

INHERENTLY LIGHT- AND HEAT-STABILIZED POLYAMIDE AND METHOD OF MAKING THE SAME

5 Description

This invention relates to polyamides. More particularly, this invention relates to inherently light- and heat-stabilized polyamides and to methods of making such polyamides. This invention
10 also relates to articles produced from such polyamides.

Polyamides tend to degrade when exposed to light and/or heat. For example, the amino end groups (*i.e.*, the primary dye sites for acid dyes) of a polyamide are reduced during melt extrusion of
15 the polyamide and during exposure of polyamide fibers or other polyamide articles to light and/or heat. In addition, polyamide fabrics such as, for example, carpets and textiles which have been dyed with certain classes of dyes, lose color and fade when exposed to light and/or heat.

20 Furthermore, the heat resistance of polyamides such as, for example, nylon 6 and nylon 6/6, is not sufficient for certain applications. For example, during the dyeing of polyamide-containing carpets, yarns, and textile fabrics and in certain heat-setting
25 processes and end-use applications, chemical changes occur which may cause problems, *e.g.*, oxidative/thermal damage. These problems may involve continuous filaments or staple fibers.

Stabilizers have been used to improve the heat resistance of
30 polyamides. The stabilizers may be added before, during, or after polymerization, and even as late as the processing stage. The conventional known stabilizers are admixed with the polymer and are not bound to the polymer chain; therefore, during processing or use of the polyamide, the stabilizers can readily migrate out
35 of the polymer, evaporate, or be washed out. This means that the activity of the stabilization is reduced in an undesired manner, and impurities are released to the surroundings (*e.g.*, air, dye bath, *etc.*).

40 Certain copper stabilizers have also been added either during extrusion or in the dye bath to minimize polyamide degradation due to exposure to light and/or heat. This practice, however, is expensive, disturbs processing, and presents environmental problems.

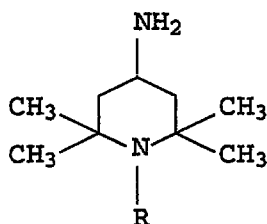
45

United States Patent Application Serial Number 09/044,031, which is assigned to BASF Corporation, relates to a process for making stabilized solution-dyed fibers by melting a polyamide comprising amide monomers polymerized in the presence of at least one hindered piperidine compound and coloring the melted polyamide with a colorant.

United States Patent Application Serial Number 08/804,312, which is assigned to BASF Corporation, relates to a process for preparing photochemically-stable, dyed nylon compositions comprising providing to a dye bath a shaped article of poly(epsilon-caprolactam) hydrolytically polymerized in the presence of water and a hindered piperidine derivative and, in the dye bath, dyeing the shaped article with one or more metalized or nonmetalized acid dyestuffs.

A PCT application, International Application No. PCT/EP 95/01349, describes an inherently stabilized polyamide containing at least one triacetone diamine compound

represented by the formula



wherein R is hydrogen, a hydrocarbon group having 1-20 carbon atoms, or a benzyl group. The triacetone diamine compound has a primary amino group ($-NH_2$) that reacts with a carboxy end group of the polyamide molecule during polymerization, thus rendering the polymer light and heat stable. The available carboxy end groups of the polyamide determine the amount of the one or more triacetone diamine compounds that may be added.

An essay in Poly. Deg. and Stab. 21, 251-262 (1988) describes how the light stability of polyamide 6/6 is improved by adding 2,2,6,6-tetramethylpiperidin-4-ol (TMP). In a recondensation of the TMP-containing polyamide 6/6 in the melt at 275°C under an atmosphere of water vapor, the authors of the essay claim that TMP reacts with the carboxyl end groups of the polyamides.

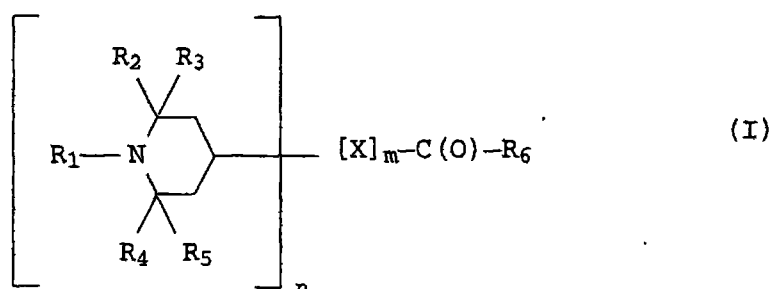
3

Although prior stabilizers are known to be considerably satisfactory, there still remain some problems to be dissolved or improved.

- 5 It has now been discovered that polyamides that are inherently stable against light and heat may be provided by polymerizing polyamide-forming monomers in the presence of (a) at least one piperidine compound represented by the formula (I):

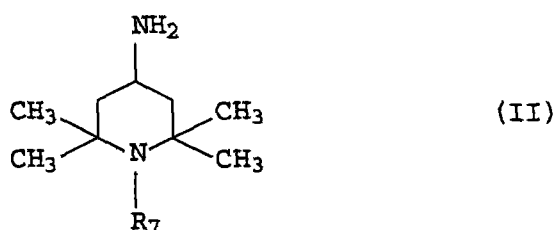
10

15



- wherein R_1 is hydrogen, benzyl, or a $\text{C}_1\text{--C}_{20}$ alkyl, $\text{R}_2\text{--R}_5$ are each
20 hydrogen or the same or a different $\text{C}_1\text{--C}_6$ alkyl, X has n free valance bonding sites and is an alkyl or substituted alkyl having from about 1 to about 30 carbon atoms or an aryl or substituted aryl having from about 6 to about 20 carbon atoms, m is 0 or 1, $\text{---C}(\text{O})\text{---R}_6$ is a group that can form an amide bond together with an
25 amine, and n is equal to 1, 2, or 3 and (b) at least one 4-amino-2,2,6,6-tetramethylpiperidine compound represented by formula (II):

30



35

wherein R_7 is hydrogen, benzyl, or a $\text{C}_1\text{--C}_{20}$ alkyl.

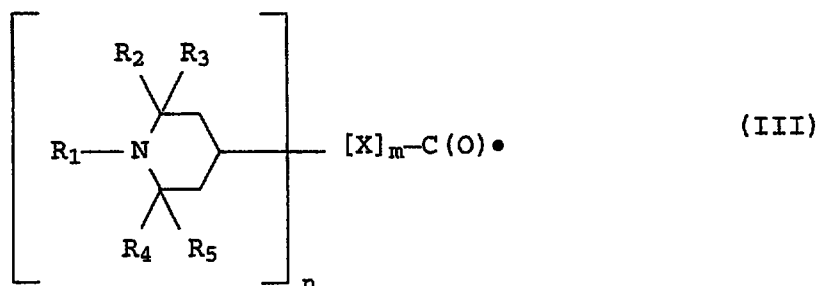
- Accordingly, one embodiment of the present invention is directed
40 to an inherently light- and heat-stabilized polyamide comprising a backbone polymer chain, at least one

piperidyl radical represented by formula (III):

45

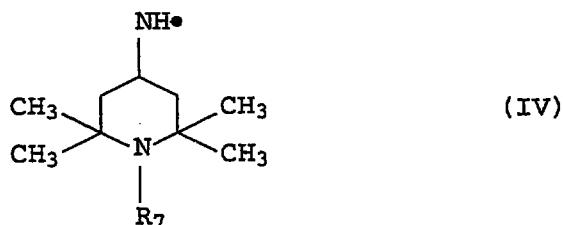
4

5



10 wherein R₁ is hydrogen, benzyl, or a C₁-C₂₀ alkyl, R₂-R₅ are each hydrogen or the same or a different C₁-C₆ alkyl, X has n free valance bonding sites and is an alkyl or substituted alkyl having from about 1 to about 30 carbon atoms or an aryl or substituted aryl having from about 6 to about 20 carbon atoms, m is 0 or 1,
 15 and n is equal to 1, 2, or 3 and at least one 4-amino-2,2,6,6-tetramethylpiperidyl radical represented by formula (IV):

20



25

wherein R₇ is hydrogen, benzyl, or a C₁-C₂₀ alkyl, wherein the one or more piperidyl radicals of formula (III) and the one or more 4-amino-2,2,6,6-tetramethylpiperidyl radicals of formula (IV) are
 30 chemically bonded to the backbone polymer chain. In the present invention, the chemical bonding of the one or more piperidyl radicals of formula (III) and the one or more 4-amino-2,2,6,6-tetramethylpiperidyl radicals of formula (IV) to the backbone polymer chain provides the polyamide with inherent,
 35 or built-in, light- and heat- stability.

