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(54) Title: MIXED PHOSPHITE STABILIZATION OF POLYETHYLENE FILM

(57) Abstract: This invention provides a process for the stabilization of thermoplastic polyolefins during melt processing operations. The stabilizer package of this invention is "phenol free" and must contain at least one solid aryl monophosphite and a specific liquid phosphite. The process of this invention is especially suitable for the manufacture of polyethylene film.



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MIXED PHOSPHITE STABILIZATION OF POLYETHYLENE FILM**TECHNICAL FIELD**

This invention relates to the melt processing of polyolefins using a stabilizer
5 which is essentially free of any phenolic antioxidant.

BACKGROUND ART

Polyolefins are conventionally stabilized with a phenolic antioxidant and a phosphite. A hindered amine light stabilizer (or "HALS") may also be included if long term stabilization is desired. These formulations generally provide adequate
10 stabilization performance during the melt processing operations which are used to produce finished plastic parts from the thermoplastic polyolefin resin and during the normal lifetime of the parts.

A general overview of phenol/phosphite stabilizer systems is provided in Polyolefins 2001 - The International Conference on Polyolefins, "Impact of
15 Stabilization Additives on the Controlled Degradation of Polypropylene", p. 521, presented by Urs Stadler of Ciba Specialty Chemicals Corporation. For convenience, a summary of the teachings of this paper is provided below. It is generally accepted that:

1. Carbon centered radicals (or "CCRs") are formed when polyolefins
20 are subjected to heat and shear during melt processing;
2. CCRs react with oxygen to form peroxy radicals (or "PRs"); and
3. PR's react with the polyolefin to form hydroperoxides (or "HPs") and more CCRs.

In a conventional phenol/phosphite stabilizer system, it is generally accepted
25 that:

1. the phenolic (which is also referred to as the "primary" antioxidant) decomposes the carbon centered radicals and peroxy radicals; and
2. the phosphite (which is also referred to as the "secondary" antioxidant) decomposes the hydroperoxides.

30 In addition, it is generally accepted that (a) the phenolic antioxidant provides a synergistic effect at the temperatures which are encountered during melt processing by reducing the rate at which the phosphite is depleted or consumed; and (b) if/when the phosphite is depleted (to below the concentration which is required for the decomposition of the hydroperoxides) then the structure of the

polyolefin is altered by the action of the free radicals. In polypropylene, this generally results in "chain scission" (a reduction in the molecular weight of the polypropylene) whereas "crosslinking" is generally believed to predominate in polyethylene (which results in an increase in apparent molecular weight).

5 Stabilizer packages which comprise a combination of a phenolic antioxidant and a phosphite are in wide spread commercial use and generally provide efficient and cost effective results.

However, the use of phenolics is associated with color development in the finished plastic parts, especially in polyethylene or polypropylene which is produced
10 with a transition metal catalyst (such as titanium, vanadium, zirconium or chromium). For example, "yellowing" and "pinkling" have been observed in plastic parts which are stabilized with a phenolic antioxidant.

Thus, as noted in United States Patent ("USP") 5,596,033: "there is a long-felt need in the market place for a stabilizer system which can prevent color
15 formation associated with the use of phenolic antioxidants".

Several "phenol free" stabilization systems have been proposed and brief overviews of several of these systems follow:

1. Phosphites plus hindered amines (HALS): these phenol free systems are reported to lack adequate process stabilization (see USP 5,596,033).
- 20 2. N,N-dialkylhydroxylamine plus HALS: these phenol free systems are expensive (due to the high cost of the hydroxylamine) and may have restricted use in certain food contact applications due to FDA regulations (again, due to the presence of the hydroxylamine) (USP 5,596,033).
3. HALS, plus hydroxylamine (or nitron) plus phosphite: as above,
25 these phenol free systems are expensive and may have restrictions upon their use (USP 6,664,317).
4. HALS plus hydroxylamine plus a mixture of two hydrolytically resistant phosphites: as above, these phenol free systems are expensive and may have restrictions upon their use (USP 6,077,890).
- 30 5. Lactones (such as benzofuranone) plus HALS: these phenol free systems are also expensive (due to the high cost of the lactone) and may have restricted use due to FDA regulations concerning the use of lactones (USP 5,883,165).

