

OXYGEN SCAVENGING COMPOSITION FOR PLASTIC MATERIAL

The present invention relates to oxygen barrier plastic materials comprising an organic polymer and an oxygen scavenger to enhance the quality and shelf-life of oxygen-sensitive products in packaging applications. These oxygen barrier plastic materials can be processed into mono- and multilayer rigid containers or flexible films to impart oxygen barrier properties at an enhanced clarity compared to other oxygen barrier compositions known in the art. Furthermore, the present invention relates to the use of oxygen barrier compositions in food, beverage and pharmaceutical packaging and to plastic material and articles comprising said oxygen barrier compositions.

For the purposes of the invention, masterbatches (MB) are compositions comprising a polymeric carrier or a liquid vehicle and an additive, where the additive is present in the masterbatch in higher concentrations than in the final application or in the final article, and the carrier does not have to be the organic polymer of the final application or of the final article. Preferred concentrations of the additives in a masterbatch range preferably of from 0.5 to 90 % by weight, more preferably of from 1 to 80 % by weight, the % by weight based in each case on the total weight of the masterbatch.

For the purposes of the invention, compounds (CO) are compositions comprising an organic polymer and an additive, where the additive is present in the compound in the desired concentration for the final application or for the final article, and the organic polymer is the organic polymer of the final application or of the final article, so that the compound is merely brought to the desired shape of the final application or of the final article by means of a physical shaping process.

Packaging for personal care, medical, pharmaceutical, household, industrial, food and beverage products require high barrier properties to oxygen to preserve the freshness and quality of the package contents. Containers made of traditional materials like glass or metal provide an excellent barrier both to egress of substances from the container and to ingress of substances from the environment.

In most instances, gas permeation through a glass or metal container is negligible. Nevertheless, due to the potentially lower cost and functional advantages (such as thermo-sealability, microwavability, optical properties, lightweight, decrease breakage and unlimited sizes and shapes) over materials such as glass and metal, there has been an increasing use of plastic materials in packaging in recent years. Polymeric material commonly used in packaging applications are polyethylene terephthalate resin (PET) and polyolefins. Both PET and polyolefins have a number of advantageous properties for use in packaging applications, but they do not possess the gas barrier properties that are required or desired in many oxygen sensitive applications.

A number of solutions to overcome barrier problems associated with plastic containers have been proposed.

- 15 The packaging industry has developed, for example, multilayer structures comprising mixed polymer layers. These laminated packaging containers offer improved barrier properties approaching, but not comparable to, those of glass and steel while sacrificing many of the recycling benefits associated with single layer containers such as PET, polyethylene naphthalate (PEN) or polyolefins bottles. Furthermore, depending on the mixtures of polymers, copolymers, blends used in the various layers, clarity of the container is often substantially diminished. Maintaining the proper balance of recyclability, barrier properties, and clarity is most critical in bottling applications.
- 25 The use of multilayer bottles that contain an inner, sometimes sandwiched, layer of a higher barrier polymer material compared to the outer polymer layers is commonplace. Typically the centre layer is a high barrier polymer that slows the permeability of oxygen through the container wall. Such a system would be categorized as a passive barrier. Examples of such high barrier polymers include ethylene-vinyl alcohol (EVOH) and polyamides, preferably a partially aromatic polyamide containing meta-xylylene groups, such as poly (m-xylylene adipamide), MXD6. A common construction for such multilayer structures would comprise inner

and outer layers of PET with a centre layer of a polyamide, or inner and outer layers of polyolefins with a centre layer of ethylene-vinyl alcohol (EVOH) polymer.

One of the advantages of using polymers such as EVOH, instead of other materials imparting oxygen barrier properties such as thin metal foil or vapour-deposited layers of inorganic oxides, is that polymer processing techniques such as extrusion, injection molding, film blowing, are available. However, EVOH suffers from the drawback of being water sensitive and to maintain its oxygen barrier properties it is usually necessary to coat or laminate it with moisture-barrier materials such as polyolefins.

MXD6 has excellent gas-barrier property and better thermal stability during melting than the other gas-barrier resins. It can be co-extruded or co-injection-molded with a thermoplastic resin such as polyethylene terephthalate (PET) and polypropylene, and positive efforts have been made to utilize it as a gas-barrier layer of multilayer structures. Nevertheless, in multilayer containers produced by using nylon MXD6, thickness unevenness and whitening are often observed, and it is very difficult to obtain multilayer containers that are satisfactory in practical applications with regards to shape, gas-barrier property and transparency.

Also, designing multilayer structures of the type described above implies increased complexity of the manufacturing process. In particular, the individual layers of said multilayer structures have to be assembled in such a manner that problems like separation of the individual layers (delamination) during use of the article are prevented.

Blends of low gas permeable polymers, such as MXD6, directly into polyesters are also commercially viable solutions although corresponding monolayer articles are prompt to haze formation due to the incompatible MXD6 domains in the PET matrix. Haziness has been particularly observed in biaxially oriented films and in stretched blown bottles. Incompatibility of PET and MXD6 results in large MXD6 particles that can effectively scatter light. Several approaches have been undertaken to reduce haze formation in PET/MXD6 blends. For example, the use

of compatibilizers reduces particle size to the submicron level thus resulting in containers with greatly improved impact delamination resistance, adhesion, colour, and transparency.

- 5 US 6346307 discloses the use of a dianhydride of a tetracarboxylic acid to reduce the dispersed domain size of a blend of MXD6 in PET.

US 6444283 discloses that low molecular weight MXD6 polyamides have lower haze than higher molecular weight MXD6 when blended with PET.

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US 4957980 discloses the use of maleic anhydride grafted copolyesters to compatibilize polyester-MXD6 blends.

- To further reduce the entry of oxygen into the contents of the package, small
15 amounts of transition metal salts can be added to PET/polyamide blends to catalyse and actively promote the oxidation of the polyamide polymer, thereby further enhancing the oxygen barrier characteristics of the package. This method affords the opportunity to eliminate unwanted oxygen from the package cavity that may have been inadvertently introduced during packaging or filling. The method of
20 providing oxygen barrier properties where a substance consumes or reacts with the oxygen is known as a reactive oxygen barrier and differs from the passive oxygen barriers which attempt to hermetically seal a product away from oxygen via the passive approach.

- 25 US 5021515A, US 5639815A and US 5955527A disclose the use of a cobalt salt as the preferred transition metal catalyst and MXD6 as the preferred polyamide. It is mentioned that the scavenging properties of the compositions do not emerge immediately after the blending, but only after ageing. There is no data on the haze of the polyamide blends.

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EP1663630B1 discloses the use of 5-sodiumsulfoisophthalic acid or 5-zinc sulfoisophthalic acid, or their dialkyl esters, as ionic compatibilizers of blends of polyester, partially aromatic polyamide and cobalt salts.

Apart from PET/polyamide blends and the catalysed oxidation of the polyamide polymer by a transition metal catalyst, incorporation into the container walls of other substances capable of intercepting and scavenging oxygen as it attempts to pass through the walls of the container is another method to limit oxygen exposure.

Among others, oxygen-scavenging compositions comprising an oxidizable ethylenically unsaturated hydrocarbon and a transition metal catalyst are well-known viable solutions. US 5310497A, US 5211875A, US 5346644A and US 5350622A disclose the use of poly(1,2-butadienes) as the ethylenically unsaturated hydrocarbons; US 5021515A and US 5211875A disclose the use of an oxidizable polymer such as polyamide, polyisoprene, polybutadiene, or copolymers thereof, specifically block copolymers thereof, such as styrene-butadiene.

Within the scope of the present invention, preferred compositions would comprise both a passive barrier and an active oxygen scavenger so to absorb oxygen at a rate faster than the permeability of oxygen through the packaging wall for the planned shelf-life of the packaged product while having enough capacity to remove oxygen from within the package headspace, if necessary. Additionally, shelf life and turnover intervals require that the oxygen scavenging should occur for extended periods of time.

Beyond pure performance and protection of the packaged product, appearance is also a key element to product differentiation. The trend towards transparent materials has become critical to the food packaging industry in recent years and continues to gain momentum. In those applications requiring clarity, and particularly for polyester applications, the packaging article should have optical properties approaching those of virgin polymer. Product visibility is a powerful tool, both functionally and aesthetically. It allows end consumers to readily see what product they are buying and check its appearance without opening the packaging

and enables product manufacturers to easily inspect the packaged product through the use of vision systems, metal detectors and manual visual inspection.

