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3,655,819

POLYAMIDE FILAMENTS CONTAINING POLY-ALKYLENE ETHERS AND PHENOLIC ANTI-OXIDANTS

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U.S. Cl. 260—857 PE

19 Claims

ABSTRACT OF THE DISCLOSURE

A filament, having improved resistance to light, of a polyamide having incorporated therethrough about 0.3 to 7 weight percent, based on the weight of the polyamide, of a poly(alkylene ether) having a molecular weight from about 600 to 3,000,000, and about 0.05 to 2 weight percent, based on the weight of the polyamide, of a sterically hindered phenolic compound.

BACKGROUND OF THE INVENTION

This invention relates to a filament of a synthetic polymer. More particularly, this invention relates to a filament, having improved resistance to light, of a polyamide having mixed therethrough a small amount of a poly(alkylene ether) and a sterically hindered phenolic compound.

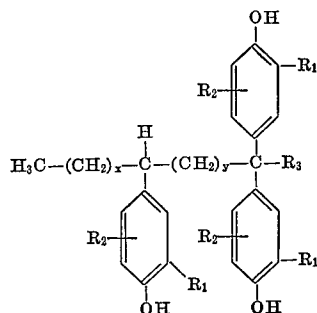
The soiling of synthetic fibers has always been a problem to the textile industry and various different chemical compounds have been used in the prior art to alleviate this problem. The poly(alkylene ethers) have been found to be particularly effective soil resistance additives for polyamide filaments, however, they have the disadvantage of reducing the resistance of the polyamide filaments to light. For example, the incorporation of a poly(alkylene ether) in a polyamide filament in an amount sufficient to impart soil resistance significantly reduces the percent breaking strength retention of the filament when it is exposed to light. In addition, the incorporation of a poly(alkylene ether) in a polyamide filament in an amount sufficient to impart soil resistance significantly reduces the dyelightfastness of a dyed filament when it is exposed to light.

It has now been discovered that a small amount of a sterically hindered phenolic compound can be incorporated along with a poly(alkylene ether) in a polyamide filament to improve its resistance to light.

SUMMARY OF THE INVENTION

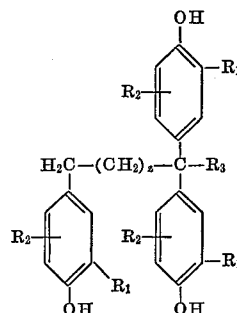
In accordance with the present invention, there is provided a filament, having improved resistance to light, of a polyamide having incorporated therethrough about 0.3 to 7, preferably about 2 to 5, weight percent, based on the weight of the polyamide, of a poly(alkylene ether) said poly(alkylene ether) having a molecular weight from about 600 to 3,000,000, preferably about 1,000 to 100,000, and about 0.05 to 2, preferably about 0.1 to 1, weight percent, based on the weight of the polyamide, of a sterically hindered phenolic compound which can be of one having the general formulas:

(I)

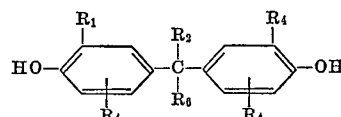


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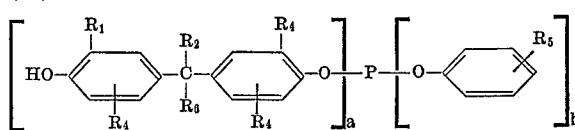
(II)



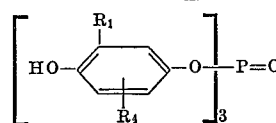
(III)



(IV)



(V)



or mixtures thereof; wherein R_1 is a sterically hindering radical selected from the group consisting of cyclohexyl, phenyl, and alkyl containing about 3 to 8 carbon atoms, which is preferably tertiary alkyl and most preferably is tertiary butyl; R_2 is a lower alkyl radical containing up to about 8 carbon atoms; R_3 is hydrogen or a lower alkyl radical containing up to about 8 carbon atoms; R_4 is hydrogen, lower alkyl containing up to about 8 carbon atoms, or R_1 ; R_5 is an alkyl radical containing about 4 to 20, preferably about 6 to 10 and most preferably 8 or 9, carbon atoms which is preferably in the meta or para position; R_6 is a lower alkyl radical containing up to about 8 carbon atoms; x is an integer of 0 to 5, preferably 0 to 3; y is an integer of 1 to 6, preferably 1 to 3; the sum of x and y is no greater than 6 and is at least 1; z is an integer of 1 to 7, preferably 1 to 3; a is an integer of 1 to 3, preferably 2 or 3; b is an integer of 0 to 2, preferably 1 or 2; and the sum of a and b is 3.

