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(54) Title: THERMOPLASTIC POLYAMIDE COMPOSITION

(57) Abstract: Disclosed is a thermoplastic polyamide composition including a) a polyamide resin; b) one or more polyhydric alcohols; c) one or more anti-whitening agents selected from the group consisting of poly(ethylene glycol), poly(ethylene glycol) diesters, po!y(propylene glycol), poly(propylene glycol) diesters; and styrene-isoprene-styrene block copolymers; and mixtures of these; d) a lubricant; e) one or more reinforcement agents; and, optionally, f) a polymeric toughener comprising a reactive functional group and/or a metal salt of a carboxylic acid.

Thermoplastic Polyamide Composition

FIELD OF THE INVENTION

The present invention relates to the field of molded and extruded thermoplastic polyamide articles having improved aging characteristics.

BACKGROUND OF THE INVENTION

High temperature resins based on polyamides possess desirable chemical resistance, processability and heat resistance. This makes them particularly well suited for demanding high performance automotive and electrical/electronics applications. There is a current and general desire in the automotive field to have high temperature resistant structures since temperatures higher than 150°C, even higher than 200°C, are often reached in under-hood areas of automobiles. When plastic parts are exposed to such high temperatures for a prolonged period, such as in automotive under-the-hood applications or in electrical/electronics applications, the mechanical properties generally tend to decrease due to the thermo-oxidation of the polymer. This phenomenon is called heat aging.

In an attempt to improve heat aging characteristics, polyhydric alcohols have been found to give significantly improved heat aging characteristics as disclosed in US patent application publication US 2010-0029819 A1 (Palmer et al). However, molded articles derived from the polyamide compositions comprising the polyhydric alcohols have a tendency to undergo surface whitening upon aging at high humidity; which is an undesirable feature for many applications.

There remains a need for thermoplastic compositions that are suitable for manufacturing articles, that exhibit good mechanical properties after long-term high temperature exposure; and have desirable visual properties; that is, exhibit no whitening or a low degree of whitening, upon aging at high humidity.

EP 1041109 discloses a polyamide composition comprising a polyamide resin, a polyhydric alcohol having a melting point of 150 to 280 °C, that has good fluidity and mechanical strength and is useful in injection welding techniques.

US Patent No. 6,262,221 discloses a polyamide resin comprising a poly(ethylene glycol) diester as a plasticizer.

US 2012/0029133 discloses a polyamide resin comprising a styrene block copolymer as a plasticizer.

[illegible] ent application abstract CN 2011-102000646 discloses a flameproof material comprising a polymer, magnesium hydroxide, triorthocresol phosphate, and a toughener selected from a group including styrene-isoprene-styrene block copolymer.

SUMMARY OF THE INVENTION

Disclosed is a thermoplastic polyamide composition comprising

a. a polyamide resin having a melting point and/or glass transition temperature;

b. 0.1 to 10 weight percent of one or more polyhydric alcohols having more than two hydroxyl groups and having a number average molecular weight (M_n) of less than 2000;

c. 0.5 to 5 weight percent of one or more anti-whitening agents selected from the group consisting of poly(ethylene glycol), poly(ethylene glycol) diesters, poly(propylene glycol), poly(propylene glycol) diesters; and styrene-isoprene-styrene block copolymers; and mixtures of these;

d. 0.02 to 1 weight percent of a lubricant;

e. 10 to 60 weight percent of one or more reinforcement agents; and

f. 0 to 50 weight percent of a polymeric toughener comprising a reactive functional group and/or a metal salt of a carboxylic acid;

with the proviso that the thermoplastic composition comprises less than 15 weight percent magnesium hydroxide and less than 0.20 weight percent zinc compounds selected from the group consisting of zinc borate and zinc oxide; and with the further proviso that at least 2 weight percent of styrene-isoprene-styrene block copolymers are present when no other anti-whitening agents selected from the group are present; and wherein all weight percentages are based on the total weight of the polyamide composition.

Also disclosed are molded or extruded articles made from the thermoplastic polyamide composition disclosed above.

DETAILED DESCRIPTION OF THE INVENTION

Herein melting points and glass transitions are as determined with differential scanning calorimetry (DSC) at a scan rate of 10 °C/min in the first heating scan, wherein the melting point is taken at the maximum of the endothermic peak and the glass transition, if evident, is considered the mid-point of the change in enthalpy.

For the purposes of the description, unless otherwise specified, "high-temperature" means a temperature at or higher than 170 °C, preferably at or higher than 210 °C, and most preferably at or higher than 230 °C.

In the present invention, unless otherwise specified, "long-term" refers to an aging period equal or longer than 500 hrs.

As used herein, the term "high heat stability", as applied to the polyamide composition disclosed herein or to an article made from the composition, refers to the retention of physical properties (for instance, tensile strength) of 2 mm thick molded test bars consisting of the polyamide composition that are exposed to air oven aging (AOA) conditions at a test temperature at 210 °C or 230 °C for a test period of at least 500 h, in an atmosphere of air, and then tested according to ISO 527-2/1BA method. The physical properties of the test bars are compared to that of unexposed controls that have identical composition and shape, and are expressed in terms of "% retention". In a preferred embodiment the test temperature is at 210 °C, the test period is at 500 hours and the exposed test bars have a % retention of tensile strength of at least 50 %. Herein "high heat stability" means that said molded test bars, on average, meet or exceed a retention for tensile strength of 50 % when exposed at a test temperature at 210 °C for a test period of at least 500 h. Compositions exhibiting a higher retention of physical properties for a given exposure temperature and time period have better heat stability.

The terms "at 170 °C," "at 210 °C" and "at 230 °C" refer to the nominal temperature of the environment to which the test bars are exposed; with the understanding that the actual temperature may vary by +/- 2 °C from the nominal test temperature.

The thermoplastic polyamide compositions of various embodiments of the invention comprise a polyamide resin. The polyamide resins are condensation products of one or more dicarboxylic acids and one or more diamines, and/or one or more aminocarboxylic acids, and/or ring-opening polymerization products of one or more cyclic lactams. Suitable cyclic lactams are caprolactam and laurolactam. Polyamides may be fully aliphatic or semi-aromatic.

Fully aliphatic polyamides are formed from aliphatic and alicyclic monomers such as diamines, dicarboxylic acids, lactams, aminocarboxylic acids, and their reactive equivalents. A suitable aminocarboxylic acid is 11-aminododecanoic acid.

[illegible] caprolactam and laurolactam. In the context of this invention, the term "fully aliphatic polyamide" also refers to copolymers derived from two or more such monomers and blends of two or more fully aliphatic polyamides. Linear, branched, and cyclic monomers may be used.

Carboxylic acid monomers comprised in the fully aliphatic polyamides include, but are not limited to aliphatic carboxylic acids, such as for example adipic acid (C6), pimelic acid (C7), suberic acid (C8), azelaic acid (C9), decanedioic acid (C10), dodecanedioic acid (C12), tridecanedioic acid (C13), tetradecanedioic acid (C14), pentadecanedioic acid (C15), hexadecanedioic acid (C16) and octadecanedioic acid (C18). Diamines can be chosen among diamines having four or more carbon atoms, including, but not limited to tetramethylene diamine, hexamethylene diamine, octamethylene diamine, decamethylene diamine, dodecamethylene diamine, 2-methylpentamethylene diamine, 2-ethyltetramethylene diamine, 2-methyloctamethylenediamine; trimethylhexamethylenediamine, meta-xylylene diamine, and/or mixtures thereof.

The semi-aromatic polyamide is a homopolymer, a copolymer, a terpolymer or more advanced polymers formed from monomers containing aromatic groups. One or more aromatic carboxylic acids may be terephthalate or a mixture of terephthalate with one or more other carboxylic acids, such as isophthalic acid, phthalic acid, 2-methyl terephthalic acid and naphthalic acid. In addition, the one or more aromatic carboxylic acids may be mixed with one or more aliphatic dicarboxylic acids, as disclosed above. Alternatively, an aromatic diamine such as meta-xylylene diamine (MXD) can be used to provide a semi-aromatic polyamide, an example of which is MXD6, a homopolymer comprising MXD and adipic acid.

Preferred polyamides disclosed herein are homopolymers or copolymers wherein the term copolymer refers to polyamides that have two or more amide and/or diamide molecular repeat units. The homopolymers and copolymers are identified by their respective repeat units. For copolymers disclosed herein, the repeat units are listed in decreasing order of mole % repeat units present in the copolymer. The following list exemplifies the abbreviations used to identify monomers and repeat units in the homopolymer and copolymer polyamides (PA):

HMD	hexamethylene diamine (or 6 when used in combination with a diacid)
T	Terephthalic acid
AA	Adipic acid

[illegible]	[illegible]nethylenediamine
6	€-Caprolactam
DDA	Decanedioic acid
DDDA	Dodecanedioic acid
TDDA	Tetradecanedioic acid
HDDA	Hexadecanedioic acid
ODDA	Octadecanedioic acid
I	Isophthalic acid
MXD	meta-xylylene diamine
TMD	1,4-tetramethylene diamine
4T	polymer repeat unit formed from TMD and T
6T	polymer repeat unit formed from HMD and T
DT	polymer repeat unit formed from 2-MPMD and T
MXD6	polymer repeat unit formed from MXD and AA
66	polymer repeat unit formed from HMD and AA
10T	polymer repeat unit formed from DMD and T
410	polymer repeat unit formed from TMD and DDA
510	polymer repeat unit formed from 1,5-pentanediamine and DDA
610	polymer repeat unit formed from HMD and DDA
612	polymer repeat unit formed from HMD and DDDA
614	polymer repeat unit formed from HMD and TDDA
616	polymer repeat unit formed from HMD and HDDA
618	polymer repeat unit formed from HMD and ODDA
6	polymer repeat unit formed from €-caprolactam
11	polymer repeat unit formed from 11-aminoundecanoic acid
12	polymer repeat unit formed from 12-aminododecanoic acid

Note that in the art the term "6" when used alone designates a polymer repeat unit formed from €-caprolactam. Alternatively "6" when used in combination with a diacid such as T, for instance 6T, the "6" refers to HMD. In repeat units comprising a diamine and diacid, the diamine is designated first. Furthermore, when "6" is used in combination with a diamine, for instance 66, the first "6" refers to the diamine HMD, and the second "6" refers to adipic acid. Likewise, repeat units derived from other amino acids or lactams are designated as single numbers designating the number of carbon atoms.