As mentioned, in barrier layers of packaging articles that are made from blends of oxygen scavenging materials with resins such as PET, haze can result from the immiscibility of the scavenging materials with the base polymer, the inability to create by mechanical blending disperse-phase domains that are small enough as not to interfere with the passage of light, and the adverse influence of the scavenging material on the crystallization behaviour of PET base resin. One approach to minimize such haze is the careful selection of base resin to improve dispersibility of the scavenger material and, thus, reduce, but not substantially eliminate, haze; and to minimize the adverse crystallization effect. This approach may restrict the choice of base polymer resin. Another approach is to use compositions that serve as compatibilizers to reduce haze. These approaches add cost to the barrier layer and the compatibilizer adds an additional material that must be evaluated for its suitability for contact with food. Thus, there is a need for improved plastic materials, which provide high oxygen scavenging capability and are substantially transparent.

Finally, the preferred thin walled container should be suitable for recycling with other polyester or polyolefin articles. In order to be meaningful, the recycling must be conducted without the need for any special physical processing such as delamination or the need for any special chemical processing such as depolymerization.

Summarising, a number of attempts have been made to prepare oxygen barrier and/or scavenging articles. There have been numerous approaches involving the use of laminated structures, and others involving the incorporation of inorganic powders, salts and/or sacrificial oxydizable compounds. Most of these systems have at least one or several disadvantages including poor processing properties, insufficient oxygen uptake and long induction periods and most of them also suffer from poor clarity and lack of recyclability.

A need exist for improved gas barrier compositions, methods for the production of said compositions and methods of using the compositions in packaging articles that satisfy all the demands as recited above, specifically the need for transparent, recyclable, thin walled articles and containers with excellent oxygen scavenging capabilities.

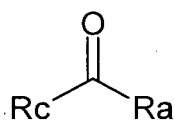
In particular, it would be desirable to obtain improved gas barrier polyester compositions that can be injection stretch blow molded as monolayer containers with reduced haze. This is particularly required for containers that require a long shelf life, such as beer and other oxygen sensitive materials.

Surprisingly, it has been found that the object of the invention can be achieved by using particular additives as oxygen scavengers in certain plastic materials as specified hereinafter.

Therefore, the present invention provides for the use of an additive as oxygen scavenger in a plastic material, wherein:

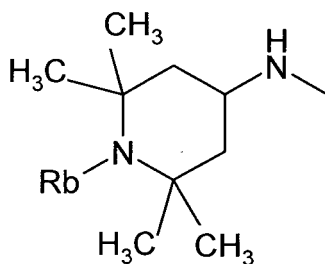
(a) the plastic material is a polyester, a polyolefin, a polyolefin copolymer or a polystyrene, and the additive is (b) and optionally (c):

(b) a compound of formula (1),



(1)

wherein Ra represents a group of formula (A),



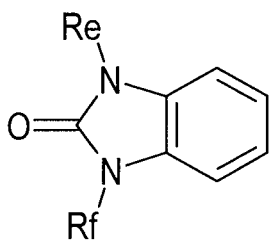
Formula (A)

wherein Rb is selected from the group consisting of hydrogen, C₁-C₆ alkyl, C₁-C₆ alkoxy and -CO-C₁-C₄ alkyl, preferably hydrogen or methyl, more preferably hydrogen;

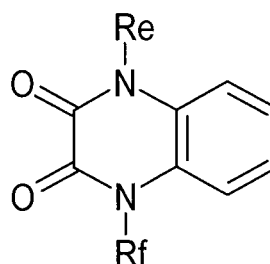
Rc represents C₇-C₂₀ alkyl, C₆-C₁₀ aryl, C₄-C₁₀ heteroaryl, wherein the heteroatoms are N, O and/or S, (C₂-C₆)-alkenylene-(C₆-C₁₀) aryl, C₁-C₆-alkylene-C₆-C₁₀-aryl, the aryl and heteroaryl radicals optionally being substituted by hydroxyl, C₁-C₆-alkyl, C₁-C₆ alkoxy, C₆-C₁₀ aryloxy, halogen, e.g. F, Cl, Br, I, cyano, nitro, C₆-C₁₀-aryl, di(C₁-C₆)alkylamino, (C₁-C₆)alkylthio, C₆-C₁₀-arylthio, SO₃H, SO₂NR⁹R¹⁰, CO₂R¹¹, CONR⁹R¹⁰, NHCOR¹² or CO-C₆-C₁₀-aryl, wherein R⁹, R¹⁰, R¹¹, R¹² are the same or different and independently represent hydrogen or C₁-C₆-alkyl;

(c) a transition metal catalyst.

In a preferred embodiment Rc represents phenyl, naphthyl, a heteroaryl of formula (B) or formula (C)



Formula (B)



Formula (C)

wherein Re and Rf are independently of each other hydrogen, C₁-C₂₀ alkyl or phenyl;

or Rc represents (C₂-C₄) alkenylen (C₆-C₁₀) aryl, C₁-C₄-alkylen-C₆-C₁₀-aryl, the aryl and heteroaryl radicals optionally being substituted by hydroxyl,

5 C₁-C₄-alkyl, C₁-C₄ alkoxyl, C₆-C₁₀ aryloxy, Cl, cyano, C₆-C₁₀-aryl, or CO-C₆-C₁₀-aryl.

In a more preferred embodiment Rc represents phenyl, naphthyl, a heteroaryl of formula (B) as shown above, wherein Re and Rf are independently of each other hydrogen or C₁-C₂ alkyl;

10 or Rc represents C₂- alkenylen (C₆-C₁₀) aryl, C₁-C₂-alkylen-C₆-C₁₀-aryl, the aryl and heteroaryl radicals optionally being substituted by hydroxyl, methyl, methoxy, C₆-C₁₀ aryloxy, Cl, C₆-C₁₀-aryl, or CO-C₆-C₁₀-aryl.

The number of the above mentioned substituents for the aryl and heteroaryl radicals is expediently 1, 2 or 3.

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Suitable oxidation catalysts include transition metal catalysts which can readily interconvert between at least two oxidation states. Preferably, the transition metal is in the form of a transition metal salt with the metal selected from the first, second or third transition series of the Periodic Table. Suitable metals include

20 manganese II or III, iron II or III, cobalt II or III, nickel II or III, copper I or II, rhodium II, III or IV and ruthenium I, II or IV. Suitable counterions for the metal include, but are not limited to, chloride, acetate, acetylacetonate, stearate, palmitate, 2-ethylhexanoate, neodecanoate, octanoate, or naphthenate, and mixtures thereof. The metal salt may also be an ionomer, in which case a polymeric counterion is employed. Such ionomers are well known in the art. Any amount of catalyst which is effective in catalysing oxygen scavenging may be used.

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Expediently, the plastic material is or is part of a packaging article, or is a masterbatch MB or a Compound CO which can be processed into a packaging material.

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Oxygen scavenging, in the sense of the present invention, refers to the reduction or elimination of unwanted oxygen from the packaging cavity by providing a substance that reacts with, absorbs and/or consumes oxygen. This is known as an active oxygen barrier and differs from the passive oxygen barriers, which attempt to hermetically seal a product away from oxygen.

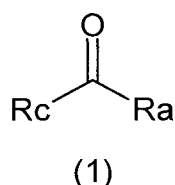
Preferably, the additive (b) is used in an amount of from 0.001 to 5 %, more preferably 0.01 to 1.5 %, most preferably 0.05 to 1 %, by weight, based on the total weight of the plastic material of the packaging article and the additive(s).

The transition metal catalyst (c) is used in an amount of from 0 to 1 %, preferably 0.001 to 1 %, more preferably 0.01 to 0.5 %, by weight, based on the total weight of the plastic material of the packaging article and the additive(s).

The present invention further provides for a method of providing an active oxygen barrier in a plastic material of a packaging article comprising incorporating an effective amount of an additive (b) and optionally (c) as specified above into a plastic material which is a polyester, a polyolefin, a polyolefin copolymer or a polystyrene.

The present invention further provides for a composition Z comprising the components A, B, and C

- the component A being a plastic material selected from the group consisting of polyesters, polyolefins, polyolefin copolymers and polystyrenes;
- the component B being an additive represented by the formula (1),



- wherein Ra and Rc are as defined above; and
- the component C being a transition metal catalyst.

Preferred transition metal catalysts are as defined above.

