol or a compound of the formula:

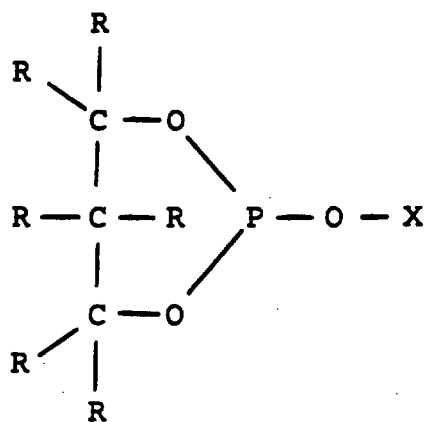


in which X, Y and Z are defined above. The
 5 desired product of Dever et al. may be recovered by distillation.

Suitable glycols are listed and include 2-ethyl-2-butyl-1,3 propane diol among others.

Dever et al. U.S. Patent 3,714,302 clearly
 10 teaches away from compounds wherein X and Z are both alkyl groups such that they create stearic hinderance. Specifically note col. 3, lines 63 to 65 thereof wherein it states that the proviso that the sum of X, Y and Z does not exceed 5
 15 excludes such phenols as 2,6-di-tertiarybutyl phenols from consideration because of stearic hinderance problems.

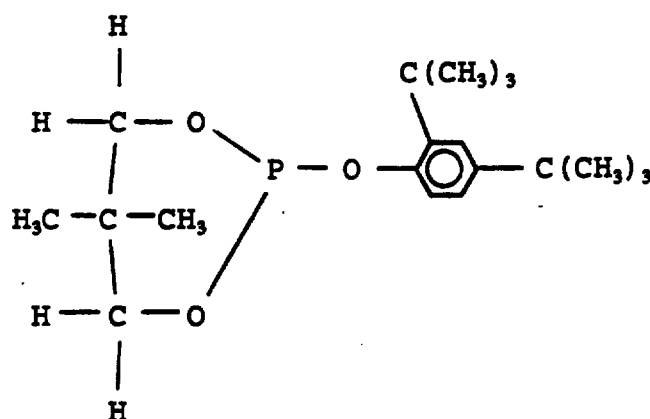
Dever et al U.S. Patent 3,467,733 discloses compounds of the formula:



wherein R is independently selected from the group consisting of hydrogen, alkyl of 1 to 6 carbon atoms, and halogen; X is a monovalent radical of the formula:



- 5 wherein R² independently selected from the group consisting of hydrogen, alkyl of 1 to 12 carbon atoms and halogen, and R³ is independently selected from the group consisting of alkyl of 1 to 12 carbon atoms and halogen, and sets forth in
10 Claim 7 a phosphite of the formula:



Many of these phosphites can, however, experience thermal stability problems, hydrolytic stability problems, and/or ultraviolet light discoloration problems.

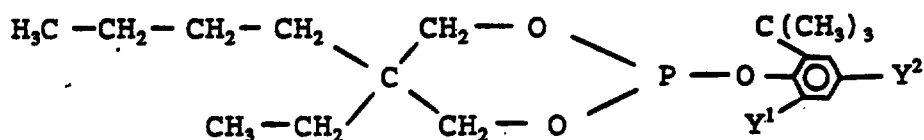
- 15 Shepard et al., U.S. Patent 3,415,906 issued December 10, 1968, discloses phosphite phospholane and phorinane compounds, and lists many diols including 2-ethyl-2-n-butyl-1,3-propane diol and many phosphorodihalidites
20 including 2,4,6-tri-tertiary-butylphenyl

phosphorsdichlordite and 2,6-di-tertiary butyl-4-butylphenyl phosphorsdichlordite.

- Consequently, there is a need for a neoalkyl aryl phosphite exhibiting improved ultraviolet and hydrolytic stability.

Summary of the Invention

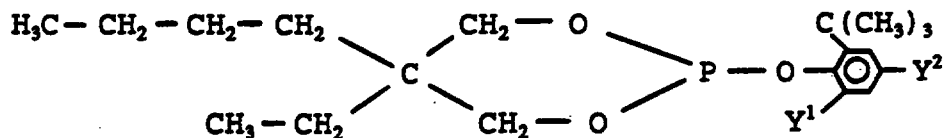
The present invention involves a liquid neoalkyl aryl phosphite composition containing a phosphite of the formula:



- wherein Y^1 is independently selected from the group consisting of alkyl radicals, and preferably Y^1 is a tert-butyl group and Y^2 is a sec-butyl group. The phosphites are useful to stabilize organic materials against thermal oxidative degradation, exhibit enhanced hydrolytic stability and are resistant to UV yellowing.

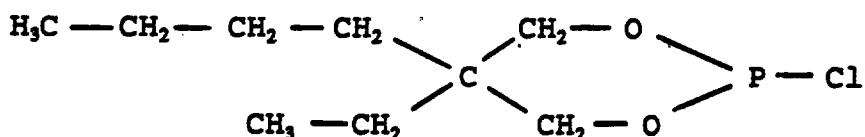
Detailed Description of the Invention

The phosphite is a compound of the formula:

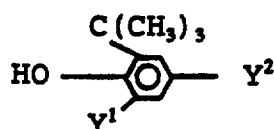


- wherein Y^2 is sec-butyl and preferably Y^1 is tert-butyl. Utilizing sec-butyl as Y^2 rather than tert-butyl as Y^2 results in liquid phosphite rather than a solid phosphite at room temperature. The surprising and unexpected

The phosphite may be made by the reaction of 2-ethyl-2-butyl-1,3-propane diol with PCl_3 in the absence of a catalyst, HCl acceptor and solvent to produce an intermediate product of the formula:



followed by the reaction with a hydroxyaryl compound of the formula:



15 wherein Y¹ and Y² are as defined above. Suitable
reaction methods are set out in Great Britain
Patent 2087399A, U.S. Patent Spivak et al.
4318845 issued 1982, and Article in Phosphorous
& Sulfur Journal by J.D. Spivak et al. 1983, vol.
20 15, pp. 9-13, all of which are incorporated
herein by reference.