[illegible]diment the polyamide composition comprises a one or more polyamides selected from the group consisting of

Group (I) polyamides having a melting point of less than 210 °C, and comprising an aliphatic or semiaromatic polyamide selected from the group consisting of poly(pentamethylene decanediamide) (PA510), poly(pentamethylene dodecanediamide) (PA512), poly(ε-caprolactam/hexamethylene hexanediamide) (PA6/66), poly(ε-caprolactam/hexamethylene decanediamide) (PA6/610), poly(ε-caprolactam/hexamethylene dodecanediamide) (PA6/612), poly(hexamethylene tridecanediamide) (PA613), poly(hexamethylene pentadecanediamide) (PA615), poly(ε-caprolactam/tetramethylene terephthalamide) (PA6/4T), poly(ε-caprolactam/hexamethylene terephthalamide) (PA6/6T), poly(ε-caprolactam/decamethylene terephthalamide) (PA6/10T), poly(ε-caprolactam/dodecamethylene terephthalamide) (PA6/12T), poly(hexamethylene decanediamide/hexamethylene terephthalamide) (PA610/6T), poly(hexamethylene dodecanediamide/hexamethylene terephthalamide) (PA612/6T), poly(hexamethylene tetradecanediamide/hexamethylene terephthalamide) (PA614/6T), poly(ε-caprolactam/ hexamethylene isophthalamide/hexamethylene terephthalamide) (PA6/6I/6T), poly(ε-caprolactam/hexamethylene hexanediamide/hexamethylene decanediamide) (PA6/66/610), poly(ε-caprolactam/hexamethylene hexanediamide/hexamethylene dodecanediamide) (PA6/66/612), poly(ε-caprolactam/hexamethylene hexanediamide/hexamethylene decanediamide/hexamethylene dodecanediamide) (PA6/66/610/612), poly(2-methylpentamethylene hexanediamide/hexamethylene hexanediamide/hexamethylene terephthamide) (PA D6/66/6T), poly(2-methylpentamethylene hexanediamide/hexamethylene hexanediamide/) (PA D6/66), poly(decamethylene decanediamide) (PA1010), poly(decamethylene dodecanediamide) (PA1012), poly(decamethylene decanediamide/decamethylene terephthalamide) (PA1010/10T) poly(decamethylene decanediamide/dodecamethylene decanediamide/ decamethylene terephthalamide/dodecamethylene terephthalamide (PA1010/1210/10T/12T), poly(11-aminoundecanamide) (PA11), poly(11-aminoundecanamide/tetramethylene terephthalamide) (PA11/4T), poly(11-aminoundecanamide/hexamethylene terephthalamide) (PA11/ 6T), poly(11-aminoundecanamide/decamethylene terephthalamide) (PA11/10T), poly(11-aminoundecanamide/dodecamethylene [illegible], (PA11/12T), poly(12-aminododecanamide) (PA12), poly(12-aminododecanamide/tetramethylene terephthalamide) (PA12/4T), poly(12-aminododecanamide/hexamethylene terephthalamide) (PA12/6T), poly(12-aminododecanamide/decamethylene terephthalamide) (PA12/10T) poly(dodecamethylene dodecanediamide) (PA1212), poly(dodecamethylene dodecanediamide/dodecamethylene dodecanediamide/dodecamethylene terephthalamide)) (PA1212/12T), poly(hexamethylene hexadecanediamide) (PA616), and poly(hexamethylene octadecanediamide) (PA618); **Group (II) polyamides** having a melting point of at least 210 °C, and comprising an aliphatic polyamide selected from the group consisting of poly(tetramethylene hexanediamide) (PA46), poly(ε-caprolactam) (PA 6), poly(hexamethylene hexanediamide/(ε-caprolactam/) (PA 66/6) poly(hexamethylene hexanediamide) (PA 66), poly(hexamethylene hexanediamide/hexamethylene decanediamide) (PA66/610), poly(hexamethylene hexanediamide/hexamethylene dodecanediamide) (PA66/612), poly(hexamethylene hexanediamide/decamethylene decanediamide) (PA66/1010), poly(hexamethylene decanediamide) (PA610), poly(hexamethylene dodecanediamide) (PA612), poly(hexamethylene tetradecanediamide) (PA614), and poly(tetramethylene hexanediamide/2-methylpentamethylene hexanediamide) (PA46/D6);

Group (III) polyamides having a melting point of at least 210 °C, and comprising

(aa) about 20 to about 35 mole percent semiaromatic repeat units derived from monomers selected from one or more of the group consisting of:

(i) aromatic dicarboxylic acids having 8 to 20 carbon atoms and aliphatic diamines having 4 to 20 carbon atoms; and

(bb) about 65 to about 80 mole percent aliphatic repeat units derived from monomers selected from one or more of the group consisting of:

(ii) an aliphatic dicarboxylic acid having 6 to 20 carbon atoms and said aliphatic diamine having 4 to 20 carbon atoms; and

(iii) a lactam and/or aminocarboxylic acid having 4 to 20 carbon atoms;

Group (IV) polyamides comprising

(cc) about 50 to about 95 mole percent semiaromatic repeat units derived from monomers selected from one or more of the group consisting of:

(i) aromatic dicarboxylic acids having 8 to 20 carbon atoms and aliphatic diamines having 4 to 20 carbon atoms; and [illegible] [illegible] 5 to about 50 mole percent aliphatic repeat units derived from monomers selected from one or more of the group consisting of:

(ii) an aliphatic dicarboxylic acid having 6 to 20 carbon atoms and said aliphatic diamine having 4 to 20 carbon atoms; and

(iii) a lactam and/or aminocarboxylic acid having 4 to 20 carbon atoms;

Group (V) polyamides having a melting point of at least 260 °C, comprising

(ee) greater than 95 mole percent semiaromatic repeat units derived from monomers selected from one or more of the group consisting of:

(i) aromatic dicarboxylic acids having 8 to 20 carbon atoms and aliphatic diamines having 4 to 20 carbon atoms; and

(ff) less than 5 mole percent aliphatic repeat units derived from monomers selected from one or more of the group consisting of:

(ii) an aliphatic dicarboxylic acid having 6 to 20 carbon atoms and said aliphatic diamine having 4 to 20 carbon atoms;

(iii) a lactam and/or aminocarboxylic acid having 4 to 20 carbon atoms; and

Group (VI) polyamides having no melting point, and selected from the group consisting of poly(hexamethylene isophthalamide/ hexamethylene terephthalamide) (6I/6T) and poly(hexamethylene isophthalamide/hexamethylene terephthalamide/hexamethylene hexanediamide) (6I/6T/66).

Group (I) polyamides may have semiaromatic repeat units to the extent that the melting point is less than 210 °C and generally the semiaromatic polyamides of the group have less than 40 mole percent semiaromatic repeat units. Semiaromatic repeat units are defined as those derived from monomers selected from one or more of the group consisting of: aromatic dicarboxylic acids having 8 to 20 carbon atoms and aliphatic diamines having 4 to 20 carbon atoms.

Another embodiment is a molded or extruded thermoplastic article wherein said polyamide resin is selected from Group (III) polyamides selected from the group consisting of poly(tetramethylene hexanediamide/tetramethylene terephthalamide) (PA46/4T), poly(tetramethylene hexanediamide/hexamethylene terephthalamide) (PA46/6T), poly(tetramethylene hexanediamide/2-methylpentamethylene hexanediamide/decamethylene terephthalamide)_PA46/D6/10T), poly(hexamethylene hexanediamide/hexamethylene terephthalamide) (PA66/6T), poly(hexamethylene hexanediamide/hexamethylene isophthalamide/hexamethylene terephthalamide PA66/6I/6T, and poly(hexamethylene hexanediamide/2-

ene hexanediamide /hexamethylene terephthalamide (PA66/D6/6T); and a most preferred Group (III) polyamide is PA 66/6T.