5 The amount of catalyst which is effective in catalysing oxygen scavenging is preferably 0.001 to 1 %, more preferably 0.01 to 0.5 %, by weight, based on the total weight of the composition Z.

Preferred plastic materials, i.e. component A or plastic material a) within the meaning of the invention, are polyesters and polyolefines.

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The polyesters of the present invention are thermoplastic. The intrinsic viscosity values of the polyesters are set forth in dL/g units as calculated from the inherent viscosity measured at 25 °C in 60/40 wt/wt phenol/tetrachloroethane. The intrinsic viscosity of the polyesters preferably ranges from about 0.55 to about 1.14 dL/g.

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Preferred polyesters are the ones resulting from the condensation reaction of dibasic acids and glycols.

Typically, the dibasic acid comprises an aromatic dibasic acid, or ester or anhydride thereof, and is selected from the group consisting of isophthalic acid, 20 terephthalic acid, naphthalene-1,4-dicarboxylic acid, naphthalene-2,6,-dicarboxylic acid, phthalic acid, phthalic anhydride, tetrahydrophthalic anhydride, trimellitic anhydride, diphenoxyethane-4,4'-dicarboxylic acid, diphenyl-4,4'-dicarboxylic acid, and mixtures thereof. The dibasic acid also can be an aliphatic dibasic acid or 25 anhydride, such as adipic acid, sebacic acid, decan-1,10-dicarboxylic acid, fumaric acid, succinic anhydride, succinic acid, cyclohexanediadicetic acid, glutaric acid, azelaic acid, and mixtures thereof. Other aromatic and aliphatic dibasic acids known to persons skilled in the art also can be used. More preferably, the dibasic acid comprises an aromatic dibasic acid, optionally further comprising up to about 30 20 % by weight of the dibasic acid component, of an aliphatic dibasic acid.

Preferably, the glycol or diol component of the polyester is selected from the group consisting of ethylene glycol, propylene glycol, butane-1,4-diol, diethylene glycol,

a polyethylene glycol, a polypropylene glycol, neopentyl glycol, a polytetramethylene glycol, 1,6-hexylene glycol, pentane-1,5-diol, 3-methylpentanediol-(2,4), 2-methylpentanediol-(1,4), 2,2,4-trimethylpentane-diol-(1,3), 2-ethylhexanediol-(1,3), 2,2-diethylpropanediol-(1,3), hexanediol-(1,3), 1,4-di-
5 (hydroxy-ethoxy) benzene, 2,2-bis-(4-hydroxycyclohexyl) propane, 2,4-dihydroxy-1,1,3,3-tetramethylcyclobutane, 2,2-bis-(3-hydroxyethoxyphenyl) propane, 2,2-bis-(4-hydroxypropoxyphenyl) propane, 1,4-dihydroxymethyl-cyclohexane, and mixtures thereof. Additional glycols known to persons skilled in the art also can be used as the glycol component of the polyester.

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Two preferred polyesters are polyethylene terephthalate (PET) and polyethylene naphthalate (PEN). The PET and PEN can be homopolymers, or copolymers further containing up to 10 mole percent of a dibasic acid different from terephthalic acid or a naphthalene dicarboxylic acid, and/or up to 10 mole percent
15 of a glycol different from ethylene glycol.

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PEN is preferably selected from the group consisting of polyethylene naphthalene 2, 6-dicarboxylate, polyethylene naphthalene 1,4-dicarboxylate, polyethylene naphthalene 1,6-dicarboxylate, polyethylene naphthalene 1,8-dicarboxylate, and
polyethylene naphthalene 2,3-dicarboxylate. More preferably, PEN is polyethylene naphthalene 2,3-dicarboxylate.

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More preferably the plastic material is selected from the group consisting of PET, e.g. virgin bottle grade PET and postconsumer PET (PC-PET), cyclohexane dimethanol/PET copolymer (PETG), polyethylene naphthalate (PEN),
polybutylene terephthalate (PBT), and mixtures thereof.

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Also preferred plastic materials are biodegradable polyester, preferably selected from the group consisting of PLAs (Polylactic acid), polycaprolactones (PCL) and polyhydroxybutyrates (PHB), and bio-based polyesters, which are derived from renewable resources such as corn and sugar cane and the by-products associated with their harvesting and processing but are not biodegradable.

Preferred polyolefins and polyolefin copolymers, i.e. component A or plastic material a) within the meaning of the invention, are thermoplastic polyolefins known in the art and are selected from the group consisting of:

- 5 Polyethylene (PE), preferably selected from the group consisting of high density polyethylene (HDPE), medium density polyethylene (MDPE), low density polyethylene (LDPE), linear low density polyethylene (LLDPE), metallocene low density polyethylene (mLDPE) and metallocene linear low density polyethylene (mLLDPE),

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Polypropylene (PP), preferably selected from the group consisting of polypropylene homopolymer (PPH), polypropylene random copolymer (PP-R) and polypropylene block copolymers (PP-block-COPO),

- 15 PE copolymers, preferably selected from the group consisting of ethylene-vinyl acetate copolymers (EVA), copolymers of ethylene and methyl acrylate (EMA), copolymers of ethylene and butyl acrylate (EBA), copolymers of ethylene and ethyl acrylate (EEA), and cycloolefin copolymers (COC), general purpose polystyrene (GPPS) and high impact polystyrene (HIPS);

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More preferably of

- high density polyethylene (HDPE) and low density polyethylene (LDPE)
- polypropylene homopolymer (PPH),
- general purpose polystyrene (GPPS).

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Preferred polystyrenes, i.e. component A or plastic material a) within the meaning of the invention, can be a styrene homopolymer, an alkylstyrene homopolymer, preferably a C₁-C₄-alkylstyrene homopolymer, for example α -methylstyrene homopolymer; a styrene copolymer, especially a high impact polystyrene (HIPS).

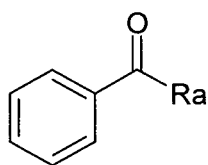
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High impact polystyrenes (HIPS) are generally prepared by polymerization by grafting mixtures of styrene and optionally of one or more copolymerizable vinyl monomers, preferably mixtures of styrene, methylstyrene, ethylstyrene,

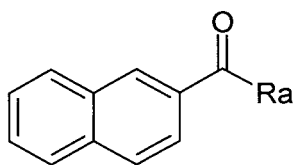
- butylstyrene, halostyrenes, vinylalkylbenzenes, such as vinyltoluene, vinylxylene, acrylonitrile, methacrylonitrile, lower alkyl esters of methacrylic acid, in the presence of a rubbery polymer trunk comprising copolymers chosen from polybutadiene, polyisoprene, rubbery styrene-diene copolymers, acrylic rubber, nitrile rubber and olefinic rubbers, such as propylene diene monomer rubber (PDM) and propylene rubber (PR). In the high impact polystyrene, the rubbery polymer trunk normally constitutes from 5 to 80 % by weight, preferably 5 to 50 % by weight, of the total weight of the grafted polymer.
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- 10 The preferred density of component P is of from 1.0 to 1.1 g/cm³, more preferably of from 1.02 to 1.06 g/cm³, even more preferably of from 1.03 to 1.05 g/cm³.

- Preferred polystyrenes are polystyrenes with a MFR at 200 °C/5 kg according to ISO 1133 of from 0.1 to 300 g/10 min, more preferably of from 1 to 200 g/10 min, even more preferably of from 5 to 100 g/10 min, especially of from 10 to 50 g/10 min, more especially of from 15 to 35 g/10 min, in particular of from 20 to 25 g/10 min.
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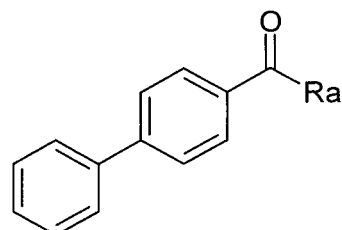
- Preferred, component B or additive b) is any compound represented by any of the formulae (1a) to (1f) with a moiety Ra as represented by formulae (A) above
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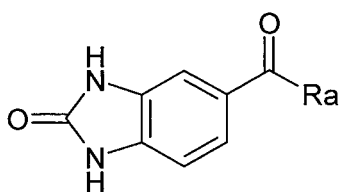
(1a)



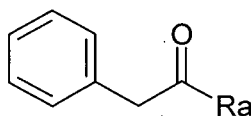
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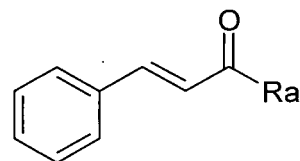
(1c)



(1d)



(1e)



(1f)

wherein the phenyl group in formula (1a), (1e) and (1f) is preferably substituted with C₁-C₄-alkoxy groups, preferably methoxy, C₁-C₄-alkyl groups, preferably methyl, or halogen, preferably chloro.