The reaction between the diol and PCl₃ may be conducted in known manner, as by mixing the reactants together at room temperature, or

preferably, by cooling the PCl_3 to a temperature between 5-15 degrees centigrade prior to addition of diol to the reactor. An excess of either reactant may be employed although it is preferred to operate with substantially stoichiometric amounts of the diol and PCl_3 . The reaction temperature is preferably maintained between 5-15 degrees centigrade. This temperature may be readily controlled by regulating the rate of diol addition. The esterification reaction is quite exothermic in the absence of a solvent, but a temperature moderating effect is produced by the cooling effect of vigorous HCl evolution. Hence, by effective control of diol addition, the reaction may be made self-regulating in the temperature range between 5-15 degrees centigrade.

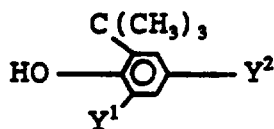
After the reaction has gone to completion, the bulk of the by-product HCl may optionally be removed by gently raising the temperature of the product to about 50 degrees centigrade and applying a vacuum.

The reaction between the intermediate product of the reaction discussed in the preceding paragraph and hydroxyaryl compound may be conducted in the same reaction vessel that was employed to produce the crude intermediate by merely introducing the hydroxyaryl compound into the reactor.

The reaction between the hydroxyaryl compound and the intermediate product in some instances may be carried out at a temperature between 35 to 100 degrees centigrade and preferably between about 45 to about 80 degrees

centigrade. The pressure of the reaction system is maintained between about 50 millimeters mercury absolute to atmospheric pressure. The reaction reaches substantial completion in from 1
 5 to about 8 hours and for practical purposes it is preferably operated under temperature and pressure conditions which will afford the maximum amount of product within 3 to about 5 hours. Although a stoichiometric excess of either
 10 reactant may be employed, it is preferred to operate with substantially stoichiometric quantities.

The hydroxyaryl compound may be any compound of the formula:



15 in which Y¹ is selected from the group consisting of alkyl groups preferably having from 1 to 8 carbon atoms, more preferably methyl or t-butyl. The reaction can be completed in the presence of a base such as an amine acceptor. Since Y¹ is an
 20 alkyl group, an amine acceptor should be added to help drive this reaction. If Y¹ is a tert-alkyl group, such as t-butyl, then a stoichiometric amount of amine acceptor should be present. Y² is sec-butyl and the phosphite is a liquid at room
 25 temperature (25°C).

After completion or near completion of the reaction, HCl generated during the process may readily be substantially removed by evacuating the reactor vessel. No special precautions need

to be taken to remove all the HCl present, as by addition of HCl acceptor or via controlled neutralization of the acidity. The product may then be recovered by distillation, or
5 crystallization.

The phosphites have Y¹ as an alkyl group such as methyl or t-butyl in order to inhibit ultraviolet light yellowing of the phosphite. If Y¹ is hydrogen the phosphite will have sensitivity
10 to UV yellowing. The preferred phosphite has a phenolic degradation product boiling point of greater than 250°C, more preferably greater than 260°C so that the volatility of the degradation product during processing of the stabilized
15 polymer, such as polyolefins such as polypropylene which processes at 240°C and above, is minimized. The problem of excessive volatiles can be minimized by employing an 2-t-butyl-4-sec-butyl-6-alkyl phenyl group because such groups
20 have corresponding 2-t-butyl-4-sec-butyl-6-alkyl phenol degradation products which have a boiling point of greater than 260°C.

The present invention also is a stabilized polymer composition which includes an effective
25 amount of one or more of the phosphites described above. An amount of the phosphites of the invention is considered to be an "effective amount" when the polymer composition containing the phosphites of the invention shows improved
30 stability in any of its physical or color properties in comparison to an analogous polymer composition which does not include a phosphite of the invention. In most polymer compositions, however, it will be preferred that the phosphites

be present in an amount equal to about 0.01 to about 2 parts by weight per 100 parts by weight resin (phr). Amounts of about 0.01 to about 1 phr are more preferred, although most

5 compositions will contain about 0.025 phr or more. The polymer composition may be thermoset in nature including unsaturated polyesters, phenolics, epoxie, urethanes, coating resins and crosslinkable latexes.

10 The polymer may also be any thermoplastic known in the art, such as polyesters, polyurethanes, polyalkylene terephthalates, polysulfones, polyimides, polyphenylene ethers, styrenic polymers, polycarbonates, acrylic
15 polymers, polyamides, polyacetals, halide containing polymers and polyolefin homopolymers and copolymers. Mixtures of different polymers, such as polyphenylene ether/styrenic resin blends, polyvinyl chloride/ABS or other impact
20 modified polymers, such as methacrylonitrile and alphas-methylstyrene containing ABS, and polyester/ABS or polycarbonate/ABS and polyester plus some other impact modifier may also be used. Such polymers are available commercially or may
25 be made by means well known in the art. However, the phosphites of the invention are particularly useful in thermoplastic polymers, such as polyolefins, polycarbonates, polyesters, polyphenylene ethers and styrenic polymers, due
30 to the extreme temperatures at which thermoplastic polymers are often processed and/or used.