Another embodiment is a molded or extruded thermoplastic article wherein said polyamide resin is selected from Group (IV) polyamides selected from the group consisting of poly(tetramethylene terephthalamide/hexamethylene hexanediamide) (PA4T/66), poly(tetramethylene terephthalamide/ε-caprolactam) (PA4T/6), poly(tetramethylene terephthalamide/hexamethylene dodecanediamide) (PA4T/612), poly(tetramethylene terephthalamide/2-methylpentamethylene hexanediamide/hexamethylene hexanediamide) (PA4T/D6/66), poly(hexamethylene terephthalamide/2-methylpentamethylene terephthalamide/hexamethylene hexanediamide) (PA6T/DT/66), poly(hexamethylene terephthalamide/hexamethylene hexanediamide) PA6T/66, poly(hexamethylene terephthalamide /hexamethylene decanediamide) (PA6T/610), poly(hexamethylene terephthalamide/hexamethylene tetradecanediamide) (PA6T/614), poly(nonamethylene terephthalamide/nonamethylene decanediamide) (PA9T/910), poly(nonamethylene terephthalamide/nonamethylene dodecanediamide) (PA9T/912), poly(nonamethylene terephthalamide/11-aminoundecanamide) (PA9T/11), poly(nonamethylene terephthalamide/12-aminododecanamide) (PA9T/12), poly(decamethylene terephthalamide/11-aminoundecanamide) (PA 10T/11), poly(decamethylene terephthalamide/12-aminododecanamide) (PA10T/12) poly(decamethylene terephthalamide/decamethylene decanediamide) (PA10T/1010), poly(decamethylene terephthalamide/decamethylene dodecanediamide) (PA10T/1012), poly(decamethylene terephthalamide/tetramethylene hexanediamide) (PA10T/46), poly(decamethylene terephthalamide/ε-caprolactam) (PA10T/6), poly(decamethylene terephthalamide/hexamethylene hexanediamide) (PA10T/66), poly(dodecamethylene terephthalamide/dodecamethylene dodecanediamide) (PA12T/1212), poly(dodecamethylene terephthalamide/ε-caprolactam) (PA12T/6), and poly(dodecamethylene terephthalamide/hexamethylene hexanediamide) (PA12T/66); and a most preferred Group (IV) polyamide is PA6T/66.

Another embodiment is a molded or extruded thermoplastic article wherein said polyamide resin is selected from Group (V) polyamides selected from the group consisting of poly(tetramethylene terephthalamide/2-methylpentamethylene terephthalamide) PA4T/DT, poly(tetramethylene terephthalamide/ hexamethylene terephthalamide), PA4T/6T, poly(tetramethylene terephthalamide/decamethylene terephthalamide) PA4T/10T, poly(tetramethylene terephthalamide/dodecamethylene terephthalamide)PA4T/12T, poly(tetramethylene terephthalamide/2-methylpentamethylene terephthalamide/ hexamethylene terephthalamide) (PA4T/DT/6T), poly(tetramethylene terephthalamide/hexamethylene terephthalamide/2-methylpentamethylene terephthalamide) (PA4T/6T/DT), poly(hexamethylene terephthalamide/2-methylpentamethylene terephthalamide) (PA6T/DT), poly(hexamethylene hexanediamide/hexamethylene isophthalamide) (PA 6T/6I), poly(hexamethylene terephthalamide/decamethylene terephthalamide) PA6T/10T, poly(hexamethylene terephthalamide/dodecamethylene terephthalamide) (PA6T/12T), poly(hexamethylene terephthalamide/2-methylpentamethylene terephthalamide/poly(decamethylene terephthalamide) (PA6T/DT/10T), poly(hexamethylene terephthalamide/decamethylene terephthalamide/ dodecamethylene terephthalamide) (PA6T/10T/12T), poly(decamethylene terephthalamide) (PA10T), poly(decamethylene terephthalamide/tetramethylene terephthalamide) (PA10T/4T), poly(decamethylene terephthalamide/2-methylpentamethylene terephthalamide) (PA10T/DT), poly(decamethylene terephthalamide/dodecamethylene terephthalamide) (PA10T/12T), poly(decamethylene terephthalamide/2-methylpentamethylene terephthalamide/(decamethylene terephthalamide) (PA10T/DT/12T). poly(dodecamethylene terephthalamide) (PA12T), poly(dodecamethylene terephthalamide)/tetramethylene terephthalamide) (PA12T/4T), poly(dodecamethylene terephthalamide)/hexamethylene terephthalamide) PA12T/6T, poly(dodecamethylene terephthalamide)/decamethylene terephthalamide) (PA12T/10T), and poly(dodecamethylene terephthalamide)/2-methylpentamethylene terephthalamide) (PA12T/DT); and a most preferred_Group (V) Polyamide is PA6T/DT.

In various embodiments the polyamide is a Group (I) Polyamide, Group (II) Polyamide, Group (III) Polyamide, Group (IV) Polyamide, Group (V) Polyamide or Group (VI) Polyamide, respectively. In one embodiment the polyamide resin is selected from the group consisting of poly(ε-caprolactam), poly(hexamethylene hexanediamide), poly(hexamethylene hexanediamide/hexamethylene [illegible], nd poly(hexamethylene terephthalamide/ hexamethylene hexanediamide).

The polyamides may also be blends of two or more polyamides. Preferred blends include those selected from the group consisting of Group (I) and Group (II) Polyamides; Group (I) and Group (III) Polyamide, Group (I) and Group (VI) Polyamides, Group (II) and Group (III) Polyamides, Group (II) and Group (IV) Polyamides, Group (II) and Group (V) Polyamides, Group (II) and Group (VI) Polyamides, Group (III) and Group (VI) Polyamides, and Group (IV) and Group (V) Polyamides.

A preferred blend includes Group (II) and (V) Polyamides, and a specific preferred blend includes poly(hexamethylene hexanediamide) (PA 66) and poly(hexamethylene terephthalamide/2-methylpentamethylene terephthalamide) (PA 6T/DT).

Another preferred blend includes Group (II) and Group (III) Polyamides and a specific preferred blend includes poly(ε-caprolactam) (PA6) and poly(hexamethylene hexanediamide/hexamethylene terephthalamide (PA66/6T).

In various embodiments 39 to 89.38 weight percent of polyamide resin, or 49 to 89.38 weight percent of polyamide resin, is present in the thermoplastic polyamide composition.

The thermoplastic polyamide composition comprises 0.1 to 10 weight percent of one or more polyhydric alcohols having more than two hydroxyl groups and a number average molecular weight (M_n) of less than 2000, as determined for polymeric materials with gel permeation chromatography (GPC)

Polyhydric alcohols may be selected from aliphatic hydroxylic compounds containing more than two hydroxyl groups, aliphatic-cycloaliphatic compounds containing more than two hydroxyl groups, cycloaliphatic compounds containing more than two hydroxyl groups, and saccharides. An aliphatic chain in the polyhydric alcohol can include not only carbon atoms but also one or more hetero atoms which may be selected, for example, from nitrogen, oxygen and sulpher atoms. A cycloaliphatic ring present in the polyhydric alcohol can be monocyclic or part of a bicyclic or polycyclic ring system and may be carbocyclic or heterocyclic. A heterocyclic ring present in the polyhydric alcohol can be monocyclic or part of a bicyclic or polycyclic ring system and may include one or more hetero atoms which may be selected, for example, from nitrogen, oxygen and sulphur atoms. The one or [illegible] polyhydric alcohols may contain one or more substituents, such as ether, carboxylic acid, carboxylic acid amide or carboxylic acid ester groups.

Examples of polyhydric alcohol containing more than two hydroxyl groups include, without limitation, triols, such as glycerol, trimethylolpropane, 2,3-di-(2'-hydroxyethyl)-cyclohexan-1-ol, hexane-1,2,6-triol, 1,1,1-tris-(hydroxymethyl)ethane, 3-(2'-hydroxyethoxy)-propane-1,2-diol, 3-(2'-hydroxypropoxy)-propane-1,2-diol, 2-(2'-hydroxyethoxy)-hexane-1,2-diol, 6-(2'-hydroxypropoxy)-hexane-1,2-diol, 1,1,1-tris-[(2'-hydroxyethoxy)-methyl]-ethane, 1,1,1-tris-[(2'-hydroxypropoxy)-methyl]-propane, 1,1,1-tris-(4'-hydroxyphenyl)-ethane, 1,1,1-tris-(hydroxyphenyl)-propane, 1,1,3-tris-(dihydroxy-3-methylphenyl)-propane, 1,1,4-tris-(dihydroxyphenyl)-butane, 1,1,5-tris-(hydroxyphenyl)-3-methylpentane, di-trimethylopropane, trimethylolpropane ethoxylates, or trimethylolpropane propoxylates; polyols such as pentaerythritol, dipentaerythritol, and tripentaerythritol; and saccharides, such as cyclodextrin, D-mannose, glucose, galactose, sucrose, fructose, xylose, arabinose, D-mannitol, D-sorbitol, D-or L-arabitol, xylitol, iditol, talitol, allitol, altritol, guilitol, erythritol, threitol, and D-gulonic-y-lactone; and the like.

Preferred polyhydric alcohols include those having a pair of hydroxyl groups which are attached to respective carbon atoms which are separated one from another by at least one atom. Especially preferred polyhydric alcohols are those in which a pair of hydroxyl groups is attached to respective carbon atoms which are separated one from another by a single carbon atom.

Preferably, the polyhydric alcohol used in the thermoplastic composition is pentaerythritol, dipentaerythritol, tripentaerythritol, di-trimethylolpropane, D-mannitol, D-sorbitol and xylitol. More preferably, the polyhydric alcohol used is dipentaerythritol and/or tripentaerythritol. A most preferred polyhydric alcohol is dipentaerythritol.

In various embodiments the content of said polyhydric alcohol in the thermoplastic composition is 0.25-10 weight percent, preferably 0.25-8 weight percent, more preferably 1.0 - 8 weight percent and 1.0 - 5 weight percent, and most preferably 1 - 4 weight percent, based on the total weight of the thermoplastic composition.

The thermoplastic polyamide composition comprises (c) 0.5 to 5 weight percent of one or more anti-whitening agents selected from the group consisting of poly(ethylene glycol), poly(ethylene glycol) diesters, poly(propylene glycol), poly(propylene glycol) diesters; and styrene-isoprene-styrene block copolymers; and with the proviso that at least 2 weight percent of styrene-isoprene-styrene block copolymer is present when no other anti-whitening agents selected from the group are present. The term poly(ethylene glycol) includes materials having M_n of about 400 and higher and includes those materials often referred to as polyethylene oxides having M_n greater than 5,000 and preferably greater than 10,000.