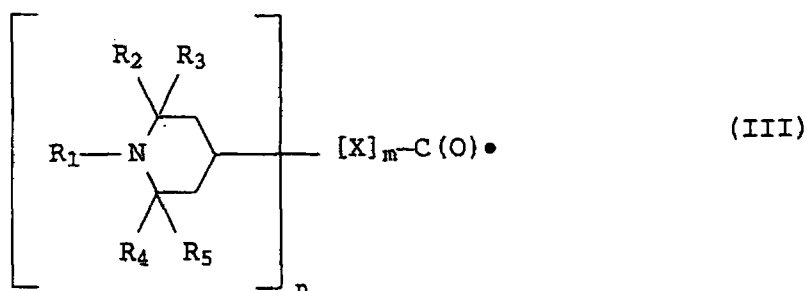
40

In a second embodiment, the present invention is directed to a method of making an inherently light- and heat-stabilized polyamide comprising at least one piperidyl radical of formula (III):

45

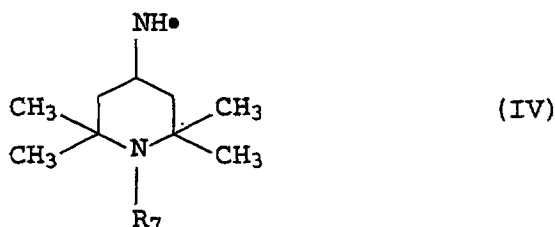
5

5



- 10 wherein R_1 is hydrogen, benzyl, or a C_1 - C_{20} alkyl, R_2 - R_5 are each hydrogen or the same or a different C_1 - C_6 alkyl, X has n free valance bonding sites and is an alkyl or substituted alkyl having from about 1 to about 30 carbon atoms or an aryl or substituted aryl having from about 6 to about 20 carbon atoms, m is 0 or 1,
 15 and n is equal to 1, 2, or 3 and at least one 4-amino-2,2,6,6-tetramethylpiperidyl radical of formula (IV):

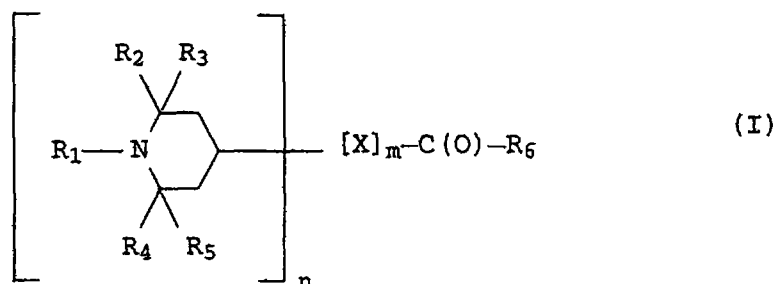
20



25

- wherein R_7 is hydrogen, benzyl, or a C_1 - C_{20} alkyl, wherein the radicals of formulae (III) and (IV) are chemically bonded to the backbone polymer chain, the method comprising subjecting poly-
 30 amide-forming monomers to a polymerization process in the presence of an effective amount of at least one piperidine compound of formula (I):

35

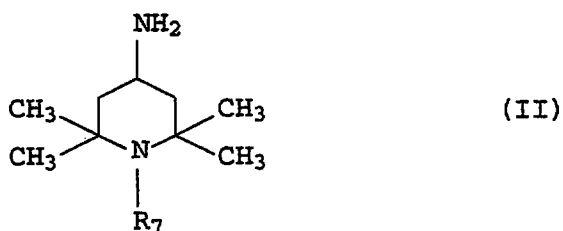


40

- wherein R_1 is hydrogen, benzyl, or a C_1 - C_{20} alkyl, R_2 - R_5 are each hydrogen or the same or a different C_1 - C_6 alkyl, X has n free valance bonding sites and is an alkyl or substituted alkyl having from about 1 to about 30 carbon atoms or an aryl or substituted
 45 aryl having from about 6 to about 20 carbon atoms, m is 0 or 1, $-C(O)-R_6$ is a group that can form an amide bond together with an

amine, and n is equal to 1, 2, or 3 and an effective amount of at least one 4-amino-2,2,6,6-tetramethylpiperidine compound of formula (II):

5



10

wherein R₇ is hydrogen, benzyl, or a C₁-C₂₀ alkyl.

15 In yet another embodiment, the present invention is directed to polyamide fibers formed from the inherently light- and heat-stabilized polyamides of the present invention.

Thus, it is a primary object of the present invention to provide
20 a light- and heat-stabilized polyamide wherein the stabilizing components are chemically bonded to the polyamide.

Another object of the present invention is to provide a method of making a light- and heat-stabilized polyamide wherein the stabi-
25 lizing components are chemically bonded to the polyamide.

A further object of the present invention is to provide polyamide fibers formed from making a light- and heat-stabilized polyamide, wherein the stabilizing components are chemically bonded to the
30 polyamide.

The above and other objects, effects, features, and advantages of the present invention will become more apparent from the following detailed description of the preferred embodiments thereof,
35 particularly when viewed in conjunction with the accompanying figures.

FIG. 1 is a graph illustrating the yellowing of scoured knitted tubes after exposure in a weatherometer for 700 hours.

40

FIG. 2 is a graph illustrating the percent strength retained for solution-dyed yarns after exposure in a weatherometer.

To promote an understanding of the principles of the present in-
45 vention, descriptions of specific embodiments of the invention follow, and specific language is used to describe the same. It will nevertheless be understood that no limitation of the scope

of the invention is intended by the use of this specific language and that alterations, modifications, equivalents, and further applications of the principles of the invention discussed are contemplated as would normally occur to one of ordinary skill in the art to which the invention pertains.

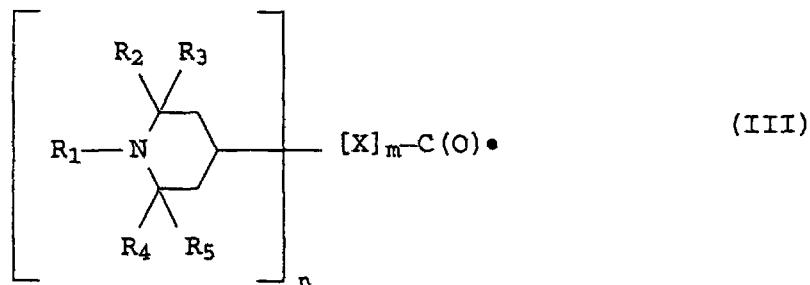
As used herein with respect to the polyamides of this invention, the term "inherently light- and heat-stabilized" means that the light- and heat-stability are built into the polyamide. In other words, the components that render the polyamide light- and heat-stabilized are chemically bonded to the backbone polymer chain of the polyamide rather than merely physically admixed with the polyamide.

As used herein with respect to the polyamides of this invention, the phrase "both end groups that are terminated and stabilized" refers to the result that occurs when the piperidyl radical of formula (III) and the 4-amino-2,2,6,6-tetramethylpiperidine radical of formula (IV) chemically bond to the backbone polymer chain of the inherently light- and heat-stabilized polymers.

In one embodiment, the present invention is an inherently light- and heat-stabilized polyamide comprising at least one piperidyl radical represented by formula (III):

25

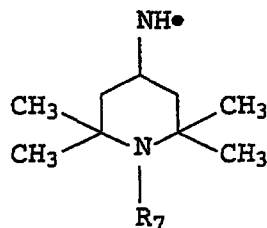
30



wherein R_1 is hydrogen, benzyl, or a C_1 - C_{20} , preferably a C_2 - C_4 , alkyl, R_2 - R_5 are each hydrogen or the same or a different C_1 - C_6 alkyl, X has n free valance bonding sites and is an alkyl or substituted alkyl having from about 1 to about 30 carbon atoms or an aryl or substituted aryl having from about 6 to about 20 carbon atoms, m is 0 or 1, and n is equal to 1, 2, or 3 and at least one 4-amino-2,2,6,6-tetramethylpiperidyl radical represented by formula (IV):

45

5

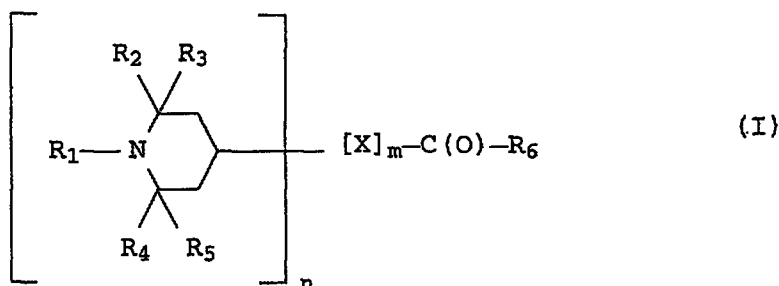


(IV)

10 wherein R_7 is hydrogen, benzyl, or a C_1 - C_{20} , preferably C_1 - C_{18} and
 more preferably C_2 - C_4 , alkyl, wherein the at least one piperidyl
 radical of formula (III) and the at least one
 4-amino-2,2,6,6-tetramethylpiperidyl radical of formula (IV) are
 chemically bonded to the backbone polymer chain of the inherently
 15 light- and heat-stabilized polyamide.