6. A combination of aryl monophosphite with a diphosphite: (USP 7,361,703). These systems may “plate out” of LLDPE compositions because the solubility of this monophosphite/diphosphite system in LLDPE is quite low.

We have now discovered an effective low cost, phenol free stabilization
5 package for the melt processing of polyolefins.

SUMMARY OF INVENTION

The present invention provides a process for stabilizing a thermoplastic polyolefin during melt processing conditions, said process comprising the step of incorporating into said thermoplastic polyolefin a stabilizer package comprising:

- 10 1) a solid aryl monophosphite; and
 2) a liquid phosphite defined by the term: phosphorous acid, triphenyl ester, polymer with α -hydro- ω -hydroxypoly[oxy(methyl-1,2-ethanediyl)], C10-16 alkyl esters

and subjecting said thermoplastic polyolefin to sufficient temperature to melt said
15 polyolefin;

with the proviso that said stabilizer package is essentially free of any additive selected from the group consisting of hindered phenolic antioxidants, lactone stabilizers and hydroxylamine stabilizers.

DESCRIPTION OF EMBODIMENTS

20 This invention generally relates to the melt processing of polyolefins using a stabilizer system which is essentially free of phenolic antioxidant.

The “phenol free” melt processing operation of this invention is generally suitable for any thermoplastic polyolefin, though thermoplastic polypropylene and polyethylene are preferred. The preferred thermoplastic polyolefins for use in this
25 invention are prepared with a transition metal catalyst such as titanium, vanadium, zirconium or chromium and the present invention is particularly suitable for polyolefins which contain from about 0.5 parts per million by weight (“ppm”) to about 15 parts per million by weight of transition metal residue. (The process of this invention may not provide complete process stabilization if the polyolefin
30 contains more than 15 parts per million transition metal and the process of this invention may not be required if the polyolefin contains less than 0.5 ppm of transition metal). In addition, the polyolefin may contain magnesium residues (in amounts up to 500 ppm); aluminum residues (in amounts up to 150 ppm); and chlorine residues (in amounts up to 200 ppm).

It is preferred that the thermoplastic polyolefin is a linear polyethylene having:

(i) a density of from 0.880 grams per cubic centimeter (g/cc) to 0.960 grams per cubic centimeter (g/cc) - especially from 0.910 to 0.945 g/cc; and

5 (ii) a melt index, I_2 , as determined by ASTM D 1238 of from 0.3 (grams per 10 minutes) to 150, especially from 1 to 100 and most preferably from 1 to 5.

The most preferred linear polyethylene are copolymers of ethylene with at least one other olefin selected from the group consisting of butene, pentene, hexene, and octene. These thermoplastic polyethylenes may be produced in any
10 of the known polymerization processes (such as a gas phase process, a slurry process or a solution process) using any known polymerization catalyst (such as a chromium catalyst, a Ziegler Natta catalyst or a single site catalyst such as a metallocene catalyst or a so-called "constrained geometry catalyst").

The melt processing process of this invention is characterized by:

15 (1) the required use of a defined solid aryl monophosphite (described in part A below);

(2) the required use of a defined liquid phosphite (described in part B below); and

(3) that the melt processing is essentially free of a phenolic antioxidant or
20 hydroxylamine or lactone stabilizer (described in part D below).

In addition to the two require phosphites, the stabilizer package used in the present invention preferably contains an acid neutralizer (described in Part C.1 below). If the finished part which is made in accordance with the present invention is intended for long term use, then the use of additional stabilizers (especially
25 HALS) is preferred as described in C.2 below. Other conventional additives may also be included.

In an embodiment, the linear polyethylene is made with two catalysts (especially a Ziegler Natta catalyst and a single site catalyst) in two or more reactors. It is known that such linear polyethylenes can be especially susceptible to
30 color formation, as disclosed in WO 2016/063200 (Sibtain et al.).

Part A. "Solid Aryl Monophosphite"

As used herein, the term solid aryl monophosphite refers to a phosphite stabilizer which contains:

(1) only one phosphorus atom per molecule; and

(2) at least one aryloxy (which may also be referred to as phenoxide) radical which is bonded to the phosphorus.

The aryl monophosphite is a solid at 20°C (for clarity, the monophosphite is a solid – not a liquid – at 20°C).