Useful anti-whitening agents for the composition include Plasthall® 809, a polyethylene glycol 400 di-2-ethylhexoate available from C.P. Hall Company; PEG 6000J, a poly(ethylene glycol) manufactured by Lion Corporation, Japan; and Kraton D1116AT, a styrene-butadiene-styrene block copolymer (SBS), available from Kraton Performance Polymers. Herein anti-whitening agents are materials, that when present in the thermoplastic compositions in the presence of lubricants disclosed herein, significantly impede or prevent the whitening of molded or extruded parts upon ageing. Herein ageing is performed at 85 °C and 85 % relative humidity for periods of time, typically 1 day and 7 days. In various embodiments 0.5 to 3.0 weight percent, 0.75 to 3.0 weight percent, and 0.75 to 2.0 weight percent of anti-whitening agent are present in the thermoplastic polyamide composition. In one embodiment the anti-whitening agent is selected from the group consisting of poly(ethylene glycol) diesters and styrene-isoprene-styrene block copolymers. In a preferred embodiment the anti-whitening agent is selected from the group consisting of polyethylene glycol and poly(ethylene glycol) diesters.

The thermoplastic polyamide composition comprises (d) 0.02 to 1 weight percent, and preferably 0.02 to 0.8 weight percent and 0.05 to 0.8 weight percent, of a lubricant. Preferably the lubricant is selected from the group consisting of fatty acids, fatty acid esters, fatty acid amides, fatty acid metal salts (e.g. aluminum stearate), and oxidized polyethylene wax. By "fatty acid" herein means carboxyl groups with the fatty acids, fatty acid esters, fatty acid amides, and fatty acid metal salts have 10, and preferably 12 or 16, or more aliphatic carbon atoms linked in a linear or branched chain. Preferably the term "fatty acid" comprises 10 to 22 carbon atoms in a linear carbon chain. Preferably 0.05 to 0.5, and more preferably 0.05 to 0.25 weight percent of lubricant (d) is present, based on the total weight of the thermoplastic composition.

Examples of fatty acids include stearic acid, oleic acid, erucic acid, and behenic acid.

[illegible] fatty acid esters include pentaerythritol tetrastearate, stearyl stearate, and montanic acid esters.

Examples of fatty acid metal salts include aluminum stearate, sodium montanate, and calcium montanate.

Examples of the fatty acid amide include methylenebisstearylamide, methylenebislaurylamide, ethylenebisstearylamide, ethylenebislaurylamide, methylenebehenylamide, ethylenebisbehenylamide, dioctadecyladipamide, dioctadecylsuccinamide, dihexyladipamide, dihexylsuccinamide, distearyladipamide, distearylsuccinamide, eruccamide, stearylamide, oleamide, oleyl palmitamide, erucyl stearamide, and N-stearylerucamide. N-stearylerucamide is a preferred fatty acid amide compound.

Useful commercial lubricants for the composition include Kemamide E180 lubricant is N-stearylerucamide, CAS No. [10094-45-8], available from Chemtura Corp., Philadelphia, PA; Crodamide® 212 lubricant, a stearyl erucamide available from Croda Chemicals, Hull UK; Licowax OP lubricant manufactured by Clariant Corp., Charlotte, NC; PED 191 lubricant, an oxidized polyethylene wax available from Clariant Corp., Charlotte, NC; Licomont® CaV 102 lubricant, a fine grain calcium montanate available from Clariant Corp.; Hostamont® NAV 101 lubricant, a sodium montanate manufactured by Clariant, Muttenz, Switzerland; aluminum distearate, a wax supplied by PMC Global, Inc. Sun Valley, CA, USA; and Loxiol® VPG 861 lubricant, a pentaerythritol tetrastearate, manufactured by Cognis, Dusseldorf, Germany; Vestowax AO1535 lubricant, available from Evonik Industries, Germany; Acrawax® C lubricant, and N,N'-ethylene bisstearamide from Lonza Chemical Co.

The thermoplastic polyamide composition comprises 10 to about 60 weight percent, and preferably about 12.5 to 55 weight percent and 15 to 50 weight percent, of one or more reinforcement agents. The reinforcement agent may be any filler with the proviso that the thermoplastic composition comprises less than 15 weight percent magnesium hydroxide and preferably less than 10 weight percent, and more preferably less than 1 weight percent magnesium hydroxide. The reinforcement agent is preferably selected from the group consisting calcium carbonate, glass fibers with circular and noncircular cross-section, glass flakes, glass beads, carbon fibers, talc, mica, wollastonite, calcined clay, kaolin, diatomite, magnesium sulfate, [illegible], barium sulfate, titanium dioxide, sodium aluminum carbonate, barium ferrite, potassium titanate and mixtures thereof. In preferred embodiments the reinforcing agent is selected from the group consisting of glass fiber and glass fiber with noncircular cross-section. The glass fiber may have sizing or coupling agents, organic or inorganic materials that improve the bonding between glass and the polyamide resin.

Glass fibers with noncircular cross-section refer to glass fiber having a cross section having a major axis lying perpendicular to a longitudinal direction of the glass fiber and corresponding to the longest linear distance in the cross section. The non-circular cross section has a minor axis corresponding to the longest linear distance in the cross section in a direction perpendicular to the major axis. The non-circular cross section of the fiber may have a variety of shapes including a cocoon-type (figure-eight) shape, a rectangular shape; an elliptical shape; a roughly triangular shape; a polygonal shape; and an oblong shape. As will be understood by those skilled in the art, the cross section may have other shapes. The ratio of the length of the major axis to that of the minor access is preferably between about 1.5:1 and about 6:1. The ratio is more preferably between about 2:1 and 5:1 and yet more preferably between about 3:1 to about 4:1. Suitable glass fiber are disclosed in EP 0 190 001 and EP 0 196 194.

The thermoplastic polyamide composition, optionally, comprises 0 to 50 weight percent of a polymeric toughener comprising a reactive functional group and/or a metal salt of a carboxylic acid. In one embodiment the composition comprises 2 to 20 weight percent polymeric toughener selected from the group consisting of: a copolymer of ethylene, glycidyl (meth)acrylate, and optionally one or more (meth)acrylate esters; an ethylene/α-olefin or ethylene/α-olefin/diene copolymer grafted with an unsaturated carboxylic anhydride; a copolymer of ethylene, 2-isocyanatoethyl (meth)acrylate, and optionally one or more (meth)acrylate esters; and a copolymer of ethylene and acrylic acid reacted with a Na, Li, or Mn compound to form the corresponding ionomer.

The thermoplastic composition of the present invention may also comprise other additives commonly used in the art, such other heat stabilizers or antioxidants referred to as “co-stabilizers”, antistatic agents, blowing agents, and colorant and pigments. In one embodiment 0.1 to 3.0 weight percent of one or more colorants is present, wherein the weight percent colorant includes the weight of the carrier colorant. In one embodiment the colorant is selected from the group of carbon black and nigrosine black pigment.

The thermoplastic polyamide of the present invention may further comprise halogenated flame retardants, preferably in the range of 2 to 30 weight percent based on the total weight of the polyamide composition. A preferred halogenated flame retardant is brominated polystyrene.

The thermoplastic polyamide composition consists of less than 15 weight percent, preferably less than 10 weight percent magnesium hydroxide; and less than 0.20 weight percent, preferably less than 0.10 weight percent, of zinc compounds selected from the group consisting of zinc borate and zinc oxide.

Co-stabilizers include copper stabilizers, secondary aryl amines, hindered amine light stabilizers (HALS), hindered phenols, and mixtures thereof, that are disclosed in US patent application publication 2010/0029819, Palmer et al, herein incorporated by reference.

Molded parts comprising the thermoplastic polyamide composition herein disclosed exhibit no whitening or only low levels of whitening upon ageing. For instance, molded parts, aged in an environmental chamber under conditions of 85% relative humidity and 85 °C for one to seven days show significantly less whitening than similar compositions absence the anti-whitening agents and lubricant. Although not met to be limiting the scope of the invention disclosed herein, whitening is thought to be related to the migration, (often referred to as blooming) and crystallization of materials onto the surface of test plaques under aging conditions. Whitening can be evaluated by visual observation and also by measuring the L value with a spectrophotometer. The L value is a common measure of whiteness on the CIELAB colorspace. Low L values correspond to darker plaques and higher L values correspond to lighter plaques. Therefore a positive ΔL means a change from darker to lighter. In one embodiment 5 in x 3 in x 3 mm test plaques prepared from the thermoplastic polyamide composition, when exposed at a test temperature at 85 °C and relative humidity of 85 %, for a test period of 7 days in an atmosphere of air, had a ΔL value, versus an untreated control of identical composition, determined at 110 ° reflection with a multi-angle spectrophotometer, of at least 25 percent less than that of the same composition absent the anti-whitening agent.

Herein the thermoplastic composition is a mixture by melt-blending, in which all polymeric ingredients are adequately mixed, and all non-polymeric ingredients are ed in a polymer matrix. Any melt-blending method may be used for mixing polymeric ingredients and non-polymeric ingredients of the present invention. For example, polymeric ingredients and non-polymeric ingredients may be fed into a melt mixer, such as single screw extruder or twin screw extruder, agitator, single screw or twin screw kneader, or Banbury mixer, and the addition step may be addition of all ingredients at once or gradual addition in batches. When the polymeric ingredient and non-polymeric ingredient are gradually added in batches, a part of the polymeric ingredients and/or non-polymeric ingredients is first added, and then is melt-mixed with the remaining polymeric ingredients and non-polymeric ingredients that are subsequently added, until an adequately mixed composition is obtained. If a reinforcing filler presents a long physical shape (for example, a long glass fiber), drawing extrusion molding may be used to prepare a reinforced composition.