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In a preferred embodiment of the present invention, the additive b) or component B contains at least one of the compounds of formula (1a) to (1f), wherein R_a independently is a moiety selected from above formula (A), wherein R_b is selected from hydrogen, methyl, ethyl, methyl-CO-, and ethyl-CO-.

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Additive c) or component C, within the meaning of the invention, is a transition metal catalyst that initiate and accelerates the rate of oxygen scavenging.

More preferably, the transition metal catalyst is in the form of a salt, with the transition metal selected from the first, second or third transition series of the

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Periodic Table. Suitable metals and their oxidation states include, but are not limited to, manganese II or III, iron II or III, cobalt II or III, nickel II or III, copper I or II, rhodium II, III or IV, and ruthenium. The oxidation state of the metal when introduced does not need necessarily to be that of the active form.

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The metal is preferably iron, nickel, manganese, cobalt or copper; more preferably manganese or cobalt; and even more preferably cobalt. Suitable counterions for the metal include, but are not limited to, chloride, acetate, propionate, oleate, stearate, palmitate, 2-ethylhexanoate, neodecanoate or naphthenate. The metal salt can also be an ionomer, in which case a polymeric counterion is employed.

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Such ionomers are well known in the art.

Even more preferably, the salt, the transition metal, and the counterion are either compliant with country regulations in the matter of food contact materials or, if part of a packaging article, exhibit substantially no migration from the oxygen

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scavenging composition to the packaged contents. Particularly preferable salts include cobalt oleate, cobalt propionate, cobalt stearate, and cobalt neodecanoate.

Optionally, composition Z comprises one or more further substances (component D), which are selected from the group consisting of aliphatic polyamides and partially aromatic polyamides.

- 5 The aliphatic polyamides are fully aliphatic polyamides and include a moiety $-\text{CO}(\text{CH}_2)_n\text{CONH}(\text{CH}_2)_m\text{NH}-$ or a moiety $-(\text{CH}_2)_p\text{CONH}-$, wherein n , m and p are integers independently from each other in the range of 1 to 10, preferably of 4 to 6.

Preferably, aliphatic polyamides include poly (hexamethylene adipamide), poly
10 (caprolactam) and poly (hexamethylene adipamide)-co-caprolactam.
Especially, the aliphatic polyamide is poly (hexamethylene adipamide)-co-caprolactam.

"Partially aromatic polyamides" within the meaning of the invention are
15 polymerized from a mixture of aromatic and non-aromatic monomers or precursors. Preferably, the partially aromatic polyamides are selected from the group consisting of polyamides formed from isophthalic acid, terephthalic acid, cyclohexanedicarboxylic acid, aliphatic diacids with 6 to 12 carbon atoms together
20 with meta- or para-xylene diamine, 1,3- or 1,4-cyclohexane(bis)methylamine, aliphatic diamines with 4 to 12 carbon atoms, or aliphatic amino acids with 6 to 12 carbon atoms, or from lactams with 6 to 12 carbon atoms, in all possible combinations, and from other generally known polyamide forming diacids and diamines. The partially aromatic polyamides may also contain small amounts of
25 trifunctional or tetrafunctional comonomers such as trimellitic anhydride, pyromellitic dianhydride, or other polyamide forming polyacids and polyamines known in the art.

More preferably, partially aromatic polyamides are selected from the group consisting of poly(m-xylene adipamide), poly (hexamethylene isophthalamide),
30 poly (hexamethylene adipamide-co-isophthalamide), poly(hexamethylene adipamide-co-terephthalamide) and poly(hexamethylene isophthalamide-co-terephthalamide).

Even more preferably, the polyamide is poly(m-xylylene adipamide).

Molecular weight M_n of the polyamides is desirably between 1000 and 45000, preferably between 2500 and 25000.

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Optionally, composition Z comprises also one or more further substances, which are selected from the group consisting of natural colorants derived from plants or animals and synthetic colorants, preferred synthetic colorants being synthetic organic and inorganic dyes and pigments,

- 10 - preferred synthetic organic pigments being azo or disazo pigments, laked azo or disazo pigments or polycyclic pigments, particularly preferably phthalocyanine, diketopyrrolopyrrole, quinacridone, perylene, dioxazine, anthraquinone, thioindigo, diaryl or quinophthalone pigments;
 - preferred synthetic inorganic pigments being metal oxides, mixed oxides, 15 aluminium sulphates, chromates, metal powders, pearlescent pigments (mica), luminescent colours, titanium oxides, cadmium lead pigments, iron oxides, carbon black, silicates, nickel titanates, cobalt pigments or chromium oxides;
 - fillers and nanosized fillers, preferably silica, zeolites, silicates, particularly 20 preferably aluminium silicates, sodium silicate, calcium silicates; chalk or talc; metal hydrates;
 - auxiliaries, preferably acid scavengers, processing aids, coupling agents, lubricants, stearates, blowing agents, polyhydric alcohols, nucleating agents, or antioxidants, e.g. stearates, or oxides such as magnesium oxide;
 - 25 - antioxidants, preferably primary or secondary antioxidants;
 - antistatic agents;
 - compatibilizers for polyester/polyamide blends;
- UV absorbers, slip agents, anti-fogging agents, anti-condensation agents, suspension stabilizers, anti-blocking agents, waxes, and a mixture of these 30 substances.

More preferably, the further substances are selected from the group consisting of compatibilizers for polyester-polyamide blends, if the plastic material is polyester, UV absorbers, antioxidants and colorants:

- 5 Preferred compatibilizers include, but are not limited to, polyester ionomers, preferably PET ionomers, isophthalic acid (IPA) modified PET, p-toluene sulfonic acid (pTSA) modified PET, pyromellitic dianhydride (PMDA) modified PET, and maleic anhydride modified PET. Other preferred compatibilizers include acrylic modified polyolefin type ionomer and low molecular weight bisphenol-A epoxy
- 10 resin-E44 which may be added directly to a PET/polyamide blend. Further, trimellitic anhydride (TMA) may be added to the polyamide, transesterified, mixed with PET and then coupled using a bifunctional coupler such as, but not limited to, diphenylmethane-4, 4'-diisocyanate (MDI), diphenylmethane-4, 4'-diisopropylurethane (DU), or bisoxazoline (BOX). When compatibilizers are used,
- 15 preferably one or more properties of the polyamide/polyester blends are improved, such properties including color, haze, and adhesion between a layer comprising a blend and a layer comprising polyester.

Preferred polyester ionomers include those disclosed in US 6500895 B1.

- 20 Preferred PET ionomers include sulfonated PET. A preferred modified PET-type compatibilizer is IPA modified PET.

Preferably, the composition Z contains

- of from 14 to 99.887 % by weight of component A;
- 25 of from 0.01 to 70 % by weight of component B;
- of from 0.003 to 15 % by weight of component C;
- of from 0 to 80 % by weight of components D;
- with the % by weight being based in each case on the total weight of the composition Z; and with the weight percent of the components A, B, C and
- 30 optionally D always adding up to 100 %.

The composition Z can be a masterbatch MB or a compound CO. The composition Z can be liquid or solid at ambient temperature.

Preferably, in case the composition Z is a masterbatch MB, the composition Z comprises

- of from 14 to 94 % by weight of component A;
- 5 of from 5 to 70 % by weight of component B;
- of from 1 to 15 % by weight of component C;
- of from 0 to 80 % by weight of components D;
- more preferably
- of from 14 to 94 % by weight of component A;
- 10 of from 5 to 50 % by weight of component B;
- of from 1 to 10 % by weight of component C;
- of from 0 to 80 % by weight of components D;
- with the % by weight being based in each case on the total weight of the composition Z; and with the weight percent of the components A, B, C and
- 15 optionally D always adding up to 100 %.

Preferably, in case the composition Z is a compound CO, the composition Z comprises

- of from 88 to 99.887 % by weight of component A;
- 20 of from 0.01 to 1.5 % by weight of component B;
- of from 0.003 to 0.5 % by weight of component C;
- of from 0 to 10 % by weight of components D;
- more preferably
- of from 90 to 99.86 % by weight of component A;
- 25 of from 0.1 to 0.8 % by weight of component B;
- of from 0.04 to 0.3 % by weight of component C;
- of from 0 to 8.9 % by weight of components D;
- with the % by weight being based in each case on the total weight of the composition Z; and with the weight percent of the components A, B, C and
- 30 optionally D always adding up to 100 %.