The inherently light- and heat-stabilized polyamide of the pre-
 sent invention is obtained by subjecting polyamide-forming
 monomers to a polymerization process in the presence of (a) an
 20 effective amount of at least one piperidine compound represented
 by formula (I):

25



(I)

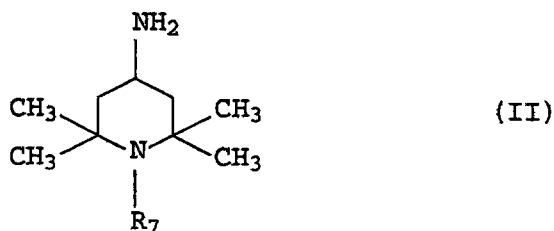
30

wherein R_1 is hydrogen, benzyl, or a C_1 - C_{20} , preferably a C_2 - C_4 ,
 alkyl, R_2 - R_5 are each hydrogen or the same or a different C_1 - C_6
 alkyl, X has n free valance bonding sites and is an alkyl or sub-
 stituted alkyl having from about 1 to about 30 carbon atoms or an
 35 aryl or substituted aryl having from about 6 to about 20 carbon
 atoms, m is 0 or 1, $-C(O)-R_6$ is a group that can form an amide
 bond together with an amine, and n is equal to 1, 2, or 3 and (b)
 an effective amount of at least one 4-amino-2,2,6,6,-tetramethyl-
 piperidine compound represented by formula (II):

40

45

5

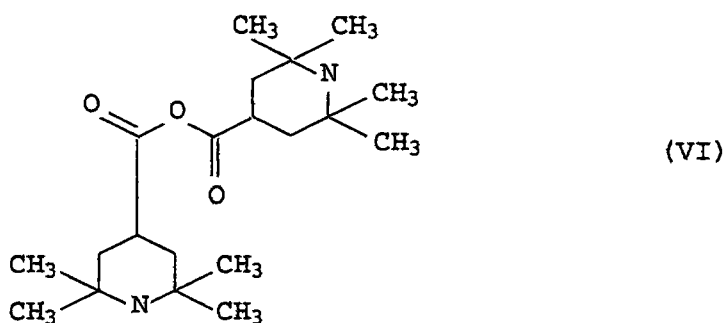


10 wherein R_7 is hydrogen, benzyl, or a C_1 - C_{20} alkyl. Preferably, R_7 is a C_1 - C_{18} alkyl and more preferably a C_2 - C_4 alkyl.

In formula (I), $-C(O)-R_6$ represents a group that can form an amide bond together with an amine such as, for example, carboxylic
 15 acid, alkyl ester, aryl ester, amide, and anhydride. Thus, R_6 may be selected from the group consisting of hydroxyl; $-OR_8$ where R_8 is a C_1 - C_{30} alkyl or a C_6 - C_{20} aryl; $-NHR_9$ where R_9 is hydrogen, a C_1 - C_{30} alkyl, or a C_6 - C_{20} aryl; $-NR_{10}R_{11}$ where R_{10} and R_{11} are each the same or a different C_1 - C_{30} alkyl or C_6 - C_{20} aryl; and $-OCOR_{12}$
 20 where R_{12} is a C_1 - C_{30} alkyl or a C_6 - C_{20} aryl. Most preferably, R_6 is hydroxyl.

With respect to the anhydride (i.e., where R_6 is $-OCOR_{12}$), it may be a symmetrical anhydride (i.e., R_{12} and the piperidine compound
 25 of formula (I) are identical) or an asymmetrical anhydride (i.e., R_{12} and the piperidine compound of formula (I) are different). A preferred anhydride is 4-carboxy-2,2,6,6-tetramethylpiperidine anhydride represented by formula (VI):

30



35

As noted above, X is an alkyl having from about 1 to about 30
 40 carbon atoms or an aryl having from about 6 to about 20 carbon atoms. Alternatively, X may also be a substituted alkyl having a C_1 - C_{30} alkyl backbone wherein one or more of the hydrogen atoms is substituted with dialkyl amine, alkoxy, chlorine, or fluorine. Alternatively, X may also be a substituted aryl having a C_6 - C_{24}
 45 aryl backbone wherein one or more of the hydrogen atoms is substituted with dialkyl amine, alkoxy, chlorine, fluorine, or a

C₁-C₃₀ alkyl. Preferably, X is selected from the group consisting of C₁-C₄ alkyl, methylene, ethylene, and, if n is 2, -CH.

The preferred piperidine compound of formula (I) is

- 5 4-carboxy-2,2,6,6-tetramethylpiperidine (also referred to as "carboxy-TAD").

The polymerization process by which the polyamide of the present invention is formed is preferably carried out according to conventional processes such as, for example, those described in U.S. Patent No. 5,149,758 to Matthies, the entirety of which is herein incorporated by reference, but with the addition of an effective amount of one or more piperidine compounds of formula (I) and an effective amount of one or more 4-amino-2,2,6,6-tetramethylpiperidine compound of formula (II). An effective amount of at least one piperidine compound of formula (I) is an amount sufficient in combination with the one or more 4-amino-2,2,6,6-tetramethylpiperidine compounds of formula (II) to render the resultant polyamide inherently light- and heat-stable. Preferably, the effective amount of the one or more piperidine compounds of formula (I) is in the range of about 0.01 to about 0.70, and more preferably about 0.08 to about 0.50, weight percent based on the weight of the polyamide-forming monomers used. An effective amount of at least one 4-amino-2,2,6,6-tetramethylpiperidine compound of formula (II) is an amount sufficient in combination with the one or more piperidine compounds of formula (I) to render the resultant polyamide inherently light- and heat-stable. Preferably, the effective amount of the one or more 4-amino-2,2,6,6-tetramethylpiperidine compounds of formula (II) is in the range of about 0.01 to about 0.70, and more preferably about 0.08 to about 0.50, weight percent based on the weight of the polyamide-forming monomers used.

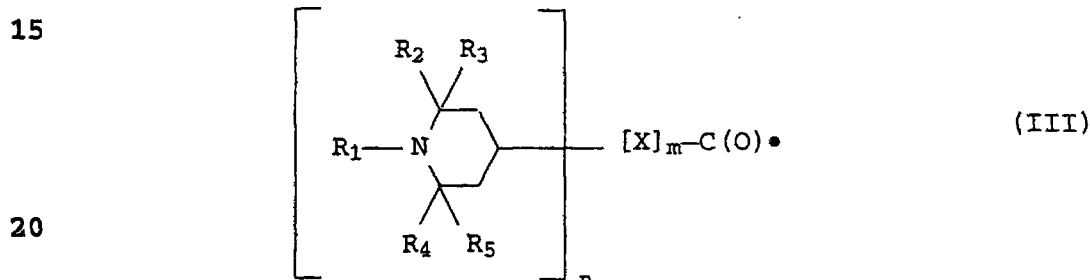
The one or more piperidine compounds of formula (I) may be added to the polyamide-forming compounds or to the polymerizing reaction mixture. Thus, the one or more piperidine compounds of formula (I) and the polyamide-forming monomers may be added separately or as a mixture to a reactor in which polymerization is effected.

40 Via the carboxy groups(s) thereof, the one or more piperidine compounds of formula (I) react with the polyamide-forming monomers or with the amine groups of the resulting polyamide such that the one or more piperidyl radicals of formula (III) becomes chemically bonded to the backbone polymer chain of the polyamide. The chemical bonding of the piperidyl radicals of formula (III)

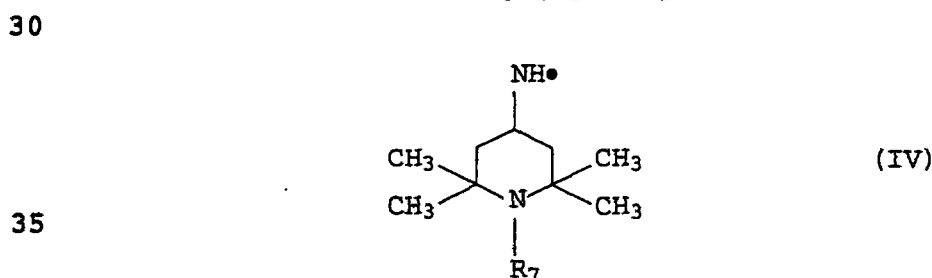
to the backbone polymer chain of the polyamide provides the polyamide with the inherent light- and heat-stability.

The one or more 4-amino-2,2,6,6-tetramethylpiperidine compounds of formula (II) also chemically bond to an end of the backbone polymer chain of the polyamide of the present invention through reaction of the primary amino groups of the one or more 4-amino-2,2,6,6-tetramethylpiperidine compounds of formula (II) with the polyamide-forming monomers themselves or with the carboxyl groups of the resulting polyamide.