In another aspect, the present invention relates to a method for manufacturing an article by shaping the thermoplastic polyamide composition disclosed herein. Examples of articles are films or laminates, automotive parts or engine parts or electrical/electronics parts. By “shaping”, it is meant any shaping technique, such as for example extrusion, injection molding, thermoform molding, compression molding or blow molding. Preferably, the article is shaped by injection molding or blow molding.

The molded or extruded thermoplastic articles disclosed herein may have application in many vehicular components that meet one or more of the following requirements: high impact requirements; significant weight reduction (over conventional metals, for instance); resistance to high temperature; resistance to oil environment; resistance to chemical agents such as coolants; and noise reduction allowing more compact and integrated design. Specific molded or extruded thermoplastic articles are selected from the group consisting of charge air coolers (CAC); cylinder head covers (CHC); oil pans; engine cooling systems, including thermostat and heater housings and coolant pumps; exhaust systems including mufflers and housings for catalytic converters; air intake manifolds (AIM); and timing chain belt front covers. As an illustrative example of desired mechanical resistance against long-term high temperature exposure, a charge air cooler can be mentioned. A charge air cooler is a part of the radiator of a vehicle that improves engine combustion efficiency. Charge air coolers reduce the charge air temperature and [illegible] of the air after compression in the turbocharger thus allowing more air to enter into the cylinders to improve engine efficiency. Since the temperature of the incoming air can be more than 200°C when it enters the charge air cooler, it is required that this part be made out of a composition maintaining good mechanical properties under high temperatures for an extended period of time. Also it is very desirable to have a shaped article that exhibits no whitening or very little whitening upon aging.

The present invention is further illustrated by the following examples. It should be understood that the following examples are for illustration purposes only, and are not used to limit the present invention thereto.

Methods

Compounding Method A

Examples and Comparative Examples listed in Tables 2-8 and 11 were prepared by melt blending the ingredients listed in the Tables in a 30 mm twin screw extruder (ZSK 30 by Coperion) operating at about 280 °C for Polyamide B and PA66 compositions and 310°C barrel setting for Polyamide A (PA 6T/66 55:45) compositions, using a screw speed of about 300 rpm, a throughput of 13.6 kg/hour and a melt temperature measured by hand of about 320 - 355°C for the all compositions. The glass fibers were added to the melt through a screw side feeder. Ingredient quantities shown in the Tables are given in weight percent on the basis of the total weight of the thermoplastic composition.

The compounded mixture was extruded in the form of laces or strands, cooled in a water bath, chopped into granules and placed into sealed aluminum lined bags in order to prevent moisture pick up.

Compounding Method B

Examples and Comparative examples listed in Tables 9 and 12 were prepared by melt blending the ingredients listed in the Tables in a 40 mm twin screw extruder (Berstorff ZE40) operating at barrel settings of about 285°C using a screw speed of about 200 rpm, a throughput of 125 kg/hour and a melt temperature measured by hand of about 310°C for all compositions. The glass fibers were added to the melt through a screw side feeder. Liquid plasticizer (Plasthall 809 and Uniplex 214) was added through a liquid injection pump to the final barrel section. Ingredient [illegible] the Tables are given in weight percent on the basis of the total weight of the thermoplastic composition.

The compounded mixture was extruded in the form of laces or strands, cooled in a water bath, chopped into granules and placed into sealed aluminum lined bags in order to prevent moisture pick up. The cooling and cutting conditions were adjusted to ensure that the materials were kept below 0.15 wt % of moisture level.

Compounding Method C

Examples and comparative examples listed in Table 10 were prepared by melt blending the ingredients listed in the Table in a 58 mm twin screw extruder operating at barrel settings of about 260°C using a screw speed of about 300 rpm, a throughput of 600 lbs/hour and a melt temperature of about 315°C for all compositions. The glass fibers were added to the melt through a screw side feeder. Liquid plasticizer (Plasthall 809) was added through a liquid injection pump to the final barrel section. Ingredient quantities shown in the Table are given in weight percent on the basis of the total weight of the thermoplastic composition.

The compounded mixture was extruded in the form of laces or strands, cooled in a water bath, chopped into granules and placed into sealed aluminum lined bags in order to prevent moisture pick up. The cooling and cutting conditions were adjusted to ensure that the materials were kept below 0.15 wt % of moisture level.

Compounding Method D

Examples and comparative examples listed in Table 13 were prepared by melt blending the ingredients listed in the Table in a 58 mm twin screw extruder (ZSK58 by Coperion) operating at barrel settings of about 270°C using a screw speed of about 300 rpm, a throughput of 275 kg/hour and a melt temperature of about 315°C for all compositions. The glass fibers were added to the melt through a screw side feeder. Liquid plasticizer (Plasthall 809) was added through a liquid injection pump to a spacer plate between the final two barrel sections. Ingredient quantities shown in the Table are given in weight percent on the basis of the total weight of the thermoplastic composition.

The compounded mixture was extruded in the form of laces or strands, cooled in a water bath, chopped into granules and placed into sealed polyethylene lined boxes in order to prevent moisture pick up. The cooling and cutting conditions were adjusted to ensure that the materials were kept below 0.15 wt % of moisture level.

Tensile Properties

Mechanical tensile properties, i.e. E-modulus, stress at break (Tensile strength) and strain at break (elongation at break) were measured according to ISO 527-2/1BA. Measurements were made on 2 mm thick injection molded ISO tensile bars at a testing speed of 5 mm/min. Mold temperature for PA 6T/DT test specimens was 145-150 °C; mold temperature for PA 6T/66 test specimens was 90 – 100 °C; and melt temperature was 325 – 330 °C for both resins.

Air Oven Ageing (AOA)

The test specimens (2 mm thick tensile bars) were heat aged in a re-circulating air ovens (Heraeus type UT6060) according to the procedure detailed in ISO 2578. At various heat aging times, the test specimens were removed from the oven, allowed to cool to room temperature and sealed into aluminum lined bags until ready for testing. The tensile mechanical properties were then measured according to ISO 527 using a Zwick tensile instrument. The average values obtained from 5 specimens are given in the Tables.

Retention of tensile strength (TS) and elongation at break (EL) corresponds to the percentage of the tensile strength and elongation at break after heat aging for 500 or 1000 hours in comparison with the value of specimens non-heat-aged control specimens considered as being 100%.

Whitening Determination Method

Two 5 in x 3 in X 3 mm plaques were treated by placing in an environmental chamber under conditions of 85% relative humidity and 85 °C. After one day one plaque was removed from the chamber and visually inspected. The L value, determined at 110 ° reflection was measured with a ChromaVision MA100 Multi-Angle Spectrophotometer (manufactured by X-Rite, Incorporated, Grandville, Michigan). L is a common measure of whiteness on the CIELAB colorspace. The L value was measured at 4 places on the plaque, both front and back and the L values averaged. A determination of L also was performed on an untreated plaque. A ΔL value was determined by subtracting the average of the four L measurements of the untreated plaque from the average of the four measurements from the treated plaque. After 7 days, the second plaque was removed from the chamber and the L value and ΔL value determined.

Low L values correspond to darker plaques and higher L values correspond to lighter plaques. Therefore a positive ΔL means a change from darker to lighter.

[illegible], [illegible]nd that, by visual observation, those of ordinary skill in the art could identify three levels of whitening, listed in Table 1, corresponding to the ΔL values determined by spectroscopic measurements means. Thus, using this relationship in some examples, visual observation was used to evaluate whitening where the L values could not be conveniently measured. For Examples and comparative examples listed In Table 10 the visual observation method was used on tensile bars rather than 5 in x 3 in plaques.

Table 1 – Characterization of Whitening

Visual observation	ΔL (110°)
none	$\Delta L < 5$
slight	$5 < \Delta L < 15$
moderate	$15 < \Delta L < 25$
severe	$\Delta L > 25$

Materials

Polyamide A refers to PA 6T/66, a Zytel® HTN502HNC010 copolyamide, made from terephthalic acid, adipic acid, and hexamethylenediamine; wherein the two acids are used in a 55:45 molar ratio; having a melting point of about 310 °C and an inherent viscosity (IV), according to ASTM D2857 method, typically about 1.07, available from E.I. DuPont de Nemours and Company, Wilmington, Delaware, USA.

Polyamide B refers to PA66/6T (75/25 molar ratio repeat units) with amine ends approximately 80 meq/kg, having a typical relative viscosity (RV) of 41, according to ASTM D-789 method, and a typical melt point of 268 °C, that was provided according to the following procedure:

Polyamide 66 salt solution (3928 lbs. of a 51.7 percent by weight with a pH of 8.1) and 2926 lbs of a 25.2% by weight of polyamide 6T salt solution with a pH of 7.6 were charged into an autoclave with 100 g of a conventional antifoam agent, 20g of sodium hypophosphite, 220g of sodium bicarbonate, 2476 g of 80% HMD solution in water, and 1584 g of glacial acetic. The solution was then heated while the pressure was allowed to rise to 265 psia at which point, steam was vented to maintain the pressure at 265 psia and heating was continued until the temperature of the batch reached 250°C. The pressure was then reduced slowly to 6 psia, while the batch temperature was allowed to further rise to 280-290 °C. The pressure was then held [illegible]mperature was held at 280-290 °C for 20 minutes. Finally, the polymer melt was extruded into strands, cooled, and cut into pellets.

PA 66 refers to an aliphatic polyamide made of 1,6-hexanedioic acid and 1,6-hexamethylenediamine having an relative viscosity in the range of 46 – 51 and a melting point of about 263 °C, commercially available from E.I. DuPont de Nemours and Company, Wilmington, Delaware, USA under the trademark Zytel® 101NC010.