The present invention further provides for a composition Z consisting of components A, B, C, and optionally D, with the components A to D and the

amounts and preferred amounts of components A to D as described in the foregoing.

5 The composition Z of the present invention is expediently formed, e.g. blow molded, into a plastic article.

Therefore, another subject of the present invention is a formed plastic article comprising said composition Z.

10 The formed plastic article according to the invention can be a packaging material, preferably

a container, a film or a sheet, especially for use in packaging of personal care, cosmetics, medical, pharmaceutical, household, industrial, food and beverage products where a high oxygen barrier is needed.

15 Packaging materials suitable for comprising oxygen scavenging composition Z can be flexible, rigid, semi-rigid or combinations thereof.

Rigid packaging articles typically have wall thicknesses in the range of 100 to 1000 micrometers. Typical flexible packages typically have thicknesses of 5 to 250 micrometers.

20 Rigid packaging articles or flexible films comprising oxygen scavenging compositions of the invention can consist of a single layer or may comprise multiple layers.

25 When a packaging article or film comprises an oxygen scavenging layer, it can further comprise one or more additional layers, one or more of the additional layers comprising an oxygen barrier layer or being permeable to oxygen. Further additional layers, such as adhesive layers, can also be used in a multi-layer packaging article or film.

Preferably, the rigid containers, e.g. bottles, or flexible films in which composition Z is used to scavenge oxygen, are monolayer.

30

Another subject of the invention is a method for the manufacture of a plastic material or an article as defined above, characterised in that the components A, B,

C, and optionally D, are physically mixed with one another and subjected to a shape forming process.

For physical mixing, it is possible to use a mixing apparatus customary in the plastics industry. Preferably, the mixing apparatus can be one used to make a liquid masterbatch or a solid masterbatch or can be a combination of those apparatuses.

A mixing apparatus for a liquid masterbatch can be a high speed dispersor (e.g. of CowlesTM type), a media mill, a three-roll mill, a submill or a rotor-stator type dispersor.

A mixing apparatus used to make solid masterbatches MB or compounds CO can be a mixer, extruder, kneader, press, mill, calender, blender, injection moulding machine, injection and stretch blow moulding machine (ISBM), extrusion blow moulding machine (EBM), compression moulding machine, compression and stretch blow moulding machine; more preferably a mixer, extruder, injection moulding machine, injection and stretch blow moulding machine, compression moulding machine, compression and stretch blow moulding machine; even more preferably a mixer, extruder, injection and stretch blow moulding machine and extrusion blow moulding machine.

The shape forming process for the article is dependent on the desired shape of article to be manufactured.

Containers are preferably made by blow moulding, injection moulding, injection and stretch blow moulding, extrusion blow moulding, compression moulding, compression and stretch blow moulding processes.

Films and sheets are preferably made by cast or blown film extrusion or co-extrusion processes, depending on the thickness required and on the number of layers needed to obtain specific properties, eventually followed by post-extrusion shaping processes like thermoforming or stretching. In the thermoforming process, the plastic sheet is heated to a pliable forming temperature, formed to a specific shape in a mold, and trimmed to create a final article. If vacuum is used, this process is generally called vacuum forming. In post-extrusion stretching

processes an extruded film can be, for example, biaxially oriented by drawing. All the above listed processes are well-known in the art.

For compositions Z comprising more than one masterbatch or components,

- 5 extruders may be equipped with a metering system for introducing said components and/or masterbatches into the main stream polymer. This metering may be carried out directly with one or more pure components or with one or more masterbatches.

- 10 The type of metering equipment used depends on the form in which the pure component or the masterbatch is metered.

- In the case of solid component, a metering device of the feed screw type is usually employed and the point of introduction may be the main inlet of the extruder jointly with the feed of the main polymer granules, or in an unpressurized injection zone located along the extruder. For a solid masterbatch, the metering device may be a
15 system comprising an additional extruder that pre-melts the masterbatch, pressurizes it and meters it by means of a metering pump, the amount of masterbatch metered being fed at a point along the main extruder advantageously without pressure.

- For a liquid pure component or a liquid masterbatch, the metering device may be a
20 system comprising one or more metering pumps which introduce the liquid masterbatch at the main inlet of the extruder jointly with the feed with the main polymer granules, without any pressure, or at a point under pressure located along the extruder.

- 25 The mixing of the components forming composition Z can occur in one step, two steps or in a plurality of steps.

- Mixing can occur in one step when the components A, B, C, and optionally component D, are directly metered and/or let down in a form of liquid or solid concentrates or as pure components, for example in an injection and stretch blow
30 molding machine.

Preferably, component B and component C are pre-dispersed into component A to form two separate masterbatches, and then these masterbatches are combined

with components A and optionally D. For either two or three step mixing process, it is most preferred that the addition of component D occurs in the last step.

5 In one preferred embodiment of the invention, in a first step, component B is dispersed into component A while component C is dispersed into component A to provide two separate masterbatches. After being melt compounded, for example in a single or twin screw extruder, the extrudates are withdrawn in strand form, and recovered as pellets according to the usual way, such as cutting. In a second step, the obtained masterbatches are metered and let down by a converter/compounder
10 into the main stream of component A pellets and optionally component D pellets, one or both optionally ground, or into the main stream of a concentrate of compound D into compound A, for example in an injection and stretch blow molding machine.

15 In another embodiment of the invention, in a first step, component B, C and optionally component D are dispersed into component A to provide a masterbatch. After being melt compounded, for example in a single or twin screw extruder, the extrudate is withdrawn in strand form, and recovered as pellets according to the usual way such as cutting. In a second step, the obtained solid
20 masterbatch is metered and let down by a converter/compounder into the main stream of component A of e.g. an injection and stretch blow molding machine, at a rate corresponding to the final desired concentration of component B, C and D in the article and without the step of separately metering component D.

25 Mixing preferably occurs continuously or batchwise, more preferably continuously; in case of a solid masterbatch MB preferably by extrusion, mixing, milling or calendaring, more preferably by extrusion; in case of a liquid masterbatch MB preferably by mixing or milling; in case of a compound CO preferably by extrusion or calendaring, more preferably by extrusion.

30

Mixing is preferably carried out at a temperature of from 0 to 330 °C.

The mixing time is preferably of from 5 sec to 36 h, preferably 5 sec to 24 h.

The mixing time in the case of continuous mixing is preferably of from 5 sec to 1 h.

The mixing time in the case of batchwise mixing is preferably of from 1 sec to 36 h.

In the case of a liquid masterbatch MB, mixing is preferably carried at a temperature of from 0 to 150 °C with a mixing time of from 0.5 minutes to 60 minutes.

In the case of a solid masterbatch MB or a compound CO, mixing is preferably carried out at a temperature of from 80 to 330 °C with a mixing time of from 5 sec to 1 h.

- 10 In another embodiment, the compositions described herein are used as a component of a wall that is used in a package article for oxygen sensitive materials. The wall may be a rigid one, such as in a container or bottle or a flexible one such as in films. It may be homogenous or a laminated or coated with other polymers. If it is laminated or coated, then the scavenging property may reside in one or more layers of the wall.

Specific articles of the present invention include preforms, containers, films and sheets 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 juices, sport drinks, beer or any other beverage where oxygen detrimentally affects the flavour, fragrance, performance (prevent vitamin degradation), or colour of the drink. The compositions of the present invention 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 of the present invention also find use in the manufacture of cosmetic containers and containers for pharmaceuticals or medical devices.

Preferred articles of the present invention are rigid packaging articles, such as bottles and thermoformed sheets and flexible films.

More preferred articles of the present invention are hollow containers which are expediently manufactured by any kind of blow moulding process known in the art. Blow molding of thermoplastic hollow containers is conventionally performed either
5 by blow molding of an extruded thermoplastic polymeric parison (extrusion blow moulding - EBM) or by blow molding of a thermoplastic polymeric preform, the latter is usually injection molded from a thermoplastic polymer (injection and stretch blow moulding - ISBM). The hot thermoplastic polymeric parison or the heated preform is received within a mold cavity whereupon pressurized gas
10 provides the blow molding of the container to the shape of the mold cavity.