5 Preferred aryl monophosphites contain three aryloxy radicals--for example, tris phenyl phosphite is the simplest member of this preferred group of aryl monophosphites.

Highly preferred solid aryl monophosphites contain C₁ to C₁₀ alkyl substituents on at least one of the aryloxy groups.

10 Non-limiting examples of solid aryl monophosphites follow.

Triphenyl phosphite; tris(2,4-di-tert-butylphenyl) phosphite [IRGAFOS® 168, available from BASF]; and bis(2,4-di-tert-butyl-6-methylphenyl) ethyl phosphite [IRGAFOS 38, available from BASF]; and 2,2',2''-nitrilo[triethyltris(3,3',5,5'-tetra-tert-butyl-1,1'-biphenyl-2,2'-diyl) phosphite [IRGAFOS 12, available from BASF].

15 As illustrated by data in the accompanying examples, the tertiary butyl substituted aryl phosphites are preferred.

The amount of solid aryl monophosphite used in the present invention is from 200 to 2,000 ppm (based on the weight of the polyolefin), preferably from 300 to 1,500 ppm and most preferably from 400 to 1,000 ppm.

20 The solid aryl monophosphite is critical to the present invention. Whilst not wishing to be bound by theory, it is postulated that (i) the aryl monophosphite decomposes during the melt processing operation of this invention and provides a phenolic structure (in-situ); and (ii) the “in-situ phenolic” provides a synergistic effect with respect to reducing the rate of decomposition of the remaining active
25 phosphite (without leading to the excessive color formation which is typically observed in a conventional phenol/phosphite stabilizers system).

In an embodiment, the aryl monophosphite is tris (2,4-ditertiary butyl) phosphite (CAS Registry Number 31570-044).

PART B. Selected Liquid Phosphite

30 The liquid phosphite is defined by the term: phosphorous acid, triphenyl ester, polymer with α -hydro- ω -hydroxypoly[oxy(methyl-1,2-ethanediyl)], C₁₀-16 alkyl esters (CAS Reg. No. 1227937-46-3).

Part C.1 Acid Neutralizers

Many commercially available polyolefins contain chloride residues. These chloride residues may generate hydrochloric acid, particularly during melt processing operations. Accordingly, an "acid neutralizer" is conventionally included in a polyolefin stabilization package and is preferably included in the process of this invention.

These acid neutralizers may be divided into "Inorganic" - such as zinc oxide, synthetic hydrotalcites and Li, Na, Ca or Al (hydroxy) carbonates; and "Organic" - such as salts of fatty acids or their derivatives including calcium stearate, zinc stearate, calcium lactate and calcium stearoyl lactylate.

When employed, these conventional acid neutralizers are used in conventional amounts. It is preferred to use a synthetic hydrotalcite (in an amount of from 100 to 1,000 ppm), zinc stearate (in an amount of from 200 to 700 ppm) or calcium stearoyl lactylate (in an amount of from 200 to 700 ppm). A combination of a hydrotalcite with an "organic" acid neutralizer is highly preferred.

Part C.2 Long Term Stabilizers

Plastic parts which are intended for long term use preferably contain at least one HALS (C.2.1).

Part C.2.1 HALS

A hindered amine light stabilizer (HALS) is preferably included in the stabilizer package used in the present invention if the plastic part is intended for more than single/short term use.

HALS are well known to those skilled in the art.

When employed, the HALS is preferably a commercially available material and is used in a conventional manner and amount.

Commercially available HALS include those sold under the trademarks CHIMASSORB® 119; CHIMASSORB 944; CHIMASSORB 2020; TINUVIN® 622 and TINUVIN 770 from Ciba Specialty Chemicals Corporation, and CYASORB® UV 3346, CYASORB UV 3529, CYASORB UV 4801, and CYASORB UV 4802 from Cytec Industries. TINUVIN 622 is preferred. Mixtures of more than one HALS are also contemplated.

Suitable HALS include: bis (2,2,6,6-tetramethylpiperidyl)-sebacate; bis-5 (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; 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; tris-(2,2,6,6-
 tetramethylpiperidyl)-nitrilotriacetate, tetrakis-(2,2,6,6-tetramethyl-4-piperidyl)-
 5 1,2,3,4butane-tetra-carbonic acid; and 1,1'-(1,2-ethanediyl)-bis-(3,3,5,5-
 tetramethylpiperazinone).