The resulting polyamide, therefore, will contain one or more piperidyl radicals of formula (III):



wherein R_1 is hydrogen, benzyl, or a C_1 - C_{20} , preferably a C_2 to C_4 , alkyl, R_2 - R_5 are each hydrogen or the same or a different C_1 - C_6 alkyl, X has n free valance bonding sites and is an alkyl or substituted alkyl having from about 1 to about 30 carbon atoms or an aryl or substituted aryl having from about 6 to about 20 carbon atoms, m is 0 or 1, and n is equal to 1, 2, or 3 and one or more 4-amino-2,2,6,6-tetramethylpiperidyl radicals of formula (IV):



wherein R_7 is hydrogen, benzyl, or a C_1 - C_{20} alkyl. Preferably, R_7 is a C_1 - C_{18} alkyl and more preferably a C_2 - C_4 alkyl.

The presence of the one or more 4-amino-2,2,6,6-tetramethylpiperidine compounds of formula (II) during the polymerization of the polyamide-forming monomers further enhances the light- and heat-stability of the polyamide of the present invention. Because of steric hindrance, it is believed that the secondary amino groups of the one or more 4-amino-2,2,6,6-tetramethylpiperidine

compounds of formula (II) do not react with the polyamide-forming monomers or the resulting polyamide. Thus, the one or more 4-amino-2,2,6,6-tetramethylpiperidine compounds of formula (II) may also function as a chain regulator.

5

The one or more 4-amino-2,2,6,6-tetramethylpiperidine compounds of formula (II) may be added to the polyamide-forming monomers or to the polymerizing reaction mixture. Preferably, the one or more 4-amino-2,2,6,6-tetramethylpiperidine compounds of formula (II) is added in an amount of from about 0.03 to about 0.80, more preferably from about 0.06 to about 0.40, mole percent, each in relation to one mole of amide groups in the polyamide.

10

Any suitable polyamide-forming monomers may be used to form the inherently light- and heat-stabilized polyamide of the present invention. Examples of such suitable polyamide-forming monomers are diamine compounds, dicarboxylic acids, caprolactam monomers, and combinations thereof.

15

According to one embodiment of the method of the present invention, the polyamide-forming monomers are composed of at least one diamine compound and at least one dicarboxylic acid. Preferred diamine compounds are hexamethylenediamine and tetramethylenediamine. Preferred dicarboxylic acids include adipic acid, sebacic acid, and terephthalic acid. Adipic acid and terephthalic acid are most preferred. Alternatively, the polyamide-forming monomers may be composed of dicarboxylic acid diamine salts.

20

25

According to another embodiment of the method of the present invention, the polyamide-forming monomers are composed of caprolactam monomers, which polymerize to form nylon 6.

30

In preferred embodiments of the present invention, the inherently light- and heat-stabilized polyamide of this invention is nylon 6, nylon 6/6, nylon 4/6, nylon 6/10, or aromatic nylons such as, for example, poly(meta-phenylene isophthalamide) and poly(para-phenylene terephthalamide), which are disclosed in U.S. Patent No. 3,287,324 to Sweeny and U.S. Patent Number 3,671,542 to Kwoleck, both of which are incorporated herein by reference.

35

40

In a more preferred embodiment of the method of the present invention, the one or more piperidine compounds of formula (I) and the one or more 4-amino-2,2,6,6-tetramethylpiperidine compounds of formula (II) are combined with an effective amount of at least one conventional chain regulator. The carboxy group(s) of the chain regulator(s) react at the amino end groups of the polyamide chain, while the amino group(s) of amine chain regulator(s) react

45

at the carboxylic end groups of the polyamide chain. Thus, the chain regulator(s) acts as a molecular weight controller.

The particular chain regulator, or combination of chain regulators, and the amount thereof are selected according to the desired amino end group content of the final polyamide product and according to the desired melt stability of the final polyamide product. The desired amino end group content of the final polyamide product will depend on the desired dyeability of the yarns or fibers produced from such polyamide product. The desired melt stability of the final polyamide product will depend on the practical requirements for the processing of the polyamide, particularly for the spinning of the polyamide.

Suitable chain regulators for use in the present invention include, for example, monocarboxylic acids, dicarboxylic acids, amines, diamines, and combinations thereof. Non-limiting examples of suitable monocarboxylic acids include acetic acid, propionic acid, and benzoic acid. Non-limiting examples of suitable dicarboxylic acids include C₄-C₁₀ alkane dicarboxylic acids, particularly adipic acid, azelaic acid, sebacic acid, decanedicarboxylic acid, and dodecanedioic acid; C₅-C₈ cycloalkane dicarboxylic acids, particularly cyclohexane-1,4-dicarboxylic acid; and benzoic dicarboxylic acids, particularly isophthalic acid, terephthalic acid, and naphthalene-2,6-dicarboxylic acid. Non-limiting examples of suitable amines include hexylamine, cyclohexylamine, octylamine, benzylamine, and 2-phenylethylamine. Non-limiting examples of suitable diamines include C₂-C₁₈ alkane diamines, particularly tetramethylene diamine, hexamethylene diamine, and dodecane diamine; C₅-C₈ cycloalkane diamines; and C₆-C₂₄ aryl diamines, particularly para-phenylene diamine, meta-phenylene diamine, meta-xylylene diamine, and para-xylylene diamine. The chain regulator(s) is preferably used in an amount of from about 0.06 to about 0.60, more preferably from about 0.10 to about 0.50, mole percent, each in relation to one mole of amide groups in the polyamide.

Preferably, the chain regulator(s) used in the present invention is one or more dicarboxylic acids or one or more diamines. The dicarboxylic acid or diamine chain regulator(s) may be the same as or different from a dicarboxylic acid or diamine that is used as a polyamide-forming compound.

In another embodiment of the present invention, the method of polymerization of polyamide-forming monomers in the presence of one or more piperidine compounds of formula (I) and one or more 4-amino-2,2,6,6-tetramethylpiperidine compounds of formula (II)

is also carried out in the presence of one or more pigments. Suitable pigments for use in the present invention include, for example, titanium dioxide and color-bearing compounds of organic or inorganic nature. The pigment(s) is preferably added to the
5 polyamide-forming monomers or to the polymerizing mixture in an amount of from about 0 to about 5, more preferably from about 0.02 to about 2, parts by weight per 100 parts by weight of the polyamide product.

10 Most preferably, the method of the present invention comprises subjecting polyamide-forming monomers to polymerization in the presence of one or more piperidine compounds of formula (I), one or more 4-amino-2,2,6,6-tetramethylpiperidine compounds of formula (II), and one or more chain regulators and/or pigments.

15

The present invention is further directed to articles produced from the inherently light- and heat-stabilized polyamides and to methods of producing such articles. Non-limiting examples of such articles include fibers, yarns, carpets, textile fabrics, and the

20 like. Fibers may be formed by subjecting the inherently light- and heat-stabilized polyamides of the present invention to any conventional fiber-forming process such as, for example, that disclosed in U.S. Patents Nos. 4,983,448 to Karageorgiou and 5,487,860 to Kent et al., the entirety of both of which are incorporated herein by reference. Preferably, the fiber-forming
25 process involves rapidly spinning the inherently light- and heat-stabilized polyamide at take-off speeds of at least about 4,000 m/min.

30 Similarly, fabrics may be formed by subjecting the inherently light- and heat-stabilized polyamides of the present invention to any conventional fabric-forming process such as, for example, that disclosed in U.S. Patent No. 4,918,947 to Speich, the entirety of which is incorporated herein by reference.

35

The articles formed from the inherently light- and heat-stabilized polyamides of the present invention may be dyed with conventional dyes used to dye nylons such as, for example, metalized and non-metalized acid dyes. Usual dyebath conditions for dyeing
40 nylon can be employed. The following general conditions are exemplary and not intended to be limiting. A dyebath is prepared at a volume equal to about 20 times the weight of the articles to be dyed. Processing chemicals are added including a chelating agent to prevent the deposition or complexing of metal ions in hard
45 water, a dye leveling agent, and, in the case of metalized acid dyes, an acid donor to slowly lower the dyebath pH. The dyestuff is added, and the dyebath pH is adjusted. The solution is heated

to the desired temperature of typically about from 95° C to about 110° C at a rate of from about 0.5° C to about 3.0° C per minute and is held at that temperature for about 30 minutes to about 60 minutes. The dyebath is cooled or emptied, and the articles are
5 thoroughly rinsed with fresh water. The dyed articles are dried in a tumble drier or an oven such as a Tenter or are passed over heater cans. The dyed articles may then be optionally heatset to improve dimensional stability.