Polymers of monoolefins and diolefins, for example polypropylene, polyisobutylene,

polybutene-1, polymethylpentene-1, polyisoprene or polybutadiene, as well as polymers of cycloolefins, for instance of cyclopentene or norbornene, polyethylene (which optionally can be crosslinked), for example high density polyethylene (HDPE), low density polyethylene (LDPE) and linear low density polyethylene (LLDPE) may be used. Mixtures of these polymers, for example, mixtures of polypropylene with polyisobutylene, polypropylene with polyethylene (for example PP/HDPE, PP/LDPE) and mixtures of different types of polyethylene (for example LDPE/HDPE), may also be used. Also useful are copolymers of monoolefins and diolefines with each other or with other vinyl monomers, such as, for example, ethylene/propylene, LLDPE and its mixtures with LDPE, propylene/butene-1, ethylene/hexene, ethylene/ethylpentene, ethylene/heptene, ethylene/octene, propylene/isobutylene, ethylene/butane-1, propylene/butadiene, isobutylene, isoprene, ethylene/alkyl acrylates, ethylene/alkyl methacrylates, ethylene/vinyl acetate (EVA) or ethylene/acrylic acid copolymers (EAA) and their salts (ionomers) and terpolymers of ethylene with propylene and a diene, such as hexadiene, dicyclopentadiene or ethylidene-norbornene; as well as mixtures of such copolymers and their mixtures with polymers mentioned above, for example polypropylene/ethylene propylene-copolymers, LDPE/EVA, LDPE/EAA, LLDPE/EVA and LLDPE/EAA.

Thermoplastic polymers may also include styrenic polymers, such as polystyrene, poly-(p-

methystyrene), poly-(α -methystyrene),
copolymers of styrene or α -methystyrene with
dienes or acrylic derivatives, such as, for
example, styrene/butadiene,
5 styrene/acrylonitrile, styrene/alkyl
methacrylate, styrene/maleic anhydride,
styrene/butadiene/ethylacrylate/styrene/acrylonit
rile/methylacrylate, mixtures of high impact
strength from styrene copolymers and another
10 polymer, such as, for example, from a
polyacrylate, a diene polymer or an
ethylene/propylene/diene terpolymer; and block
copolymers of styrene, such as, for example,
styrene/-butadiene/styrene,
15 styrene/isoprene/styrene,
styrene/ethylene/butylene/styrene or
styrene/ethylene/propylene styrene. Styrenic
polymers may additionally or alternatively
include graft copolymers of styrene or α -
20 methystyrene such as, for example, styrene on
polybutadiene, styrene on polybutadiene-styrene
or polybutadiene-acrylonitrile; styrene and
acrylonitrile (or methacrylonitrile) on
polybutadiene and copolymers thereof; styrene and
25 maleic anhydride or maleimide on polybutadiene;
styrene, acrylonitrile and maleic anhydride or
maleimide on polybutadiene; styrene,
acrylonitrile and methyl methacrylate on
polybutadiene, styrene and alkyl acrylates or
30 methacrylates on polybutadiene, styrene and
acrylonitrile on ethylene/-propylene/diene
terpolymers, styrene and acrylonitrile on
polyacrylates or polymethacrylates, styrene and
acrylonitrile on acrylate/butadiene copolymers,

as well as mixtures of with the styrenic copolymers indicated above.

Nitrile polymers are also useful in the polymer composition of the invention. These
5 include homopolymers and copolymers of acrylonitrile and its analogs, such as polymethacrylonitrile, polyacrylonitrile, acrylonitrile/-butadiene polymers, acrylonitrile/alkyl acrylate polymers,
10 acrylonitrile/alkyl methacrylate/butadiene polymers, and various ABS compositions as referred to above in regard to styrenics.

Polymers based on acrylic acids, such as acrylic acid, methacrylic acid, methyl
15 methacrylic acid and ethacrylic acid and esters thereof may also be used. Such polymers include polymethylmethacrylate, and ABS-type graft copolymers wherein all or part of the acrylonitrile-type monomer has been replaced by
20 an acrylic acid ester or an acrylic acid amide. Polymers including other acrylic-type monomers, such as acrolein, methacrolein, acrylamide and methacrylamide may also be used.

Halogen-containing polymers may also be
25 useful. These include resins such as polychloroprene, epichlorohydrin homo-and copolymers, polyvinyl chloride, polyvinyl bromide, polyvinyl fluoride, polyvinylidene chloride, chlorinated polyethylene, chlorinated
30 polypropylene, fluorinated polyvinylidene, brominated polyethylene, chlorinated rubber, vinyl chloride-vinylacetate copolymers, vinyl chloride-ethylene copolymer, vinyl chloride-propylene copolymer, vinyl chloride-styrene

copolymer, vinyl chloride-isobutylene copolymer,
 vinyl chloride-vinylidene chloride copolymer,
 vinyl chloride-styrene-maleic anhydride
 tercopolymer, vinyl chloride-styrene-
 5 acrylonitrile copolymer, vinyl chloride-butadiene
 copolymer, vinyl chloride isoprene copolymer,
 vinyl chloride-chlorinated propylene copolymer,
 vinyl chloride-vinylidene chloride-vinyl acetate
 tercopolymer, vinyl chloride-acrylic acid ester
 10 copolymers, vinyl chloride-maleic acid ester
 copolymers, vinyl chloride-methacrylic acid ester
 copolymers, vinyl chloride-acrylonitrile
 copolymer and internally plasticized polyvinyl
 chloride.

