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(54) Title: OXYGEN SCAVENGING COMPOSITIONS

(57) Abstract: The disclosure relates to transition metal compositions, methods of making the compositions, articles prepared from the compositions, and methods of making the articles. This abstract is intended as a scanning tool for purposes of searching in the particular art and is not intended to be limiting of the present invention.



WO 2013/165971 A1

## **OXYGEN SCAVENGING COMPOSITIONS**

### **CROSS REFERENCE TO RELATED APPLICATIONS**

**[0001]** This application claims the benefit of priority to United States Provisional Patent Application number 61/640,168, filed April 30, 2012, the entire disclosure of which is incorporated by reference herein for all purposes.

### **BACKGROUND**

**[0002]** Many polymers used in packaging materials and other articles are permeable to oxygen. When oxygen permeates a polymeric composition or article, it can cause oxidative damage to the contents of the package. It is therefore desirable for certain polymer compositions and articles to have oxygen scavenging capability, such that when oxygen permeates the composition or article, oxidative damage can be mitigated.

**[0003]** It is known in the art to include an oxygen scavenger in the packaging structure for the protection of oxygen sensitive materials. Such scavengers are believed to react with oxygen that is trapped in the package or that permeates from outside of the package, thus extending to life of package contents. These packages include films, bottles, containers, and the like. Food, beverages (such as beer and fruit juices), cosmetics, medicines, and the like are particularly sensitive to oxygen exposure and require high barrier properties to oxygen to preserve the freshness of the package contents and avoid changes in flavor, texture and color.

**[0004]** Furthermore, it is known in the art that it is advantageous in some applications to use transition metal catalysts, such as cobalt II neodecanoate ("CoNDA") or octoate (US Patent 6,083,585; US Patent 7,097,890; Devlieghere F., Vermeiren L., Debevere J. (2004) International Dairy Journal, 14: 273-285), in order to accelerate the scavenging rate. Although such transition metal catalysts are currently used, they suffer from several shortcomings. For example, these materials require drying immediately before process use unless they are predried and immediately sealed for protection against exposure to oxygen. Furthermore, the currently available compositions are of a form such that they are not

feasible to mill for co-compaction with a powdered oxygen scavenger due to the high ratio required and drying requirements.

[0005] Thus, there is a need for oxygen scavenging compositions that can be manufactured in a form that is easier to handle, amenable to milling, and can be combined with a powdered oxygen scavenger composition for use as a single component in the manufacturing process of packaging materials and other articles. These needs and other needs are satisfied by the present invention.

### SUMMARY

[0006] In accordance with the purpose(s) of the invention, as embodied and broadly described herein, the invention, in one aspect, relates to oxygen scavenging polymer compositions, methods of making the compositions, articles prepared from the compositions, and methods of making the articles.

[0007] Disclosed are transition metal master batch compositions comprising: (a) a polymer carrier; and (b) a transition metal composition dispersed in the solid polymer carrier; wherein the transition metal composition is present in an amount greater than about 30,000 ppm (by metal) based on the weight of the transition metal master batch composition.

[0008] Also disclosed are transition metal compact compositions comprising: (a) an oxygen scavenger composition; and (b) a transition metal master batch composition dispersed in the oxygen scavenger composition; wherein the oxygen scavenger composition is present in an amount greater than about 85 weight percent; wherein the transition metal master batch composition comprises: (i) a polymer carrier; and (ii) a transition metal composition dispersed in the solid polymer carrier; wherein the transition metal composition is present in an amount greater than about 30,000 ppm (by metal) based on the weight of the transition metal master batch composition.

[0009] Also disclosed are methods for the manufacture of a transition metal master batch composition comprising the step of extruding a transition metal master batch composition, the composition comprising: (a) a polymer carrier; and (b) a transition metal composition;

wherein the transition metal composition is present in an amount greater than about 30,000 ppm (by metal) based on the weight of the transition metal master batch composition.

**[0010]** Also disclosed are methods for the manufacture of transition metal compacted pellets comprising the steps of (1) extruding a transition metal master batch composition, the composition comprising: (a) a solid polymer carrier; and (b) a transition metal composition; wherein the transition metal composition is present in an amount greater than about 30,000 ppm (by metal) based on the weight of the transition metal master batch composition; (2) processing the extrudate comprising the transition metal master batch composition to particulate form by milling or pulverization, wherein the particle size is less than about 5.0 mm screen size; (3) preparing a homogeneous mixture comprising the particulate transition metal master batch composition and a powdered oxygen scavenger composition, wherein the powdered oxygen scavenger composition is present in an amount greater than about 85 weight percent based on the combined weight of the particulate transition metal master batch composition and the powdered oxygen scavenger composition; and (4) forming compacted single pellets from the homogeneous mixture comprising the particulate transition metal master batch composition and a powdered oxygen scavenger composition, thereby producing transition metal compacted pellets.

**[0011]** Also disclosed are methods for the manufacture of an article comprising comprising the steps of (1) combining polyester pellets with transition metal compacted pellets in a melt processing zone; wherein the transition metal compacted pellets comprise an oxygen scavenger composition present in an amount greater than about 85 weight percent and a transition metal master batch composition present in an amount greater than about 10 weight percent; wherein the let down ratio of the transition metal compacted pellets is greater than about 1%; (2) forming a melt; and (3) extruding the melt, thereby forming the article.

**[0012]** Also disclosed are the products of the disclosed methods.

**[0013]** Additional advantages of the invention will be set forth in part in the description which follows, and in part will be obvious from the description, or can be learned by practice of the invention. The advantages of the invention will be realized and attained by means of the elements and combinations particularly pointed out in the appended claims. It is to be

understood that both the foregoing general description and the following detailed description are exemplary and explanatory only and are not restrictive of the invention, as claimed.

### DETAILED DESCRIPTION

[0014] The present invention can be understood more readily by reference to the following detailed description of the invention and the Examples included therein.

[0015] Before the present compounds, compositions, articles, systems, devices, and/or methods are disclosed and described, it is to be understood that they are not limited to specific synthetic methods unless otherwise specified, or to particular reagents unless otherwise specified, as such may, of course, vary. It is also to be understood that the terminology used herein is for the purpose of describing particular aspects only and is not intended to be limiting. Although any methods and materials similar or equivalent to those described herein can be used in the practice or testing of the present invention, example methods and materials are now described.

[0016] Disclosed are the components to be used to prepare the compositions of the invention as well as the compositions themselves to be used within the methods disclosed herein. These and other materials are disclosed herein, and it is understood that when combinations, subsets, interactions, groups, etc. of these materials are disclosed that while specific reference of each various individual and collective combinations and permutation of these compounds can not be explicitly disclosed, each is specifically contemplated and described herein. For example, if a particular compound is disclosed and discussed and a number of modifications that can be made to a number of molecules including the compounds are discussed, specifically contemplated is each and every combination and permutation of the compound and the modifications that are possible unless specifically indicated to the contrary. Thus, if a class of molecules A, B, and C are disclosed as well as a class of molecules D, E, and F and an example of a combination molecule, A-D is disclosed, then even if each is not individually recited each is individually and collectively contemplated meaning combinations, A-E, A-F, B-D, B-E, B-F, C-D, C-E, and C-F are considered disclosed. Likewise, any subset or combination of these is also disclosed. Thus, for example, the sub-group of A-E, B-F, and C-E would be considered disclosed. This

concept applies to all aspects of this application including steps in methods of making and using the compositions of the invention. Thus, if there are a variety of additional steps that can be performed it is understood that each of these additional steps can be performed with any specific embodiment or combination of embodiments of the methods of the invention.

[0017] While aspects of the present invention can be described and claimed in a particular statutory class, such as the system statutory class, this is for convenience only and one of skill in the art will understand that each aspect of the present invention can be described and claimed in any statutory class. Unless otherwise expressly stated, it is in no way intended that any method or aspect set forth herein be construed as requiring that its steps be performed in a specific order. Accordingly, where a method claim does not specifically state in the claims or descriptions that the steps are to be limited to a specific order, it is no way intended that an order be inferred, in any respect. This holds for any possible non-express basis for interpretation, including matters of logic with respect to arrangement of steps or operational flow, plain meaning derived from grammatical organization or punctuation, or the number or type of aspects described in the specification.

[0018] Throughout this application, various publications are referenced. The disclosures of these publications in their entireties are hereby incorporated by reference into this application in order to more fully describe the state of the art to which this pertains. The references disclosed are also individually and specifically incorporated by reference herein for the material contained in them that is discussed in the sentence in which the reference is relied upon. Nothing herein is to be construed as an admission that the present invention is not entitled to antedate such publication by virtue of prior invention. Further, the dates of publication provided herein may be different from the actual publication dates, which can require independent confirmation.

#### **A. DEFINITIONS**

[0019] As used in the specification and the appended claims, the singular forms “a,” “an” and “the” include plural referents unless the context clearly dictates otherwise. Thus, for example, reference to “a functional group,” “an alkyl,” or “a residue” includes mixtures of two or more such functional groups, alkyls, or residues, and the like. Alternatively, for

example, reference to processing or making a “polymer,” “preform,” “article,” “container,” or “bottle” is intended to include the processing or making of a plurality of polymers, preforms, articles, containers, or bottles.

**[0020]** For example, when a “polymer” is referred to in the specification and the claims, the term should be construed to include not just the reaction product of a single polymerization, but also to blends or physical mixtures of more than one polymer, since the thermoplastic polymers described herein may be satisfactorily blended with one another so that it may be difficult to afterward identify the source. Thus, the phrase a “PET homopolymer or copolymer” (sometimes hereinafter described simply as a “PET polymer”) should be construed, for example, to include both the product of a single polymerization as well as mixtures of more than one PET homopolymer or copolymer. Likewise, the phrase a “polyolefin polymer” or a “polybutadiene homopolymer or copolymer” should be construed, for example, to include both the reaction product of a single polymerization as well as mixtures of more than one polybutadiene homopolymer or copolymer.

**[0021]** References to a composition or a polymer blend containing “an” ingredient or “a” polymer is intended to include other ingredients or other polymers, respectively, in addition to the one named.

**[0022]** By “comprising” or “containing” or “having” it is intended that at least the named compound, element, particle, or method step, etc., is present in the composition or article or method, but does not exclude the presence of other compounds, catalysts, materials, particles, method steps, etc., even if the other such compounds, material, particles, method steps, etc., have the same function as what is named, unless expressly excluded in the claims.

**[0023]** When it is stated, for example, that an oxygen-scavenging polymer is added to, blended with, or reacted with the PET polymer, the oxygen-scavenging polymer may either be added neat or as a concentrate, unless the context indicates otherwise. Furthermore, when the oxygen-scavenging polymer is functionalized and capable of reacting with the PET polymer, the oxygen-scavenging polymer may be added as a copolycondensate.

**[0024]** Ranges can be expressed herein as from “about” one particular value, and/or to “about” another particular value. When such a range is expressed, another aspect includes

from the one particular value and/or to the other particular value. Similarly, when values are expressed as approximations, by use of the antecedent “about,” it will be understood that the particular value forms another aspect. It will be further understood that the endpoints of each of the ranges are significant both in relation to the other endpoint, and independently of the other endpoint. It is also understood that there are a number of values disclosed herein, and that each value is also herein disclosed as “about” that particular value in addition to the value itself. For example, if the value “10” is disclosed, then “about 10” is also disclosed. It is also understood that each unit between two particular units are also disclosed. For example, if 10 and 15 are disclosed, then 11, 12, 13, and 14 are also disclosed.

**[0025]** As used herein, the terms “optional” or “optionally” means that the subsequently described event or circumstance may or may not occur, and that the description includes instances where said event or circumstance occurs and instances where it does not.

**[0026]** As used herein, the term “substantially” means that the subsequently described event or circumstance completely occurs or that the subsequently described event or circumstance generally, typically, or approximately occurs. For example, when the specification discloses that substantially all of an agent is released, a person skilled in the relevant art would readily understand that the agent need not be completely released. Rather, this term conveys to a person skilled in the relevant art that the agent need only be released to an extent that an effective amount is no longer unreleased.

**[0027]** As used herein, the term “polymer” refers to a relatively high molecular weight organic compound, natural or synthetic, whose structure can be represented by a repeated small unit, the monomer (e.g., polyethylene, rubber, cellulose). Synthetic polymers are typically formed by addition or condensation polymerization of monomers. The number of monomers/constitutional units within a given polymer may vary widely, ranging, for example, from 5 to 10 to 25 to 50 to 100 to 1000 to 10,000 or more monomer units.

**[0028]** As used herein, the term “monomers” may refer to the free monomers and those that are incorporated into polymers, with the distinction being clear from the context in which the term is used.



**[0029]** As used herein, the term “homopolymer” refers to a polymer formed from a single type of monomer are called homopolymers

**[0030]** As used herein, the term “copolymer” refers to a polymer formed from two or more different repeating units (monomer residues). The two or more types of monomers within a given copolymer may be present in any of a variety of distributions including random, statistical, gradient and periodic (e.g., alternating) distributions, among others. One particular type of copolymer is a “block copolymer,” which as used herein is a copolymer that contains two or more polymer chains of different composition, which chains may be selected from homopolymer chains and copolymer chains (e.g., random, statistical, gradient or periodic copolymer chains). As used herein, a polymer “chain” is a linear assembly of monomers and may correspond to an entire polymer or to a portion of a polymer. By way of example and without limitation, a copolymer can be an alternating copolymer, a random copolymer, a block copolymer, or a graft copolymer. It is also contemplated that, in certain aspects, various block segments of a block copolymer can themselves comprise copolymers.