Suitable polyamides for use in the present invention include, for example, those prepared by condensation of hexamethylene diamine and adipic acid, condensation of hexamethylene diamine and sebacic acid known as nylon 6,6 and nylon 6,10, respectively, condensate of bis(para-aminocyclohexyl)methane and azelaic acid, condensation of bis(para-aminocyclohexyl)methane and dodecanedioic acid, or by polymerization of 6-caprolactam, 7-aminoheptanoic acid, 8-capryllactam, 9-aminopelargonic acid, 11-aminoundecanoic acid, and 12-dodecalactam, known as nylon 6, nylon 7, nylon 8, nylon 9, nylon 11, and nylon 12, respectively.

The poly(alkylene ethers) which can be incorporated in the polyamide are either ethylene oxide, propylene oxide or ethylene oxide-propylene oxide condensation products including ethylene oxide-propylene oxide copolymers, that is, the products contain from two to three carbon atoms in the alkylene group with two of the carbon atoms being intralinear carbon atoms connecting intralinear ether-oxygen atoms. Preferably, the poly(alkylene ether) is an ethylene oxide polymer. The poly(alkylene ether) can be a glycol ether, and thus terminated or capped by hydroxyl groups, or it can be an oxyalkylated ether of a monohydric or polyhydric alcohol. Suitable alcohols are methanol, eth-

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anol, i-octanol, decanol, lauro, tridecanol, glycerol, pentaerythritol, sorbitol, mannitol, their partial esters and the like. Other suitable terminating or capping agents are primary and secondary amines, mercaptans, and amides. Alternatively, the poly(alkylene ether) can be an oxyalkylated condensation product of a phenol. The preferred poly(alkylene ethers) are those which are substantially linear, and are terminated by hydroxyl groups, or by one or two ether end groups of the formula —OR, wherein R is an alkyl, aryl, or aralkyl, such as methyl, ethyl, i-octyl, decyl, lauryl, tridecyl, nonylphenyl, dodecylphenyl, phenyl, naphthyl and the like. They are preferably water soluble or readily water dispersible. Residues of coupling compounds or chain-initiating agents, such as bis-phenol, can be present. The poly(alkylene ether) can, as just mentioned, be a propylene oxide polymer or an ethylene oxide-propylene oxide copolymer. Indeed, when the specified number of ethylene oxide units are present, copolymer, constituents in addition to those mentioned can be included in the polymer chain. Other elements or radicals may be introduced into the R groups provided they are not reactive with the hydrophobic polymer. The necessity for the absence of groups which are reactive with the synthetic polymer will be readily apparent since durability, molecular weight and other physical properties of the hydrophobic polymer are adversely affected by copolymerization with poly(alkylene ether).

The polyether compound employed should preferably be of high purity. In addition, it should be free from color forming compounds, particularly those of an aldehyde nature. This is especially important where the polyether compound is to be subjected to the high temperatures involved in melt extrusion.

The poly(alkylene ethers) can have a molecular weight of about 600 to 3,000,000, preferably about 1,000 to 100,000. The preferred poly(alkylene ethers) are the polyethylene glycols having a molecular weight of about 1,000 to 30,000.

The sterically hindered phenolic compounds used in this invention are well-known compounds. The phenolic group is sterically hindered by the presence of at least one alkyl substituent on the ring ortho to the phenolic group. Alkyl groups of from about 3 to 8 carbon atoms are effective. Tertiary alkyl groups are preferred. Typical examples of sterically hindered phenolic compounds and methods for their preparation are disclosed in U.S. Pats. 2,877,209 and 3,112,286.

Representative sterically hindered phenolic compounds suitable for use in this invention are 1,1,3 tris(5-tert-butyl, 4-hydroxy, 2 methylphenyl)butane; 2,2 bis(3-tert-butyl, 4 hydroxyphenyl)propane; 2,2 bis(3,5-di-tert-butyl, 4 hydroxyphenyl)propane; 2(3-tert-butyl, 4 hydroxyphenyl) 2(4 hydroxyphenyl)propane; mono-4-(1,1,3,3 tetramethylbutyl)phenyl, bis{2-tert-butyl, 4-[dimethyl(3-tert-butyl, 4 hydroxyphenyl)methyl]phenyl}phosphite; bis(4 nonylphenyl), mono{2-tert-butyl, 4-[dimethyl(3-tert-butyl, 4 hydroxyphenyl)methyl]phenyl} phosphite; tris(3,5-di-tert-butyl, 4-hydroxyphenyl) phosphate; and mixtures thereof.