PA 6-1 refers to Ultramid® B27 polyamide 6 resin (polycaprolactam) available from BASF Corporation, Florham Park, NJ, 07932.

PA6 -2 refers to Durethan B29 poly(e-caprolactam) available from Lanxess Germany.

Glass fiber B refers to CPIC 301HP chopped glass fiber available from Chongqing Polycomp International Corp., Chongqing, China.

Glass fiber C refers to PPG 3610 chopped glass fiber available from PPG Industries, Pittsburgh, PA.

Glass fibers D refer NEG 262H glass fibers manufactured by Nippon Electric Glass, Osaka, Japan.

Black Pigment A refers to ZYTEL® FE3786 BK031C black concentrate, a 40 wt % nigrosine black pigment concentrate in a PA66 carrier.

Black Pigment B refers ZYTEL ® FE3779 BK031C black concentrate, a 25 wt % carbon black in a PA6 carrier.

Cu heat stabilizer refers to a mixture of 7 parts of potassium iodide and 1 part of copper iodide in 0.5 part of aluminum stearate wax binder.

Plasthall 809 is a polyethylene glycol 400 di-2-ethylhexoate available from C.P. Hall Company, Chicago, Illinois 60606.

Loxiol HOB 7119 lubricant is a pentaerythritol tetrastearate manufactured by Cognis, Dusseldorf, Germany.

PEG 6000J is a poly(ethylene glycol) manufactured by Lion Corporation, Japan.

PEG refers to a polyethylene glycol of MW about 18,500 from Polysciences Inc. Warrington, PA,18976, USA.

Uniplex 214 plasticizer refers to N-butylbenzenesulfonamide available from Unitex Chemical Corp., Greensboro, NC.

Kraton D1161 PT is a styrene-isoprene-styrene block copolymer (SIS), available from Kraton Performance Polymers, Houston, TX, USA.

[illegible]6AT is a styrene-butadiene-styrene block copolymer (SBS), available from Kraton Performance Polymers, Houston, TX, USA.

Kemamide E180 lubricant is N-stearylerucamide, CAS No. [10094-45-8], available from Chemtura Corp., Philadelphia, PA.

Saytex 7010G is brominated polystyrene used as a flame retardant manufactured by Albermarle.

Thermoguard S PE80/20 is antimony oxide [CAS 1309-64-4] masterbatch in polyethylene, manufactured by Chemtura.

Examples

Comparative Example C1, having no DPE, exhibits no whitening.

Comparative Examples C3 and C4, having DPE but absent an anti-whitening agent, exhibits severe whitening.

Comparative Example C2, having DPE and an anti-whitening agent, but absent a lubricant shows moderate whitening.

The Examples, comprising a polyhydric alcohol, anti-whitening agent, and lubricant, show significantly less whitening than the Comparative Examples.

Table 2

Example	C1	C2	C3	C4
Polyamide B (66/6T)	63.27	60.77	61.67	60.17
Glass Fiber B	35.00	35.00	35.00	35.00
Kemamide E180			0.10	0.10
Cu Heat Stabilizer	0.30	0.30	0.30	0.30
Dipentaerythritol		1.50	1.50	3.00
Plasthall 809		1.00		
Black Pigment A	0.60	0.60	0.60	0.60
Black Pigment B	0.83	0.83	0.83	0.83
Whitening Properties				
ΔL (110°), 24 h	1.2	4.4	12.7	23.6
Visual observation, 24 h	none	none	slight	moderate
ΔL (110°), 7 days	1.9	22.2	38.6	52.8
Visual observation, 7 days	none	moderate	severe	severe
Tensile Properties, Dry-As-Molded				
Tensile Strength [MPa]	180	185	205	207
Elongation at Break [%]	5.4	5.8	3.6	3.8
Tensile Properties, 500 hrs at 230 °C				
Tensile Strength [MPa]	56	161	155	158
Tensile Strength Retention [%]	31%	87%	76%	77%
Elongation at Break [%]	1.3	4.0	2.1	2.0
Elongation Retention [%]	25%	69%	57%	53%
Tensile Properties, 1000 hrs at 230 °C				
Tensile Strength [MPa]	4	121	107	61
Tensile Strength Retention [%]	2%	66%	52%	30%
Elongation at Break [%]	0.4	4.4	1.9	1.1
Elongation Retention [%]	7%	76%	51%	30%

Table 3

Example	C1	C6	C7	C8	1	C9
Polyamide B (66/6T)	63.27	63.17	61.77	60.77	60.67	60.17
Glass Fiber B	35.00	35.00	35.00	35.00	35.00	35.00
Kemamide E180		0.10			0.10	0.10
Cu Heat Stabilizer	0.30	0.30	0.30	0.30	0.30	0.30
Pentaerythritol			0.75	0.75	0.75	1.50
Dipentaerythritol			0.75	0.75	0.75	1.50
Plasthall 809				1.00	1.00	
Black Pigment A	0.60	0.60	0.60	0.60	0.60	0.60
Black Pigment B	0.83	0.83	0.83	0.83	0.83	0.83
Whitening Properties						
ΔL (110°), 24 h	1.2	1.8	9.0	6.5	9.0	40.3
Visual observation, 24 h	none	none	slight	slight	slight	severe
ΔL (110°), 7 days	1.9	1.9	11.6	15.3	11.0	46.9
Visual observation, 7 days	none	none	slight	moderate	slight	severe
Tensile Properties, Dry-As-Molded						
Tensile Strength [MPa]	180	190	188	184	184	187
Elongation at Break [%]	5.4	6.6	5.6	5.8	6.8	6.2
Tensile Properties, 500 h at 230 °C						
Tensile Strength [MPa]	56	52	100	122	98	122
Tensile Strength Retention [%]	31%	28%	53%	66%	53%	65%
Elongation at Break [%]	1.3	1.8	2.8	3.0	3.2	3.4
Elongation Retention [%]	25%	27%	50%	5.2%	47%	55%
Tensile Properties, 1000 h at 230 °C						
Tensile Strength [MPa]	4	1	5	10	1	5
Tensile Strength Retention [%]	2%	1%	2%	6%	1%	3%
Elongation at Break [%]	0.4	0.2	0.3	0.3	0.4	0.3
Elongation Retention [%]	7%	3%	5%	5%	6%	5%

Table 4

Example	2	3	4	5	6	7	8	9	10
Polyamide B (66/6T)	60.67	60.92	61.17	60.67	60.92	61.17	60.67	60.92	61.17
Glass Fiber B	35.00	35.00	35.00	35.00	35.00	35.00	35.00	35.00	35.00
Kemamide E180	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10
Cu Heat Stabilizer	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.30
Pentaerythritol	0.75	0.75	0.75	1.00	1.00	1.00	0.50	0.50	0.50
Dipentaerythritol	0.75	0.75	0.75	0.50	0.50	0.50	1.00	1.00	1.00
Plasthall 809	1.00	0.75	0.50	1.00	0.75	0.50	1.00	0.75	0.50
Black Pigment A	0.60	0.60	0.60	0.60	0.60	0.60	0.60	0.60	0.60
Black Pigment B	0.83	0.83	0.83	0.83	0.83	0.83	0.83	0.83	0.83
Whitening Properties									
ΔL (110°), 24 h	9.3	9.6	12.6	7.4	8.0	9.3	8.6	8.2	11.6
Visual observation, *24 h*	slight	slight	slight	slight	slight	slight	slight	slight	slight
ΔL (110°), 7 days	12.3	11.4	20.3	4.4	13.2	11.3	11.9	6.3	10.6
Visual observation, *7 days*	slight	slight	moderate	none	slight	slight	slight	slight	slight
Tensile Properties, Dry-As-Molded									
Tensile Strength [MPa]	188	187	189	182	188	187	185	187	190
Elongation at Break [%]	6.7	6.7	6.6	6.9	6.7	6.7	6.8	6.9	6.5
Tensile Properties, 500 h at 230 °C									
Tensile Strength [MPa]	84	118	105	101	102	107	122	119	124
Tensile Strength Retention [%]	45%	63%	56%	55%	54%	57%	66%	64%	66%
Elongation at Break [%]	3.0	4.0	3.8	3.5	3.2	3.4	3.9	4.3	4.1
Elongation Retention [%]	44%	58%	57%	51%	50%	51%	56%	63%	60%
Tensile Properties, 1000 h at 230 °C									
Tensile Strength [MPa]	6	6	5	4	4	7	8	9	9
Tensile Strength Retention [%]	3%	3%	3%	2%	2%	4%	4%	5%	5%
Elongation at Break [%]	0.2	0.3	0.3	0.3	0.3	0.3	0.2	0.3	0.3
Elongation Retention [%]	3%	4%	4%	4%	4%	4%	3%	4%	4%