15 Other useful thermoplastic polymers include
 homopolymers and copolymers of cyclic ethers,
 such as polyalkylene glycols, polyethylene oxide,
 polypropylene oxide or copolymers thereof with
 bis-glycidyl ethers; polyacetals, such as
 20 polyoxymethylene and those polyoxymethylene which
 contain ethylene oxide as a comonomer;
 polyacetals modified with thermoplastic
 polyurethanes, acrylates or methacrylonitrile
 containing ABS; polyphenylene oxides and
 25 sulfides, and mixtures of polyphenylene oxides
 with polystyrene or polyamides; polycarbonates
 and polyester-carbonates; polysulfones,
 polyethersulfones and polyetherketones; and
 polyesters which are derived from dicarboxylic
 30 acids and diols and/or from hydroxycarboxylic
 acids or the corresponding lactones, such as
 polyethylene terephthalate, polybutylene
 terephthalate, poly-1,4-dimethylol-cyclohexane
 terephthalate, poly-2(2,2,4(4-hydroxyphenyl)-

propane) terephthalate and polyhydroxybenzoates as well as block-copolyetheresters derived from polyethers having hydroxyl end groups.

- Polyamides and copolyamides which are
- 5 derived from diamines and dicarboxylic acids and/or from aminocarboxylic acids or the corresponding lactams, such as polyamide, 4, polyamide 6, polyamide 6/6, 6/10, 6/9, 6/12 and 4/6, polyamide 11, polyamide 12, aromatic
- 10 polyamides obtained by condensation of m-xylene, diamine and adipic acid; polyamides prepared from hexamethylene diamine and isophthalic or/and terephthalic acid and optionally an elastomer as modifier, for example poly-2,4,4-
- 15 trimethylhexamethylene terephthalamide or poly-m-phenylene isophthalamide may be useful. Further copolymers of the aforementioned polyamides with polyolefins, olefin copolymers, ionomers or chemically bonded or grafted elastomers; or with
- 20 polyethers, such as for instance, with polyethylene glycol, polypropylene glycol or polytetramethylene glycols and polyamides or copolyamides modified with EPDM or ABS may be used.
- 25 Polyolefin, polyalkylene terephthalate, polyphenylene ether and styrenic resins, and mixtures thereof are more preferred, with polyethylene, polypropylene, polyethylene terephthalate, polyphenylene ether homopolymers
- 30 and copolymers, polystyrene, high impact polystyrene, polycarbonates and ABS-type graft copolymers and mixtures thereof being particularly preferred.

The resulting stabilized polymer compositions of the invention may optionally also contain (or be free of) various conventional additives, such as the following:

- 5 1. Antioxidants
 - 1.1 Alkylated monophenols, for example:
 2,6-di-tertbutyl-4-methylphenol, 2-tert-butyl-
 4,6-dimethylphenol, 2,6-di-tert-butyl-4-
 ethylphenol, 2,6-di-tert-butyl-4-n-butylphenol,
 10 2,6-di-tert-butyl-4-isobutylphenol, 2,6-
 dicyclopentyl-4-methylphenol, 2-(alpha-
 methylcyclohexyl)-4,6 dimethylphenol, 2,6-di-
 octadecyl-4-methylphenol, 2,4,6,-
 tricyclohexylphenol, 2,6-di-tert-butyl-4-
 15 methoxymethylphenol.
 - 1.2 Alkylated hydroquinones, for example,
 2,6-di-tert-butyl-4-methoxyphenol, 2,5-di-tert-
 butyl-hydroquinone, 2,5-di-tert-amyl-
 hydroquinone, 2,6-diphenyl-4octadecyloxyphenol.
 - 20 1.3 Hydroxylated thiodiphenyl ethers, for
 example, 2,2'-thio-bis-(6-tert-butyl-4-
 methylphenol), 2,2'-thio-bis-(4-octylphenol),
 4,4'-thio-bis-(6-tert-butyl-3-methylphenol), 4,4'-
 thio-bis-(6-tert-butyl-2-methylphenol).
 - 25 1.4 Alkylidene-bisphenols, for example,
 2,2'-methylene-bis-(6-tert-butyl-4-methylphenol),
 2,2'-methylene-bis-(6-tert-butyl-4-ethylphenol),
 2,2'-methylene-bis-(4-methyl-6-(alpha-
 methylcyclohexyl)(phenol), 2,2'-methylene-bis-(4-
 30 methyl-6-cyclohexylphenol), 2,2'-methylene-bis-
 (6-nonyl-4-methylphenol), 2,2'-methylene-bis-(6-
 nonyl-4-methylphenol), 2,2'-methylene-bis-(6-
 (alpha-methylbenzyl)-4-nonylphenol), 2,2'-
 methylene-bis-(6-(alpha,alpha-dimethylbenzyl)-4-

nonyl-phenol). 2,2'-methylene-bis-(4,6-di-tert-butylphenol), 2,2'-ethyldiene-bis-(6-tert-butyl-4-isobutylphenol), 4,4'-methylene-bis-(2,6-di-tert-butylphenol), 4,4'-methylene-bis-(6-tert-butyl-2-methylphenol), 1,1-bis-(5-tert-butyl-4-hydroxy-2-methylphenol)butane. 2,6-di-(3-tert-butyl-5-methyl-2-hydroxybenzyl)-4-methylphenol, 1,1,3-tris-(5-tert-butyl-4-hydroxy-2-methylphenyl)butane, 1,1-bis-(5-tert-butyl-4-hydroxy-2-methylphenyl)-3-dodecyl-mercaptobutane, ethyleneglycol-bis-(3,3'-bis-(3'-tert-butyl-4'-hydroxyphenyl)-butyrate)-di-(3-tert-butyl-4-hydroxy-5-methylphenyl)-dicyclopentadiene, di-(2-(3'-tert-butyl-2'-hydroxy-5'-methyl-benzyl)-6-tert-butyl-4-methylphenyl)terephthalate.