ISBM processes are generally divided into two main types. The first is a one-step process, in which the preform is molded, conditioned, and then transferred to the stretch blow molding operation before the preform has cooled below its softening
15 temperature. The second type of ISBM process is a two-step process in which the preform is prepared ahead of time and stored for later use. In the two-step process, the preform is reheated prior to the initiation of the stretch blow molding step. The two-step process has the advantage of faster cycle times, as the stretch blow molding step does not depend on the slower injection molding operation to
20 be completed. However, the two-step process presents the problem of reheating the preform to the stretch blow molding temperature. This is usually done using infrared heating, which provides radiant energy to the outside of the preform. It is sometimes difficult to heat the preform uniformly using this technique and unless done carefully, a large temperature gradient can exist from the outside of the
25 preform to the centre. Conditions usually must be selected carefully to heat the interior of the preform to a suitable molding temperature without overheating the outside. The result is that the two-step process usually has a smaller operating window than the one-step process.

30 To determine the oxygen scavenging capabilities of the invention, the rate of oxygen scavenging can be calculated by measuring the time elapsed until the article has depleted a certain amount of oxygen from a sealed container.

Another definition of acceptable oxygen scavenging is derived from testing actual packages.

The oxygen scavenging capacity of an article comprising the invention can be measured by determining the amount of oxygen consumed until the article

5 becomes ineffective as a scavenger.

In actual use, the oxygen scavenging capacity requirement of the article will largely depend on three parameters of each application:

- the quantity of oxygen initially present in the package,
- 10 - the rate of oxygen entry into the package in the absence of the scavenging property, and
- the intended shelf life for the package.

The composition Z allows the use of transition metal-based polyester compositions
15 as oxygen scavenging systems with significantly improved oxygen scavenging performance and greatly increased transparency of the final plastic articles.

Another advantage of using an oxygen scavenging composition comprising the organic compound B, compared to the use of oxygen scavenging materials commonly used in polymeric articles, is due to the lower amount of material
20 needed to achieve the same oxygen scavenging performance.

Synthesis of additives of formulae (B1) to (B13):

The manufacturing method of the additives of formula (B1) to (B13) is not
25 particularly limited and can be done by any means known to those skilled in the art.

All solvents and reagents were obtained from commercial sources and used as received. The synthesis was performed under a nitrogen atmosphere.

In a typical experiment, the carboxamide compounds were prepared as follows:

30 To a two liter three neck roundbottom flask under nitrogen fitted with a mechanical stirrer, addition funnel and condenser, was charged successively 250 ml of dioxane, 0.5 mol of the acylchloride (see Table 1) 0.55 mole of triethylamine, 0.5 mole of 2,2,6,6-tetramethyl-piperidin-4-yl amine (TAD). The reaction mixture is

heated to reflux for 2 hours and cooled to room temperature. The precipitate formed is filtered, washed twice with methanol (2*100 ml) and water (2*200 ml). The presscake is then dried in the oven or may be optionally recrystallized. For diacyl chloride compounds, two equivalents of triethylamine and TAD are used per chlorine atom.

The mass spectrometry and the elementary analysis are indicated in Table 1 below.

10 Table 1

Component	Acyl chloride	MS. m/z	Elementary Analysis
B1	3-methoxy benzoyl chloride	290	C: 70.5 (th:70.31), H: 9.3 (th:9.02), N: 9.2 (th: 9.65)
B2	2,5-dimethoxy benzoyl chloride	320	C: 67.6 (th: 67.47), H: 8.6 (th:8.81), N: 9.0 (th: 8.74)
B3	biphenyl-4-carbonyl chloride	336	C: 78.3 (th:78.53), H: 8.2 (th:8.39), N: 8.1 (th:8.33)
B4	Naphthalene-2-carbonyl chloride	310	C: 76.9 (th: 77.38), H: 8.2 (th: 8.44), N: 9.1 (th:9.02)
B5	2-methyl benzoyl chloride	274	C: 74.5 (th:74.41), H:9.6 (th: 9.55), N: 10.4 (th: 10.21)
B6	4-Methoxy Benzoyl chloride	290	C: 70.5 (th:70.31), H: 9.2 (th: 9.02), N: 10.0 (th: 9.65)
B7	2,4-dichloro-benzoyl chloride	329	C: 58.2 (th:58.36), H: 6.9 (th:6.73), N: 9.0 (th: 8.51)
B8	2,4,6--trimethylphenylacetyl chloride	316	C: 76.2 (th:75.90), H: 10.3 (th: 10.19), N: 9.0 (th: 8.85)
B9	2,5-dimethylphenylacetyl chloride	302	C: 75.8 (th:75.45), H: 10.2 (th:10.00), N: 9.1 (th: 9.26)
B10	4-chloro-benzoyl chloride	294	C: 64.7 (th: 65.18), H: 7.5 (th:7.86), N: 9.1 (th:9.50)

B11	Cinnamoyl chloride	286	C: 75.7 (th: 75.48), H: 9.4 (th: 9.15), N: 9.6 (th:9.78)
B12	2-naphthoyl-benzoyl chloride	414	C: 78.5 (th: 78.2), H: 7.6 (th: 7.29), N: 7.0 (th:6.76)
B13	2-Oxo-2,3-dihydro-1H- benzimidazole-5- carbonyl	316	C: 65.2 (th: 64.5), H: 8.0 (th: 7.65), N: 17.5 (th:17.7)

Measurement method for oxygen scavenging activity

In case of bottles:

For a typical carbonated beverage shelf-life test, a 500 ml bottle is (i) filled with deoxygenated water up to a headspace of 10 ml, inside a nitrogen circulation glove box where the oxygen level of the water inside the bottle was stabilized at a level well below 50 ppb, (ii) carbonated with CO₂ to a carbonation level of 2.8 volumes (i.e. the amount of gas dissolved in every cm³ of water is of 2.8 cm³) and then capped. Measurement of the oxygen level in the free headspace of the bottle is then carried out using a non-invasive oxygen measurement sensor and a Fibox[®] transmitter. Data are collected in parallel for at least two sample bottles of the same composition, at regular time intervals. For each sample bottle, the oxygen ingress at a certain time is calculated as the difference between the oxygen content measured at that time and the level of oxygen measured at time 0. The oxygen ingress is then averaged over the number of sample bottles measured for each composition and plotted against time. Due to the sensitivity of the Fibox[®] method, measurements are stopped when oxygen ingress increases above 2 ppm.

In case of films:

A proprietary steel cell with an open surface of 20x20 cm² is used to simulate the conditions of a typical tray for food stuff. The cell is prepared within a nitrogen circulation glove box, covered by a barrier film and sealed at the edges via a steel frame. Measurement of the oxygen level in the free headspace of the cell is then carried out using a non-invasive oxygen measurement sensor and a Fibox[®] transmitter. Data are collected at regular time intervals. For each sample, the oxygen ingress at a certain time is calculated as the difference between the

oxygen content measured at that time and the level of oxygen measured at time 0. The oxygen ingress is then plotted against time.

Haze measurement:

- 5 Values of haze are determined on the sidewall of stretch blow molded bottles in accordance with ASTM D1003, Procedure A (% of transmitted light which, in passing through a specimen, deviates from the incident beam by forward scattering)

$$\% \text{Haze} = (T_{\text{diffuse}} / T_{\text{total}}) * 100$$

- 10 where T = % transmission.

Bottles were manufactured as described below and the haze of the bottle walls was measured with a hazemeter haze-gard dual (BYK Gardner). D65 illuminant was used with a CIE 1964 10° standard observer. The haze is defined as the percent of the CIE Y diffuse transmittance to the CIE Y total transmission.

15

Examples

% by weight mentioned in the following examples are based on the total weight of the mixture, composition or article; parts are parts by weight;

20

“ex” means example; “cpex” means comparative example; MB means masterbatch; CO means compound; unless indicated otherwise.

Substances used

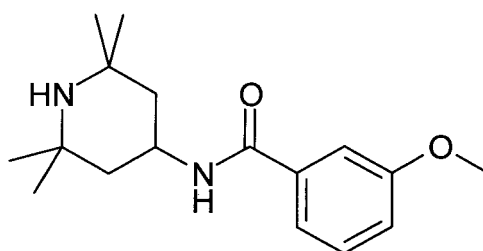
- 25 Component A1:

Polyethylene terephthalate (PET) having a density from 1.35 to 1.45 g/cm³ and intrinsic viscosity from 0.74 to 0.78 dl/g (ASTM D3236-88).