**[0031]** As used herein, “polyester polymer” refers to a condensation polymer in which more than 50 percent of the groups connecting repeat units are ester groups. Thus polyesters may include polyesters, poly(ester-amides) and poly(ester-imides), so long as more than half of the connecting groups are ester groups. For example, suitable polyester polymers can have at least 70% of the connecting groups as esters. Alternatively, suitable polyester polymers can have at least 90% of the connecting groups as ester. In a further example, polyester polymers can have essentially all of the connecting groups as esters. The proportion of ester connecting groups can be estimated to a first approximation by the molar ratios of monomers used to make the polyester.

**[0032]** As used herein, the terms “polyethylene terephthalate” and “PET” refer to a polyester polymer in which the diol repeat units are from ethylene glycol and the dicarboxylic acid repeat units are from terephthalic acid. These terms are meant to include PET no matter how prepared. For example, a monomer used in the preparation of PET can be synthesized by the esterification reaction between terephthalic acid and ethylene glycol with water as a byproduct. Alternatively, a monomer used in the preparation of PET can be prepared by the transesterification reaction between ethylene glycol and dimethyl terephthalate with methanol

as a byproduct. Polymerization can be through a polycondensation reaction of the monomers with ethylene glycol as the byproduct.

**[0033]** Furthermore, these terms, PET or polyethylene terephthalate, are meant to include polyethylene terephthalate polymers which are reacted with minor, e.g., less than about 20 percent by weight of the polymer, amounts of modifying agents. Such modifying agents include various diols such as 1,4 butane diol, cyclohexane dimethanol and 1,3 propane diol. Other modifying agents include various diacids such as isophthalic acid, adipic acid, 2,6 naphthalene dicarboxylic acid and p-hydroxy benzoic acid. Minor amounts of chain branching agents and/or chain terminating agents may also be used. Such chain branching agents include, for example, polyfunctional acids and/or polyfunctional alcohols such as trimethylol propane and pentaerythritol. Chain terminating agents include monofunctional alcohols and/or monofunctional carboxylic acids such as stearic acid and benzoic acid. Mixtures of the chain branching and chain terminating agents may also be used. PET which contains such chain branching agents and chain terminating agents is described in U.S. Ser. No. 894,674 filed Apr. 10, 1978 (now U.S. Pat. No. 4,161,579) by Edelman et al and entitled " Extrusion Grade Polyethylene Terephthalate". The disclosure of this patent application is hereby incorporated by reference. Although the terms "polyethylene terephthalate" and "PET" are meant to include polyethylene terephthalate polymers containing minor amounts of modifying agents or chain branching agents, the remainder of this specification, for purposes of illustration, is generally directed to PET which does not contain these modifying agents or chain branching agents.

**[0034]** Furthermore, these terms, PET or polyethylene terephthalate, refer to a thermoplastic polyester resin that can exist both as an amorphous (transparent) and as a semi-crystalline (opaque and white) material. PET can also exist as a semicrystalline transparent material, as used in the side walls of PET bottles. In such aspects, the crystals are smaller than the wavelength of visible light and thus do not make the material opaque and white.

**[0035]** It is understood that these terms, " polyethylene terephthalate" and "PET," include both PET polymers and copolymers. For example, PET can be provided as a copolymer having, in addition to terephthalic acid residues and ethylene glycol residues, additional

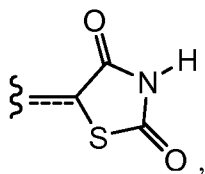
isophthalic acid residues and/or cycloheptanedimethanol residues. It is also understood that PET polymer and/or copolymer can be provided as part of a polymer blend.

[0036] As used throughout the specification, “ppm” is parts per million by weight.

[0037] As used herein, nomenclature for compounds, including organic compounds, can be given using common names, IUPAC, IUBMB, or CAS recommendations for nomenclature. When one or more stereochemical features are present, Cahn-Ingold-Prelog rules for stereochemistry can be employed to designate stereochemical priority, *E/Z* specification, and the like. One of skill in the art can readily ascertain the structure of a compound if given a name, either by systemic reduction of the compound structure using naming conventions, or by commercially available software, such as CHEMDRAW<sup>TM</sup> (Cambridgesoft Corporation, U.S.A.).

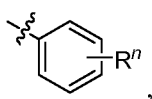
[0038] A residue of a chemical species, as used in the specification and concluding claims, refers to the moiety that is the resulting product of the chemical species in a particular reaction scheme or subsequent formulation or chemical product, regardless of whether the moiety is actually obtained from the chemical species. Thus, an ethylene glycol residue in a polyester refers to one or more -OCH<sub>2</sub>CH<sub>2</sub>O- units in the polyester, regardless of whether ethylene glycol was used to prepare the polyester. Similarly, a sebacic acid residue in a polyester refers to one or more -CO(CH<sub>2</sub>)<sub>8</sub>CO- moieties in the polyester, regardless of whether the residue is obtained by reacting sebacic acid or an ester thereof to obtain the polyester.

[0039] A very close synonym of the term “residue” is the term “radical,” which as used in the specification and concluding claims, refers to a fragment, group, or substructure of a molecule described herein, regardless of how the molecule is prepared. For example, a 2,4-thiazolidinedione radical in a particular compound has the structure

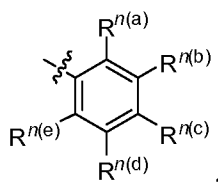


regardless of whether thiazolidinedione is used to prepare the compound. In some embodiments the radical (for example an alkyl) can be further modified (i.e., substituted alkyl) by having bonded thereto one or more “substituent radicals.” The number of atoms in a given radical is not critical to the present invention unless it is indicated to the contrary elsewhere herein.

**[0040]** In some aspects, a structure of a compound can be represented by a formula:



which is understood to be equivalent to a formula:



wherein  $n$  is typically an integer. That is,  $R^n$  is understood to represent five independent substituents,  $R^{n(a)}$ ,  $R^{n(b)}$ ,  $R^{n(c)}$ ,  $R^{n(d)}$ ,  $R^{n(e)}$ . By “independent substituents,” it is meant that each R substituent can be independently defined. For example, if in one instance  $R^{n(a)}$  is halogen, then  $R^{n(b)}$  is not necessarily halogen in that instance.

**[0041]** As used herein, the term “substituted” is contemplated to include all permissible substituents of organic compounds. In a broad aspect, the permissible substituents include acyclic and cyclic, branched and unbranched, carbocyclic and heterocyclic, and aromatic and nonaromatic substituents of organic compounds. Illustrative substituents include, for example, those described below. The permissible substituents can be one or more and the same or different for appropriate organic compounds. For purposes of this disclosure, the heteroatoms, such as nitrogen, can have hydrogen substituents and/or any permissible substituents of organic compounds described herein which satisfy the valences of the heteroatoms. This disclosure is not intended to be limited in any manner by the permissible substituents of organic compounds. Also, the terms “substitution” or “substituted with” include the implicit proviso that such substitution is in accordance with permitted valence of

the substituted atom and the substituent, and that the substitution results in a stable compound, *e.g.*, a compound that does not spontaneously undergo transformation such as by rearrangement, cyclization, elimination, etc.

## B. COMPOSITIONS

[0042] In one aspect, the invention relates to transition metal master batch compositions comprising (a) a polymer carrier; and (b) a transition metal composition dispersed in the solid polymer carrier; wherein the transition metal composition is present in an amount greater than about 30,000 ppm (by metal) based on the weight of the transition metal master batch composition. The transition metal master batch composition advantageously achieves a high load level of a transition metal composition dispersed in a carrier polymer. The transition metal master batch compositions provide a transition metal oxygen scavenging catalyst in an easy to handle solid that can be processed to a form with desired solid handling characteristics. Thus, the transition metal master batch composition can be milled, pelletized, pulverized, or powdered to appropriate size and solid handling characteristics. For example, the transition metal composition can be readily milled to a size suitable for blending, *e.g.* less than about 1.0 mm, with another material, *e.g.* a powdered oxygen scavenger, for use in co-compaction and other applications. Moreover, the transition metal master batch compositions of the invention make feasible co-compaction of a transition metal composition with a powdered oxygen scavenger.

[0043] In one aspect, the invention also relates to compositions comprising a transition metal compact composition comprising: (a) an oxygen scavenger composition; and (b) a transition metal master batch composition dispersed in the oxygen scavenger composition; wherein the oxygen scavenger composition is present in an amount greater than about 85 weigh percent; wherein the transition metal master batch composition comprises: (i) a polymer carrier; and (ii) a transition metal composition dispersed in the solid polymer carrier; wherein the transition metal composition is present in an amount greater than about 30,000 ppm (by metal) based on the weight of the transition metal master batch composition. The transition metal compact composition can be readily compacted into pellets or granules, which advantageously can be used as a single component oxygen scavenger/catalyst system for use in packaging applications.

## 1. POLYMER CARRIER

[0044] A variety of different polymers can be used as the carrier polymer. The disclosed compositions enable oxygen scavenging, and thus the carrier polymer generally includes those polymers that can be subject to oxidation. For example, polymers that exhibit at least some oxygen permeability are useful with the disclosed compositions, at least inasmuch as the disclosed compositions can reduce the oxidative damage to the polymer. In one aspect, the polymer carrier comprises a polyester polymer. In a further aspect, the polyester polymer is a polyalkyl terephthalate, or a copolymer thereof. In a yet further aspect, the polyester polymer is polyethylene terephthalate, or a copolymer thereof. In an even further aspect, the polyester polymer is a polymer comprising repeating aromatic units selected from terephthalic acid residues, isophthalic acid residues, and naphthalenic acid residues. In a still further aspect, the polyester polymer is selected from polyethylene terephthalate, poly(dimethyl cyclohexane terephthalate), polytrimethylene terephthalate, polynaphthalate, or a copolymer thereof.

[0045] The carrier polymer can be a polymer commonly used in packaging materials including polyethylene, such as low density polyethylene, very low density polyethylene, ultra-low density polyethylene, high density polyethylene, and linear low density polyethylene; polyesters such as (PET), (PEN) and their copolymers such as PET/IP; polyvinyl chloride (PVC); polyvinylidene chloride (PVDC); and ethylene copolymers such as ethylene/vinyl acetate copolymer, ethylene/alkyl (meth)acrylate copolymers, ethylene/(meth)acrylic acid copolymers, and ionomers. Blends of different base polymers also can be used.

[0046] In a further aspect, the carrier polymer can include one or more polymers approved by the U.S. Food and Drug Administration (FDA). Examples include polyethylene terephthalate, polypropylene, and polyethylene.

[0047] In a further aspect, the carrier polymer comprises a polyester polymer or copolymer. Preferred polyesters include polymers of phthalic acids, such as polyethylene terephthalate (PET), or a copolymer thereof. PET, for example, can be made from terephthalic acid and ethylene glycol. PET can also be made using dimethyl terephthalate and ethylene glycol.

Preferred copolymers of phthalic acids include copolymers of a phthalic acid and one or more hydroxylated organic compounds. Examples of suitable hydroxylated organic compounds include 1, 4-cyclohexanedimethanol, 1,2-propanediol, 1, 4-butanediol, 2,2- dimethyl-1, 3 -propanediol, 2-methyl -1, 3 -propanediol (2MPDO), 1,6-hexanediol, 1,2- cyclohexanediol, 1,4-cyclohexanediol, 1, 2-cyclohexanedimethanol, 1,3- cyclohexanedimethanol, and diols containing one or more oxygen atoms in the chain, e.g., diethylene glycol, triethylene glycol, dipropylene glycol, tripropylene glycol, or mixtures of these, and the like.

**[0048]** In a still further aspect, the carrier polymer includes a polyethylene terephthalate homopolymer and copolymer modified with one or more polycarboxylic acid modifiers in a cumulative amount of less than about 15 mole %, or about 10 mole % or less, or about 8 mole % or less, or one or more hydroxyl compound modifiers in an amount of less than about 60 mol %, or less than about 50 mole %, or less than about 40 mole %, or less than about 15 mole %, or about 10 mole % or less, or about 8 mole % or less and polyethylene naphthalate homopolymers and copolymers modified with a cumulative amount of less than about 15 mole %, or about 10 mole % or less, or about 8 mole % or less, of one or more polycarboxylic acid modifiers or modified with less than about 60 mol %, or less than about 50 mole %, or less than about 40 mole %, or less than about 15 mole %, or about 10 mole % or less, or about 8 mole % or less of one or more hydroxyl compound modifiers, and blends thereof. In some aspects, the base polymer comprises at least 90 mole %, 92 mole %, or 94 mole % ethylene terephthalate repeat units based on the moles of all repeat units in the polyester polymers.