Table 5

Example	C6	C11	C12	C13	11	12	13
Polyamide B (66/6T)	63.17	61.77	60.77	61.67	60.67	59.17	44.67
Glass Fiber B	35.00	35.00	35.00	35.00	35.00	35.00	50.00
Kemamide E180	0.10			0.10	0.10	0.10	0.10
Cu Heat Stabilizer	0.30	0.30	0.30	0.30	0.30	0.30	0.30
Dipentaerythritol		0.75	0.75	0.75	0.75	1.50	1.25
Tripentaerythritol		0.75	0.75	0.75	0.75	1.50	1.25
Plasthall 809			1.00		1.00	1.00	1.00
Black Pigment A	0.60	0.60	0.60	0.60	0.60	0.60	0.60
Black Pigment B	0.83	0.83	0.83	0.83	0.83	0.83	0.83
Whitening,Properties							
ΔL (110°), 24 h	1.8	12.0	13.2	21.4	1.0	4.0	11.0
Visual observation, 24 h	none	slight	slight	moderate	none	none	slight
ΔL (110°), 7 days	1.9	15.0	13.8	26.1	1.0	6.7	13.9
Visual observation, 7 days	none	slight	slight	severe	none	slight	slight
Tensile Properties, Dry-As-Molded							
Tensile Strength [MPa]	190	190	182	187	181	181	182
Elongation at Break [%]	6.6	5.6	5.8	6.4	6.6	6.5	6.5
Tensile Properties, 500 h at 230 °C							
Tensile Strength [MPa]	52	115	135	114	120	157	182
Tensile Strength Retention [%]	28%	61%	74%	61%	66%	87%	100%
Elongation at Break [%]	1.8	3.0	3.4	3.0	3.2	4.0	4.4
Elongation Retention [%]	27%	53%	58%	47%	49%	60%	68%
Tensile Properties, 1000 h at 230 °C							
Tensile Strength [MPa]	1	7	20	7	11	38	74
Tensile Strength Retention [%]	1%	4%	11%	4%	6%	21%	41%
Elongation at Break [%]	0.2	0.4	0.6	0.2	0.3	0.8	1.6
Elongation Retention [%]	3%	7%	11%	3%	4%	13%	25%

Table 6

Example	C14	C15	14
Polyamide A (6T/66)	63.67	53.67	52.67
Glass Fiber B	35.00	35.00	35.00
Licowax OP	0.25	0.25	0.25
Cu Heat Stabilizer	0.40	0.40	0.40
TRX-301		2.50	2.50
PA66		5.00	5.00
Dipentaerythritol		2.50	1.25
Pentaerythritol			1.25
Plasthall 809			1.00
Black Pigment A	0.68	0.68	0.68
Whitening Properties			
ΔL (110°), 24 h	-1.6	4.1	4.4
Visual observation, 24 h	none	none	none
ΔL (110°), 7 days	0.9	23.9	7.3
Visual observation, 7 days	none	moderate	slight
Tensile Properties, Dry-As-Molded			
Tensile Strength [MPa]	208	202	199
Elongation at Break [%]	5.2	5.4	5.6
Tensile Properties, 500 hrs at 230 °C			
Tensile Strength [MPa]	73	190	167
Tensile Strength Retention [%]	35%	94%	84%
Elongation at Break [%]	1.9	4.4	4.0
Elongation Retention [%]	37%	81%	71%
Tensile Properties, 1000 hrs at 230 °C			
Tensile Strength [MPa]	17	133	120
Tensile Strength Retention [%]	8%	66%	60%
Elongation at Break [%]	0.4	2.6	2.7
Elongation Retention [%]	7%	49%	48%

Table 7

Example	C16	C17	C18	C19	15	C20	C21
Polyamide B (66/6T)	61.67	61.67	56.45	60.17	59.17	45.35	42.30
Glass Fiber B	35.00	35.00	35.00	35.00	35.00	50.00	45.00
Kemamide E180	0.10	0.10	0.075	0.10	0.10	0.125	0.15
Aluminum Stearate			0.075			0.125	0.15
Cu Heat Stabilizer	0.30	0.30	0.30	0.30	0.30	0.30	0.30
TRX-301							2.50
PA6-1			5.00				5.00
Tripentaerythritol	1.50	1.50	1.50	3.00	3.00	2.50	3.00
Plasthall 809					1.00		
Black Pigment A	0.60	0.60	0.60	0.60	0.60	0.60	0.60
Black Pigment B	0.83	0.83	1.00	0.83	0.83	1.00	1.00
Whitening Properties							
ΔL (110°), 24 h	17.4	22.6	16.8	8.0	5.5	12.1	15.0
Visual observation, 24 h	moderate	moderate	moderate	slight	none	slight	moderate
ΔL (110°), 7 days	18.0	23.7	26.5	10.2	4.5	21.0	20.7
Visual observation, 7 days	moderate	moderate	severe	slight	none	moderate	moderate
Tensile Properties, Dry-As-Molded							
Tensile Strength [MPa]	187	191	204	180	186	243	214
Elongation at Break [%]	6.4	6.1	6.0	6.5	6.6	5.4	5.7
Tensile Properties, 500 h at 230 °C							
Tensile Strength [MPa]	125	130	185	159	197	203	222
Tensile Strength Retention [%]	67%	68%	91%	90%	106%	84%	104%
Elongation at Break [%]	3.3	3.6	4.3	4.0	4.7	3.9	4.8
Elongation Retention [%]	52%	58%	71%	62%	72%	72%	84%
Tensile Properties, 1000 h at 230 °C							
Tensile Strength [MPa]	8	11	121	61	102	92	150
Tensile Strength Retention [%]	4%	6%	59%	34%	55%	38%	*70%*
Elongation at Break [%]	0.3	0.4	3.0	1.3	2.3	2.4	3.0
Elongation Retention [%]	4%	6%	50%	20%	36%	45%	*53%*

Table 8

Example	16	C22	C23	C24	17	18	19	C25
Polyamide B (66/6T)	42.40	42.40	42.40	55.50	54.50	54.00	43.15	44.65
Glass Fiber B	45.00	45.00	45.00	35.00	35.00	35.00	50.00	50.00
Kemamide E180	0.20	0.20	0.20	0.10	0.10	0.10	0.25	0.25
Cu Heat Stabilizer	0.30	0.30	0.30	0.30	0.30	0.30		
TRX-301	0.50	1.00	1.50			0.50	0.50	
Kraton D1161 PT	2.00	1.50	1.00	1.00	1.00	2.00	2.00	1.00
PA6-1	5.00	5.00	5.00	5.00	5.00	5.00		
Dipentaerythritol	3.00	3.00	3.00	1.50	1.50	1.50	2.50	2.50
Plasthall 809					1.00			
Black Pigment A	0.60	0.60	0.60	0.60	0.60	0.60	0.60	0.60
Black Pigment B	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Whitening Properties								
ΔL (110°), 24 h	8.1	10.0	8.5	7.9	3.4	2.3	5.2	10.1
visual observation, 24 h	slight	slight	slight	slight	none	none	none	slight
ΔL (110°), 7 days	17.1	22.6	39.8	29.5	1.5	13.9	13.1	21.9
visual observation, 7 days	moderate	moderate	severe	severe	none	slight	slight	moderate
Tensile Properties, Dry-As-Molded								
Tensile Strength [MPa]	220	220	216	203	190	193	228	238
Elongation at Break [%]	5.3	5.3	5.4	5.6	5.7	5.8	5.0	5.2
Tensile Properties, 500 h at 230 °C								
Tensile Strength [MPa]	228	220	218	170	209	169	189	188
Tensile Strength Retention [%]	103%	100%	101%	84%	110%	88%	83%	79%
Elongation at Break [%]	4.5	4.3	4.2	3.5	4.8	3.6	3.3	3.4
Elongation Retention [%]	84%	80%	79%	63%	85%	63%	67%	66%
Tensile Properties, 1000 h at 230 °C								
Tensile Strength [MPa]	77	55	174	54	186	41	173	145
Tensile Strength Retention [%]	35%	25%	80%	27%	98%	21%	76%	61%
Elongation at Break [%]	0.9	1.0	2.9	0.8	3.5	0.8	3.2	3.1
Elongation Retention [%]	16%	18%	54%	14%	61%	13%	63%	59%

Table 9

Example	C26	C27	20
Polyamide B (66/6T)	42.40	42.40	42.40
Glass fiber C	45.00	45.00	45.00
PA6-2	5.00	5.00	5.00
Dipentaerythritol	3.00	3.00	3.00
Black Pigment A	0.60	0.60	0.60
Black Pigment B	1.00	1.00	1.00
Cu Heat Stabilizer	0.30	0.30	0.30
Kemamide E180	0.20	0.20	0.20
TRX-301	2.50	0.50	0.50
Kraton D1116AT - SBS		2.00	
Kraton D1161PT - SIS			2.00
Whitening Properties			
Visual observation, 24 h	Moderate	Moderate	None
visual observation, 7 days	Moderate	Moderate	slight
Tensile Properties, Dry-As-Molded			
Tensile Strength [MPa]	211.7	212.5	209.5
Elongation at Break [%]	3.4	3.2	3.3

Table 10

Example[a]	C28	C29	21	22
PA6-1	62.15	61.30	60.55	59.55
Glass Fiber B	35.00	35.00	35.00	35.00
Dipentaerythritol	1.50	1.50	1.50	1.50
Black Pigment A	0.60	0.60	0.60	0.60
Black Pigment B	0.60	1.00	1.00	1.00
Cu Heat Stabilizer		0.45	0.45	0.45
Kemamide E180	0.075	0.075	0.075	0.075
Aluminum distearate	0.075	0.075	0.075	0.075
Plasthall 809			0.75	0.75
TRX-301				0.20
Kraton D1161PT - SIS				0.80
Whitening Properties				
Visual observation, 24 h	Moderate	Moderate	None	None
Visual observation, 7 days	Severe	Severe	slight	None
Tensile Properties, Dry-As-Molded				
Tensile Strength [MPa]	209	206	202	192
Elongation at Break [%]	4.2	3.6	3.6	3.7