Part C.2.2 Other Optional Additives

C.2.2.1 2-(2'-hydroxyphenyl)-benzotriazoles

For example, the 5'-methyl-,3'5'-di-tert-butyl-,5'-tert-butyl-,5'-(1,1,3,3-
 10 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-di
 methylbenzyl)-derivatives.

C.2.2.2 2-Hydroxy-Benzophenones

For example, the 4-hydroxy-4-methoxy-,4-octoxy,4-decyloxy-, 4-dodecyloxy-
 15 ,4-benzyloxy,4,2',4' -trihydroxy-and 2'-hydroxy-4,4'-dimethoxy derivative.

C.2.2.3 Esters of Substituted and Unsubstituted Benzoic Acids

For example, phenyl salicylate; 4-tertbutylphenyl-salicylate; octylphenyl
 salicylate; dibenzoylresorcinol; bis-(4-tert-butylbenzoyl)-resorcinol;
 benzoylresorcinol; 2,4-di-tert-butyl-phenyl-3,5-di-tert-butyl-4-hydroxybenzoate; and
 20 hexadecyl-3,5-di-tert-butyl-4-hydroxybenzoate.

C.2.2.4 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-
 25 methoxy-cinnamic acid methyl ester; and N-(beta-carbomethoxy-beta-cyano-vinyl)-
 2-methyl-indoline.

C.2.2.5 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
 30 n-butylamine, triethanolamine or N-cyclohexyl-diethanolamine; 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; and nickel

complexes of 1-phenyl-4-lauroyl-5-hydroxy-pyrazole, optionally with additional ligands.

C.2.2.6 Oxalic Acid Diamides

For example, 4,4'-di-octyloxy-oxanilide; 2,2'-di-octyloxy-5,5'-ditert-butyl-
 5 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-butyl-oxanilide; and mixtures of ortho-and para-methoxy as well as of o- and p-ethoxy-disubstituted oxanilides.

10 C.2.2.7 Hydroxyphenyl-s-triazines

For example, 2,6-bis-(2,4-dimethylphenyl)-4-(2-hydroxy-4-octyloxyphenyl)-s-triazine; 2,6-bis(2,4-dimethylphenyl)-4-(2,4-dihydroxyphenyl)-s-triazine; 5 2,4-bis(2,4-dihydroxyphenyl)-6-(4-chlorophenyl)-s-triazine; 2,4-bis(2-hydroxy-4-(2-hydroxyethoxy)phenyl)-6-(4-chlorophenyl)-s-triazine; 2,4-bis(2-hydroxy-4-(2-
 15 hydroxyethoxy)phenyl)-6-phenyl-s-triazine; 2,4-bis(2-hydroxy-4-(2-hydroxyethoxy)-phenyl)-6-(2,4-dimethylphenyl)-s-triazine; 2,4-bis(2-hydroxy-4-(2-hydroxyethoxy)phenyl)-6-(4-bromo-phenyl)-s-triazine; 2,4-bis(2-hydroxy-4-(2-acetoxyethoxy)phenyl)-6-(4-chlorophenyl)-s-triazine; and 2,4-bis(2,4-dihydroxyphenyl)-6-(2,4-dimethylphenyl)-1-s-triazine.

20 C.2.2.8 Metal Deactivators

For example, N,N'-diphenyloxalic acid diamide; N-salicylal-N'-salicyloylhydrazine; N,N'-bis-salicyloylhydrazine; N,N'-bis-(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)-2-hydrazine; salicyloylarnino-1,2,4-triazole; and bis-benzyliden-oxalic acid dihydrazide.

25 C.2.2.9 Peroxide Scavengers

For example, esters of betathiodipropionic acid, for example the lauryl, stearyl, myristyl or tridecyl esters; mercaptobenzimidazole or the zinc salt of 2-mercaptobenzimidazole; zinc-dibutyldithiocarbamate; dioctadecyldisulfide; and pentaerythritotetrakis-(beta-dodecylmercapto)-propionate.

30 C.2.2.10 Polyamide Stabilizers

For example, copper salts in combination with iodides and/or phosphorus compounds and salts of divalent manganese.