**[0049]** Polyesters such as PET can be prepared by polymerization procedures known in the art sufficient to effect esterification and polycondensation. Polyester melt phase manufacturing processes include direct condensation of a dicarboxylic acid with a diol, optionally in the presence of one or more esterification catalysts, in the esterification zone, followed by polycondensation in the prepolymer and finishing zones in the presence of a polycondensation catalyst; or ester exchange usually in the presence of a transesterification catalyst in the ester exchange zone, followed by prepolymerization and polymerization in the presence of a polycondensation catalyst.

**[0050]** In one aspect, the polymer carrier of the invention relates to a polyester polymer. Thus, the polyester polymer is any thermoplastic polyester polymer, e.g. partially aromatic polyester polymers or polyester polymers mainly derived from an aromatic diacid and an aliphatic diol. In a further aspect, the polyester polymer is polyethylene terephthalate. In a still further aspect, the polyethylene terephthalate polymer has ethylene terephthalate units in an amount of at least 60 mole %, in an amount of at least 85 mole %, in an amount at least 90 mole %, and in an amount at least 92 mole %, as measured by the mole % of ingredients added to the reaction mixture. Thus, a polyethylene terephthalate polymer may comprise a copolyester of ethylene terephthalate units and other units derived from an alkylene glycol or aryl glycol with a aliphatic or aryl dicarboxylic acid.

**[0051]** Polyethylene terephthalate polymers can be manufactured by reacting a diacid or diester component comprising at least 60 mole % terephthalic acid or C<sub>1</sub>-C<sub>4</sub> dialkylterephthalate, preferably at least 70 mole %, more preferably at least 85 mole %, even more preferably, at least 90 mole %, and for many applications will be at least 95 mole %, and a diol component comprising at least 60 mole % ethylene glycol, preferably at least 70 mole %, more preferably at least 85 mole %, even more preferably at least 90 mole %, and for many applications, will be at least 95 mole %. It is also preferable that the diacid component is terephthalic acid and the diol component is ethylene glycol. The mole percentage for all of the diacid component totals 100 mole %, and the mole percentage for all of the diol component totals 100 mole %.

**[0052]** In a further aspect, the polyester pellet composition may be formed by admixing polyester polymers with other thermoplastic polymers, such as polycarbonate (PC) and polyamides. The polyester pellet composition can comprise a majority of a polyester polymer, e.g. a polyester polymer present in an amount of at least 80 wt. %, present in an amount at least 95 wt. %, and an in an amount at least 98 wt. %, based on the weight of polymers (excluding fillers, fibers, impact modifiers, or other polymers which may form a discontinuous phase). The polyester polymer can comprise at least 60 wt. % of a polyethylene terephthalate, at least 90 wt. % of a polyethylene terephthalate, and 100 wt. % of a polyethylene terephthalate. A polyethylene terephthalate polymer can contain at least 60 mole % of ethylene terephthalate units. In this embodiment, the polyethylene terephthalate can be made from at least 90 mole % terephthalic acid and at least 90 mole % of ethylene glycol.



**[0053]** Typically, polyesters such as polyethylene terephthalate polymer are made by reacting a glycol with a dicarboxylic acid as the free acid or its dimethyl ester to produce a prepolymer compound which is then polycondensed to produce the polyester. If required, the molecular weight of the polyester can then be increased further by solid state polymerization. In one aspect, after melt phase and/or solid state polycondensation the polyesters have an intrinsic viscosity (It.V.) of at least 0.60 dL/g, and at least 0.70 dL/g measured at 25° C in a 60/40 ratio by weight of phenol/tetrachloroethane.

**[0054]** In addition to units derived from terephthalic acid, the acid component of the polyester polymer can be modified with units derived from one or more additional dicarboxylic acids. Such additional dicarboxylic acids include aromatic dicarboxylic acids preferably having 8 to 14 carbon atoms, aliphatic dicarboxylic acids preferably having 4 to 12 carbon atoms, or cycloaliphatic dicarboxylic acids preferably having 8 to 12 carbon atoms. Examples of dicarboxylic acid units useful for modifying the acid component are units from phthalic acid, isophthalic acid, naphthalene-2,6-dicarboxylic acid, cyclohexanedicarboxylic acid, cyclohexanediacetic acid, diphenyl-4,4'-dicarboxylic acid, succinic acid, glutaric acid, adipic acid, azelaic acid, sebacic acid, and the like, with isophthalic acid, naphthalene-2,6-dicarboxylic acid, and cyclohexanedicarboxylic acid being most preferable. It should be understood that use of the corresponding acid anhydrides, esters, and acid chlorides of these acids is included in the term "dicarboxylic acid".

**[0055]** In addition to units derived from ethylene glycol, the diol component of the present polyester can be modified with units from additional diols including cycloaliphatic diols preferably having 6 to 20 carbon atoms and aliphatic diols preferably having 3 to 20 carbon atoms. Examples of such diols include diethylene glycol, triethylene glycol, 1,4-cyclohexanedimethanol, propane-1,3-diol, butane-1,4-diol, pentane-1,5-diol, hexane-1,6-diol, 3-methylpentanediol-(2,4), 2-methylpentanediol-(1,4), 2,2,4-trimethylpentane-diol-(1,3), 2,5-ethylhexanediol-(1,3), 2,2-diethyl propane-diol-(1,3), hexanediol-(1,3), 1,4-di-(hydroxyethoxy)-benzene, 2,2-bis-(4-hydroxycyclohexyl)-propane, 2,4-dihydroxy-1,1,3,3-tetramethyl-cyclobutane, 2,2-bis-(3-hydroxyethoxyphenyl)-propane, and 2,2-bis-(4-hydroxypropoxyphenyl)-propane.

**[0056]** Polyesters can be prepared by conventional polymerization procedures well-known in the art sufficient to effect esterification and polycondensation. Polyester polycondensation processes include direct condensation of dicarboxylic acid with the diol, ester interchange, and solid state polymerization methods. Typical polyesterification catalysts which can be used include titanium alkoxides, dibutyl tin dilaurate, and antimony oxide or antimony triacetate, used separately or in combination, optionally with zinc, manganese, or magnesium acetates or benzoates and/or other such catalyst materials as are well known to those skilled in the art. Phosphorus and cobalt compounds may also optionally be present.

**[0057]** For example, a mixture of one or more dicarboxylic acids, preferably aromatic dicarboxylic acids, or ester forming derivatives thereof, and one or more diols may be heated in the presence of esterification and/or transesterification catalysts in an esterification zone, optionally with a polycondensation catalyst, at temperatures in the range of about 150° C. to about 300° C., or alternatively, about 200° C. to about 300° C., and in conventional reactions, typically between about 260° C. to about 300° C., and pressures ranging from atmospheric to about 0.2 mmHg. Normally, the dicarboxylic acid is esterified with the diol(s) at elevated pressure and at a temperature of about 240° C. to about 270° C. Polycondensation reactions are initiated and continued in the melt phase in a prepolymerization zone and finished in the melt phase in a finishing zone, after which polycondensation reactions are continued in the solid state in a solid stating zone. In the prepolymerization zone, molecular weight build up is effected by increasing the temperature from about 260° C. up to about 280° C. and lowering the pressure while excess diol is removed from the mixture. Polycondensation can be continued in a finishing zone in a series of finishing vessels ramped up to higher temperatures until an ItV of about 0.70 dL/g or less is achieved. The catalyst material such as antimony oxide or triacetate may be added to the prepolymerization zone along with phosphorus, cobalt compounds, and colorants, which may optionally be added to the finishing zone. In a typical DMT based process, those skilled in the art recognize that other catalyst material and points of adding the catalyst material and other ingredients vary from a typical direct esterification process.

**[0058]** Other components can be added to the polyester polymer composition to enhance the performance properties. For example, crystallization aids, impact modifiers, surface lubricants, denesting agents, stabilizers, antioxidants, ultraviolet light absorbing agents, metal

deactivators, colorants, nucleating agents, acetaldehyde reducing compounds, other reheat rate enhancing aids such as elemental antimony or reduced antimony, carbon black, graphite, black iron oxide, red iron oxide and the like, sticky bottle additives such as talc, and fillers and the like can be included. The resin may also contain small amounts of branching agents such as trifunctional or tetrafunctional comonomers such as trimellitic anhydride, trimethylol propane, pyromellitic dianhydride, pentaerythritol, and other polyester forming polyacids or polyols generally known in the art. All of these additives and many others and their use are well known in the art and do not require extensive discussion.

## 2. TRANSITION METAL COMPOSITION

[0059] The compositions of the present invention relate to a transition metal composition, wherein the transition metal is in a positive oxidation state. The transition metal composition in the presence of a suitable oxygen scavenger composition is believed to catalyze the oxygen scavenging properties of the oxygen scavenger composition. Thus, in one aspect, the transition metal composition enhances the oxygen scavenging properties of the oxygen scavenger composition.

[0060] In one aspect, the transition metal can be a transition metal from the first, second, or third transition series of the Periodic Table. The metal can be Rh, Ru, Pd, Os, Ir, Pt, or one of the elements in the series of Sc to Zn (*e.g.*, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, and Zn). In one aspect, the transition metal is cobalt. Cobalt can be used in +2 or +3 oxidation states. In some aspects, it is preferred to use cobalt in the +2 oxidation state. In a further aspect, the transition metal is rhodium. For example, rhodium in the +2, +3, or +4 oxidation state can be used. In a still further aspect, the transition metal is manganese. For example, manganese in the +2 or +3 oxidation state can be used. In a yet further aspect, the transition metal is iron. For example, iron in the +2 or +3 oxidation state can be used. In an even further aspect, the transition metal is nickel. For example, nickel in the +2 or +3 oxidation state can be used. In a yet further aspect, the transition metal is copper. For example, copper in the +1 or +2 oxidation state can be used. The transition metal can also be a positive oxidation form of zinc. Alternatively, the transition metal can be ruthenium. The transition metal composition may also be an ionomer, in which case a polymeric counter-ion is employed.

**[0061]** The transition metal can be present as a salt. The cation of the salt can be the transition metal in a positive oxidation state. A variety of anions can stabilize the positively charged transition metal. Suitable anions for the salts include, but are not limited to, halides, such as chloride; carboxylates, such as neodecanoate, octanoate, acetate, butyrate, lactate, naphthalate, malate, stearate, acetate, acetylacetonate, linoleate, oleate, palmitate, 2-ethylhexanoate, tallate, resinate, 3,5,5-trimethylhexoate, valerate, cyclohexanebutyrate, acetylacetonate, benzoylacetonate, dodecylacetylacetonate, benzoate, oxalate, citrate, tartrate or ethylene glycolate; or as their oxides, borates, carbonates, dioxides, hydroxides, nitrates, phosphates, sulfates, silicates, , dialkyldithiocarbamate, disalicylalethylenediamine chelate, or phythalocyanine, among others.

**[0062]** In one aspect, the transition metal is selected from cobalt 2-ethylhexanoate, cobalt oleate, cobalt neodecanoate, cobalt 2-ethylhexanoate, cobalt acetate, cobalt stearate, and cobalt benzoate. In a further aspect, the transition is cobalt neodecanoate.

**[0063]** In a further aspect, the transition metal composition is in the form of a concentrated solid, semi-solid, gel or paste. In a still further aspect, the transition metal composition is in the form of a pastille.

**[0064]** In a further aspect, the transition metal is present in the pastille in a weight percent amount of about 15% to about 30% (by metal). In a yet further aspect, the transition metal is present in the pastille in an weight percent amount of about 17% to about 25% (by metal). In a still further aspect, the transition metal is present in the pastille in an weight percent amount of about 19% to about 22% (by metal).

**[0065]** In a further aspect, the transition metal comprises cobalt, copper, rhodium, platinum, rhenium, ruthenium, palladium, tungsten, osmium, cadmium, silver, tantalum, hafnium, vanadium, titanium, chromium, nickel, zinc, or manganese. In a still further aspect, the transition metal comprises cobalt.

**[0066]** In a further aspect, the transition metal in the transition metal composition comprises cobalt. In a yet further aspect, the source of cobalt in the transition metal composition comprises a cobalt carboxylate or cobalt neodecanoate, or mixtures thereof. In a

still further aspect, the source of cobalt in the transition metal composition comprises cobalt neodecanoate.

[0067] In a further aspect, at least a portion of the cobalt in the transition metal composition is present in the +2 or +3 oxidation state. In a still further aspect, at least a portion of the cobalt in the transition metal composition is present in the +2 oxidation state.

[0068] In a further aspect, the transition metal in the transition metal composition comprises zinc. In a still further aspect, the source of cobalt in the transition metal composition comprises a zinc carboxylate or zinc neodecanoate, or mixtures thereof. In a yet further aspect, the source of zinc in the transition metal composition comprises zinc neodecanoate.