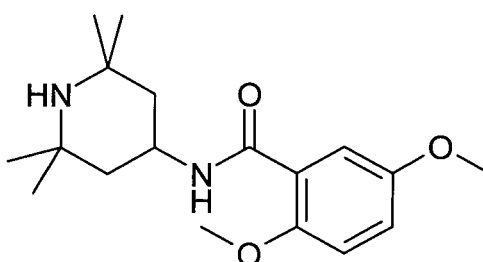
Component A2:

- 30 Polybutylene terephthalate (PBT) having a density from 1.28 to 1.32 g/cm³ and intrinsic viscosity from 0.90 to 1.00 dl/g (ASTM D3236-88).

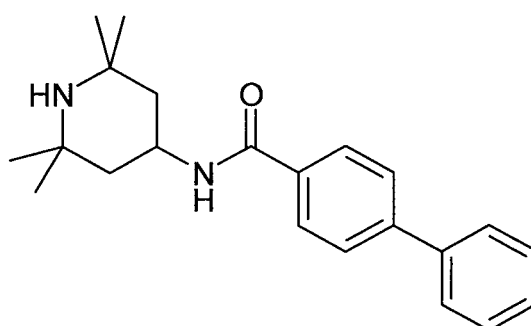
Component B1:



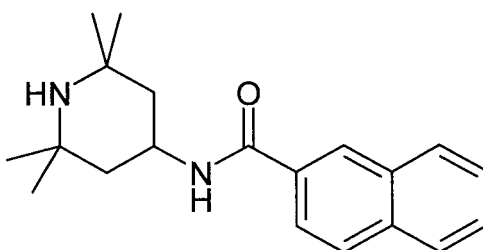
Component B2:



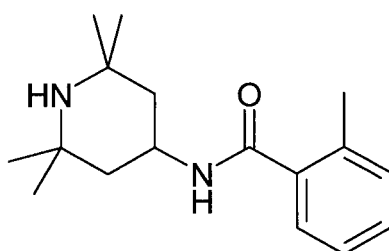
5 Component B3:



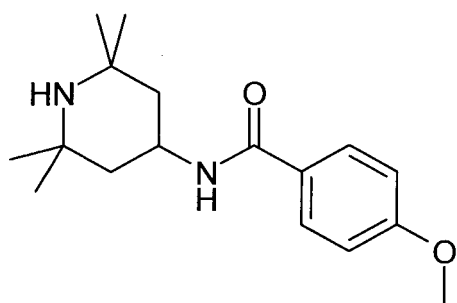
Component B4:



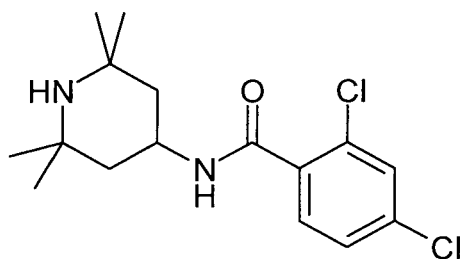
Component B5:



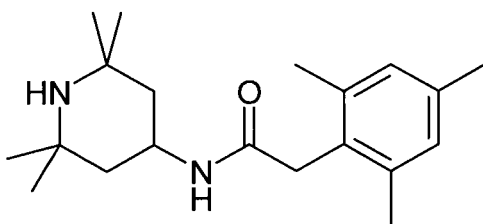
Component B6:



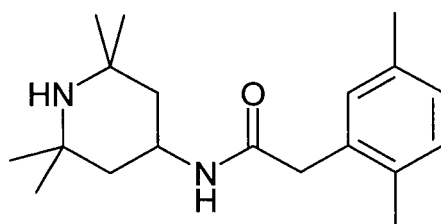
Component B7:



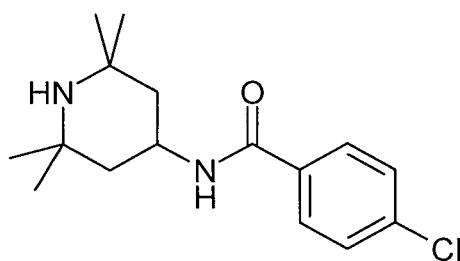
5 Component B8:



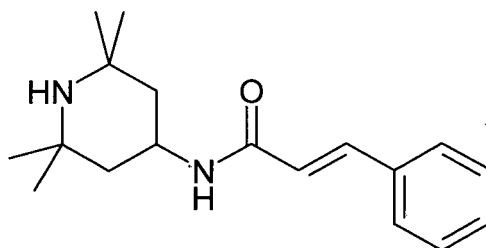
Component B9:



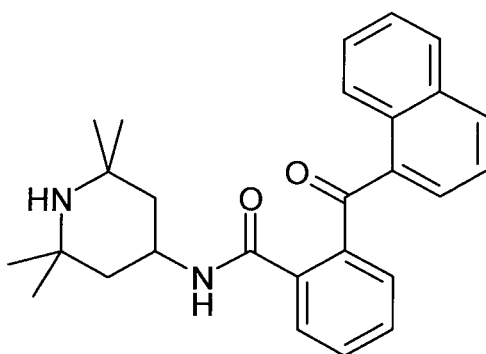
Component B10:



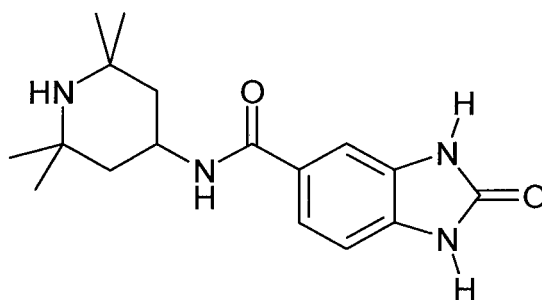
Component B11:



Component B12:



5 Component B13:



Component C1:

Cobalt stearate (9.5 % Cobalt concentration).

10

Component D1:

Poly(m-xylylene adipamide) (MXD6) having a density from 1.20 to 1.30 g/cm³ and MFR of 2 g/10 min (measured at 275 °C/0.325 kg).

15 Component D2:

Comparative product: Amosorb® 4020E polyester resin (ColorMatrix, US), which is a PET copolymer containing polybutadiene segments and a cobalt salt to give elemental cobalt level of 50 ppm.

Masterbatches MB1 to MB13

Component A1 was dried at 160 °C for 7 hrs and then the other components were homogenized and mixed in the ratios according to Table 2. The components were

5 homogenized together on a Leistritz® ZSE18HP extruder at a temperature of 230 °C to obtain solid masterbatches MB1 to MB13.

Table 2

	A1	B1	B2	B3	B4	B5	B6	B7	B8	B9	B10	B11	B12	C1	D1	D2
MB1	95	4												1		
MB2	95		4											1		
MB3	95			4										1		
MB4	95				4									1		
MB5	95					4								1		
MB6	95						4							1		
MB7	95							4						1		
MB8	95								4					1		
MB9	95									4				1		
MB10	95										4			1		
MB11	95											4		1		
MB12	95												4	1		
MB13 (comp)														8	92	

10 ex1 to ex3 and cpex1 to cpex3:

Component A1 was dried at 160 °C for 7 hrs and then the other components were homogenized and mixed in the ratios according to Table 3.

15 The obtained Compounds CO1 to CO6 were used to manufacture 500 ml bottles via a two-step ISBM process. 23 gram preforms were firstly prepared on an

injection molding machine Arburg® 420C 1000-150 and then cooled to room temperature prior to the stretch blow molding step on a Sidel® SBO-1.

5 As an example of operational mode, preforms were obtained via injection molding by using the Arburg® 420C 1000-150 by inserting the component A1, pre-dried for 6 hours at 160 °C, into the main hopper of the machine, and by adding the other components (MB1 to MB13 or D2) through dosing units applied to the main stream of component A1 before entering the injection unit barrel. Barrel temperatures can be kept at temperatures between 270 and 295 °C; cycle time can vary between 10 14 and 16 seconds.

The weight of the preforms is chosen accordingly to the standard preforms found in the market, and can be set e.g. at 23 g per preform. The mould can be cooled by using water at e.g. 8 °C. Once extracted from the mould, preforms can be 15 collected in order to be successively blown by using a Sidel® SBO-1 blow forming unit. This unit, equipped e.g. with a mould for 500 ml (nominal capacity) bottle, comprises a heating zone where preforms are heated at temperatures variable with the design of the preform and of the final bottle; the final temperature of the preforms is kept between 105 and 110 °C; preforms are then inserted in the bottle 20 moulds and blown by injecting dry air or nitrogen with a profile of pressure reaching 35-40 bar at its maximum, the blowing process requiring 2 to 3 seconds time. The average production rate was 900 bottles per hour.

