Innovation, Sciences et Développement économique Canada
Office de la Propriété Intellectuelle du Canada

Innovation, Science and Economic Development Canada
Canadian Intellectual Property Office

CA 2819930 C 2020/06/02

(11)(21) **2 819 930**

(12) BREVET CANADIEN CANADIAN PATENT

(13) **C**

(22) **Date de dépôt/Filing Date:** 2013/06/25

(41) **Mise à la disp. pub./Open to Public Insp.:** 2014/12/25

(45) **Date de délivrance/Issue Date:** 2020/06/02

(51) **Cl.Int./Int.Cl.** ***C08J 7/12*** (2006.01),
C08J 3/20 (2006.01), ***C08K 5/3492*** (2006.01),
C08L 23/04 (2006.01), ***C09K 3/10*** (2006.01)

(72) **Inventeurs/Inventors:**
LIGHTBODY, OWEN C., CA;
TIKUISIS, TONY, CA;
AUBEE, NORMAN D.J., CA

(73) **Propriétaire/Owner:**
NOVA CHEMICALS CORPORATION, CA

(74) **Agent:** CHISHOLM, P. SCOTT

(54) **Titre : FILMS DE POLYETHYLENE TRAITES A L'EFFET COURONNE**
(54) **Title: CORONA TREATED POLYETHYLENE FILMS**

(57) **Abrégé/Abstract:**
A process for improving the sealing characteristics of corona treated polyolefin films through the use of a stabilizer system comprising i) 1,3,5-tris(4-tert-butyl-3-hydroxy-2,6-dimethyl benzyl)-1,3,5-triazine-2,4,6-(1H,3H,5H)-trione (CAS registry number 040601-76-1) and ii) an organic phosphite or phosphonite.

CORONA TREATED POLYETHYLENE FILMS

ABSTRACT OF THE DISCLOSURE

A process for improving the sealing characteristics of corona treated polyolefin films through the use of a stabilizer system comprising i) 1,3,5-tris(4-tert-butyl-3-hydroxy-2,6-dimethyl benzyl)-1,3,5-triazine-2,4,6-(1H,3H,5H)-trione (CAS registry number 040601-76-1) and ii) an organic phosphite or phosphonite.

CORONA TREATED POLYETHYLENE FILMS

FIELD OF THE INVENTION

This invention relates to improving the sealing characteristics of polyolefin films that have been corona treated.

BACKGROUND OF THE INVENTION

Polyolefin films are widely used to prepare packaging. It is difficult to apply color printing to these films as the films are generally non polar and the printing inks are typically polar. There are several methods to improve ink adhesion, including the use of a primer coating; flame treatment of the surface and corona treatment.

Corona treatment is well known to those skilled in the art and is discussed for example, in U.S. patent 4,145,386 and in a paper by Lahti et al. entitled, "The Effects of Corona and Flame Treatment: Part 1: PE-LD Coated Packaging Board." In general, the corona treated oxidizes the surface of the film. It is generally accepted that this surface oxidation causes the formation of polar functional groups on the film surface. In particular, hydroxyl, carbonyl, and carboxyl groups have been reported to be formed by corona treatment. While not wishing to be bound by theory, it is believed that those polar groups help to improve the adhesion of printing inks to the surface of the treated film.

However, corona treatment has also been observed to cause problems with the seal strength of treated films. While not wishing to be bound by theory, it is believed that corona treatment can cause crosslinking and/or chain scission on the film surface (and that, in turn, these crosslinking or chain scission phenomena can cause problems with seal formation and seal strength). We have now discovered that the use of a stabilizer system comprising i) 1,3,5-tris(4-tert-butyl-3-hydroxy-2,6-dimethyl benzyl)-1,3,5-triazine-2,4,6-(1H,3H,5H)-trione (CAS registry number 040601-76-1) and ii) a secondary antioxidant (a phosphite) mitigates this problem and provides a method to improve the sealing performance of corona treated polyethylene film.

SUMMARY OF THE INVENTION

The present invention provides a method for preparing a sealed polyethylene package having incorporated therein a stabilizer system sufficient to mitigate the deleterious effect of corona treatment on seal strength, said method comprising:

1) providing polyethylene film;
2) subjecting said polyethylene film to corona treatment;
3) forming a heat seal by subjecting two layers of said polyethylene film to a sealing bar at a temperature of from 120 to 220°C;

wherein said stabilizer system is characterized by comprising i) from 100 to 1000 parts per million by weight of 1,3,5-tris(4-tert-butyl-3-hydroxy-2,6-dimethyl benzyl)-1,3,5-triazine-2,4,6-(1H,3H,5H)-trione, and ii) from 100 to 1000 parts per million by weight of a secondary antioxidant selected from the group consisting of organic phosphites and phosphonites.