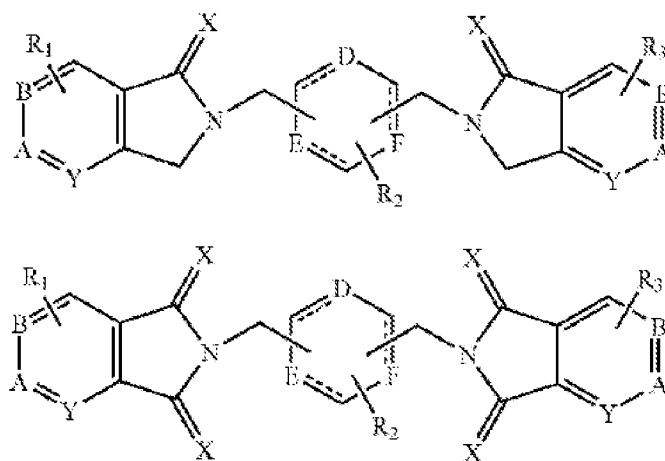
### 3. OXYGEN SCAVENGER COMPOSITION

[0069] The compositions of the present invention relate to oxygen scavenger compositions. The oxygen scavenger compositions comprise various materials which are selected by one skilled in the art based on their material handling characteristics, end-use, and specifications of the finished articles. The materials may be single or multi-component which can be further mixed, compounded, or blended with additional materials as required. Oxygen scavenger compositions can comprise organic molecules, including monomers or polymers, and/or transition metal compositions. When included in the manufacture of packaging materials, such oxygen scavenger compositions are believed to react with oxygen that is trapped in the package or that permeates from outside of the package, thus extending to life of package contents. These packages include films, bottles, containers, and the like. Food, beverages (such as beer and fruit juices), cosmetics, medicines, and the like are particularly sensitive to oxygen exposure and require high barrier properties to oxygen to preserve the freshness of the package contents and avoid changes in flavor, texture and color.

[0070] Use of certain polyamides in combination with a transition metal is known to be useful as the oxygen scavenging material. One particularly useful polyamide is MXD6 which contains meta-xylene residues in the polymer chain. See, for example, U.S. Pat. Nos. 5,639,815; 5,049,624; and 5,021,515. Other oxygen scavenger compositions include

potassium sulfite (U.S. Pat. No. 4,536,409), unsaturated hydrocarbons (U.S. Pat. No. 5,211,875), and ascorbic acid derivatives (U.S. Pat. No. 5,075,362).

**[0071]** In one aspect, the oxygen scavenger compositions useful in the present comprise:  
(a) a base polymer; (b) at least one compound of Formula I or II:

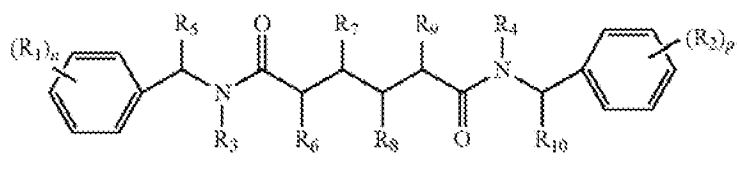


wherein X is selected from the group consisting of O, S and NH; Y, A and B are independently selected from the group consisting of N and CH; D, E and F are independently selected from the group consisting of CH, N, O and S; the symbol--when used in conjunction with a bond line represents a single or a double bond; and R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> are independently selected from the group consisting of H, electron withdrawing groups and electron releasing groups and a transition metal; and (c) at least one transition metal in a positive oxidation state, said metal being present in the composition in an amount of 10 to 400 ppm; wherein said compound is present in an amount of about 0.10 to 10 weight percent of said composition, which are described in the patent US 7,994,245 and is incorporated herein by reference.

**[0072]** In a further aspect, the oxygen scavenger composition of the transition metal compact composition comprises the material DC-100. In a still further aspect, the oxygen scavenger composition of the transition metal compact composition comprises the material DC-300. The material DC-100 and DC-300 are manufactured by and are commercially available from Constar International. Preparation of these materials and other material useful as oxygen scavenger compositions of the present invention are described in the patents US

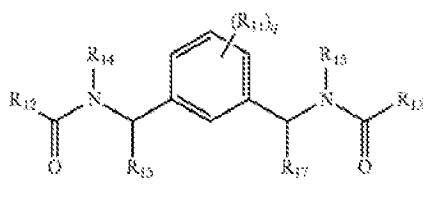
7,691,290 and US 7,994,245; and in the patent applications US 12/945,351 (Publ. No. US 2011/0172335) and US 12/945,355 (Publ. No. US 2011/0117301), which are herein incorporated by reference.

**[0073]** In various aspects, the oxygen scavenger compositions comprises a compound represented by the formula:



wherein  $n$  and  $p$  are independently 0 or an integer from 1 to 5; each  $R_1$  and  $R_2$  is independently selected from H,  $C_1$ - $C_{12}$  alkyl,  $C_1$ - $C_6$  alkoxy,  $C_6$ - $C_{20}$  aryloxy, hydroxy,  $C_2$ - $C_6$  alkenyl,  $NR_{19}R_{20}$ , acetyl, nitro, glyceryl, carbohydrate,  $-C(=O)H$ , L, or two  $R_1$  or two  $R_2$  groups can form a group of the formula  $-O-R_{18}-O$ ;  $R_3$  and  $R_4$  are each H;  $R_5$  to  $R_{10}$  are independently selected from H or  $C_1$ - $C_3$  alkyl; and  $R_{18}$  is  $C_2$ - $C_6$  alkyl. In a further aspect,  $n$  and  $p$  are each 0, 1, or 2. In a still further aspect,  $R_1$  and  $R_2$  are independently selected from H,  $C_1$ - $C_4$  alkyl, hydroxy,  $C_1$ - $C_3$  alkoxy, or carbohydrate. In a yet further aspect,  $R_1$  and  $R_2$  are independently selected from H, methyl, ethyl, hydroxy, methoxy, ethoxy, or glucose. In an even further aspect, each of  $R_5$  to  $R_{10}$  are H. In a still further aspect,  $R_1$  and  $R_2$  are each H.

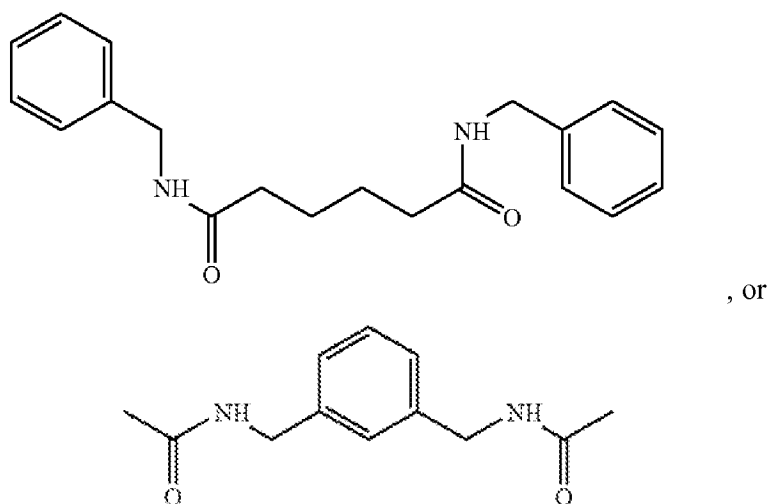
**[0074]** In various aspects, the oxygen scavenger compositions comprises a compound represented by the formula:



wherein  $q$  is 0 or an integer from 1 to 4; L is a linking group of the formula  $-(O-R_{21})_z-$ ,  $O-$ ,  $-(NH-R_{21})_z-NH-$ ,  $-(NH-C(=O)R_{22})_t-NH-$ ,  $-NH-R_{25}-$ ,  $NH(C(=O)R_{26}NHR_{25}NH)_u-$ ,  $-(O-R_{23}-O-R_{24}-C(=O))_s-O-$  where L is attached to a

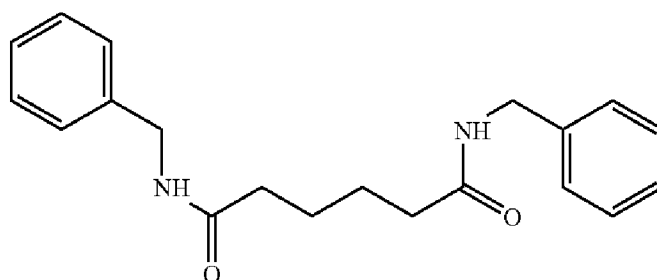
carbon atom of Ar (for example, replaces a H atom of the Ar) in structure (I) or where  $R_{12}$  or  $R_{13}$  of structure (II) is L;  $R_{11}$  is selected from H,  $C_1$ - $C_{12}$  alkyl,  $C_1$ - $C_6$  alkoxy,  $C_6$ - $C_{20}$  aryloxy, hydroxy,  $C_2$ - $C_6$  alkenyl,  $NR_{19}R_{20}$ , acetyl, nitro, glyceryl, carbohydrate,  $-C(=O)H$ , L, or two  $R_1$  or two  $R_2$  groups can form a group of the formula  $-O-R_{18}-O$ ;  $R_{12}$  and  $R_{13}$  are each, independently, H,  $C_1$ - $C_6$  alkyl,  $C_6$ - $C_{20}$  aryl,  $C_1$ - $C_6$  alkoxy, or L;  $R_{14}$ , and  $R_{15}$  are each H;  $R_{16}$ , and  $R_{17}$  are independently selected from H or  $C_1$ - $C_3$  alkyl; and  $R_{18}$  is  $C_2$ - $C_6$  alkyl. In a further aspect,  $R_{16}$  and  $R_{17}$  are each H. In a still further aspect, each  $R_{11}$  is independently selected from H,  $C_1$ - $C_4$  alkyl, hydroxy, or  $C_1$ - $C_3$  alkoxy, or carbohydrate. In a yet further aspect, each  $R_{11}$  is independently selected from H, methyl, ethyl, hydroxy, methoxy, or ethoxy.

**[0075]** In a further aspect, the oxygen scavenger composition comprises a compound represented by a formula:

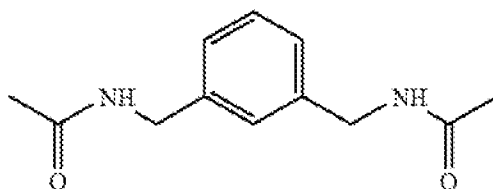


**[0076]** In a further aspect, the oxygen scavenger composition comprises a compound represented by a formula:

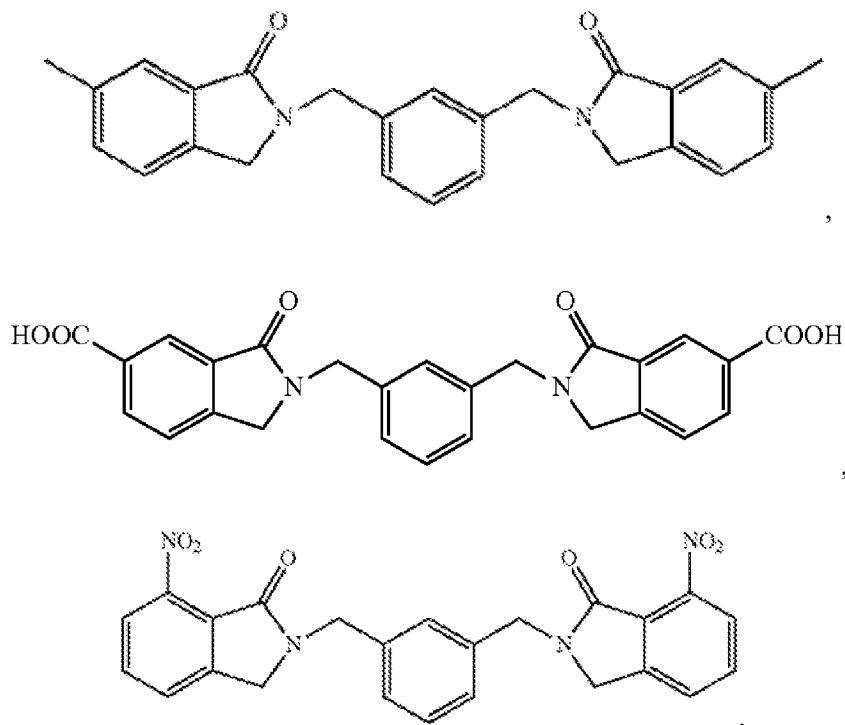


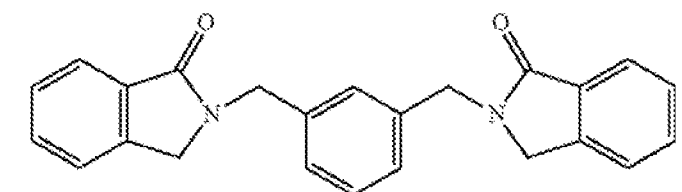


[0077] In a further aspect, the oxygen scavenger composition comprises a compound represented by a formula:

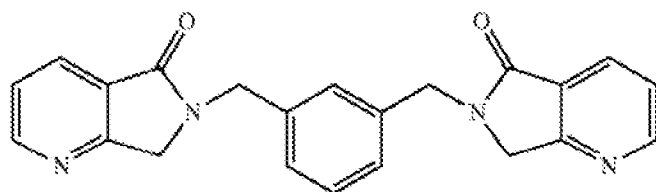


[0078] In a further aspect, the oxygen scavenger composition comprises a compound represented by a formula:

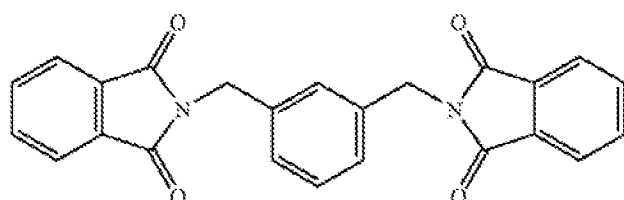




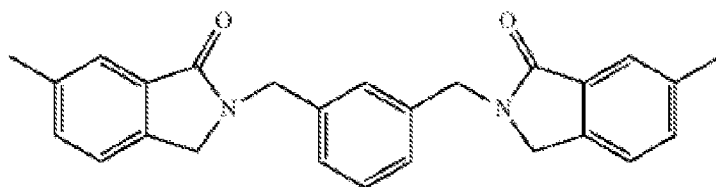
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, or

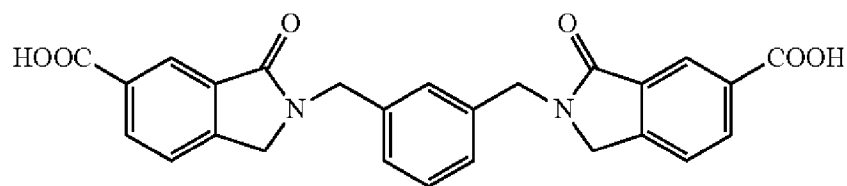


[0079] In a further aspect, the oxygen scavenger composition comprises a compound represented by a formula:



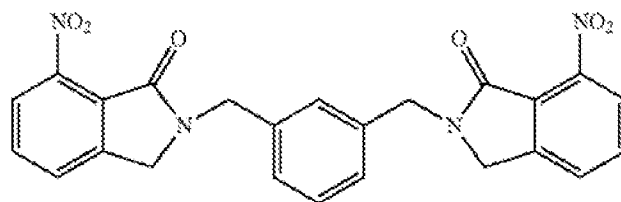
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[0080] In a further aspect, the oxygen scavenger composition comprises a compound represented by a formula:

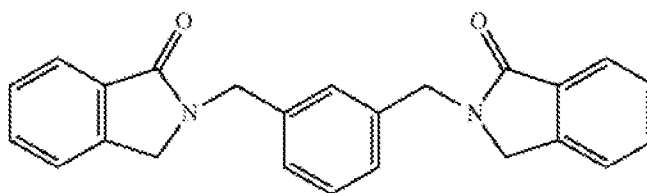


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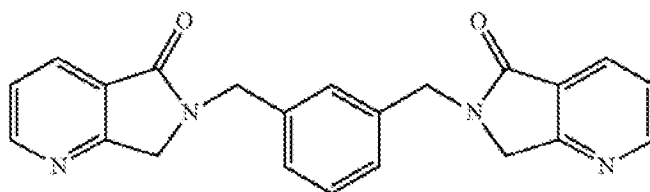
[0081] In a further aspect, the oxygen scavenger composition comprises a compound represented by a formula:



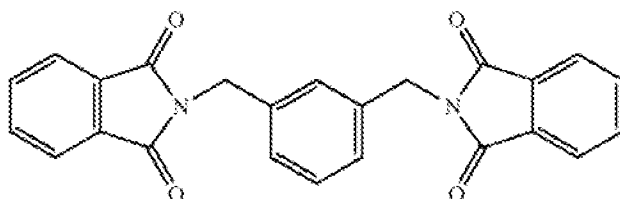
[0082] In a further aspect, the oxygen scavenger composition comprises a compound represented by a formula:



[0083] In a further aspect, the oxygen scavenger composition comprises a compound represented by a formula:



[0084] In a further aspect, the oxygen scavenger composition comprises a compound represented by a formula:



#### 4. TRANSITION METAL MASTER BATCH COMPOSITION

[0085] In one aspect, the invention relates to a transition metal master batch composition comprising: (a) a polymer carrier; and (b) a transition metal composition dispersed in the solid polymer carrier; wherein the transition metal composition is present in an amount

greater than about 30,000 ppm (by metal) based on the weight of the transition metal master batch composition.

[0086] In a further aspect, the polymer carrier of the transition master batch composition comprises a polyester polymer. In a still further aspect, the polyester polymer is a polyalkyl terephthalate, or a copolymer thereof. In a yet further aspect, the polyester polymer is polyethylene terephthalate, or a copolymer thereof. In an even further aspect, the polyester polymer is a polymer comprising repeating aromatic units selected from terephthalic acid residues, isophthalic acid residues, and naphthalenic acid residues. In a still further aspect, the polyester polymer is selected from polyethylene terephthalate, poly(dimethyl cyclohexane terephthalate), polytrimethylene terephthalate, polynaphthalate, or a copolymer thereof.

[0087] In a further aspect, the amount of the polymer carrier present in the transition metal master batch composition is at least about 75 weight percent. In a still further aspect, the amount of the polymer carrier present in the transition metal master batch composition is from about 70 weight percent to about 90 weight percent. In a yet further aspect, the amount of the polymer carrier present in the transition metal master batch composition is from about 75 weight percent to about 85 weight percent. In an even further aspect, the amount of the polymer carrier present in the solid concentrate composition is from about 77 weight percent to about 82 weight percent.

[0088] In a further aspect, the polymer carrier present in the transition metal master batch composition is a polyester polymer and is present in an amount that is at least about 75 weight percent. In a still further aspect, the polymer carrier present in the transition metal master batch composition is a polyester polymer and is present in an amount that is from about 70 weight percent to about 90 weight percent. In a further aspect, the polymer carrier present in the transition metal master batch composition is a polyester polymer and is present in an amount that is from about 75 weight percent to about 85 weight percent. In a further aspect, the polymer carrier present in the transition metal master batch composition is a polyester polymer and is present in an amount that is from about 77 weight percent to about 82 weight percent.

[0089] In a further aspect, the polymer carrier present in the transition metal master batch composition is PET and is present in an amount that is at least about 75 weight percent. In a still further aspect, the polymer carrier present in the transition metal master batch composition is PET and is present in an amount that is from about 70 weight percent to about 90 weight percent. In a further aspect, the polymer carrier present in the transition metal master batch composition is PET and is present in an amount that is from about 75 weight percent to about 85 weight percent. In a further aspect, the polymer carrier present in the transition metal master batch composition is PET and is present in an amount that is from about 77 weight percent to about 82 weight percent.

[0090] In a further aspect, the transition metal composition is present in the transition metal master composition in an amount greater than about 35,000 ppm (by metal) based on the weight of the transition metal master batch composition. In a still further aspect, the transition metal composition is present in the transition metal master composition in an amount greater than about 40,000 ppm (by metal) based on the weight of the transition metal master batch composition. In a yet further aspect, the transition metal composition is present in the transition metal master composition in an amount from about 30,000 ppm to about 60,000 ppm (by metal) based on the weight of the transition metal master batch composition. In an even further aspect, the transition metal composition is present in the transition metal master composition in an amount from about 35,000 ppm to about 55,000 ppm (by metal) based on the weight of the transition metal master batch composition. In a still further aspect, the transition metal composition is present in the transition metal master composition in an amount from about 37,500 ppm to about 52,500 ppm (by metal) based on the weight of the transition metal master batch composition. In a yet further aspect, the transition metal composition is present in the transition metal master composition in an amount from about 37,500 ppm to about 47,500 ppm (by metal) based on the weight of the transition metal master batch composition. In an even further aspect, the transition metal composition is present in the transition metal master composition in an amount from about 38,950 ppm to about 47,500 ppm (by metal) based on the weight of the transition metal master batch composition. In a still further aspect, the transition metal composition is present in the transition metal master composition in an amount from about 40,000 ppm to about 60,000 ppm (by metal) based on the weight of the transition metal master batch composition. In a yet further aspect, the

transition metal composition is present in the transition metal master composition in an amount from about 40,000 ppm to about 50,000 pm (by metal) based on the weight of the transition metal master batch composition. In an even further aspect, the transition metal composition is present in the transition metal master composition in an amount from about 30,000 ppm to about 47,500 pm (by metal) based on the weight of the transition metal master batch composition.

[0091] In a further aspect, the transition metal composition is in the form of a concentrated solid, semi-solid, gel or paste. In a still further aspect, the transition metal composition is in the form of a pastille. In a yet further aspect, the let down ratio of the pastille into the solid polymer carrier is about 10% to about 30%. In an even further aspect, the let down ratio of the pastille into the solid polymer carrier is about 15% to about 25%. In a still further aspect, the let down ratio of the pastille into the solid polymer carrier is about 17% to about 22%. In a yet further aspect, the let down ratio of the pastille into the solid polymer carrier is about 19% to about 22%.

## 5. TRANSITION METAL COMPACT COMPOSITION

[0092] In one aspect, the invention relates to a transition metal compact composition comprising: (a) an oxygen scavenger composition; and (b) a transition metal master batch composition dispersed in the oxygen scavenger composition; wherein the oxygen scavenger composition is present in an amount greater than about 85 weigh percent; wherein the transition metal master batch composition comprises: (i) a polymer carrier; and (ii) a transition metal composition dispersed in the solid polymer carrier; wherein the transition metal composition is present in an amount greater than about 30,000 ppm (by metal) based on the weight of the transition metal master batch composition.

[0093] In a further aspect, the oxygen scavenger composition of the transition metal compact composition is present in a weight percent amount of about 70% to about 90% based on the weight of the transition metal compact composition. In a still further aspect, the oxygen scavenger composition of the transition metal compact composition is present in a weight percent amount of about 80% to about 90% based on the weight of the transition metal compact composition. In a yet further aspect, the oxygen scavenger composition of the

transition metal compact composition is present in a weight percent amount of from about 85% to about 89% based on the weight of the transition metal compact composition. In an even further aspect, the oxygen scavenger composition of the transition metal compact composition is present in a weight percent amount of from about 70% to about 90% based on the weight of the transition metal compact composition. In a yet further aspect, the oxygen scavenger composition of the transition metal compact composition is present in a weight percent amount of from about 80% to about 90% based on the weight of the transition metal compact composition. In a still further aspect, the oxygen scavenger composition of the transition metal compact composition is present in a weight percent amount of from about 85% to about 89% based on the weight of the transition metal compact composition.

[0094] In a further aspect, the transition metal master batch composition of the transition metal compact composition is present in a weight percent amount of from about 10% to about 20% based on the weight of the transition metal compact composition. In a still further aspect, the transition metal master batch composition of the transition metal compact composition is present in a weight percent amount of from about 10% to about 15% based on the weight of the transition metal compact composition. In a yet further aspect, the transition metal master batch composition of the transition metal compact composition is present in a weight percent amount of from about 10% to about 13% based on the weight of the transition metal compact composition.

[0095] In a further aspect, the transition metal of the transition metal compact composition is present in an amount greater than about 4,000 ppm (by metal) based on the weight of the transition metal compact composition. In a still further aspect, the transition metal of the transition metal compact composition is present in an amount greater than about 5,000 ppm (by metal) based on the weight of the transition metal compact composition. In a yet further aspect, the transition metal of the transition metal compact composition is present in an amount of from about 4,000 ppm to about 6,000 ppm (by metal) based on the weight of the transition metal compact composition. In an even further aspect, the transition metal of the transition metal compact composition is present in an amount of about from 5,000 ppm to about 6,000 ppm (by metal) based on the weight of the transition metal compact composition. In a still further aspect, the transition metal of the transition metal compact composition is

present in an amount of about from 5,000 ppm to about 5,500 ppm (by metal) based on the weight of the transition metal compact composition.

### **C. METHODS OF MAKING**

[0096] In one aspect, the invention relates to methods of making transition metal master batch compositions. In a further aspect, the invention relates to methods of making transition metal compacted pellets. In a yet further aspect, the invention relates to making an article.

[0097] The compositions of this invention can be prepared by employing the methods as described in the following, in addition to other standard manipulations that are known in the literature, exemplified in the experimental sections or clear to one skilled in the art.

[0098] Reactions, processes, procedures, and methodologies used to generate the compositions of this invention are prepared by employing reactions as described in this invention (hereinabove and hereinbelow), in addition to other standard manipulations known in the literature or to one skilled in the art. The following examples are provided so that the invention might be more fully understood, are illustrative only, and should not be construed as limiting.

#### **1. METHOD OF MAKING A TRANSITION METAL MASTER BATCH COMPOSITION**

[0099] In one aspect, the invention relates to methods of making a transition metal master batch composition comprising the step of extruding a transition metal master batch composition, the composition comprising: (a) a polymer carrier; and (b) a transition metal composition; wherein the transition metal composition is present in an amount greater than about 30,000 ppm (by metal) based on the weight of the transition metal master batch composition.

[00100] In a further aspect, the method further comprises the step of milling the transition metal master batch composition following the step of extrusion. In a yet further aspect, the transition metal master batch composition is milled to a size less than about 5.0 mm screen size. In a still further aspect, the transition metal master batch composition is milled to a size less than about 4.0 mm screen size. In an even further aspect, the transition metal master batch composition is milled to a size less than about 3.0 mm screen size. In a still further



aspect, the transition metal master batch composition is milled to a size less than about 2.0 mm screen size. In a yet further aspect, the transition metal master batch composition is milled to a size less than about 1.0 mm screen size. In an even further aspect, the method further comprises the step of drying the transition metal master batch composition following the step of milling. The milled transition metal master batch composition can be dried in an atmosphere of dried air or other inert gas, such as nitrogen, and if desired, under sub-atmospheric pressure.