[a] tensile bar samples were used for visual observation

Table 11

Example	C30	C31	C32	23	24	25	26	27
Polyamide B (66/6T)	61.57	60.07			60.57	58.57	60.57	58.57
PA66			61.57	60.57				
Glass fiber D	35.00	35.00	35.00	35.00	35.00	35.00	35.00	35.00
Dipentaerythritol	1.50	3.00	1.50	1.50	1.50	1.50	1.50	1.50
Black Pigment A	0.60	0.60	0.60	0.60	0.60	0.60	0.60	0.60
Black Pigment B	0.83	0.83	0.83	0.83	0.83	0.83	0.83	0.83
Cu Heat Stabilizer	0.40	0.40	0.40	0.40	0.40	0.40	0.40	0.40
Kemamide E180	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10
Plasthall 809				1.00	1.00	3.00		
PEG 6000J							1.00	3.00
Whitening Properties								
ΔL (110°), 24 h	10.6	23.2	21.9	-2.7	-2.1	0.0	5.8	2.6
Visual observation, 24 h	slight	moderate	moderate	none	none	none	slight	none
ΔL (110°), 7 days	44.1	46.9	51.3	-5.3	-3.5	-4.7	6.4	2.4
Visual observation, 7 days	*severe*	*severe*	*severe*	*none*	*none*	*none*	*slight*	*none*
Tensile Properties, Dry-As-Molded								
Tensile Strength [MPa]	203	202	208	189	189	177	194	188
Elongation at Break [%]	3.5	3.3	3.3	3.4	3.5	3.3	3.3	3.5

Table 12

Example	C33	C34	C35	C36	28	29
PA66/6T	57.80	56.75	56.30	55.55	55.55	55.55
PA 6-1	5.00	5.00	5.00	5.00	5.00	5.00
Glass Fiber C	35.00	35.00	35.00	35.00	35.00	35.00
DPE		1.50	1.50	1.50	1.50	1.50
Black Pigment A	0.60	0.60	0.60	0.60	0.60	0.60
Black Pigment B	1.00	1.00	1.00	1.00	1.00	1.00
Cu Heat Stabilizer	0.45		0.45	0.45	0.45	0.45
Kemamide E180	0.075	0.075	0.075	0.075	0.075	0.075
Aluminum distearate	0.075	0.075	0.075	0.075	0.075	0.075
Uniplex 214 (NBBS)				0.75		
Plasthall 809					0.75	
PEG						0.75
Properties						
Whitening, visual observation, 7 days	None	Moderate	Moderate	Slight	None	None
ΔL (110°), 24 h	0	18	17	12	4	0
Whitening, visual observation, 7 days	None	Severe	Severe	Moderate	Slight	None
ΔL (110°), 7 days	0	27	29	20	6	1
Tensile Properties, Dry-As-Molded						
Tensile Strength [MPa]	203.8	199.3	204.4	209.4	205.8	202.9
Elongation at Break [%]	4.2	4.2	4.1	4.1	4.0	4.3

Table 13

Examples	C36	31	32	C37	33
PA 66/6T	52.30	51.30	51.05	52.25	51.25
PPG 3610 glass	15.00	15.00	15.00	15.00	15.00
Dipentaerythritol	2.50	2.50	2.50	2.50	2.50
Thermoguard S PE80/20	5.00	5.00	5.00	5.00	5.00
Saytex 7010G	23.00	23.00	23.00	23.00	23.00
Kemamide E180	0.20	0.20	0.20	0.125	0.125
Aluminum Distearate				0.125	0.125
FE3786 (black concentrate)	1.00	1.00	1.00	1.00	1.00
FE3779 (black concentrate)	1.00	1.00	1.00	1.00	1.00
Plasthall 809			1.25		
PEG 20,000		1.00			1.00
Whitening Properties					
ΔL (110°), 24 h at 85 °C, 85% RH	24.8	1.4	10.5	8.9	0.5
Whitening Characterization, 24 h	moderate	none	slight	slight	none
ΔL (110°), 7 days at 85 °C, 85% RH	43.8	1.9	16.5	45.1	2.5
Whitening Characterization, 7 days	severe	none	moderate	severe	none

CLAIMS

We Claim:

1. A thermoplastic polyamide composition comprising

a) a polyamide resin having a melting point and/or glass transition temperature;

b) 0.1 to 10 weight percent of one or more polyhydric alcohols having more than two hydroxyl groups and having a number average molecular weight (M_n) of less than 2000;

c) 0.5 to 5 weight percent of one or more anti-whitening agents selected from the group consisting of poly(ethylene glycol), poly(ethylene glycol) diesters, poly(propylene glycol), poly(propylene glycol) diesters; and styrene-isoprene-styrene block copolymers; and mixtures of these;

d) 0.02 to 1 weight percent of a lubricant;

e) 10 to 60 weight percent of one or more reinforcement agents; and

f) 0 to 50 weight percent of a polymeric toughener comprising a reactive functional group and/or a metal salt of a carboxylic acid;

with the provisos that the thermoplastic composition comprises less than 15 weight percent magnesium hydroxide and less than 0.20 weight percent zinc compounds selected from the group consisting of zinc borate and zinc oxide; and with the further proviso that at least 2 weight percent of styrene-isoprene-styrene block copolymers are present when no other anti-whitening agents selected from the group are present; and wherein all weight percentages are based on the total weight of the polyamide composition.

2. The thermoplastic polyamide composition of Claim 1 wherein the lubricant is selected from the group consisting of fatty acids, fatty acid esters, fatty acid amides, fatty acid metal salts, and oxidized polyethylene wax.

3. The thermoplastic polyamide composition of Claim 1 wherein the lubricant is present at 0.05 to 0.5 weight percent based on the weight of the total thermoplastic polyamide composition.

4. The thermoplastic polyamide composition of Claim 1 wherein the anti-whitening agent is selected from polyethylene glycol and poly(ethylene glycol) diesters.

5. The thermoplastic polyamide composition of Claim 1 wherein the reinforcing agent is selected from the group consisting of glass fiber and noncircular glass fiber.

6. The thermoplastic polyamide of Claim 1 wherein the composition further comprises: 0.1 to 3.0 weight percent of one or more colorants.

7. The thermoplastic polyamide of Claim 1wherein the composition further comprises: 1 to 30 weight percent of one or more halogenated flame retardants.

8. The thermoplastic polyamide composition of Claim 1 wherein the polyamide resin is selected from the group consisting of **Group (II) polyamides** having a melting point of at least 210 °C, and comprising an aliphatic polyamide selected from the group consisting of poly(tetramethylene hexanediamide), poly(ε-caprolactam), poly(hexamethylene hexanediamide/(ε-caprolactam/) poly(hexamethylene hexanediamide), poly(hexamethylene hexanediamide/hexamethylene decanediamide), poly(hexamethylene hexanediamide/hexamethylene dodecanediamide), poly(hexamethylene hexanediamide/decamethylene decanediamide), poly(hexamethylene decanediamide), poly(hexamethylene dodecanediamide), poly(hexamethylene tetradecanediamide), and poly(tetramethylene hexanediamide/2-methylpentamethylene hexanediamide);

Group (III) polyamides having a melting point of at least 210 °C, and comprising

(aa) about 20 to about 35 mole percent semiaromatic repeat units derived from monomers selected from one or more of the group consisting of:

(i) aromatic dicarboxylic acids having 8 to 20 carbon atoms and aliphatic diamines having 4 to 20 carbon atoms; and

(bb) about 65 to about 80 mole percent aliphatic repeat units derived from monomers selected from one or more of the group consisting of:

(ii) an aliphatic dicarboxylic acid having 6 to 20 carbon atoms and said aliphatic diamine having 4 to 20 carbon atoms; and

(iii) a lactam and/or aminocarboxylic acid having 4 to 20 carbon atoms;

and **Group (IV) polyamides** comprising:

(cc) about 50 to about 95 mole percent semiaromatic repeat units derived from monomers selected from one or more of the group consisting of:

(iv) aromatic dicarboxylic acids having 8 to 20 carbon atoms and aliphatic diamines having 4 to 20 carbon atoms; and

(gg) about 5 to about 50 mole percent aliphatic repeat units derived from monomers selected from one or more of the group consisting of:

(v) an aliphatic dicarboxylic acid having 6 to 20 carbon atoms and said aliphatic diamine having 4 to 20 carbon atoms; and

(vi) a lactam and/or aminocarboxylic acid having 4 to 20 carbon atoms.

9. The thermoplastic polyamide composition of Claim 8 wherein the polyamide resin is selected from the group consisting of poly(ε-caprolactam), poly(hexamethylene hexanediamide), poly(hexamethylene hexanediamide/hexamethylene terephthalamide), and poly(hexamethylene terephthalamide/ hexamethylene hexanediamide).

10. The polyamide composition of Claim 1 wherein 5 in x 3 in X 2 mm test plaques prepared from said polyamide composition, when exposed at a test temperature at 85 °C and relative humidity of 85 %, for a test period of 7 days in an atmosphere of air, had a ΔL value, versus an untreated control of identical composition, determined at 110 ° reflection with a multi-angle spectrophotometer, of at least 25 percent less than that of the same composition absent the anti-whitening agent.

11. A molded or extruded article made from the thermoplastic polyamide composition of Claim 1.

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2013/037280

A. CLASSIFICATION OF SUBJECT MATTER

INV. C08L77/02 C08L77/06

ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C08L

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2011/028628 A1 (MARTENS MARVIN M [US] ET AL) 3 February 2011 (2011-02-03) claim 1 example 19 -----	1-11
A	US 2011/028621 A1 (MARTENS MARVIN M [US] ET AL) 3 February 2011 (2011-02-03) example 19 -----	1-11
A	EP 1 323 766 A1 (ASAHI CHEMICAL IND [JP]) 2 July 2003 (2003-07-02) example 9 -----	1-11

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

☒ See patent family annex.

* Special categories of cited documents :

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Date of the actual completion of the international search 2 July 2013	Date of mailing of the international search report 22/07/2013
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Barrère, Matthieu

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
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