C.2.2.11. Nucleating Agents

For example, 4-tert-butylbenzoic acid; adipic acid; diphenylacetic acid; sodium salt of methylene bis-2,4-dibutylphenyl; cyclic phosphate esters; sorbitol tris-benzaldehyde acetal; and sodium salt of bis(2,4-di-t-butylphenyl) phosphate or Na salt of ethylidene bis(2,4-di-t-butyl phenyl)phosphate.

C.2.2.12. Fillers and Reinforcing Agents

For example, calcium carbonate; silicates; glass fibers; asbestos; talc; kaolin; mica; barium sulfate; metal oxides and hydroxides; carbon black and graphite.

C.2.2.13. Miscellaneous Additives

For example, plasticizers; epoxidized vegetable oils, such as epoxidized soybean oils; lubricants; emulsifiers; polymer process additives (e.g. fluoroelastomers); pigments; optical brighteners; flameproofing agents; anti-static agents; blowing agents and thiosynergists, such as dilaurythiodipropionate or distearylthiodipropionate.

The term "phenol free" has been used herein to refer to a stabilizer package which is "essentially free" of any "primary" antioxidant such as a phenolic, lactone or hydroxylamine. The phrase "essentially free" is meant to convey a plain meaning, namely that none of the phenolic (or lactone or hydroxylamine) is deliberately added to the polyolefin in order to achieve the melt stabilization of this invention. The "excluded" stabilizers (i.e. the stabilizers which are not deliberately added to the polyolefin according to this invention) are described in Part D below.

Part D. Excluded Stabilizers

The process of this invention utilizes a stabilizer package which is essentially free of phenolic antioxidants, hydroxyl amines (and amine oxides) and lactones.

Part D.1 Phenolic Antioxidants

D.1.1 Alkylated Mono-Phenols

For example, 2,6-di-tert-butyl-4-methylphenol; 2-tert-butyl-4,6-dimethylphenol; 2,6-di-tert-butyl-4-ethylphenol; 2,6-di-tert-butyl-4-n-butylphenol; 2,6-di-tert-butyl-4isobutylphenol; 2,6-dicyclopentyl-4-methylphenol; 2-(.alpha.-methylcyclohexyl)-4,6 dimethylphenol; 2,6-di-octadecyl-4-methylphenol; 2,4,6,-tricyclohexylphenol; and 2,6-di-tert-butyl-4-methoxymethylphenol.

D.1.2 Alkylated Hydroquinones

For example, 2,6-di-tert-butyl-4-methoxyphenol; 2,5-di-tert-butylhydroquinone; 2,5-di-tert-amyl-hydroquinone; and 2,6-diphenyl-4-octadecyloxyphenol.

5 D.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); and 4,4'-thio-bis-(6-tert-butyl-2-methylphenol).

D.1.4 Alkylidene-Bisphenols

10 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-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-nonylphenol); 2,2'-methylene-bis-(4,6-di-tert-butylphenol); 2,2'-ethyleneglycol-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-dodecylmercaptobutane; 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'-methylbenzyl)-6-tert-butyl-4-methylphenyl)terephthalate; and other phenolics such as monoacrylate esters of bisphenols such as ethyleneglycol bis-2,4-di-tert-butylphenol monoacrylate ester.

D.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-mercaptoacetate; bis-(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl)dithiol-terephthalate; 1,3,5-tris-(3,5-di-tert-butyl-4,10-hydroxybenzyl)isocyanurate; 1,3,5-tris-(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl)isocyanurate; dioctadecyl 3,5-di-tert-butyl-4-hydroxybenzylphosphonate; calcium salt of monoethyl 3,5-di-tert-butyl-4-

hydroxybenzylphosphonate; and 1,3,5-tris-(3,5-dicyclohexyl-4-hydroxybenzyl)isocyanurate.

D.1.6 Acylaminophenols

For example, 4-hydroxy-lauric acid anilide; 4-hydroxy-stearic acid anilide;

5 2,4-bis-octylmercapto-6-(3,5-tert-butyl-4-hydroxyanilino)-s-triazine; and octyl-N-(3,5-di-tert-butyl-4-hydroxyphenyl)-carbamate.