**[00101]** In a further aspect, the method further comprises the step of pulverizing the transition metal master batch composition following the step of extrusion. In a yet further aspect, the transition metal master batch composition is pulverized to a size less than about 5.0 mm screen size. In a still further aspect, the transition metal master batch composition is pulverized to a size less than about 4.0 mm screen size. In an even further aspect, the transition metal master batch composition is pulverized to a size less than about 3.0 mm screen size. In a still further aspect, the transition metal master batch composition is pulverized to a size less than about 2.0 mm screen size. In a yet further aspect, the transition metal master batch composition is pulverized to a size less than about 1.0 mm screen size. In an even further aspect, the method further comprises the step of drying the transition metal master batch composition following the step of pulverizing. The pulverized transition metal master batch composition can be dried in an atmosphere of dried air or other inert gas, such as nitrogen, and if desired, under sub-atmospheric pressure.

**[00102]** In a further aspect, the method further comprises the step of drying the the transition metal master batch composition following the step of extrusion. The transition metal master batch composition can be dried in an atmosphere of dried air or other inert gas, such as nitrogen, and if desired, under sub-atmospheric pressure.

**[00103]** The transition metal master batch compositions of the present invention may be prepared by a variety of extrusion or melt compounding methods known in the art. Any suitable equipment designed to melt the carrier polymer pellets, to combine the components of the concentrate, and mix them may be used. Alternatively, the functions may be performed in more than one piece of equipment. This may be in continuous or batch processes. Example of equipment that may be used include, but are not limited to, two-roll mills, two rotor mixers

with open mixing chambers, internal mixers with a single rotor, internal mixers with multiple counterrotating rotors, internal mixers with multiple corotating rotors, internal mixers with multiple mixing chambers, single screw extruders, planetary screw extruders, corotating twin screw extruders, counterrotating twin screw extruders conical extruders, and the like. These mixing devices are well known in the art and described in many references, such as W. Michaeli, "Plastics Processing: An Introduction", Carl Hanser Verlag, Munich, 1995; "Polymer Mixing: Technology and Engineering", J. L. White, A. Y. Coran and A. Moet, Eds., Carl Hanser Verlag, Munich, 2001; and "Plastics Compounding: Equipment and Processing", D. B. Todd, Ed., Carl Hanser Verlag, Munich, 1998.

**[00104]** Alternatively, the components may also be mixed using static mixers in which the mixing elements are stationary and the mixing is accomplished by multiple reorientations of a melt stream containing the molten carrier polymer and the transition metal composition as it flows through the static elements, or molten polymer may be mixed with the cobalt salt in stirred vessels.

**[00105]** In a further aspect, manufacture of a transition metal master batch composition is accomplished by either dry feeding a separate stream or streams of carrier polymer pellet base resin(s) and a separate stream of transition metal composition or by dry blending the polyester with the cobalt additive which may then be fed together to the melt processing zone of a twin-screw compounder for melt mixing at an appropriate temperature (i.e. that melts the carrier polymer) and dispersing of the transition metal composition into the carrier polymer matrix. The carrier polymer/transition metal composition melt mixture is then quenched in water and cut into cylindrical pellets for further use in downstream application. The solidified pellets or concentrate can be used either in its amorphous form or it can be crystallized by agitating and heating at an appropriate temperature for an extended time, e.g. greater than about 300° F for a polyester carrier polymer such as PET.

**[00106]** In a further aspect, any conventional process used to add concentrates to a bulk stream of polymer in a melt processing zone for making the article is suitable. For example, pellets of carrier polymer, e.g. a polyester polymer such as PET, and a transition metal composition, e.g. cobalt neodecanoate in pastilles comprising about 20.5% cobalt, can be blended, either prior to or after drying, and fed to an injection molding machine or extruder,

followed by melt blending and forming into an article such as a preform. Alternatively, the pellets may be fed to the melt processing zone as individual streams, or in a combination of streams with one or more of the streams being a combination of two or more types of pellets.

## 2. METHOD OF MAKING TRANSITION METAL COMPACTED PELLETS

[00107] In one aspect, the invention relates to methods of making transition metal compacted pellets comprising the steps of: (1) extruding a transition metal master batch composition, the composition comprising: (a) a solid polymer carrier; and (b) a transition metal composition; wherein the transition metal composition is present in an amount greater than about 30,000 ppm (by metal) based on the weight of the transition metal master batch composition; (2) processing the extrudate comprising the transition metal master batch composition to particulate form by milling or pulverization, wherein the particle size is less than about 5.0 mm screen size; (3) preparing a homogeneous mixture comprising the particulate transition metal master batch composition and a powdered oxygen scavenger composition, wherein the powdered oxygen scavenger composition is present in an amount greater than about 85 weight percent based on the combined weight of the particulate transition metal master batch composition and the powdered oxygen scavenger composition; and (4) forming compacted single pellets from the homogeneous mixture comprising the particulate transition metal master batch composition and a powdered oxygen scavenger composition, thereby producing transition metal compacted pellets.

[00108] Manufacture of the compacted pellets of the invention can be by methods known to one skilled in the art involving various compactors and sifters to obtain compacted pellets of a desired size distribution. For example, compaction can be accomplished using a roller compactor such as a Bepex or Fitzpatrick Chilsonator roller compactor. A 7 x 10 chilsonator roller compactor is commonly found in industrial use, but a chilsonator of this particular configuration is not required. A non-limiting example of manufacture of the compacted can comprise the following steps: a) the homogeneous mixture as described in the foregoing paragraph can be fed in a chilsonator roller compactor, which initially generates a somewhat continuous stick; b) the somewhat continuous stick generated by the chilsonator roller compactor is fed into a mill with about a 3/8 inch screen, thereby producing smaller granules; c) the granules from the preceding step can then pass through a separator, e.g. a

screen sifter such as a 48 inch Sweco or similar screen sifter with a ring cleaner option; and d) then the material can then be discharged through a rare earth station into drums. The screen sifter can be equipped with a #4 and/or #12 mesh sizes. The exact nature of the screen meshes in each deck of the sifter can be adjusted to optimize production efficiency and quality standards required of the compacted pellets. In various further aspects, attrition testing can be carried out on random drums to monitor the effectiveness of the compaction process. Alternatively, attrition testing can occur on every nth drum, e.g. every fifth drum.

[00109] In various aspects, the compacted pellets of the present invention can have the attrition test specifications following the last step of compaction and sifting as shown in Table 1.

Table 1.

<b>Attrition Test</b>	<b>Mesh/Sieve Size</b>	<b>SPEC</b>
	<b>Drum #</b>	n/a
	% >4 mesh	5 max
	% <4 >12 mesh	up to 100
	% <12 >30 mesh	40 max
	% <30 (fines) bottom pan	Target <2: 5 max

Attrition testing can be carried as deemed appropriate, and are known to one skilled in the art. For example, the attrition test results of Table 1 can be obtained as follows: a) a 50 g sample is placed onto the top 4-mesh screen of a 4/12/30/Pan stack and shaken 3 minutes using the Rotap; b) after Rotap, material on each screen is weighed and converted to a percentage of the entire sample; c) material in the pan (the initial <30mesh fines) is discarded; d) sample on the remaining screens is combined back together, and 25g of this combined sample is placed onto the 30-mesh screen along with five pennys; e) the screen stack is placed in the Rotap, and shaken for 3 minutes; and f) <30 mesh material in the pan after the attrition test is weighed and converted to a percentage.

### 3. METHOD OF MAKING AN ARTICLE

[00110] In one aspect, the invention relates to methods of making an article comprising the steps of (1) combining polyester pellets with transition metal compacted pellets in a melt

processing zone; wherein the transition metal compacted pellets comprise an oxygen scavenger composition present in an amount greater than about 85 weight percent and a transition metal master batch composition present in an amount greater than about 10 weight percent; wherein the let down ratio of the transition metal compacted pellets is greater than about 1%; (2) forming a melt; and (3) extruding the melt, thereby forming the article.

**[00111]** In a further aspect, extrusion is injection molding. In a still further aspect, extrusion is sheet or film extrusions. In a yet further aspect, the article is a preform. In an even further aspect, the article is a bottle.

**[00112]** In a further aspect, the method further comprises addition of one or more additives selected from colorants, acetaldehyde scavengers, reheat agents, UV absorbers or inhibitors, stabilizers, thermal stabilizers, and nonionic colorant harmonizers. In a still further aspect, the additive is a visually effective amount of colorant in the melt processing zone. In a yet further aspect, the additive is a nonionic colorant harmonizer in an amount of from about 0.010 to about 10 weight percent in the melt processing zone. In a yet further aspect, the nonionic colorant harmonizer is an aliphatic ester having 6 to 24 carbons.

**[00113]** In a further aspect, the method further comprises a first stream comprising the transition metal to a melt processing zone for making the article, a second stream comprising polyester polymer particles, and optionally a third stream comprising other additives such as colorant, acetaldehyde scavengers, reheat agents, UV absorbers or inhibitors, stabilizers, thermal stabilizers; and wherein first, second and optional third streams are fed to a melt processing zone for making the article.

**[00114]** In a further aspect, the polyester pellets comprise polyethylene terephthalate or a copolymer thereof.

**[00115]** In a further aspect, the polyester pellets and the transition metal compacted pellets are combined in the melt processing zone as individual streams or as pellet/pellet dry blends, or as combinations thereof. In a still further aspect, the let down ratio of the transition metal compacted pellets is from about 1.3% to about 3.5%. In a yet further aspect, the let down ratio of the transition metal compacted pellets is from about 1.5% to about 3.0%. In an even further aspect, the let down ratio of the transition metal compacted pellets is from about 2.5%

to about 3.0%. In a still further aspect, the let down ratio of the transition metal compacted pellets is from about 1.3% to about 1.8%. In a yet further aspect, the let down ratio of the transition metal compacted pellets is from about 1.3% to about 1.6%.

[00116] In a further aspect, articles such as bottle performs are prepared from polyester polymer particles (e.g. PET) and the transition metal compacted pellet by feeding them into the melt processing zone as individual streams or as combined streams of particle/particle dry blends. Thus, there is provided a process for the manufacture of a preform comprising combining solid polyester particles comprising polyester polymers and solid transition metal compacted pellet obtained by the methods described in the invention, into an melt processing zone, forming a melt, and forming an article directly from the melt.

[00117] In a yet further aspect, a blend comprising solid polyester particles comprising polyester polymers and a solid transition metal compacted pellets can be simultaneously dried in a drying zone, under conditions effective to at least partially remove moisture from the blend. The moisture level of the blend of solid polyester particles and transition metal compacted pellets can be reduced down to less than 0.015 wt. %, or less than 0.010 wt. %, or less than 0.005 wt. %. In an apparatus containing a drying zone, radiant or convective heat, or electromagnetic or microwave radiation, or any other source for removal of moisture, is emitted from a drying zone or is passed through at least a portion of the mechanical drying zone and contacts the particle blend to remove at least a portion of surface and/or internal water moisture.

[00118] The articles obtained by the concentrates of the invention may be extruded products such as sheets and fibers, or injection molded articles such as bottle preforms and other shapes. In a preferred embodiment, the articles produced from the melt processing zone are the preforms, sheets, and trays for packaging food, pharmaceuticals, medical supplies, and beverages.

#### **D. ARTICLES**

[00119] Various articles can be prepared from the disclosed compositions. Thus, the articles prepared from the compositions will also have the composition present in the article. Suitable articles include vessels and films, such as flexible sheet films, flexible bags, pouches, semi-

rigid and rigid containers such as bottles (e.g. PET bottles) or metal cans, or combinations thereof. Typical flexible films and bags include those used to package various food items and can be made up of one or a multiplicity of layers to form the overall film or bag-like packaging material. The composition of the present invention can be used in one, some or all of the layers of such packaging material.

**[00120]** Specific articles include preforms, containers and films for packaging of food, beverages, cosmetics, pharmaceuticals, and personal care products where a high oxygen barrier is needed. Examples of beverage containers are bottles for holding water and carbonated soft drinks, and the invention is particularly useful in bottle applications containing juices, sport drinks, beer or any other beverage where oxygen detrimentally affects the flavor, fragrance, performance (*e.g.*, vitamin degradation), or color of the drink. The compositions are also particularly useful as a sheet for thermoforming into rigid packages and films for flexible structures. Rigid packages include food trays and lids. Examples of food tray applications include dual ovenable food trays, or cold storage food trays, both in the base container and in the lidding (whether a thermoformed lid or a film), where the freshness of the food contents can decay with the ingress of oxygen. The compositions can also be used in the manufacture of cosmetic containers and containers for pharmaceuticals or medical devices.