DETAILED DESCRIPTION

The method of this invention is generally believed to be suitable for any thermoplastic polyolefin, though polyethylene is preferred. The preferred thermoplastic polyolefins for use in this 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. 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 0.88 grams per cubic centimeter (g/cc) to 0.95 grams per cubic centimeter (g/cc) - especially from 0.910 to 0.945 g/cc; and

(ii) a melt index, I_2, as determined by ASTM D 1238 of from 0.3 (grams per 10 minutes) to 20, especially from 1 to 100 and most preferably from 1.5 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 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 additive package used in the present invention contains a selected primary antioxidant (part A, below), a secondary antioxidant (a phosphite or phosphonite, Part B, below) and (preferably) also contains an acid neutralizer (described in part C.1 below). If the film part which is made in accordance with the present invention is intended for long term use, then the use of additional stabilizers (especially HALS) is preferred as described in C.2 below. Other conventional additives may also be included.

Part A: Primary Antioxidant

The present invention requires the use of the trione additive described above (i.e. the molecule to which CAS registry number 040601-76-1 is assigned). This additive may be referred to as a primary antioxidant because it has the ability to scavenge free radicals. It is known to use this additive to stabilize polyolefins but it is of higher cost than other primary antioxidants (and hence is in more limited use than other, less costly antioxidants).

Examples of more commonly used (less costly) primary antioxidants include the hindered phenols which have been assigned CAS registry numbers 6683-19-8 and 2082-79-3. While not wishing to be bound by theory, it is believed that the primary antioxidant used in tis invention is less sterically encumbered (less hindered) than the more commonly used primary antioxidants and that, in turn, this allows the primary antioxidant of this invention to reduce the level of crosslinking that is caused by corona treatment. Ultimately, the process of this invention provides corona treated polyethylene films having improved sealing characteristics and it is believed that the improvement in sealing characteristics may be associated with a lower level of crosslinking in the film.

The primary antioxidant that characterizes this invention (CAS Registry number 040601-76-1) is used in an amount of from 100 to 1000 parts per million by weight (ppm), based on the weight of the polyethylene, especially from 300 to 500 ppm.

It is permissible to use the other primary antioxidants described in this section and doing so may help to lower costs (by allowing a lower amount of the more expensive antioxidant to be employed).

Part B: Secondary Antioxidant: Organic Phosphites and Phosphinites

The stabilizer system used in this invention includes a secondary antioxidant, especially a phosphite. The phosphite may be an alkyl phosphite, an aryl phosphite or a diphosphite – all of which are in commercial use.

Non-limiting examples of suitable aryl monophosphites follow with preferred aryl monophosphites being indicated by the use of trademarks in square brackets.

Triphenyl phosphite; diphenyl alkyl phosphites; phenyl dialkyl phosphites; tris(nonylphenyl) phosphite [WESTON™ 399, available from GE Specialty Chemicals];

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

Another suitable type of phosphite is a diphosphite. As used herein, the term diphosphite refers to a phosphite stabilizer which contains at least two phosphorus atoms per phosphite molecule.

Non-limiting examples of suitable diphosphites follow: distearyl pentaerythritol diphosphite, diisodecyl pentaerythritol diphosphite, bis(2,4 di-tert-butylphenyl) pentaerythritol diphosphite [ULTRANOX™ 626, available from GE Specialty Chemicals]; bis(2,6-di-tert-butyl-4-methylpenyl) pentaerythritol diphosphite; bisisodecyloxy-pentaerythritol diphosphite, bis(2,4-di-tert-butyl-6-methylphenyl) pentaerythritol diphosphite, bis(2,4,6-tri-tert-butylphenyl) pentaerythritol diphosphite, tetrakis(2,4-di-tert-butylphenyl)4,4'-bipheylene-diphosphonite [IRGAFOS™ P-EPQ, available from Ciba] and bis(2,4-dicumylphenyl)pentaerythritol diphosphite [DOVERPHOS™ S9228-T or DOVERPHOS™ S9228-CT].