- 10 Alternatively, fibers made from the inherently light- and heat-stabilized polyamides of the present invention may be solution-dyed before being formed into articles. Usual conditions for solution-dyeing nylon can be employed. The following general conditions are exemplary and not intended to be limiting. The
15 polyamide of the present invention is melted and colored with a colorant selected from the group consisting of pigments, dyes, any colored compound with properties between pigments and dyes, and combinations thereof. The colored polyamide is then spun into fibers or fabric according to conventional methods such as, for
20 example, those disclosed in U.S. Patent No. 4,983,448 to Kara-georgiou, U.S. Patent No. 5,487,860 to Kent et al., and U.S. Patent No. 4,918,947 to Speich.

The present invention will be further described by reference to
25 the following detailed examples. The examples are set forth by way of illustration and are not intended to limit the scope of the invention. As used in the examples, the following terms and test procedures are defined as follows:

30 **Weight Percent.**

The weight percentage of that component in the charge.

Relative Viscosity (RV).

- The relative viscosity compares the viscosity of a solution of
35 polymer in formic acid with the viscosity of the formic acid itself (ASTM D 789). The test results reported herein were obtained using 0.20 g of nylon 6 dissolved in 20 cc. of formic acid at 25°C.

40 **Color Measurements.**

Color measurements are made using an Applied Color Systems ("ACS") Spectrophotometer generating 1976 CIE LAB (D6500 illuminant, 10 degree observer) values. Total color difference (or
Delta E, wherein higher Delta E values indicate more color

- 45 change) calculations are made against unexposed controls. Details of CIE LAB measurements and the calculation of total color difference (Delta E) are found in color science literature such as,

for example, Billmeyer and M. Saltzman, *Principles of Color Technology*, 2nd edition.

End Group Content.

- 5 The amino end group content is determined by dissolving about 2.0 g of nylon 6 in about 60 cc. of a phenol-methanol mixture (68:32). This solution is titrated with about 0.20 normal HCl at about 25° C by a potentiometric method, wherein the endpoint is determined by a steep potential increase.

10

The carboxy end group content is determined by dissolving about 0.30 g of nylon 6 in about 40 cc. of a mixture of benzyl alcohol at 180° C. The solution is titrated with about 0.03 normal t-butyl ammonium hydroxide at about 80° C to about 100° C by a poten-

15 tiometric method, wherein the endpoint is determined by a steep potential increase.

EXAMPLE 1 (Control I)

20 Polymer Containing No Stabilizers

- In a polymerization of a nylon 6 polymer (RV 2.4), 4 kg caprolactam, 400 g water, 6.0 g (0.15 weight percent) of propionic acid are charged into a 11-liter autoclave. The mixture is heated
- 25 to about 260° C in one hour, while the pressure increases to about 60 psi (3,102 mm Hg). After holding the mixture at about 60 psi (3,102 mm Hg) for about 30 minutes, the pressure is slowly released. To accelerate polymerization, the system is placed under a vacuum of 300 mbar over the last 15 minutes. The polymer is
- 30 then extruded under a positive nitrogen pressure and cut into chips. The chips are washed 6 times with 6 L of hot water (about 100° C) and dried under nitrogen. The polymer is postcondensed at 160° C to increase the viscosity to 2.7. The amino end group content measures about 33 meq/kg, and the carboxylic end group con-
- 35 tent measures about 50 meq/kg.

EXAMPLE 2 (Control II)

40 Polymer Containing TAD Stabilizer

- In a polymerization of a nylon 6 polymer (RV 2.4), 4 kg caprolactam, 400 g water, 22.8 g (0.57 weight percent) of terephthalic acid, 10.8 g (0.27 weight percent) of 4-amino-2,2,6,6-tetramethylpiperidine are charged into a 11-liter autoclave. The mixture
- 45 is heated to about 260° C in one hour, while the pressure increases to about 60 psi (3,102 mm Hg). After holding the mixture at about 60 psi (3,102 mm Hg) for about 30 minutes, the pressure is

slowly released. To accelerate polymerization, the system is placed under a vacuum of 300 mbar over the last 15 minutes. The polymer is then extruded under a positive nitrogen pressure and cut into chips. The chips are washed 6 times with 6 L of hot water (about 100° C) and dried under nitrogen. The polymer is postcondensed at 160°C to increase the viscosity to 2.4. The amino end group content measures about 35 meq/kg, and the carboxylic end group content measures about 71 meq/kg.

10 EXAMPLE 3

Polymer Containing TAD and Carboxy-TAD Stabilizers

In a polymerization of a nylon 6 polymer (RV 2.4), 4 kg caprolactam, 400 g water, 22.8 g (0.57 weight percent) of terephthalic acid, 10.8 g (0.27 weight percent) of 4-amino-2,2,6,6-tetramethylpiperidine, and 12.8 g (0.32 weight percent) of 4-carboxy-2,2,6,6-tetramethylpiperidine are charged into a 11-liter autoclave. The mixture is heated to about 260° C in one hour, while the pressure increases to about 60 psi (3,102 mm Hg). After holding the mixture at about 60 psi (3,102 mm Hg) for about 30 minutes, the pressure is slowly released. To accelerate polymerization, the system is placed under a vacuum of 300 mbar over the last 15 minutes. The polymer is then extruded under a positive nitrogen pressure and cut into chips. The chips are washed 6 times with 6 L of hot water (about 100° C) and dried under nitrogen. The polymer is postcondensed at 160°C to increase the viscosity to 2.4. The amino end group content measures about 36 meq/kg, and the carboxylic end group content measures about 89 meq/kg.

EXAMPLE 4

Polymer Containing TAD and Carboxy-TAD Stabilizers

In a polymerization of a nylon 6 polymer (RV 2.4), 75 kg caprolactam, 1800 g water, 412.5 g (0.55 weight percent) of terephthalic acid, 202.5 g (0.27 weight percent) of 4-amino-2,2,6,6-tetramethylpiperidine, and 75 g (0.10 weight percent) of 4-carboxy-2,2,6,6-tetramethylpiperidine are charged into a 250-liter autoclave. The mixture is heated to about 270° C in one hour, while the pressure increases to about 60 psi (3,102 mm Hg). After holding the mixture at about 60 psi (3,102 mm Hg) for about 30 minutes, the pressure is slowly released. To accelerate polymerization, the system is placed under a vacuum of 500 mm Hg for less than 5 minutes. The polymer is then extruded under a positive nitrogen pressure and cut into chips. The chips are washed

with hot water (about 90° C) and dried in a tumble dryer. The amino end group content measures about 41 meq/kg, and the carboxylic end group content measures about 78 meq/kg.

5 EXAMPLE 5

Polymer Containing TAD and Carboxy-TAD Stabilizers with Titanium Dioxide

- 10 In a polymerization of a nylon 6 polymer (RV 2.4), 74 kg caprolactam, 1800 g water, 412.5 g (0.55 weight percent) of terephthalic acid, 202.5 g (0.27 weight percent) of 4-amino-2,2,6,6-tetramethylpiperidine, 75 g (0.10 weight percent) of 4-carboxy-2,2,6,6-tetramethylpiperidine, and 750 g (0.30
- 15 weight percent) of a nylon-6 master batch containing about 30 percent titanium dioxide are charged into a 250-liter autoclave. The mixture is heated to about 270° C in one hour, while the pressure increases to about 60 psi (3,102 mm Hg). After holding the mixture at about 60 psi (3,102 mm Hg) for about 30 minutes,
- 20 the pressure is slowly released. To accelerate polymerization, the system is placed under a vacuum of 500 mm Hg for less than 5 minutes. The polymer is then extruded under a positive nitrogen pressure and cut into chips. The chips are washed with hot water (about 90° C) and dried in a tumble dryer. The amino end group
- 25 content measures about 41 meq/kg, and the carboxylic end group content measures about 78 meq/kg.

EXAMPLE 6

30 Polymer Containing TAD and Carboxy-TAD Stabilizers

- In a polymerization of a nylon-6 polymer (RV 2.7), 75 kg caprolactam, 1800 g water, 225 g (0.30 weight percent) of terephthalic acid, 112.5 g (0.15 weight percent) of 4-amino-2,2,6,6-tetramethylpiperidine, and 75 g (0.10 weight percent) of
- 35 4-carboxy-2,2,6,6-tetramethylpiperidine are charged into a 250-liter autoclave. The mixture is heated to about 270° C in one hour, while the pressure increases to about 60 psi (3,102 mm Hg). After holding the mixture at about 60 psi (3,102 mm Hg) for about
- 40 30 minutes, the pressure is slowly released. To accelerate polymerization, the system is placed under a vacuum of 500 mm Hg for 30 minutes. The polymer is then extruded under a positive nitrogen pressure and cut into chips. The chips are washed with hot water (about 90° C) and dried in a tumble dryer. The amino end
- 45 group content measures about 41 meq/kg, and the carboxylic end group content measures about 65 meq/kg.