**[00121]** Other suitable articles include rigid or semi-rigid articles including plastic, such as those utilized for juices, soft drinks, as well as thermoformed trays or cup normally having thickness in the range of from 100 to 1000 micrometers. The walls of such articles can comprise single or multiple layers of materials. The article can also take the form of a bottle or can, or a crown, cap, crown or cap liner, plastisol or gasket. The composition of the present invention can be used as an integral layer or portion of, or as an external or internal coating or liner of, the formed semi-rigid or rigid packaging article. As a liner, the composition can be extruded as a film along with the rigid article itself, *e.g.*, by coextrusion, extrusion coating, or an extrusion lamination process, so as to form the liner *in situ* during article production; or alternatively can be adhered by heat and/or pressure, by adhesive, or by any other suitable method.

[00122] When the compositions are used in a wall or as a layer of a wall, the permeability of the composition for oxygen is advantageously not more than about 3.0, or about 1.7, or about 0.7, or about 0.2, or about 0.03 cm<sup>3</sup>-mm/(m<sup>2</sup>-atm-day). In some aspects, the permeability of the composition is not more than about three-quarters of that in the absence of the amide compound. In some aspects, the permeability is not more than about one half, one-tenth in certain embodiments, one twenty-fifth in other embodiments, and not more than one-hundredth of that in the absence of the amide compound.

[00123] Besides articles applicable for packaging food and beverage, articles for packaging other oxygen-sensitive products can also benefit from the present invention. Such products would include pharmaceuticals, oxygen sensitive medical products, corrodible metals or products, electronic devices and the like.

[00124] Oxygen permeability of an article can be maintained for a longer period of time by storing the article in a sealed container or under an inert atmosphere such as nitrogen prior to use with oxygen sensitive materials.

[00125] The articles can be made by various methods known in the art. Generally, the articles are prepared by melt processing methods (*i.e.*, a melt of the composition). Such processes generally include injection molding, stretch blow molding, extrusion, thermoforming, extrusion blow molding, and (specifically for multilayer structures) co-extrusion and lamination using adhesive tie layers. Orientation, *e.g.*, by stretch blow molding, of the polymer can be used with phthalate polyesters because of the known mechanical advantages that result.

[00126] The melt processing zone for making the article can be operated under customary conditions effective for making the intended articles, such as preforms, bottles, trays, and other articles mentioned above. In one aspect, such conditions are effective to process the melt without substantially increasing the intrinsic viscosity of the melt and which are ineffective at promoting transesterification reactions. In some preferred aspects, suitable operating conditions effective to establish a physical blend of the base polymer, oxidizable organic component, and transition metal are temperatures in the melt processing zone within a range of about 250 °C to about 300 °C at a total cycle time of less than about 6 minutes, and



typically without the application of vacuum and under a positive pressure ranging from about 0 psig (pound-force per square inch gauge) to about 900 psig. In some embodiments, the residence time of the melt on the screw can range from about 1 to about 4 minutes.

## **E. EXPERIMENTAL**

[00127] The following examples are put forth so as to provide those of ordinary skill in the art with a complete disclosure and description of how the compounds, compositions, articles, devices and/or methods claimed herein are made and evaluated, and are intended to be purely exemplary and are not intended to limit the disclosure. Efforts have been made to ensure accuracy with respect to numbers (*e.g.*, amounts, temperature, etc.), but some errors and deviations should be accounted for. Unless indicated otherwise, parts are parts by weight, temperature is in °C or is at ambient temperature, and pressure is at or near atmospheric.

### **1. EXAMPLE 1: PREPARATION OF TRANSITION METAL MASTER BATCH COMPOSITION**

[00128] Batches of the transition metal master batch were prepared by melt blending as described herein. Briefly, PET (DAK C61A PET; 1600 lb) was dried in 400 lb batches and packed into 55 lb foil bags for ease of handling. The extruder used in this study was a 50 mm twin screw extruder that had a 5 heat zones, 11 barrel sections. The configuration of was such that barrel section #1 was closet to the gear box and barrel section #11 was closest to the die. The configuration used in the study is further described as follows: PET was loaded into barrel section #1; cobalt pastilles (Shepherd Chemical Company, Norwood, Ohio; cobalt neodecanoate, 20.5% Co by weight; referred to hereinafter as CoNDA) were loaded with a side stuffer into barrel section #4 (where turbo-mixing element sections of the screw were co-located); atmospheric vent at barrel section #6; and vacuum was pulled at barrel section #10 with a vacuum of 30" Hg. The system ended with a 14-hole (4 mm) die.

[00129] Pre-dried PET was hand-loaded into feed hoppers above the extruder, with PET extruded at 338 lbs/hour. The CoNDA pastilles were dropped into the funnel hopper of a high capacity, twin auger side stuffer (the maximum rate was about 40% of extruder capacity). The CoNDA pastilles were fed into the side stuffer using a high capacity Brabender vibratory feeder at a rate of 15% (weight percent of the CoNDA pastille) from the

upper mezzanine (maximum rate about 6000 lbs/hour). The resulting extrusion was fed onto a pre-wetted surface, and then quenched by hand periodically with water from a stainless steel beaker.

[00130] Once it was visually apparent that the extrudate was constant, cake samples were taken by collection of the extruded material into a large metal pan containing minimal water to expedite cooling. The rate of feeding of the CoNDA pastilles into the extrusion mixture was sequentially increased from 15% to 17%, 19%, and 21%, with cake samples collected as described herein. The metal pans were floated in a water bath during this time and periodically sprayed with water to facilitate cooling of the samples. It was noted that surprisingly the viscosity notably decreased when the CoNDA component of the mixture reached 21%. The aspects of viscosity noted were an obvious change in the viscosity of the die drool, notably thinner extruded streams, and the flow pattern of extrudate when collected on a solid surface. The extrusion rate was 428 lbs/hour when the change in viscosity was noted.

[00131] At the level of 21% CoNDA in the extrudate, strands were collected into a large water bath, pulled through an air knife to blow off excess water, coiled and packed into a foil-lined fiber drum. Cake samples were also collected, and it was noted that at this level of CoNDA, the brittleness was in excess of what was anticipated. It was observed that cake samples in excess of 2" thick were easily broken into smaller pieces with minimal pressure.

## **2. EXAMPLE 2: ANALYSIS OF CO LEVELS IN TRANSITION METAL MASTER BATCH COMPOSITION**

[00132] Samples of the transition metal master batch composition comprising 21% CoNDA pastille and 79% PET were analyzed by Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) at Gas Technology Institute (Des Plaines, Illinois). The samples were microwave digested in a sulfuric acid/nitric acid solution. For ICP-OES analysis of the samples at least two spectral lines were used and yttrium was used as an internal standard. Analysis was carried out on triplicate samples and the results averaged. Results were obtained as shown in Table 2.

**Table 2.**

<b>Sample Number</b>	<b>Sample Description</b>	<b>Cobalt, wt%</b>	<b>Notes</b>
101709-001	TR-8501-A	3.89	Dried and then sealed against air exposure; exposure to air limited
101709-002	TR-8501-B	3.82	Exposed to air

[00133] The analysis of the foregoing was carried out on freshly prepared samples.

### 3. EXAMPLE 3: EXEMPLARY TRANSITION METAL MASTER BATCH COMPOSITIONS

[00134] The methods described in Example 1, or similar methods known to one skilled in the art, can be used to prepare the transition metal master batch compositions as described in Table 3 below. It is anticipated that transition metal master batch compositions prepared in this manner can be further processed (e.g. milling, pelletization, or pulverization) to pellets, granules, particulates or powders using methods known to one skilled in the art.

[00135] The transition metal master batch compositions that have been processed to a powder or fine particulate form can be used in the preparation of transition metal compact compositions according to the ratios of transition metal master batch compositions and powdered oxygen scavenger described in Table 3, wherein the oxygen scavenger exemplified is Constar International DC-300. It is understood that other oxygen scavengers in fine particulate or powder form can be substituted as required by the specific application or end-use. Briefly, the powdered transition metal master batch compositions are combined with a powdered oxygen scavenger, e.g. Constar International DC-300, physically blended to obtain a homogenous mixture, and then compacted into pellets comprising transition metal compact compositions and an oxygen scavenger to provide transition metal compacted pellets.

**[00136]** The transition metal compacted pellets can then be used in the production of preforms, e.g. a preform can be manufactured by blending the transition metal compacted pellets with a suitable preform polymer, e.g. PET, and then formed into a suitable preform by blow extrusion.

**[00137]** For the data shown in Table 3, the column headings have the following meaning:

Co Pastille (LDR, %): CoNDA (see Example 1 above) let down ratio (“LDR”) given as percent of the master batch (“MB”) comprising the Co pastille and polymer carrier, e.g. a PET polymer.

Co. Conc. (% in MB): provides the final Co concentration in the MB comprising the Co pastille and polymer carrier; the data in the table are based upon a Co pastille comprising 20.5 wt% Co.

DC300 (wt%): provides the amount of the oxygen scavenger, DC300, present in the transition metal compacted pellets comprising the Co MB and oxygen scavenger.

Co MB (wt%): provides the amount of the Co MB present in the transition metal compacted pellets comprising the Co MB and oxygen scavenger.

Compact (LDR, %): provides the LDR for the compacted pellet material into a preform, e.g. a PET preform.

Scavenger (% in PF): provides the percent of the oxygen scavenger, DC300, in the preform after addition of the transition metal compacted pellets.

Catalyst In PF (ppm): provides the ppm of Co in the preform after addition of the transition metal compacted pellets.

Water in Co MB PET (%): represents the percent water present in the Co MB.

Water added to PF by Co MB (wt%/wt%): represents the percent water present in the in the preform after addition of the compacted pellet material.

Table 3.

No.	Co Pastille (LDR, %)	Co. Conc. (% in MB)	DC300 (wt%)	Co MB (wt%)	Compact (LDR, %)
1	15	3.0750	85	15	1.7
2	16	3.2800	85	15	1.6
3	17	3.4850	86	14	1.6
4	18	3.6900	86	14	1.6
5	19	3.8950	87	13	1.6
6	20	4.1000	87	13	1.6
7	21	4.3050	88	12	1.6
8	22	4.5100	88	12	1.6
9	23	4.7150	88	12	1.5
10	24	4.9200	89	11	1.5
11	25	5.1250	89	11	1.5
12	19	3.8950	87	13	1.6
13	20	4.1000	87	13	1.6
14	19	3.8950	87	13	1.5
15	20	4.1000	87	13	1.5
16	19	3.8950	87	13	1.4
17	20	4.1000	87	13	1.4
18	19	3.8950	87	13	1.3
19	20	4.1000	87	13	1.3
20	19	3.8950	87	13	2.70
21	20	4.1000	87	13	2.70
22	19	3.8950	87	13	2.80
23	20	4.1000	87	13	2.80
24	19	3.8950	87	13	2.90
25	20	4.1000	87	13	2.90
26	19	3.8950	87	13	3.00
27	20	4.1000	87	13	3.00

Table 3 (continued).

No.	Scavenger (% in PF)	Catalyst In PF (ppm)	Water in Co MB PET (%)	Water added to PF by Co MB (wt%/wt%)
1	1.445	78.4125	0.30%	0.000765%
2	1.360	78.7200	0.30%	0.000720%
3	1.376	78.0640	0.30%	0.000672%
4	1.376	82.6560	0.30%	0.000672%
5	1.392	81.0160	0.30%	0.000624%
6	1.392	85.2800	0.30%	0.000624%
7	1.408	82.6560	0.30%	0.000576%
8	1.408	86.5920	0.30%	0.000576%

No.	Scavenger (% in PF)	Catalyst In PF (ppm)	Water in Co MB PET (%)	Water added to PF by Co MB (wt%/wt%)
9	1.320	84.8700	0.30%	0.000540%
10	1.335	81.1800	0.30%	0.000495%
11	1.335	84.5625	0.30%	0.000495%
12	1.392	81.0160	0.30%	0.000624%
13	1.392	85.2800	0.30%	0.000624%
14	1.305	75.9525	0.30%	0.000585%
15	1.305	79.9500	0.30%	0.000585%
16	1.218	70.8890	0.30%	0.000546%
17	1.218	74.6200	0.30%	0.000546%
18	1.131	65.8255	0.30%	0.000507%
19	1.131	69.2900	0.30%	0.000507%
20	2.349	136.7145	0.30%	0.001053%
21	2.349	143.9100	0.30%	0.001053%
22	2.436	141.7780	0.30%	0.001092%
23	2.436	149.2400	0.30%	0.001092%
24	2.523	146.8415	0.30%	0.001131%
25	2.523	154.5700	0.30%	0.001131%
26	2.610	151.9050	0.30%	0.001170%
27	2.610	159.9000	0.30%	0.001170%

[00138] The transition metal compacted pellets can be used in various end-use applications such as manufacture of bottle performs. For example, as shown in Table 3, the transition metal compacted pellets of varied cobalt and oxygen scavenger levels can be utilized to obtain the desired or preferred cobalt levels in the bottle perform.

[00139] It will be apparent to those skilled in the art that various modifications and variations can be made in the present invention without departing from the scope or spirit of the invention. Other embodiments of the invention will be apparent to those skilled in the art from consideration of the specification and practice of the invention disclosed herein. It is intended that the specification and examples be considered as exemplary only, with a true scope and spirit of the invention being indicated by the following claims.