1.5 Benzyl compounds, for example, 1,3,5-tris-(3,5-di-tert-butyl-4-hydroxybenzyl)-2,4,6-trimethylbenzene, bis-(3,5-di-tert-butyl-4-hydroxybenzyl)sulfide, isooctyl 3,5-di-tert-butyl-4-hydroxybenzyl-mercapto-acetate, bis-(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl)dithiol-terephthalate. 1,3,5-tris-(3,5-di-tert-butyl-4-hydroxybenzyl)isocyanurate. 1,3,5-tris-(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl)isocyanurate, dioctadecyl 3,5-di-tert-butyl-4-hydroxybenzyl-phosphonate, calcium salt of monoethyl 3,5-di-tert-butyl-4-hydroxybenzylphosphonate, 1,3,5-tris-(3,5-dicyclohexyl-4-hydroxybenzyl)isocyanurate.

1.6 Acylaminophenols, for example, 4-hydroxy-lauric acid anilide, 4-hydroxy-stearic acid anilide, 2,4-bis-octylmercapto-6-(3,5-tert-butyl-4-hydroxyanilino)-s-triazine, octyl-N-(3,5-di-tert-butyl-4-hydroxyphenyl)-carbamate.

1.7 Esters of beta-(3,5-di-tert-butyl-4-hydroxyphenol)-propionic acid with monohydric or polyhydric alcohols, for example, methanol, diethyleneglycol, octadecanol, triethyleneglycol,
 5 1,6-hexanediol, penta-erythritol, neopentylglycol, tris-hydroxyethyl isocyanurate, thiodiethyleneglycol, di-hydroxyethyl oxalic acid diamide.

1.8 Esters of beta-(5-tert-butyl-4-hydroxy-3-methylphenyl)-propionic acid with monohydric or
 10 polyhydric alcohols, for example, methanol, diethyleneglycol, octadecanol, triethyleneglycol, 1,6-hexanediol, pentaerythritol, neopentylglycol, tris-hydroxyethyl isocyanurate,
 15 thiodiethyleneglycol, dihydroxyethyl oxalic acid diamide.

1.9 Esters of beta-(5-tert-butyl-4-hydroxy-3-methylphenyl) propionic acid with mono-or polyhydric alcohols, e.g., with methanol,
 20 diethylene glycol, octadecanol, triethylene glycol, 1,6-hexanediol, pentaerythritol, neopentyl glycol, tris(hydroxyethyl) isocyanurate, thiodiethylene glycol, N,N-bis(hydroxyethyl) oxalic acid diamide.

25 1.10 Amides of beta-(3,5-di-tert-butyl-4-hydroxyphenol)-propionic acid for example, N,N'-di-(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)-hexamethylen-diamine, N,N'-di-(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)trimethylenediamine,
 30 N,N'-di-(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)-hydrazine.

2. UV absorbers and light stabilizers.

2.1 2-(2'-hydroxyphenyl)-benzotriazoles, for example, the 5'-methyl-, 3'5'-di-tert-butyl-

,5'-tert-butyl-,5'(1,1,3,3-tetramethylbutyl)-,5-chloro-3',5'-di-tert-butyl-,5-chloro-3'tert-butyl-5'methyl-,3'sec-butyl-5'tert-butyl-,4'-octoxy,3',5'-ditert-amyl-3',5'-bis-(alpha, alpha-dimethylbenzyl)-derivatives.

2.2 2-Hydroxy-benzophenones, for example, the 4-hydroxy-4-methoxy-,4-octoxy,4-decloy-,4-dodecyloxy-,4-benzyloxy,4,2',4'-trihydroxy-and 2'hydroxy-4,4'-dimethoxy derivative.

2.3 Esters of substituted and unsubstituted benzoic acids for example, phenyl salicylate, 4-tert-butylphenyl-salicylate, octylphenyl salicylate, dibenzoylresorcinol, bis-(4-tert-butylbenzoyl)-resorcinol, benzoylresorcinol, 2,4-di-tert-butyl-phenyl-3,5-di-tert-butyl-4-hydroxybenzoate and hexadecyl-3,5-di-tert-butyl-4-hydroxybenzoate.

2.4 Acrylates, for example, alpha-cyano-beta, beta-diphenylacrylic acid-ethyl ester or isooctyl ester, alpha-carbomethoxy-cinnamic acid methyl ester, alpha-cyano-beta-methyl-p-methoxy-cinnamic acid methyl ester or butyl ester, alpha-carbomethoxy-p-methoxy-cinnamic acid methyl ester, N-(beta-carbomethoxy-beta-cyano-vinyl)-2-methyl-indoline.