D.1.7 Esters of beta-(5-tert-butyl-4-hydroxy-3-methylphenyl)-propionic acid with Monohydric or Polyhydric Alcohols

For example, methanol; diethyleneglycol; octadecanol; triethyleneglycol; 1,6-
10 hexanediol; pentaerythritol; neopentylglycol; tris-hydroxyethyl isocyanurate; thidiethyleneglycol; and dihydroxyethyl oxalic acid diamide.

D.1.8 Amides of beta-(3,5-di-tert-butyl-4-hydroxyphenyl)-propionic acid

For example, N,N'-di-(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)-
hexamethylenediamine; N,N'-di-(3,5-di-tert-butyl-4-

15 hydroxyphenylpropionyl)trimethylenediamine; and N,N'-di(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)-hydrazine.

Part D.2 Hydroxylamines and Amine Oxides

The process of this invention is essentially free of hydroxylamine stabilizers. For example, N,N-dibenzylhydroxylamine; N,N-diethylhydroxylamine; N,N-
20 dioctylhydroxylamine; N,N-dilaurylhydroxylamine; N,N-ditetradecylhydroxylamine; N,N-dihexadecylhydroxylamine; N,N-dioctadecylhydroxylamine; N-hexadecyl-N-octadecylhydroxylamine; N-heptadecyl-N-octadecylhydroxylamine; and N,N-dialkylhydroxylamine derived from hydrogenated tallow amine. The analogous
amine oxides (as disclosed in USP 5,844,029, Prachu et al.) are also meant to be
25 included by the definition of hydroxylamine (and thus are not used in the process of this invention).

Part D.3 Lactones

The process of this invention is essentially free of lactone stabilizers.

The use of lactones such as benzofuranone (and derivatives thereof) or
30 indolinone (and derivatives thereof) as stabilizers is described in USP 4,611,016.

Melting Processing Operations

In general, the process of this invention is suitable for processing molten thermoplastic polyolefins. The melt processing operations are conducted at

temperatures from above the melting point of the thermoplastic polyolefin to as high as 400°C.

The present process is particularly suitable for extrusion operations, injection molding operations and rotomolding operations.

5 The extrusion of polyethylene film is particularly preferred. Examples of polyethylene film extrusion process include the blown film process and cast film process which are briefly described below.

10 In a blown film process, the polyethylene is melted in a screw extruder (preferably at a temperature of from 200 to 290°C, especially from 210 to 250°C) and then forced through an annular die to form a tube of molten polyethylene. The tube is inflated with air from the interior of the tube, then cooled and finally flattened by nip rolls. It is also known to co-extrude multi layers of film by this process.

15 In a cast film process, the polyethylene is also melted in a screw extruder (preferably at temperatures of from 450°F (232°C) to 600°F (316°C) especially from 500°F (260°C) to 550°F (288°C) and then forced through a flat die. The molten polyethylene web is then cooled (typically, through the use of a water bath or, alternatively, temperature controlled casting rolls).

20 In an injection molding process, the polyethylene is typically melted in a screw extruder and then rammed under very high pressures into a hollow mold.

25 In a rotomolding process, the polyethylene resin is ground into a fine powder, then charged into a hollow mold. The mold is then placed in a furnace and heated to temperatures of from 250°C to 325°C (especially from 520°F (271°C) to 600°F (316°C)) while the mold is rotated. The molten plastic flows through the mold under the gentle (low shear) forces from the rotation.

30 The cast film process is especially challenging for stabilization systems because it combines high temperatures and high shear rates.

EXAMPLES

Example 1

30 Phenolic antioxidants provide a synergistic effect at the temperatures which are encountered during melt processing by reducing the rate at which the phosphite is depleted or consumed. When the phosphite is depleted (to below the concentration which is required for the decomposition of the hydroperoxides) then the structure of the polyolefin is altered by the action of the free radicals. In

polypropylene, this generally results in "chain scission" (a reduction in the molecular weight of the polypropylene) whereas "crosslinking" is generally believed to predominate in polyethylene (which results in an increase in apparent molecular weight).

5 Stabilizer packages which comprise a combination of a phenolic antioxidant and a phosphite are in wide spread commercial use and generally provide efficient and cost effective results. However, the use of phenolics is associated with color development in the finished plastic parts, especially in polyethylene or polypropylene which is produced with a transition metal catalyst (such as titanium, 10 vanadium, zirconium or chromium). For example, "yellowing" and "pinkening" have been observed in plastic parts which are stabilized with a phenolic antioxidant.