## CLAIMS

### What is claimed is:

1. A transition metal master batch composition comprising:
  - (a) a polymer carrier; and
  - (b) a transition metal composition dispersed in the solid polymer carrier;wherein the transition metal in the transition metal composition is present in an amount greater than about 30,000 ppm (by metal) based on the weight of the transition metal master batch composition.
2. The composition of claim 1, wherein the polymer carrier comprises a polyester polymer.
3. The composition of claim 2, wherein the polyester polymer is a polyalkyl terephthalate, or a copolymer thereof.
4. The composition of claim 2, wherein the polyester polymer is polyethylene terephthalate, or a copolymer thereof.
5. The composition of claim 2, wherein the polyester polymer is selected from polyethylene terephthalate, poly(dimethyl cyclohexane terephthalate), polytrimethylene terephthalate, polynaphthalate, or a copolymer thereof.
6. The composition of claim 1, wherein the amount of the polymer carrier present in the transition metal master batch composition is from about 75 weight percent to about 85 weight percent.
7. The composition of claim 1, wherein the transition metal comprises cobalt.
8. The composition of claim 7, wherein the source of cobalt comprises a cobalt carboxylate or cobalt neodecanoate, or mixtures thereof.

9. The composition of claim 1, wherein the transition metal composition is present in an amount greater than about 40,000 ppm (by metal) based on the weight of the transition metal master batch composition.

10. A transition metal compact composition comprising:

(a) an oxygen scavenger composition; and

(b) a transition metal master batch composition dispersed in the oxygen scavenger composition;

wherein the oxygen scavenger composition is present in an amount greater than about 85 weigh percent;

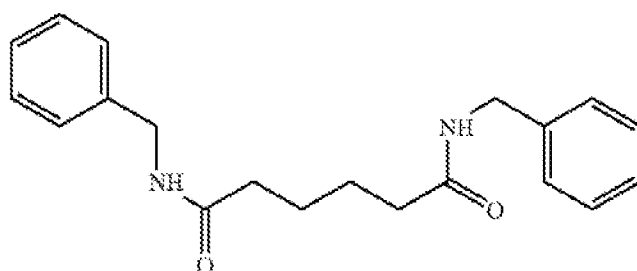
wherein the transition metal master batch composition comprises:

(i) a polymer carrier; and

(ii) a transition metal composition dispersed in the solid polymer carrier;

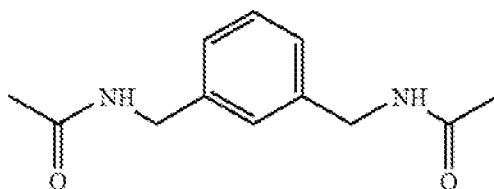
wherein the transition metal composition is present in an amount greater than about 30,000 ppm (by metal) based on the weight of the transition metal master batch composition.

11. The composition of claim 10, wherein the oxygen scavenger composition comprises a compound represented by a formula:

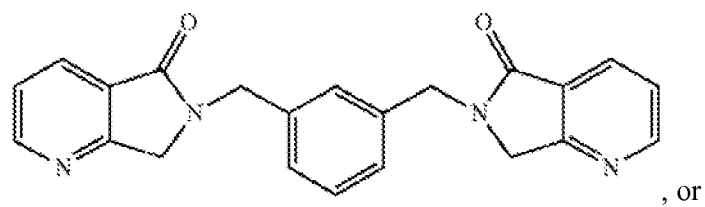
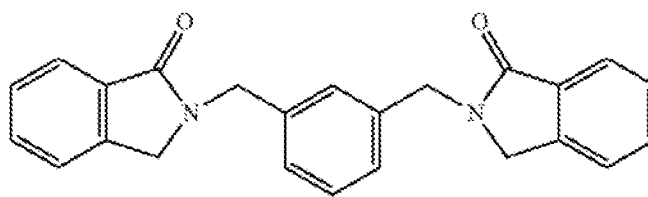
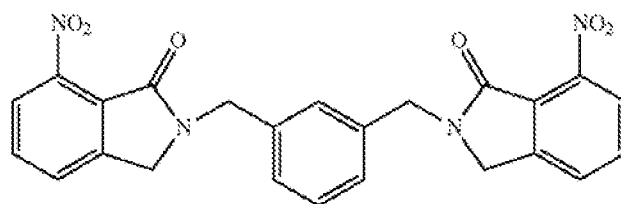
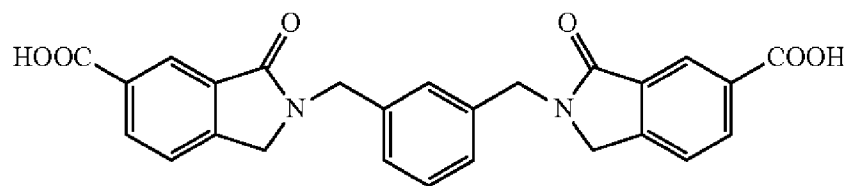
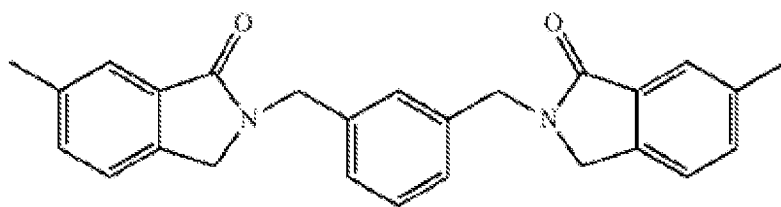


, or

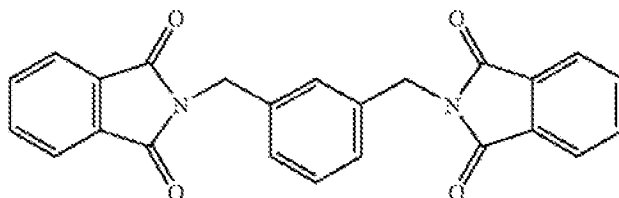




12. The composition of claim 10, wherein the oxygen scavenger composition comprises a compound represented by a formula:



, or



13. A method of making a transition metal master batch composition comprising the step of extruding a transition metal master batch composition, the composition comprising:
- (a) a polymer carrier; and
  - (b) a transition metal composition;
- wherein the transition metal composition is present in an amount greater than about 30,000 ppm (by metal) based on the weight of the transition metal master batch composition.
14. The method of claim 13, further comprising the step of milling the transition metal master batch composition following the step of extrusion.
15. The method of claim 14, wherein the transition metal master batch composition is milled to a size less than about 1.0 mm screen size.
16. The method of claim 13, wherein the polymer carrier comprises a polyester polymer.
17. The method of claim 16, wherein the polyester polymer is polyethylene terephthalate, or a copolymer thereof.
18. The method of claim 13, wherein the transition metal composition is present in an amount greater than about 40,000 ppm (by metal) based on the weight of the transition metal master batch composition.
19. A method of making transition metal compacted pellets comprising the steps of:
- (1) extruding a transition metal master batch composition, the composition comprising:
    - (a) a solid polymer carrier; and

(b) a transition metal composition;

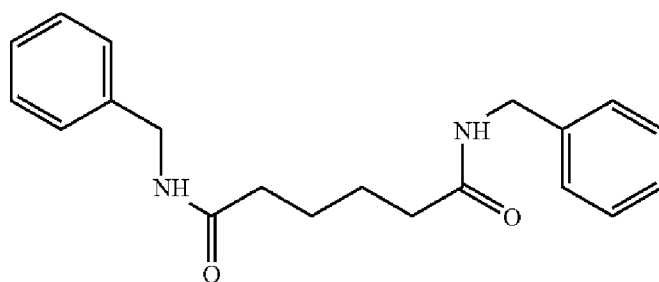
wherein the transition metal composition is present in an amount greater than about 30,000 ppm (by metal) based on the weight of the transition metal master batch composition;

(2) processing the extrudate comprising the transition metal master batch composition to particulate form by milling or pulverization, wherein the particle size is less than about 5.0 mm screen size;

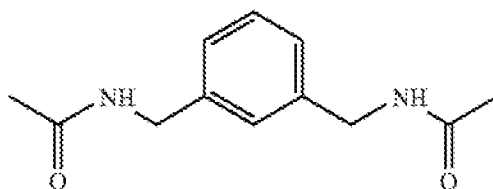
(3) preparing a homogeneous mixture comprising the particulate transition metal master batch composition and a powdered oxygen scavenger composition, wherein the powdered oxygen scavenger composition is present in an amount greater than about 85 weigh percent based on the combined weight of the particulate transition metal master batch composition and the powdered oxygen scavenger composition; and

(4) forming compacted single pellets from the homogeneous mixture comprising the particulate transition metal master batch composition and a powdered oxygen scavenger composition, thereby producing transition metal compacted pellets.

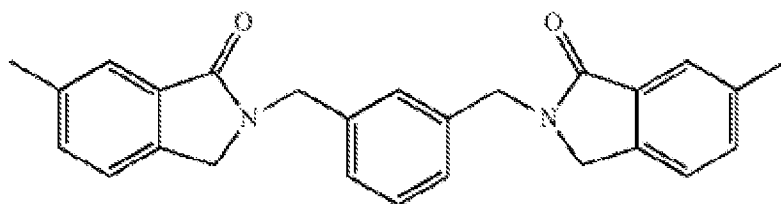
20. The method of claim 19, wherein the oxygen scavenger composition comprises a compound represented by a formula:



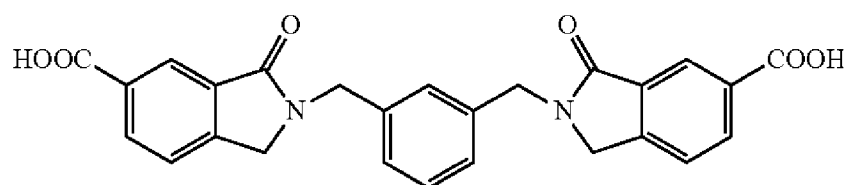
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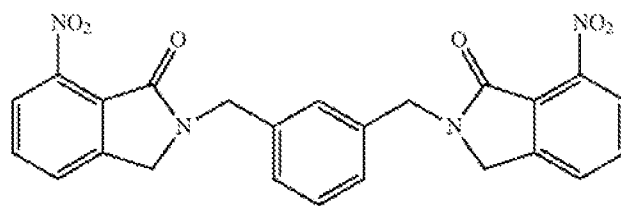
21. The method of claim 19, wherein the oxygen scavenger composition comprises a compound represented by a formula:



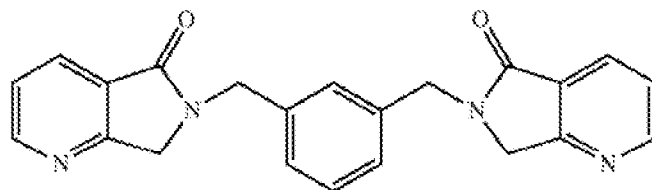
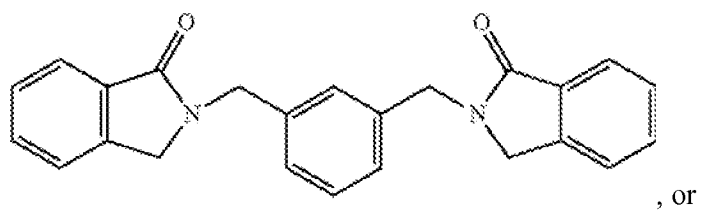
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# INTERNATIONAL SEARCH REPORT

International application No.

PCT/US13/38801

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - C08K 5/16, 3/08, 3/10 (2013.01)

USPC - 524/440, 87, 102

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)

IPC(8): C08K 5/16, 3/08, 3/10; C09K 15/22 (2013.01)

USPC: 524/440, 87, 102, 99, 92, 94, 91, 599; 428/35.7, 35.8; 252/181.6

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)

MicroPatent (US-G, US-A, EP-A, EP-B, WO, JP, DE-G, DE-A, DE-T, DE-U, GB-A, FR-A); Google; Google Scholar; DialogPro; iron, transition-metal, nickel, copper, titanium, manganese, chrome, vanadium, cobalt, ppm, polymer, polyester, polyethylene, terephthalate, batch, masterbatch, composite, blend, loaded, oxygen, O2, sequester, absorb, sorb, getter, powder, milling, milled, pulverize, comminute

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2006/0069197 A1 (TAMMAJI, KS et al.) March 30, 2006; paragraphs [0059]-[0060], [0096]	1-6, 9, 13, 16-18
Y		7-8, 10-12, 14-15, 19-21
Y	US 2006/0148957 A1 (STEWART, ME et al.) July 6, 2006; paragraphs [0088], [0091]	7-8
Y	US 2011/0251395 A1 (DESHPANDE, GN et al.) October 13, 2011; paragraphs [0021], [0029], [0072]-[0074], [0162]	10-12, 19-21
Y	WO 2012/000614 A1 (FAVA, F) January 5, 2012; page 14, lines 6-7	14-15, 19-21
Y	US 2006/0180790 A1 (DESHPANDE, GN et al.) August 17, 2006; paragraph [0080]-[0095]	11, 20

☐ Further documents are listed in the continuation of Box C.

\* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"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

Date of the actual completion of the international search

28 August 2013 (28.08.2013)

Date of mailing of the international search report

**05 SEP 2013**

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