2.5 Nickel compounds, for example, nickel complexes of 2,2'-thio-bis(4-(1,1,1,3-tetramethylbutyl)-phenol), such as the 1:1 or 1:2 complex, optionally with additional ligands such as n-butylamine, triethanolamine or N-cyclohexyldiethanolamine, nickel dibutyldithiocarbamate, nickel salts of 4-hydroxy-3,5-di-tert-butylbenzylphosphonic acid monoalkyl esters, such as of the methyl, ethyl, or butyl ester, nickel

complexes of ketoximes such as of 2-hydroxy-4-methyl-phenyl undecyl ketoxime, nickel complexes of 1-phenyl-4-lauroyl-5-hydroxy-pyrazole, optionally with additional ligands.

- 5 2.6 Sterically hindered amines, for example bis(2,2,6,6-tetramethylpiperidyl)-sebacate, bis-(1,2,2,6,6-pentamethylpiperidyl)-sebacate, n-butyl-3,5-di-tert-butyl-4-hydroxybenzyl malonic acid bis(1,2,2,6,6,-pentamethylpiperidyl)ester, 10 condensation product of 1-hydroxyethyl-2,2,6,6-tetramethyl-4-hydroxy-piperidine and succinic acid, condensation product of N,N'-(2,2,6,6-tetramethylpiperidyl)-hexamethyldiamine and 4-tert-octylamino-2,6-dichloro-1,3,5-s-triazine, 15 tris-(2,2,6,6-tetramethylpiperidyl)-nitrilotriacetate, tetrakis-(2,2,6,6-tetramethyl-4-piperidyl)-1,2,3,4-butane-tetra-carbonic acid, 1,1'(1,2-ethanediyl)-bis-(3,3,5,5-tetramethylpiperazinone). Such amines include 20 hydroxylamines derived from hindered amines, such as di(1-hydroxy-2,2,6,6-tetramethylpiperidin-4-yl)sebacate: 1-hydroxy 2,2,6,6-tetramethyl-4-benzoxypiperidine; 1-hydroxy-2,2,6,6-tetramethyl-4-(3,5-di-tert-butyl-4-hydroxy 25 hydrocinnamoyloxy)-piperidine; and N-(1-hydroxy-2,2,6,6-tetramethyl-piperidin-4-yl)-epsilon-caprolactam.

- 2.7 Oxalic acid diamides, for examples, 4,4'-dioctyloxy-oxanilide, 2,2'-di-octyloxy- 30 5',5'-di-tert-butyloxanilide, 2,2'-di-dodecyloxy-5',5'-di-tert-butyl-oxanilide, 2-ethoxy-2'-ethyl-oxanilide, N,N'-bis(3-dimethylaminopropyl)-oxalamide, 2-ethoxy-5-tert-butyl-2'-ethyloxanilide and its mixture with 2-ethoxy-

2'ethyl-5,4-di-tert-butyloxanilide and mixtures of ortho-and para-methoxy-as well as of o-and p-ethoxy-disubstituted oxanilides.

3. Metal deactivators, for example, N,N'-
 5 diphenyloxalic acid diamide, N-salicylal-N'-salicyloylhydrazine, N,N'-bis-salicyloylhydrazine, N,N'-bis-(3,5-di-tert-butyl-4-hydrophenylpropionyl)-hydrazine, salicyloylamino-1,2,4-triazole, bis-benzyliden-
 10 oxalic acid dihydrazide.

4. Phosphites and phosphonites, for example, triphenyl phosphite, diphenylalkyl phosphites, phenyldialkyl phosphites, tris(nonyl-phenyl)phosphite, trilauryl phosphite,
 15 trioctadecyl phosphite, distearyl pentaerythritol diphosphite, tris(2,4-di-tert-butylphenyl)phosphite, diisodecyl pentaerythritol diphosphite, bis(2,4-di-tert-butylphenyl)pentaerythritol diphosphite
 20 tristearyl sorbitol triphosphite, and tetrakis(2,4-di-tert-butylphenyl)4,4'-biphenylene diphosphonite.

5. Peroxide scavengers, for example, esters of betathiodipropionic acid, for example the
 25 lauryl, stearyl, myristyl or tridecyl esters, mercaptobenzimidazole or the zinc salt of 2-mercaptobenzimidazole, zinc-dibutyldithiocaramate, dioctadecyldisulfide, pentaerythritoltetrakis-(beta-dodecylmercapto)-
 30 propionate.

6. Polyamide stabilizers, for example copper salts in combination with iodides and/or phosphorus compounds and salts of divalent manganese.

7. Basic co-stabilizers, for example, melamine, polyvinylpyrrolidone, dicyandiamide, triallyl cyanurate, urea derivatives, hydrazine derivatives, amines, polyamides, polyurethanes, 5 alkali metal salts and alkaline earth metal salts of higher fatty acids, for example, Ca stearate, calcium stearoyl lactate, calcium lactate, Zn stearate, Mg stearate, Na ricinoleate and K palmitate, antimony pyrocatecholate or zinc 10 pyrocatecholate.

8. Nucleating agents, for example, 4-tert butylbenzoic acid, adipic acid, diphenylacetic acid.

9. Fillers and reinforcing agents, for 15 example, calcium carbonate, silicates, glass fibers, asbestos, talc, kaolin, mica, barium sulfate, metal oxides and hydroxides, carbon black and graphite.