25 Blown bottles are then collected from the blowing unit for the necessary testing.

CO5 consists of a transition metal-based polyester/polyamide composition, prepared according to the state of the art and thus, not comprising component B.

30 CO6 consists of a composition formulated with Amosorb® resin, not comprising component B.

Table 3

ex-cpex	Compounds	Components used [parts]					
		A1	MB1	MB4	MB11	MB13	D2
cpex 1	CO1 (virgin PET)	100					
ex1	CO2	85	15				
ex2	CO3	85		15			
ex3	CO4	85			15		
cpex2	CO5	95				5	
cpex3	CO6	98					2

Total haze is the preferred method of measuring the clarity of polyester articles, which can determine its suitability for packaging application as clear barrier compositions. Haze was measured on polyester bottles obtained from compounds CO1 to CO6 as described above. Table 4 gives the details.

Compositions CO2 to CO4 of the present invention clearly show a significant improvement in clarity compared to the state-of-the-art compositions CO5 and CO6 not comprising component B. The level of clarity from inventive compositions is very similar to the virgin PET in CO1 (Haze: 1.5%).

Table 4

compound	CO1	CO2	CO3	CO4	CO5	CO6
Haze (%)	1.5	1.9	1.8	1.9	9.5	8

The oxygen scavenging activity corresponding to bottles prepared with compounds CO1 to CO6 was then measured by following the method described above. In table 5, the ingress of oxygen (in ppm) measured for compositions CO1 to CO6 is reported against the time elapsed from the filling of the container

(measured in days). Inventive compositions CO2 to CO4 show an oxygen uptake well below 1 ppm after 120 days of measurement.

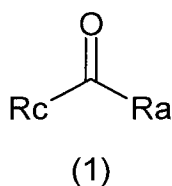
Table 5

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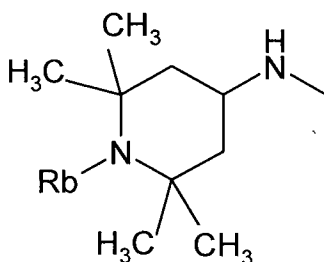
Time [days]	Ingress of oxygen [ppm]				
	CO1	CO2	CO3	CO4	CO6
0	0	0	0	0	0
26	1.50	0.70	0.76	0.80	0
35	2.00	0.70	0.80	0.83	0.03
68		0.76	0.78	0.8	0.65
89		0.73	0.72	0.78	1.7
120		0.65	0.61	0.76	2.3

Patent Claims

1. Use of an additive as oxygen scavenger in a plastic material, wherein:
- (a) the plastic material is a polyester, a polyolefin, a polyolefin copolymer or a polystyrene, and the additive is (b) and optionally (c):
- (b) a compound of formula (1),



wherein Ra represents a group of formula (A),



Formula (A)

wherein Rb is selected from the group consisting of hydrogen, C₁-C₆ alkyl, C₁-C₆ alkoxy and -CO-C₁-C₄ alkyl;

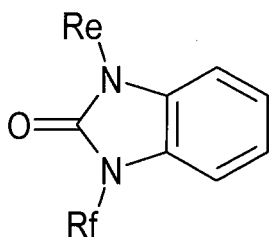
Rc represents C₇-C₂₀ alkyl, C₆-C₁₀ aryl, C₄-C₁₀ heteroaryl, wherein the heteroatoms are N, O and/or S, (C₂-C₆)-alkenylen-(C₆-C₁₀) aryl, C₁-C₆-alkylen-C₆-C₁₀-aryl, the aryl and heteroaryl radicals optionally being substituted by hydroxyl, C₁-C₆-alkyl, C₁-C₆ alkoxy, C₆-C₁₀ aryloxy, halogen, cyano, nitro, C₆-C₁₀-aryl, di(C₁-C₆)alkylamino, (C₁-C₆)alkylthio, C₆-C₁₀-arylthio, SO₃H, SO₂NR⁹R¹⁰, CO₂R¹¹, CONR⁹R¹⁰, NHCOR¹² or CO-C₆-C₁₀-aryl,

wherein R^9 , R^{10} , R^{11} , R^{12} are the same or different and independently represent hydrogen or C_1 - C_6 -alkyl;

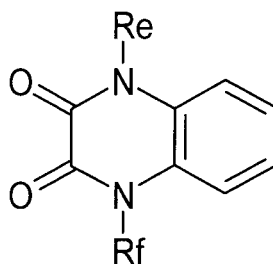
(c) a transition metal catalyst.

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2. The use as claimed in claim 1 wherein R_c represents phenyl, naphthyl, a heteroaryl of formula (B) or formula (C)



Formula (B)



Formula (C)

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wherein R_e and R_f are independently of each other hydrogen, C_1 - C_{20} alkyl or phenyl;

or R_c represents (C_2 - C_4) alkenylen (C_6 - C_{10}) aryl, C_1 - C_4 -alkylen- C_6 - C_{10} -aryl, the aryl and heteroaryl radicals optionally being substituted by hydroxyl, C_1 - C_4 -alkyl, C_1 - C_4 alkoxy, C_6 - C_{10} aryloxy, Cl, cyano, C_6 - C_{10} -aryl, or CO - C_6 - C_{10} -aryl.

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3. The use as claimed in claims 1 or 2, wherein R_c represents phenyl, naphthyl, a heteroaryl of formula (B) as defined in claim 2, wherein R_e and R_f are independently of each other hydrogen or C_1 - C_2 alkyl;

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or R_c represents C_2 - alkenylen (C_6 - C_{10}) aryl, C_1 - C_2 -alkylen- C_6 - C_{10} -aryl, the aryl and heteroaryl radicals optionally being substituted by hydroxyl, methyl, methoxy, C_6 - C_{10} aryloxy, Cl, C_6 - C_{10} -aryl, or CO - C_6 - C_{10} -aryl.

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4. The use as claimed in at least one of claims 1 to 3, wherein the transition metal catalyst is in the form of a transition metal salt with the metal selected from the first, second or third transition series of the Periodic Table.

5. The use as claimed in claim 4, wherein the metal is selected from the group consisting of manganese II, manganese III, iron II, iron III, cobalt II, cobalt III, nickel II, nickel III, copper I, copper II, rhodium II, rhodium III, rhodium IV, ruthenium I, ruthenium II and ruthenium IV.

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6. The use as claimed in anyone of claims 1 to 5 wherein the plastic material is or is part of a packaging article.

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7. The use as claimed in claim 6 wherein the packaging article is a container, a film or a sheet.

8. The use as claimed in anyone of claims 1 to 7 wherein the additive (b) is used in an amount of from 0.001 to 5 % by weight, based on the total weight of the plastic material and the additive(s).

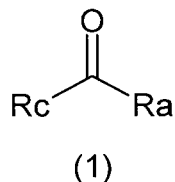
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9. The use as claimed in anyone of claims 1 to 8 wherein the transition metal catalyst (c) is used in an amount of from 0 to 1 %, preferably 0.001 to 1 %, more preferably 0.01 to 0.5 %, by weight, based on the total weight of the plastic material and the additive(s).

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10. A composition Z comprising the components A, B, and C,
- the component A being a plastic material selected from the group consisting of polyesters, polyolefins, polyolefin copolymers and polystyrenes;
 - the component B being an additive represented by the formula (1),

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wherein Ra and Rc are as defined in anyone of claims 1 to 3; and

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- the component C being a transition metal catalyst.

11. The composition as claimed in claim 10 further comprising component D, which is selected from the group consisting of aliphatic polyamides and partially aromatic polyamides.

- 5 12. The composition as claimed in claims 10 or 11, containing
of from 14 to 99.887 % by weight of component A;
of from 0.01 to 70 % by weight of component B;
of from 0.003 to 15 % by weight of component C;
of from 0 to 80 % by weight of components D;
10 with the % by weight being based in each case on the total weight of the
composition Z; and with the weight percent of the components A, B, C and
optionally D always adding up to 100 %.

13. The composition as claimed in anyone of claims 10 to 12 which is a
15 masterbatch MB or a compound CO.