Organic phosphonites may also be employed. A non-limiting example is tetrakis (2,4-di-t-butylphenyl),[1,1-biphenyl]-4,4'diylbisphosphonite (sold under the trademark PEP-Q). The phosphite is preferably used in an amount of from 100 ppm to 2,000 ppm, especially from 100 to 1,000 ppm.

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 2000 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)-hexamethylendiamine 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)-1,2,3,4butane-tetra-arbonic 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-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-,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-salicilate; 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.

C.2.2.4 Acrylates

For example, alpha-cyano-.beta,.beta.-diphenylacrylic acid-ethyl ester or isooctyl ester; alpha-carbomethoxy-cinnarnic acid methyl ester; alpha-cyano-.beta.-methyl-p-methoxy-cinnamic acid methyl ester or butyl ester; alpha-carbomethoxy-p-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 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-penyl 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-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.

C.2.2.7 Hydroxyphenyl-s-triazines

For example, 2,6-bis-(2,4-dimethylphenyl)-4-(2-hydroxy-4octyloxyphenyl)-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(2hydroxy-4-(2-hydroxyethoxy)phenyl)-6-phenyl-s-triazine; 2,4-bis(2-hydroxy-4-(2-hydroxyethoxy)-

phenyl)-6-(2,4-dimethylphenyl)-s-tri azine; 2,4-bis(2-hydroxy-4-(2-hydroxyethoxy)phenyl)-6-(4-bromo-phenyl)-s-triazine; 2,4-bis(2-hydroxy-4-(2-acetoryethoxy)phenyl)-6-(4-chlorophenyl)-s-triazine; and 2,4-bis(2,4-dihydroxyphenyl)-6-(2,4-dimethylphenyl)-1-s-triazine.

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-hydrophenylpropionyl)-2-hydrazine; salicyloylarnino-1,2,4-triazole;and bis-benzyliden-oxalic acid dihydrazide.

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 pentaerythritottetrakis-(beta-dodecylmercapto)-propionate.

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 Hydroxylamines and Amine Oxides

For example, N,N-dibenzylhydroxylamine; N,N-diethylhydroxylamine; N,N-dioctylhydroxylamine; N,N-dilaurylhydroxylamine; N,N-ditetradecylhydroxylamine; N,N-dihexadecylhydroxylamine; N,N-dioctadecylhydroxylamine; N-hexadecyl-N-octadecylhydroxylamnine; N-heptadecyl-N-octadecylhydroxylamine; and N,N-dialkylhydroxylamine derived from hydrogenated tallow amine.

C.2.2.14 Lactones

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

C.2.2.15. 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.

Part D.1 Other 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,-tricyclohexyphenol; and 2,6-di-tert-butyl-4-methoxymethylphenol.

D.1.2 Alkylated Hydroquinones

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

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-tertbutyl-3-methylphenol); and 4,4'-thio-bis-(6-tert-butyl-2-methylphenol).

D.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-methyl-6-cyclohexyiphenol); 2,2'-methylene-bis-(6-nonyl-4-methylphenol); 2,2'-methylene-bis-(6-nonyl-4methylphenol); 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'-ethylidene-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-hydroxy2-methylphenyl)-3-dodecyl-mercaptobutane; ethyleneglycol-bis-(3,3,-bis-(3'-tert-butyl-4'-hydroxyphenyl)-butyrate)-di-(3-tert-butyl-4-hydroxy-5-methylpenyl)-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 ethylidiene bis-2,4-di-t-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-3hydroxy-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-tertbutyl-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; 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-hexanediol; pentaerythritol; neopentylglycol; tris-hydroxyethyl isocyanurate; thidiethyleneglycol; and dihydroxyethyl oxalic acid diamide.

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

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

Polyethylene Film

The present invention starts with a conventional polyethylene film, especially a “blown” film or a “cast” film.

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 annuler 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.

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).

Example

Blown films having a thickness of 2 mils were prepared on a conventional blown film line sold by Gloucester Engineering. The resin used for all experiments was a linear low density polyethylene having a melt index (I_2) of 1 g/10 minutes and a density of 0.920 g/cm^3. More specifically, the resin was an ethylene-octene copolymer, produced in a solution polymerization process with a titanium catalyst and it contained residual titanium in an amount estimated at 9 ± 2 ppm (based on typical values).

The resin contained 5000 ppm of the primary antioxidant that is essential to the process of this invention (i.e. 1,3,5-tris(4-tert-butyl-3-hydroxy-2,6-dimethyl benzyl)-1,3,5-triazine-2,4,6-(1H,3H,5H)-trione, CAS registry number 040601-76-1).