The present invention mitigates this problem by eliminating the use of the phenolic antioxidant.

15 Stabilizer packages according to this invention comprise at least one solid aryl monophosphite and at least one liquid monophosphate. The solid aryl monophosphite may be tris(2-4-di-tert-butylphenyl)phosphite (CAS Reg. No. 31570-04-4) (IRGAFOS I-168). The liquid phosphite is phosphorous acid, triphenyl ester, polymer with α -hydro- ω -hydroxypoly[oxy(methyl-1,2-ethanediyl)], C10-16 alkyl esters (CAS Reg. No. 1227937-46-3), sold by Dover Chemicals under the 20 trademark DOVERPHOS® LGP-11.

Example 1:

A series of small scale experiments were completed to investigate the performance of various stabilizers. The experiments were undertaken in a fusion-head mixer (manufactured by C.W. Brabender Instruments, Inc.) equipped with 25 roller mixing blades in a mixing bowl having a 40 cc capacity. The stabilizer formulations (shown in Table 1) were mixed with a polyethylene in the fusion-head mixer for a period of 10 minutes at 160°C.

The polyethylene used in all experiments of example 1 was an ethylene-octene copolymer having a density of 0.920 g/cc and a melt index, I₂ (as 30 determined by ASTM D 1238, at 190°C, using a 2.16 kg load) of 1.0 gram per 10 minutes. This polyethylene was produced in a solution phase polymerization process using a Zeigler-Natta type catalyst containing magnesium and titanium and

was activated with an aluminum containing activator. The polyethylene contained residual titanium in an amount of greater than 5 but less than 15 ppm.

The polyethylene was removed from the Brabender mixer after the ten minute test and pressed into plaques. Color measurements were performed on the plaques in accordance with ASTM standards (yellow index or "YI" was determined according to ASTM D 1925 and whiteness index or "WI" was determined according to ASTM E313).

Low YI values and high WI values are desirable. Color data are provided in Table 1.

TABLE 1

Color Data for Various Additive Formulations

Formulation	AO1¹	AO2²	P1³	P2⁴	Color (YI)	Color (WI)
C1	500		500		-1.8	67
C2		500	500		-0.6	64
IE1			500	500	-3.9	72

¹AO1 = IRGANOX 1076, ²AO2 = IRGANOX1010, ³P1 = IRGAFOS 168, ⁴P2 = DOVERPHOS LGP-11

The two control experiments (C1 and C2) were conducted using a conventional stabilizer package that contains a phenolic antioxidant (C1 contained 500 ppm of a phenolic and 500 ppm of a phosphite sold under the trademarks IRGANOX® 1076 and IRGAFOS 168, respectively, by BASF).

C2 contained 500 ppm of a different phenolic antioxidant (sold under the trademark IRGANOX 1010) and the same phosphite used in C1. The stabilizer formulations of C1 and C2 are well known and in wide commercial use.

The color data shown in Table 1 clearly indicate that the comparative stabilizer packages generate undesirable color under the conditions of this experiment. The YI and WI of the resin of experiment C1 were -1.8 and 67, respectively, while the color levels produced in C2 were marginally worse.

Inventive formulation IE1 was prepared using a blend of two phosphite stabilizers at a loading level of 500 ppm each (500 ppm P1 and 500 ppm P2 under the trademarks IRGAFOS 168 by BASF and DOVERPHOS LGP-11 by Dover Chemicals, respectively).

Example 2 - Multipass Study

The experiments of this example were performed on a Leistritz twin screw extruder. For the purpose of this evaluation the temperature profile was set to obtain a melt temperature 225°C. The compositions were put through the extruder 3 times (or 3 “passes”). High load melt index (also known as “I₂₁”) was measured after passes 0, 1, and 3 in accordance with ASTM standards D1238 at 190°C, using a 21.6 kg load. Experimental data are provided in Table 2 (color) and Table 3 (melt flow stability). I₂₁ values are reported in grams per 10 minutes (and the smallest deviation from pass 0 MI is desirable).