The poly(alkylene ether) and the sterically hindered phenolic compound can be dry blended with the polyamide granules or pellets prior to the melting of the polymer by conventional addition and dry mixing procedures. In a preferred embodiment of this invention, the sterically hindered phenolic compound and the poly(alkylene ether) are mixed together and added to the

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molten polyamide by, for example, injection into the mixing portion of the extruder prior to the melt extrusion of the filament. In this manner, the poly(alkylene ether) and the sterically hindered phenolic compound are mixed throughout the polyamide.

PREFERRED EMBODIMENTS

The following examples illustrate the practice and principles of this invention and a mode of carrying out the invention.

Example I

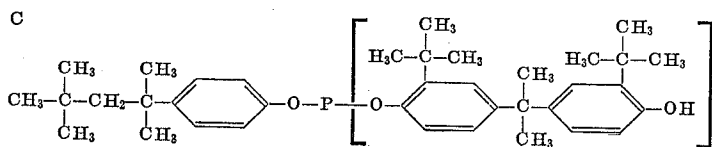
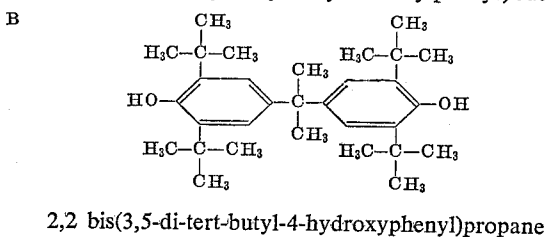
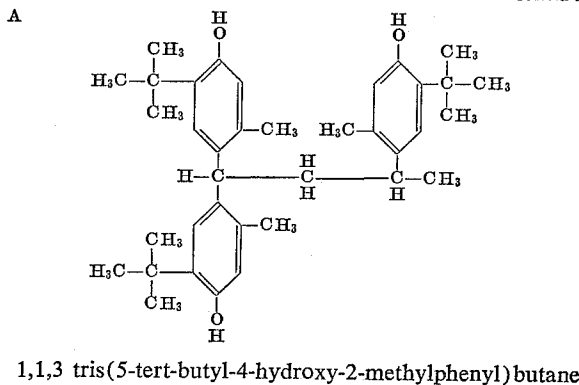
Synthetic multifilament yarns were produced in the following manner. 0.5 weight percent of a sterically hindered phenolic compound (chosen from those indicated in Table I) and 3.0 weight percent of a poly(ethylene ether) having a molecular weight of about 15,000 and a softening point of about 50 to 55° C. (marketed by Union Carbide Corporation under the tradename of Carbowax 20M or polyethylene glycol compound 20M) were added to nylon 6 (polycapromide) pellets or granules and the mixtures were blended in a double cone blender for one hour. The granular blends were then melted at 260° C. and melt extruded under a pressure of 3,000 p.s.i.g. through a 14-orifice spinnerette, each of the orifices having a diameter of $28/1000$ inch, to produce 840 denier yarns. The yarns were collected at about 800 feet per minute and were drawn about 4 times their extruded length to produce 210 denier yarns. The yarns had a relative viscosity of 55, as determined at a concentration of 11 grams of polymer in 100 ml. of 90 percent formic acid at 25° C. (ASTMD-789-62T), and a tenacity of 3.8 grams per denier.

Swatches of knit sleeves were prepared from the above yarns and the knit sleeves were subjected to ageing in an Atlas carbon arc Weather-Ometer for 100 and 200 hours, respectively. The percent breaking strengths retained by the various knit sleeves after ageing for 100 and 200 hours, respectively, are contained in Table II below.

TABLE I

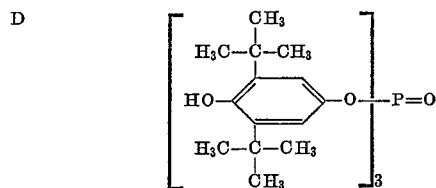
Sterically hindered phenolic compound

Chemical formula



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TABLE I.—Continued

mono 4 - (1,1,3,3 tetramethylbutyl)phenyl, bis(2 - tert-butyl, 4 - [dimethyl(3 - tert - butyl, 4 hydroxyphenyl)methyl]phenyl)phosphite