10. The present invention may also be used 20 in conjunction with aminoxy propanoate derivatives such as methyl-3-(N,N-dibenzylaminoxy)propanoate; ethyl-3-(N,N-dibenzylaminoxy)propanoate; 1,6-hexamethylene-bis(3-N,N-dibenzylaminoxy)propanoate; methyl-(2- 25 (methyl)-3-(N,N-dibenzylaminoxy)propanoate); octadecyl-3-(N,N-dibenzylaminoxy)propanoic acid; tetrakis (N,N-dibenzylaminoxy)ethyl carbonyl oxymethylmethane; octadecyl-3-(N,N-diethylaminoxy)-propanoate; 3-(N,N- 30 dibenzylaminoxy)propanoic acid potassium salt; and 1,6-hexamethylene bis(3-(N-allyl-N-dodecyl aminoxy)propanoate).

11. Other additives, for example, plasticizers, epoxidized vegetable oils, such as

epoxidized soybean oils, lubricants, emulsifiers, pigments, hydroxylamines such as R_2NOH wherein R is a C_1 to C_{30} alkyl group, such as propyl or stearyl, optical brighteners, flameproofing agents, anti-static agents, blowing agents and thiosynergists such as dilaurythiodipropionate or distearylthiodipropionate.

Polymeric particles may be coated with the present phosphites alone or in combination with other stabilizers for stabilization of the polymeric material. Particles may be spherical in shape and may be made by processes such as "Reactor Granule Technology" as disclosed in P. Galli and J.C. Hallock, The Reactor Granule - A Unique Technology for the Production of a New Generation of Polymer Blends, Society of Plastics Engineers, Polyolefin III International Conference February 24-27, 1991 and as disclosed in Pedrazzeth et al. U.S. 4708979 entitled Process for the Stabilization of Spherically Polymerized Polyolefins issued November 24, 1987 both of which are disclosed herein by reference. Particle formation may be achieved by support Ziegler-Natta Catalyst systems. Suitable commercial processes are known by the trademarks: Spheripol, Addipol and Spherilene.

Olefin polymers may be produced by polymerization of olefins in the presence of Ziegler-Natta catalysts optionally on supports such as but not limited to $MgCl_2$, chromium salts and complexes thereof, optionally supported on Silica or other materials. They may also be produced utilizing catalysts based on

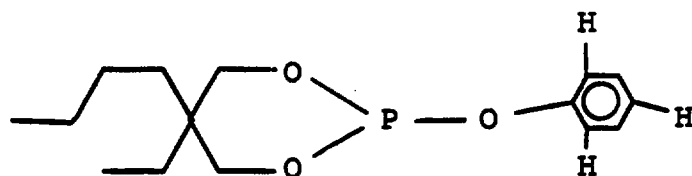
cyclopentadiene complexes of metals typically complexes of Ti and Zr.

Consistent with the invention, the phosphites of the invention may be added to the polymer at any time prior to or during fabrication into articles and may be combined with the polymer by any of a variety of means known in the art, such as by preblending or by being fed directly into fabrication equipment.

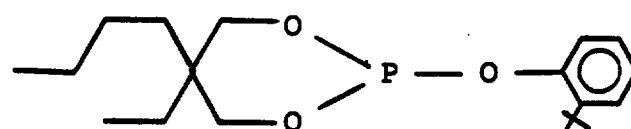
The following examples illustrate the present invention.

Examples:

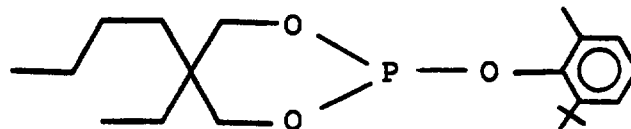
Phos 1



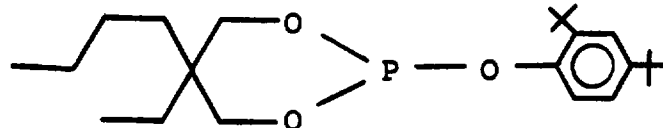
Phos 2



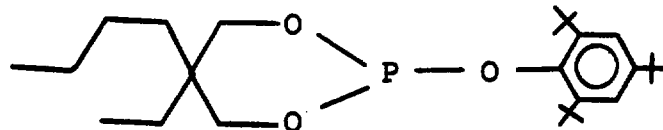
Phos 3



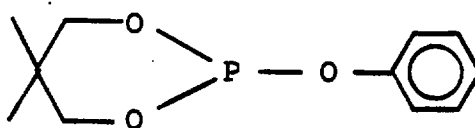
Phos 4



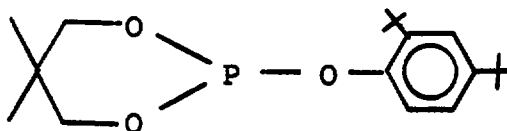
Phos 5



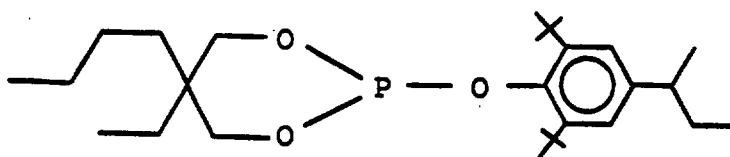
Phos 6



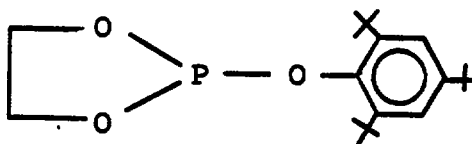
Phos 7



Phos 8



Phos 9



The Examples set out the half-life of phosphites
 in films pressed from a polypropylene resin
 composition containing 1% by weight of the
 respective phosphite. Half-life was measured at
 5 the time to 1/2 depletion of the initial
 phosphite loading upon exposure of the film to a
 temperature of 60°C and a nominal relative
 humidity of 75%. It is believed that degradation
 of the phosphite in the film was due primarily to
 10 hydrolysis of the phosphite. Phos 8 illustrates
 the phosphites of the present invention and their
 results are shown in example 1. Examples A, B,
 C, D, E & F are comparative examples. The
 additive is compounded into polymer at 5000-10000
 15 ppm, and the initial color recorded. The polymer
 sample is then exposed to short wave UV light (as
 the 254 mm light from a Mineralite[®] Lamp. Model