The desirable “color” performance illustrated in Example 1 is of little practical value unless the stabilizer package also provides “melt flow stability”. As previously noted, a useful stabilizer package must protect against chain scission reactions in polypropylene (leading to an increase in melt index) and crosslinking reactions in polyethylene. The problems caused by crosslinking of polyethylene are manifested in changes in the physical properties of the finished polyethylene good. For example, a crosslinking reaction in polyethylene used to prepare film may cause a loss of elongation, impact strength and machine direction (MD) tear strength.

TABLE 2**Color Stability Data (YI) for Various Additive Formulations After Multiple Extrusion Pass Experiment (225°C)**

Extrusion Pass #	C1	C2	IE1
0	-1.8	-0.6	-3.9
1	3.2	5.2	-3.1
3	8.2	9.8	-1.4

TABLE 3**Change In (I₂₁) for Various Additive Formulations After Multiple Extrusion Pass Experiment (225°C)**

Extrusion Pass #	C1	C2	IE1
0	24.9	25.2	25.5
1	23.3	23.8	23.8
3	20.8	21.1	19.2

The present multipass study provides additional data which further reinforce the excellent color performance of the present stabilizer system. Most notably, the data in Table 2 shows that the inventive composition (IE1) still maintained a Y1 of - 1.4 after 3 passes while the comparative compositions turned yellow Y1 values of

5 8.2 and 9.8.

Furthermore, the data in Table 3 illustrate that inventive composition IE1 also exhibits good melt flow stability after three passes at 225°C.

INDUSTRIAL APPLICABILITY

A process to prepare a phenol free stabilized polyolefin composition that has good melt flow stability and excellent resistance to color formation. The process is suitable for the preparation of a wide variety of packages, especially film packages that are made with polyethylene.

10

CLAIMS

1. A process for stabilizing a thermoplastic polyolefin during melt processing conditions said process comprising the step of incorporating into said thermoplastic polyolefin a stabilizer package comprising:

- 5 (i) a solid aryl monophosphite; and
 (ii) a liquid phosphite defined by the term: phosphorous acid, triphenyl ester, polymer with α -hydro- ω -hydroxypoly[oxy(methyl-1,2-ethanediyl)], C10-16 alkyl esters

and subjecting said thermoplastic polyolefin to sufficient temperature to melt said polyolefin;

with the proviso that said stabilizer package is essentially free of any additive selected from the group consisting of hindered phenolic antioxidants, lactone stabilizers and hydroxylamine stabilizers.

2. The process according to claim 1 wherein said stabilizer formulation contains an acid neutralizer.

3. The process according to claim 1 wherein said stabilizer formulation contains a hindered amine light stabilizer.

4. The process according to claim 1 wherein said thermoplastic polyolefin is a linear polyethylene which contains from 0.5 to 15 ppm of at least one transition metal selected from the group consisting of titanium, vanadium, zirconium and chromium.

5. The process according to claim 4 wherein said linear polyethylene is a copolymer of ethylene and at least one olefin selected from the group consisting of butene, pentene, hexene and octene.

6. The process according to claim 5 wherein said linear polyethylene has a density of from 0.880 to 0.960 g/cc and a melt index, I_2 , as determined by ASTM D1238 of from 0.3 to 150 g/10 minutes.

7. The process according to claim 6 wherein said melting processing conditions comprise a film extrusion at a temperature of from 200°C to 320°C.

INTERNATIONAL SEARCH REPORT

International application No

PCT/IB2017/057743

A. CLASSIFICATION OF SUBJECT MATTER

INV. C08K5/526 C08J3/20 C08J5/18 C08L23/04 C08K5/00
C08L85/02

ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C08K C08J C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2016/237264 A1 (JAKUPCA MICHAEL R [US] ET AL) 18 August 2016 (2016-08-18) figure 10 paragraphs [0065], [0098] - [0099] examples 1-3	1-7
Y	WO 2011/102861 A1 (DOVER CHEMICAL CORP [US]; JAKUPCA MICHAEL [US]; LANCE JACOB M [US]; ST) 25 August 2011 (2011-08-25) paragraphs [0068], [0074] claims 9,18	1-7
Y	US 2005/261403 A1 (TIKUISIS TONY [CA] ET AL) 24 November 2005 (2005-11-24) paragraph [0044] examples claims	1-7



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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