EXAMPLE 7

Spinning of Bright 40 Denier/12 Filament Yarn

- 5 The resulting nylon 6 polymers of Examples 1 through 3 are each extruded at 265-275° C. The extruded filaments are cooled and solidified by a stream of quench air at 15° C. The filaments are lubricated with spin finish below the quench cabinet and are air interlaced to improve filament cohesion. Yarns are taken up on a
10 winder at speeds greater than about 1300 m/min. The yarns are drawn prior winding, and the draw ratio varies from about 3.0 to about 3.3.

EXAMPLE 8

15

Yellowing of Scoured Knitted Tubes

- The yarns (made in Example 7) from the polymers of Examples 1 through 3 are knitted into tubes. These three knitted tubes are
20 scoured in a 20:1 bath at 1.0 percent on weight of fabric (hereinafter "owf") Kierlon NB-OL® (an anionic scouring agent available from BASF Corporation of Mount Olive, New Jersey) and 1.0 percent owf tetrasodium pyrophosphate to remove spin finish and are rinsed and dried. The three knitted tubes are then exposed in
25 an Atlas Ci65 Xenon-Arc Weather-Ometer® for 700 hours (987 kJ) in 100 hour (141 kJ) increments by the conditions specified in the GM SAE J1885 Test Method. The exposed tubes are measured at each increment of exposure for yellowing on an ACS Spectrophotometer. The Delta b* values are a measure of yellowing. A higher Delta b*
30 value indicates a more yellow sample. The results of these exposures, which are plotted in FIG. 1, show that the tubes spun from 0.15 weight percent propionic acid (control I) and 0.57 weight percent terephthalic acid /0.27 weight percent
35 4-amino-2,2,6,6-tetramethylpiperidine (control II) yellow significantly more than the tubes spun from 0.57 weight percent terephthalic acid/0.27 weight percent 4-amino-2,2,6,6-tetramethylpiperidine/0.32 weight percent 4-carboxy-2,2,6,6-tetramethylpiperidine (invention).

40 EXAMPLE 9

Heat Aging of Yarns

- Another set of knitted tubes made in accordance with Example 8
45 are exposed in a forced air heated oven at 170° C for about 23 minutes to determine the relative yellowing between the different yarns when exposed to this extreme condition. After this heat ex-

posure, the samples are measured for yellowing on the ACS Spectrophotometer, and their color difference relative to an unexposed control is determined. These Delta b* values are given in Table 1 below (each Delta b* value in Table 1 is the average of two readings per sample from two samples for each condition). The results in Table 1 show that the tube spun from 0.57 weight percent terephthalic acid/0.27 weight percent 4-amino-2,2,6,6-tetramethylpiperidine/0.32 weight percent 4-carboxy-2,2,6,6-tetramethylpiperidine (invention) yellows less than the tubes spun from the other polymers (control I and control II).

TABLE 1

Heat Aging (Yellowing) of Scoured/Knitted Yarns

15

Sample	Delta b* Value
0.15 weight percent propionic acid (Example 1)	8.0
0.57 weight percent terephthalic acid/0.26 weight percent 4-amino-2,2,6,6-tetramethylpiperidine (Example 2)	7.3
0.57 weight percent terephthalic acid/0.27 weight percent 4-amino-2,2,6,6-tetramethylpiperidine/0.32 weight percent 4-carboxy-2,2,6,6-tetramethylpiperidine (Example 3)	2.6

25

EXAMPLE 10

Strength Retention

30

Three more sets of knitted tubes made in accordance with Example 8 are dyed in separate equivalent dye baths in typical automotive headliner shades of green, gray, and burgundy. The dyeings are done in a 30:1 dye liquor ratio using the following: 0.5 percent owf Supralev AC[®] (a dyeing assistant and leveler available from Rhone-Poulenc, Inc. of Lawrenceville, Georgia), 1.0 percent owf Sandogen NH[®] (a dye leveling agent available from Clariant Corporation of Charlotte, North Carolina), and 0.5 percent owf Amquest LDS[®] (a dye solubilizer available from American Emulsions Company of Dalton, Georgia). The dye baths are adjusted to a pH of 6.5 with acetic acid and heated to 95° C at 1° C per minute. The dye baths are run for about 45 minutes at 95° C after which they are cooled, and the dyed samples are rinsed and dried. The following dyes are used to formulate the dye shades: Intralan[®] Yellow GRL 200 percent, Intralan[®] Bordeaux RLB 200 percent, and Intralan[®] Bordeaux EL 200 percent, Irgalan[®] Yellow 2GL 250 percent, Irgalan[®] Yellow 3RL, Irgalan[®] Yellow GRL 200 percent, Irgalan[®] Black

45

RBL 200 percent, Irgalan® Blue 3GL 200 percent, Irgalan® Red Brown RL 200 percent and Irgalan® Grey GL 200 percent all available from Ciba Specialty Chemicals Corporation of High Point, North Carolina, and Lanasyn® Yellow LNW available from Clariant Corporation.

After dyeing, the samples are tested for automotive dye light-fastness by exposure in an Atlas Ci65 Xenon-Arc Weather-Ometer® for 112.8 kJ, 225.6, 300.8 and 488.8 kJ by the conditions specified in the GM SAE J1885 Test Method. The strength of the yarns unraveled from the knitted tubes, as well as the strength retention of an original dyed, non-exposed sample, is measured before exposure and after each increment of exposure. These results are shown in FIG. 2. The results indicate that, for each of the dyed shades, the sample with 0.57 weight percent terephthalic acid/0.27 weight percent 4-amino-2,2,6,6-tetramethylpiperidine/0.32 weight percent 4-carboxy-2,2,6,6-tetramethylpiperidine (invention) has less strength loss than the controls (0.15 weight percent propionic acid and 0.57 weight percent terephthalic acid/0.27 weight percent 4-amino-2,2,6,6-tetramethylpiperidine).

While the invention has been described in connection with what is presently considered to be the most practical and preferred embodiment, it is to be understood that the invention is not to be limited to the disclosed embodiment, but on the contrary, is intended to cover various modifications and equivalents arrangements included within the spirit and scope of the appended claims.

30

35

40

45

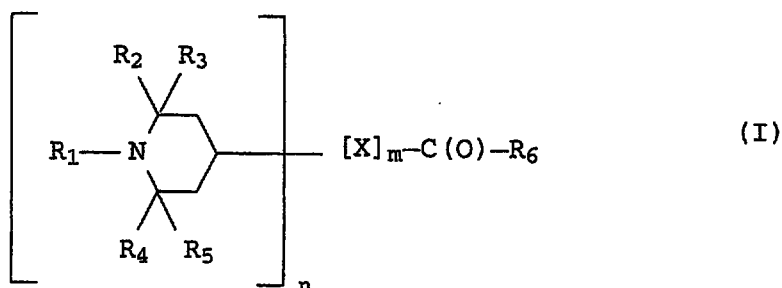


We claim:

1. A method of making an inherently light- and heat-stabilized polyamide comprising subjecting one or more polyamide-forming monomers to a polymerization process in the presence of (a) an effective amount of at least one piperidine compound represented by formula (I):

10

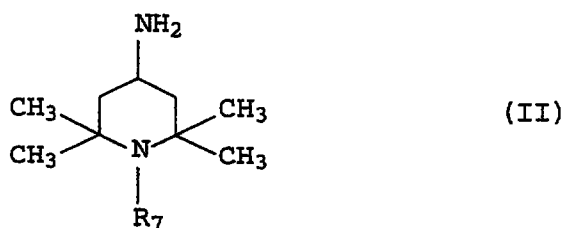
15



wherein R_1 is hydrogen, benzyl, or a $\text{C}_1\text{-C}_{20}$ alkyl, $\text{R}_2\text{-R}_5$ are each hydrogen or the same or a different $\text{C}_1\text{-C}_6$ alkyl, X has n free valance bonding sites and is an alkyl or substituted alkyl having, from about 1 to about 30 carbon atoms or an aryl or substituted aryl having from about 6 to about 20 carbon atoms, m is 0 or 1, $\text{-C}(\text{O})\text{-R}_6$ is a group that can form an amide bond together with an amine, and n is equal to 1, 2, or 3 and (b) an effective amount of at least one 4-amino-2,2,6,6-tetramethylpiperidine compound represented by formula (II):

30

35



wherein R_7 is hydrogen, benzyl, or a $\text{C}_1\text{-C}_{20}$ alkyl.

2. The method of claim 1 wherein R_1 and R_7 are hydrogen, $\text{R}_2\text{-R}_5$ are each a methyl group, R_6 is a hydroxyl group, m is 0, and n is 1.