tris(3,5-di-tert-butyl, 4-hydroxyphenyl)phosphate

TABLE II

Yarn in knit sleeve swatch	Percent breaking strength retained after:	
	100 hours	200 hours
Nylon 6 (control).....	81	64
Nylon 6 plus 3% poly(ethylene ether) (control).....	62	49
Nylon 6 plus 3% poly(ethylene ether) plus 0.5% phenolic compound A.....	74	70
Nylon 6 plus 3% poly(ethylene ether) plus 0.5% phenolic compound B.....	79	67
Nylon 6 plus 3% poly(ethylene ether) plus 0.5% phenolic compound C.....	80	65
Nylon 6 plus 3% poly(ethylene ether) plus 0.5% phenolic compound D.....	91	71

The Weather-Ometer data contained in Table II show that the incorporation of poly(ethylene ether) in nylon yarn reduces its percent breaking strength retention upon ageing but the incorporation of at least one of the phenolic compounds listed in Table I with poly(ethylene ether) in nylon yarn will improve the percent breaking strength retention after ageing. Thus the phenolic compounds used in the present invention permit the incorporation of poly(ethylene ether) in nylon yarn to impart antisoiling properties to nylon yarn with no appreciable reduction of percent breaking strength retention upon ageing.

Example II

Swatches of knit sleeves were prepared from the yarns produced in Example I. The knit sleeves were scoured in a conventional manner and the knit sleeves were then dyed blue in an aqueous dye bath containing the following:

	Percent(O.W.F.)
Merpacyl Blue SW ¹	0.5
Ammonium acetate	2.0
Merpol ND ²	1.0

¹ An acid dyestuff marketed by E. I. du Pont de Nemours & Co., Inc.
² A leveling agent marketed by E. I. du Pont de Nemours & Co., Inc.

The weight ratio of dye bath to fabric was maintained at 40:1. The knit sleeves were immersed in the above aqueous dye bath for one hour at a temperature of 205° F. The knit sleeves were then rinsed in warm water and dried. The knit sleeves were tested for fading in an Atlas carbon arc Fade-Ometer and the number of hours of exposure required for the dyed samples to break, that is to show evidence of fading, was observed. The results are contained in Table III.

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TABLE III

Blue Dyed Yarn in Knit Sleeve Swatch: Hours to break

5	Nylon 6 (control)	40
	Nylon 6+3% poly(ethylene ether) (control) ..	20
	Nylon 6+3% poly(ethylene ether)+0.5% Phenolic Compound A	40
	Nylon 6+3% poly(ethylene ether)+0.5 Phenolic Compound B	40
10	Nylon 6+3% poly(ethylene ether)+0.5% Phenolic Compound C	40
	Nylon 6+3% poly(ethylene ether)+0.5% Phenolic Compound D	40

15 Similar Fade-Ometer results were obtained on the yarns containing the same additives as illustrated in Table III above when the knit sleeves were dyed grey in the aqueous dye bath containing Nylomine Yellow A-GS,¹ Nylomine Red A-2BS,¹ and Nylomine Blue A-GS¹ as the dyes and when the knit sleeves were dyed greenish-yellow in the aqueous dye bath containing Nylomine Yellow A-GS,¹ Nylomine Red A-2BS,¹ Nylomine Blue A-GS,¹ and Fastolon Rubine 5 BLL² as the dyes.

20 The Fade-Ometer data contained in Table III above show that the incorporation of poly(ethylene ether) in nylon yarn reduces its dyelightingfastness but the incorporation of at least one of the phenolic compounds listed in Table I with poly(ethylene ether) in nylon yarn will improve the dyelightingfastness. Thus the phenolic compounds used in the present invention permit the incorporation of poly(ethylene ether) in nylon yarn to impart antisoiling properties to nylon yarn with no appreciable loss of dyelightingfastness.

EXAMPLE III

The yarns prepared in Example I were texturized and carpet samples were prepared. The carpet samples were then mock-dyed and tested for soiling at ambient temperature and 15-20 percent relative humidity. The apparent soiling, $\Delta(K/S)$, of each carpet sample was calculated according to the Kubelka-Munk equation:

$$\frac{K}{S} = \frac{(1-R)^2}{2R}$$

wherein:

50 K=light absorption coefficient
S=light scattering coefficient
R=reflectance

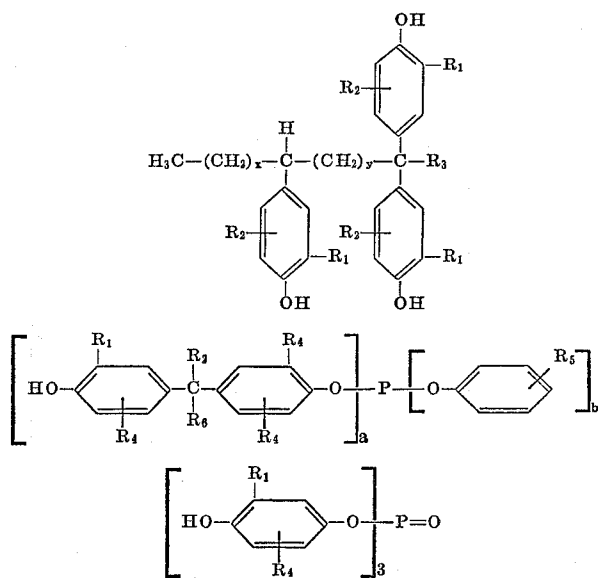
The carpet sample prepared from the nylon 6 yarn containing no additive had a $\Delta(K/S)$ value of 1.49; the carpet sample prepared from the nylon 6 yarn containing only poly(ethylene ether) had a $\Delta(K/S)$ value of 1.02; and the carpet samples prepared from the nylon 6 yarn containing the poly(ethylene ether) and a sterically hindered phenolic compound also had $\Delta(K/S)$ values of about 1.02. Thus the phenolic compounds used in the present invention permit the incorporation of poly(ethylene ether) in nylon yarn to impart antisoiling properties to nylon yarn without any substantial sacrifice to resistance to light.

65 ¹ Acid dyestuff marketed by Imperial Chemical Industries, Ltd.
² An acid dyestuff marketed by Allied Chemical Corporation.

It is claimed:

70 1. A filament, having improved resistance to light, of a polyamide having incorporated therethrough about 0.3 to 7 weight percent, based on the weight of the polyamide, of a poly(alkylene ether) said poly(alkylene ether) having a molecular weight from about 600 to 3,000,000 and about 0.05 to 2 weight percent, based on the weight of the polyamide, of a sterically hindered phenolic com-

pound selected from the group having the general formulas:



and mixtures thereof; wherein R₁ is a sterically hindering radical selected from the group consisting of cyclohexyl, phenyl, and alkyl containing about 3 to 8 carbon atoms; R₂ is a lower alkyl radical containing up to about 8 carbon atoms; R₃ is selected from the group consisting of hydrogen and a lower alkyl radical containing up to about 8 carbon atoms; R₄ is selected from the group consisting of hydrogen, lower alkyl containing up to about 8 carbon atoms, and R₁; R₅ is an alkyl radical containing about 4 to 20 carbon atoms which is positioned on the benzene ring in positions selected from the meta and para positions; R₆ is a lower alkyl radical containing up to about 8 carbon atoms; x is an integer of 0 to 5; y is an integer of 1 to 6; the sum of x and y is no greater than 6 and is at least 1; z is an integer of 1 to 7; a is an integer of 1 to 3; b is an integer of 0 to 2; and the sum of a and b is 3.

2. The polyamide filament of claim 1 wherein R₁ is a tertiary alkyl radical containing about 3 to 8 carbon atoms and R₅ is an alkyl radical containing about 6 to 10 carbon atoms.

3. The polyamide filament of claim 1 wherein the poly(alkylene ether) is present in an amount of about 2 to 5 weight percent, based upon the weight of the polyamide, and the sterically hindered phenolic compound is present in an amount of about 0.1 to 1 weight percent, based on the weight of the polyamide.

4. The polyamide filament of claim 1 wherein the poly(alkylene ether) has a molecular weight from about 1,000 to 100,000.

5. The polyamide filament of claim 4 wherein the poly(alkylene ether) is a poly(ethylene ether) having a molecular weight from about 1,000 to 30,000.

6. The polyamide filament of claim 1 wherein the sterically hindered phenolic compound comprises 1,1,3 tris(5-tert-butyl, 4-hydroxy, 2 methylphenyl)butane.

7. The polyamide filament of claim 1 wherein the sterically hindered phenolic compound comprises mono-4-(1,1,3,3 tetramethylbutyl)phenyl, bis{2-tert-butyl, 4-[dimethyl(3-tert-butyl, 4-hydroxyphenyl)methyl]phenyl}phosphite.

8. The polyamide filament of claim 1 wherein the sterically hindered phenolic compound comprises bis-(4 nonylphenyl), mono{2-tert-butyl, 4-[dimethyl(3-tert-butyl, 4-hydroxyphenyl)methyl]phenyl}phosphite.