UVGL-5) for a set time interval (usually 10 min.) at a set distance from the light source (usually less than 1 inch). The color of the polymer sample is recorded and the change in yellowness index (ΔYI) is calculated. Samples that fail the UV yellowing test will have a $\Delta YI > 5$, typically in the 20-40 range. Samples that pass the UV yellowing test will have $\Delta YI < 5$, typically in the 0-2 range.

<u>Table I</u>				
<u>Example</u>	<u>Phos Type</u>	<u>t 1/2 (days)</u>	<u>U.V.</u>	<u>Liquid (25°C)</u>
			<u>Yellowing</u>	
A	Phos 1	4	No	Yes
B	Phos 2	15	Yes	Yes
C	Phos 3	21	No	Yes
D	Phos 4	22	Yes	No
E	Phos 6	<2	No	Yes
F	Phos 7	12	Yes	No
1	Phos 8	>36	No	Yes
G	Phos 9	5	No	Yes

Note the greater hydrolytic stability of the phosphites of the present invention over the comparative phosphites. Also note the resistance of Example 1 to U.V. yellowing. Table II illustrates the high boiling point of the degradation phenolic of Example 1. The data herein demonstrates the improved properties and combination of properties of the phosphites of the present invention. The phosphite of the present invention exhibits enhanced hydrolytic stability over Phos 6 and Phos 7 (compare Phos 8 with Phos 7). Phos 1, 2, 3 and 6 are liquids at room temperature.

Table II

<u>Phenolic</u>	<u>Boiling Point</u>
HO	230°C
HO	235°C
HO	237°C
HO	263°C
HO	269°C

Table II (cont'd)

<u>Phenolic</u>	<u>Boiling Point</u>
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HO	278°C
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HO	275°C
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Table III

	H	I	2
Phos 10	600	0	0
Phos 11	0	600	0
Phos 8	0	0	600
CaSt	500	500	500
HPAO	500	500	500
Melt Flow (12 @ 230°C)			
1st Pass	4.58	5.95	4.75
3rd Pass	5.51	8.45	5.01
5th Pass	6.2	11.49	5.72
Color (Yellowness Index)			
1st Pass	2.98	2.96	1.3
3rd Pass	4.31	4.76	2.04
5th Pass	5.01	5.87	3.6

Phos 8 = (2-Butyl-2-ethyl-1,3-propanediol) (2,6-di-tert-butyl-4-sec-butylphenyl)phosphite.

5 Phos 10 is bis(2,4-di-t-butyl pentaerythritol) diphosphite.

Phos 11 is tri(2,4-di-t-butylphenyl)phosphite.

HPAO is a hindered phenolic commercially available as Irganox-1010.

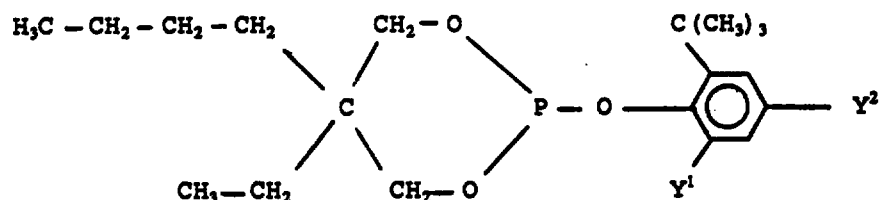
10 CaSt is calcium stearate.

Note the relatively low (stable) melt flow of example 2 on the 5th pass, and note the relatively low yellowness index on the fifth pass.

**Claims:**

I claim:

1. A phosphite of the formula:



wherein Y^1 is selected from the group consisting of alkyl groups and Y^2 is sec-butyl, said phosphite being a liquid at 25°C .

2. The phosphite of Claim 1 wherein Y^1 is methyl.
3. A thermoplastic polymeric composition comprising a thermoplastic resin and from 0.01 to 1.0 percent by weight of a phosphite as claimed in Claim 1 based on the total weight of the composition.
4. A thermoplastic polymeric composition comprising a thermoplastic resin and from 0.01 to 1.0 percent by weight of a phosphite as claimed in Claim 2 based on the total weight of the composition.
5. A thermoplastic polymeric composition comprising a thermoplastic resin and from 0.01 to 1.0 percent by weight of a phosphite as claimed in Claim 3 based on the total weight of the composition.
6. A thermoplastic composition as claimed in Claim 4 wherein said thermoplastic resin is selected from the group consisting of



polyolefins, polycarbonates, polyesters,
polyvinyl chloride and polystyrenes.

7. A thermoplastic composition as claimed in Claim 4 wherein said thermoplastic resin is polypropylene.
8. A thermoplastic composition as claimed in Claim 4 wherein said composition consists essentially of said thermoplastic resin and said phosphite.