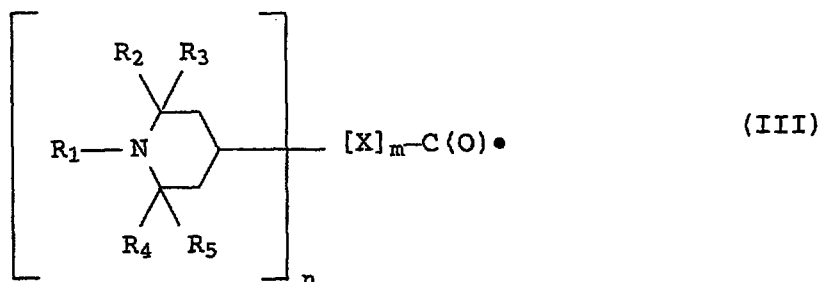
45



3. The method of claim 1 wherein R_1 and R_7 are hydrogen, R_2 - R_5 are each a methyl group, R_6 is a hydroxyl group, m is 1, n is 1, and X is selected from the group consisting of C_1 - C_4 alkyl, methylene, and ethylene.
- 5
4. The method of claim 3 wherein X is CH_2 .
5. The method of claim 1 wherein the polyamide-forming monomers comprise caprolactam monomers.
- 10
6. The method of claim 1 wherein the polyamide-forming monomers comprise at least one diamine compound and at least one dicarboxylic acid.
- 15
7. The method of claim 6 wherein the at least one diamine compound is selected from the group consisting of hexamethylenediamine and tetramethylenediamine and the at least one dicarboxylic acid is selected from the group consisting of adipic acid, sebacic acid, and terephthalic acid.
- 20
8. The method of claim 1 wherein the polyamide-forming monomers comprise dicarboxylic acid diamine salts.
- 25
9. The method of claim 1 wherein the polymerization process is further carried out in the presence of at least one chain-regulating compound other than the compounds represented by formulae (I) and (II).
- 30
10. The method of claim 9 wherein the at least one chain-regulating compound is selected from the group consisting of monocarboxylic acids, dicarboxylic acids, amines, diamines, and combinations thereof.
- 35
11. The method of claim 10 wherein the at least one chain-regulating compound comprises one or more dicarboxylic acids.
- 40
12. The method of claim 11 wherein the one or more dicarboxylic acids is selected from the group consisting of C_4 - C_{10} alkane dicarboxylic acids, C_5 - C_8 cycloalkane dicarboxylic acids, benzoic dicarboxylic acids, and combinations thereof.
- 45
13. The method of claim 12 wherein the one or more dicarboxylic acids is selected from the group consisting of adipic acid, terephthalic acid, sebacic acid, decanedicarboxylic acid, isophthalic acid, and combinations thereof.



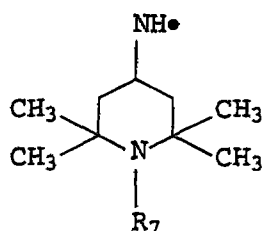
14. The method of claim 10 wherein the at least one chain-regulating compound comprises one or more diamines.
15. The method of claim 14 wherein the one or more diamines is selected from the group consisting of C₂-C₁₈ alkane diamines, C₅-C₈ cycloalkane diamines, C₆-C₂₄ aryl diamines, and combinations thereof.
16. The method of claim 1 wherein the polymerization process is further carried out in the presence of at least one pigment.
17. The method of claim 1 wherein the inherently light- and heat-stabilized polyamide is selected from the group consisting of nylon 6, nylon 6/6, nylon 4/6, nylon 6/10, and aromatic nylons selected from the group consisting of poly(meta-phenylene isophthalamide) and poly(para-phenylene terephthalamide).
18. An inherently light- and heat-stabilized polyamide comprising:
- (a) a backbone polymer chain having two chain ends;
 - (b) at least one piperidyl radical chemically bonded to one end of the backbone polymer chain of the inherently light- and heat-stabilized polyamide, the at least one piperidyl radical represented by formula (III):



wherein R₁ is hydrogen, benzyl, or a C₁-C₂₀ alkyl, R₂-R₅ are each hydrogen or the same or a different C₁-C₆ alkyl, X has n free valance bonding sites and is an alkyl or substituted alkyl having from about 1 to about 30 carbon atoms or an aryl or substituted aryl having from about 6 to about 20 carbon atoms, m is 0 or 1, and n is equal to 1, 2, or 3; and

- (c) at least one 4-amino-2,2,6,6-tetramethylpiperidyl radical chemically bonded to the other end of the backbone polymer chain of the inherently light- and heat-stabilized

polyamide, the at least one 4-amino-2,2,6,6-tetramethyl-piperidyl radical represented by formula (IV):



(IV)

wherein R_7 is hydrogen, benzyl, or a C_1 - C_{20} alkyl.

- 15 19. The polyamide of claim 18 wherein R_1 and R_7 are hydrogen, R_2 - R_5 are each a methyl group, R_6 is a hydroxyl group, m is 0, and n is 1.
- 20 20. The polyamide of claim 18 wherein R_1 and R_7 are hydrogen, R_2 - R_5 are each a methyl group, R_6 is a hydroxyl group, m is 1, X is a CH_2 , and n is 1.
- 25 21. The polyamide of claim 18 further comprising at least one radical of at least one chain-regulating compound other than the compounds represented by formulae (III) and (IV), the at least one radical being chemically bonded to the backbone polymer chain.
- 30 22. The polyamide of claim 21 wherein the at least one chain-regulating compound is selected from the group consisting of monocarboxylic acids, dicarboxylic acids, amines, diamines, and combinations thereof.
- 35 23. The polyamide of claim 22 wherein the at least one chain-regulating compound comprises one or more dicarboxylic acids.
- 40 24. The polyamide of claim 23 wherein the one or more dicarboxylic acids is selected from the group consisting of C_4 - C_{10} alkane dicarboxylic acids, C_5 - C_8 cycloalkane dicarboxylic acids, benzoic dicarboxylic acids, and combinations thereof.
- 45 25. The polyamide of claim 24 wherein the one or more dicarboxylic acids is selected from the group consisting of adipic acid, terephthalic acid, sebacic acid, decanedicarboxylic acid, isophthalic acid, and combinations thereof.

26. The polyamide of claim 22 wherein the at least one chain-regulating compound comprises one or more diamines.
27. The polyamide of claim 26 wherein the diamine is selected
5 from the group consisting of C₂-C₁₈ alkane diamines, C₅-C₈ cycloalkane diamines, C₆-C₂₄ aryl diamines, and combinations thereof.
28. The polyamide of claim 18 where in the polyamide further com-
10 prises at least one pigment.
29. The polyamide of claim 18 wherein the inherently light- and heat-stabilized polyamide is selected from the group consisting of nylon 6, nylon 6/6, nylon 4/6, nylon 6/10, and aromatic
15 nylons selected from the group consisting of poly(meta-phenylene isophthalamide) and poly(para-phenylene terephthalamide).
30. An article comprising the inherently light- and heat-stabilized
20 polyamide of claim 18.
31. The article of claim 30 wherein the article is selected from the group consisting of fibers, yarns, carpets, and textile fabrics.
- 25 32. The article of claim 31 wherein the article is a pigmented fiber.
33. The article of claim 31 wherein the article is a dyed fiber.
30