9. The polyamide filament of claim 1 wherein the sterically hindered phenolic compound comprises tris(3,5-di-tert-butyl, 4-hydroxyphenyl)phosphate.

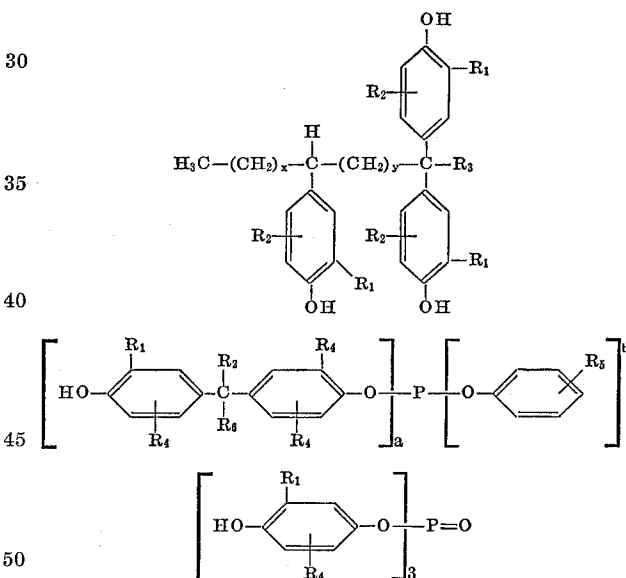
10. The polyamide filament of claim 1 wherein the polyamide is polycaproamide.

11. The polyamide filament of claim 1 wherein the polyamide is poly(hexamethylene adipamide).

12. The polyamide filament of claim 1 wherein the polyamide is poly(methylenedicyclohexylazelaamide).

13. The polyamide filament of claim 1 wherein the polyamide is poly(methylenedicyclohexyl dodecanedioicamide).

14. A process for producing a filament, having improved resistance to light, extruded from a polyamide which comprises mixing in the polyamide prior to extrusion thereof about 0.3 to 7 weight percent, based on the weight of the polyamide, of a poly(alkylene ether) said poly(alkylene ether) having a molecular weight from about 600 to 3,000,000 and about 0.05 to 2 weight percent, based on the weight of the polyamide, of a sterically hindered phenolic compound selected from the group having the general formulas:



and mixtures thereof; wherein R₁ is a sterically hindering radical selected from the group consisting of cyclohexyl, phenyl, and alkyl containing about 3 to 8 carbon atoms; R₂ is a lower alkyl radical containing up to about 8 carbon atoms; R₃ is selected from the group consisting of hydrogen and a lower alkyl radical containing up to about 8 carbon atoms; R₄ is selected from the group consisting of hydrogen, a lower alkyl radical containing up to about 8 carbon atoms, and R₁; R₅ is an alkyl radical containing about 4 to 20 carbon atoms which is positioned on the benzene ring in positions selected from the meta and para positions; R₆ is a lower alkyl radical containing up to about 8 carbon atoms; x is an integer of 0 to 5; y is an integer of 1 to 6; the sum of x and y is no greater than 6 and is at least 1; z is an integer of 1 to 7; a is an integer of 1 to 3; b is an integer of 0 to 2; and the sum of a and b is 3; and melt extruding the mixture of polyamide, poly(alkylene ether) and sterically hindered phenolic compound to form a filament having improved resistance to light.

15. The process of claim 14 wherein the poly(alkylene ether) is a poly(ethylene ether) having a molecular weight from about 1,000 to 30,000.

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16. The process of claim 14 wherein the sterically hindered phenolic compound is 1,1,3 tris(5-tert-butyl, 4-hydroxy, 2 methyphenyl)butane.

17. The process of claim 14 wherein the sterically hindered phenolic compound is mono-4-(1,1,3,3 tetramethylbutyl)phenyl, bis{2-tert-butyl, 4-[dimethyl(3-tert-butyl, 4 hydroxyphenyl)methyl]phenyl}phosphite.

18. The process of claim 14 wherein the sterically hindered phenolic compound is bis(4 nonylphenyl), mono{2-tert-butyl, 4-[dimethyl(3-tert-butyl, 4 hydroxyphenyl)methyl]phenyl}phosphite.

19. The process of claim 14 wherein the sterically hindered phenolic compound is tris(3,5-di-tert-butyl, 4-hydroxyphenyl)phosphate.

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PAUL LIEBERMAN, Primary Examiner

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