The line was operated at a rate of about 55 kilograms of extruded polyethylene per hour. The polyethylene was extruded through an annular die have a gap of 35 mils.

The film line was equipped with a commercially available corona treatment unit (sold by Sherman Treaters Inc.). A wetting tension of at least 35 dynes/cm (especially from 35 – 50) is preferred for commercial films. The corona treatment apparatus was adjusted so as to provide a wetting surface tension of 44 dynes/cm (as determined by ASTM D2578) for the films of this example.

The films were allowed to "condition" for 48 hours before sealing. After the conditioning period, 1 inch wide film strips were sealed (treated side to treated side) over a temperature range of 140-180°C using a two bar sealing system sold by Sencorp Inc. Heat was applied only to the upper seal bar. The sealing pressure was 15 pounds per square inch (psi) and the dwell time was 0.5 seconds. Once the seals were made, they were allowed to sit for 24 hours before being tested. The cold seal strength of these samples were determined using a 5-head universal tester according to ASTM F88 with a 2 inch grip separation and a test speed of 20 inches/min.

Data are compiled in Table 1 as "Seal Strength (Newtons)". The data correspond to the break load (or seal strength) – in Newtons – as determined by ASTM F88. For example/clarity: a force of 18.9 Newtons was required to break the inventive seal that was formed at 180°C (as shown in Table 1).

Comparative films were prepared with a conventional antioxidant package containing 500 ppm of a hindered phenolic (sold under the trademark IRGANOX 1076) and 500 ppm of a phosphite (sold under the trademark IRGAFOS 168). These films exhibited very poor sealing behavior after being corona treated (at a level sufficient to provide 44 dynes/cm of surface tension).

Another set of films was prepared with an additive package containing 750 ppm of IRGAFOS 168 and 500 ppm of a diphosphite sold under the trademark DOVERFOS 9228. Results from these films are shown in Table 1 (as "Comparative"). As shown in Table 1, this formulation provided seals at sealing temperatures of 170 – 180°C (though these seals were weak). For clarity – this comparative formulation provided a seal strength of 1.1 Newtons at a sealing temperature of 160°C and 3.0 Newtons (at 180°C).

Inventive films were prepared by adding a further 500 ppm of 1,3,5-tris(4-tert-butyl-3-hydroxy-2,6-dimethyl benzyl)-1,3,5-triazine-2,4,6-(1H,3H,5H)-trione to the additives package of comparative formulation 1. As shown in Table 1 (under the column "Inventive") these films exhibited higher sealing strengths (up to 18.9 Newtons at a sealing temperature of 180°C) across a broader sealing window.

TABLE 1: Seal Strength (Newtons)

	Comparative	Inventive
Sealing Temperature		
140 °C	0.1	2.6
145 °C	0.5	6.8
150 °C	0.8	13.8
160 °C	1.1	15.0
170 °C	2.8	16.4
180 °C	3.0	18.9

The embodiments of the invention in which an exclusive property or privilege is claimed are as follows:

1. A method for preparing a sealed polyethylene package having incorporated therein a stabilizer system sufficient to mitigate the deleterious effect of corona treatment on seal strength, said method comprising:

   1) providing polyethylene film;

   2) subjecting said polyethylene film to corona treatment;

   3) forming a heat seal by subjecting two layers of said polyethylene film to a sealing bar at a temperature of from 120 to 220°C;

wherein said stabilizer system is characterized by comprising i) from 100 to 1000 parts per million by weight of 1,3,5-tris(4-tert-butyl-3-hydroxy-2,6-dimethyl benzyl)-1,3,5-triazine-2,4,6-(1H,3H,5H)-trione, and ii) from 100 to 1000 parts per million by weight of a secondary antioxidant selected from the group consisting of organic phosphites and phosphonites, wherein said corona treatment is sufficient to provide a wetting tension of from 35-50 dyne/cm.

2. The method of claim 1 wherein said polyethylene is a linear low density polyethylene.

3. The method of claim 2 wherein said linear low density polyethylene is a copolymer of ethylene with at least one olefin selected from the group consisting of butene, hexene, and octene.

4. The method of claim 3 wherein said linear low density polyethylene has a density of from 0.88 to 0.95 grams per cubic centimeter and a melt index, I_2, as determined by ASTM D1238 of from 0.3 to 20 grams/10 minutes.