35



40

45

FIG.1

1/2

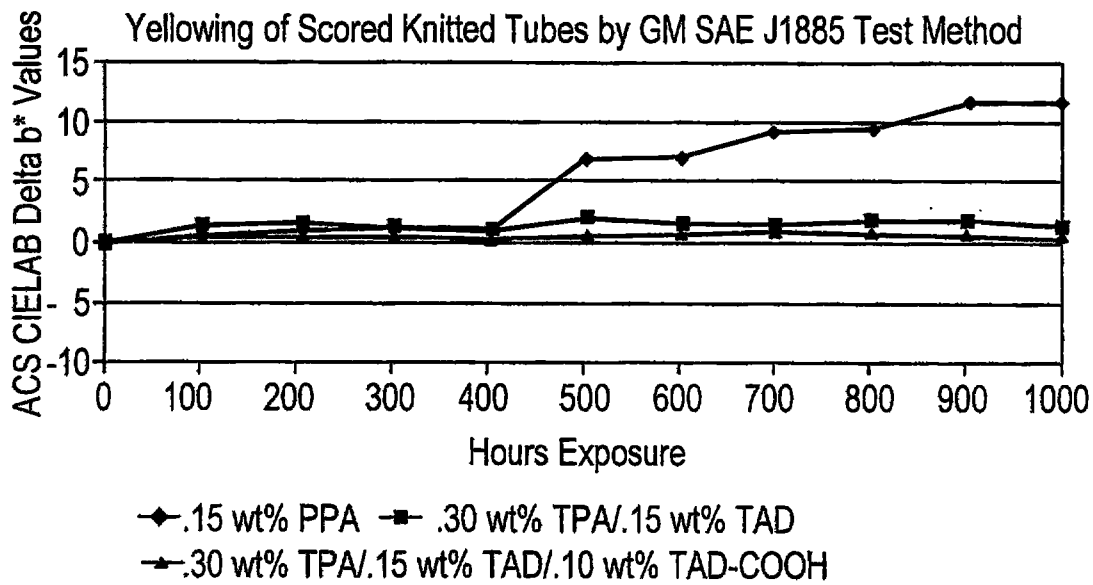


FIG.2

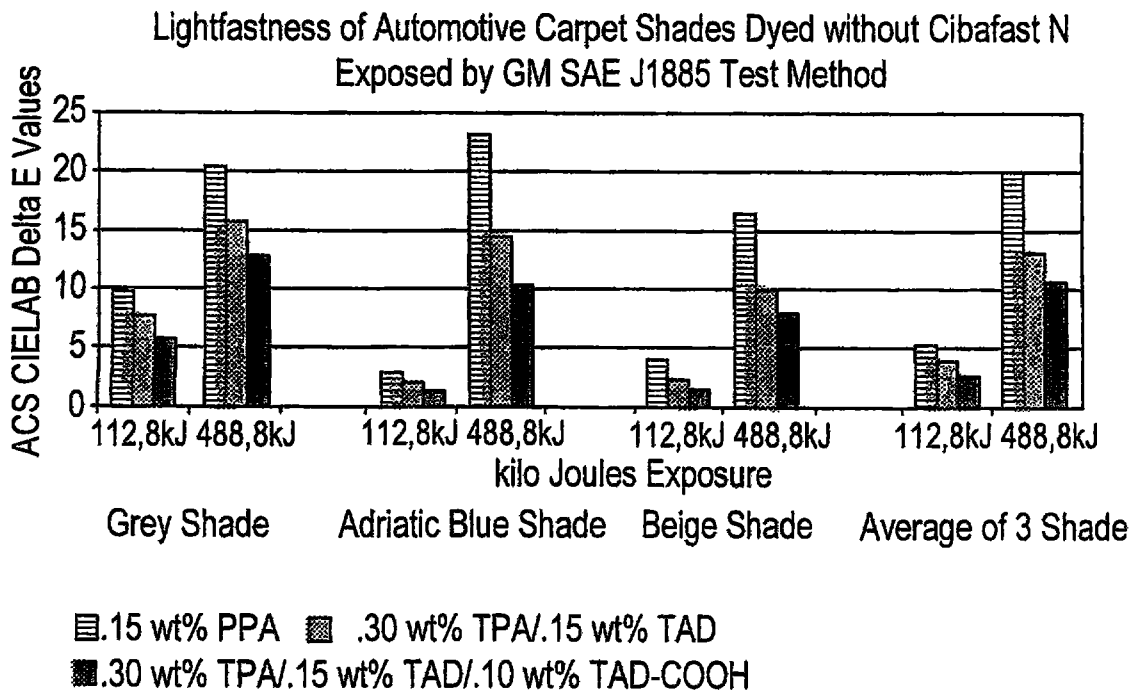
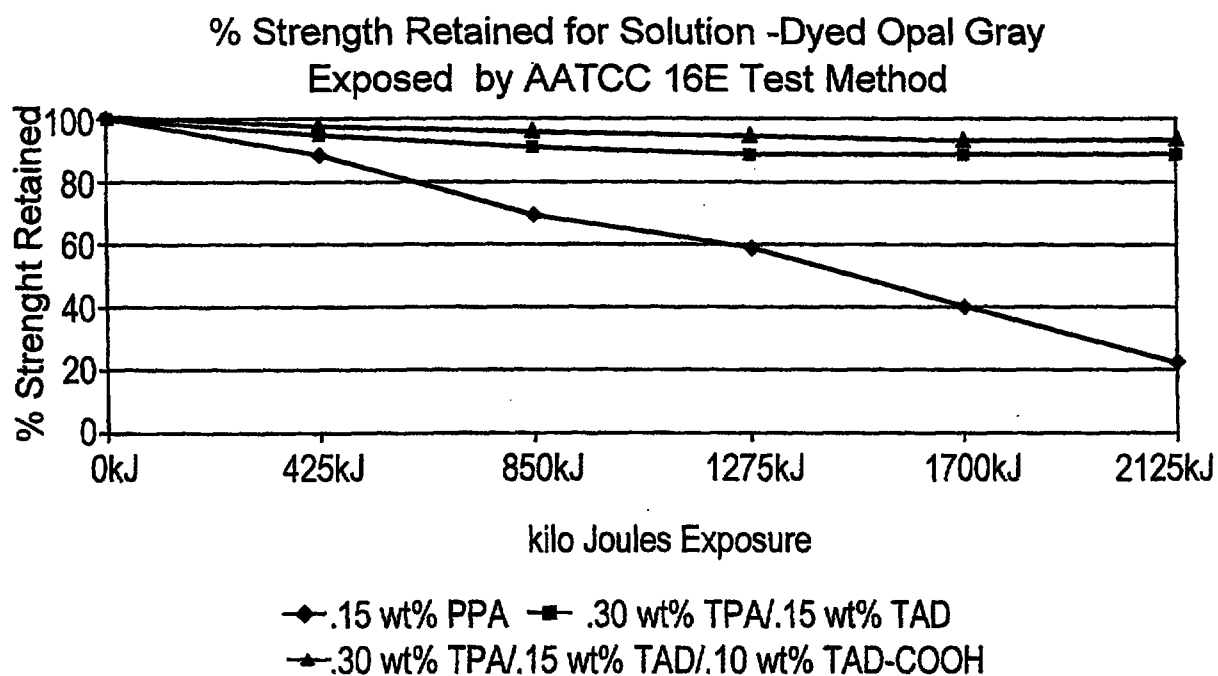


FIG.3

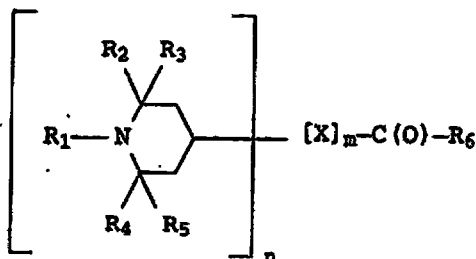




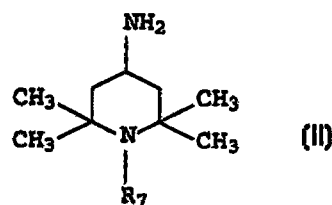
INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶: C08G 69/00, C08K 5/3435	A1	(11) International Publication Number: WO 99/41297 (43) International Publication Date: 19 August 1999 (19.08.99)
(21) International Application Number: PCT/EP99/00932 (22) International Filing Date: 12 February 1999 (12.02.99) (30) Priority Data: 60/074,578 13 February 1998 (13.02.98) US (71) Applicant (for all designated States except US): BASF AKTIENGESSELLSCHAFT [DE/DE]; D-67056 Ludwigshafen (DE). (72) Inventors; and (75) Inventors/Applicants (for US only): ILG, Otto [DE/US]; 6 Westwood Road, Asheville, NC 28803 (US). BREINER, Ulrike [DE/DE]; Spessartstrasse 7, D-68642 Birstadt (DE). JULIUS, Manfred [DE/DE]; Albert-Einstein-Allee 13a, D-67117 Limburgerhof (DE). (74) Common Representative: BASF AKTIENGESSELLSCHAFT; D-67056 Ludwigshafen (DE).		(81) Designated States: AL, AU, BG, BR, BY, CA, CN, CZ, GE, HU, ID, IL, IN, JP, KR, KZ, LT, LV, MK, MX, NO, NZ, PL, RO, RU, SG, SI, SK, TR, UA, US, UZ, VN, Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>

(54) Title: INHERENTLY LIGHT- AND HEAT-STABILIZED POLYAMIDE AND METHOD OF MAKING THE SAME



(I)



(II)

(57) Abstract

An inherently light- and heat-stabilized polyamide is prepared by polymerizing polyamide forming monomers in the presence of (a) an effective amount of at least one 4-carboxy-2,2,6,6-tetramethylpiperidine compound represented by formula (I): wherein R_1 is hydrogen, benzyl, or a C_1 - C_{20} alkyl; R_2 - R_5 are each hydrogen or the same or a different C_1 - C_6 alkyl; X has n free valance bonding sites and is an alkyl or substituted alkyl having from about 1 to about 30 carbon atoms or an aryl or substituted aryl having from about 6 to about 20 carbon atoms; m is 0 or 1; $-C(O)-R_6$ is a group that can form an amide bond together with an amine, and n is equal to 1, 2 or 3 and (b) an effective amount of at least one 4-amino-2,2,6,6-tetramethylpiperidine compound represented by formula (II): wherein R_7 is hydrogen, benzyl, or a C_1 - C_{20} alkyl. The inherently light- and heat-stabilized polyamide comprises at least one radical of the at least one piperidine compound of formula (I) chemically bonded to the backbone polymer chain and at least one radical of the at least one 4-amino-2,2,6,6-tetramethylpiperidine compound of formula (II) chemically bonded to the backbone polymer chain. The inherently light- and heat-stabilized polyamide may be used to form articles such as, for example, fibers, carpets, yarns, and textile fabrics.