United States Patent Office

3,533,986

Patented Oct. 13, 1970

3,533,986

# POLYAMIDES

Geoffrey Spencer Davy, Manchester, England, assignor to Imperial Chemical Industries Limited, London, England, a corporation of Great Britain

No Drawing. Filed Feb. 28, 1967, Ser. No. 619,144
Claims priority, application Great Britain, Mar. 7, 1966, 9,763/66; Oct. 28, 1966, 48,486/66
Int. Cl. C08g *51/58, 51/60*
U.S. Cl. 260—37 15 Claims

## ABSTRACT OF THE DISCLOSURE

Polyamides are stabilized to heat by a mixture of a phenol stable in the polyamide when molten and an organic phosphorus compound which is a phosphorous acid or a salt or ester thereof, a phosphonic acid or an ester thereof, or a phosphinic acid or a salt or ester thereof.

This invention relates to synthetic linear polyamides which have been stablised especially against the degradative effects of high temperature.

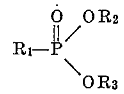
By synthetic linear polyamides we mean condensation poylmers obtained by the polycondensation of amino-carboxylic acids or of mixtures of diamines with dicarboxylic acids, including interpolyamides obtained by the poly-condensation of mixtures of different polyamide-forming components. More particularly we mean the class of polyamides known generically as nylons of which polyhexamethylene adipamide and polycaprolactam are familiar examples. Within this class are also included interpolyamides, for example that obtained by the polycondensation of a mixture of hexamethylene diammoniumadipate with caprolactam.

The nylons are eminently suitable for spinning, usually by a melt spinning technique, into filaments or fibres which are subsequently fashioned into textile articles for example yarns or knitted or woven fabrics. Nylon textiles are frequently subjected to operations involving exposure to high temperatures. For example, they may be heat set in order to stablise the dimensions and shape of the article so that it is not distorted during subsequent processing. In particular nylon textiles, especially fabrics, which are to be dyed are heat set before dyeing in order to avoid distortion and creasing during the dyeing operation. Nylon fabrics, for example, are heat set on a stenter. Exposure of nylon textiles to heat, however, may result in some degradation of the polyamide. This degradation may manifest itself in a discolouration of the nylon textile so that a white material appears less white. The degradation may also manifest itself, however, in a modification of the dyeing properties of the nylon textile. The end groups of the polymer chains of the polyamide molecules of nylon are usually either carboxyl or amino groups. The proportions of these groups relative to each other and relative to the polymer as a whole influence the dyeing properties of the nylon textile. In particular the dyeing properties with anionic dyestuffs are influenced by the proportion of amine end groups, and the affinity for anionic dyestuffs is reduced if the proportion of amine end groups is reduced. It is well known that exposure of nylon textiles to high temperatures results in a reduction of the proportion of amine end groups, and causes a reduction in the affinity for anionic dyestuffs. However, in practice the effect is not obtained in a uniform manner, so that when fabrics which have been heat set are subsequently dyed with anionic dyestuffs, for example acid dyestuffs, it is frequently found that the fabric has a stripy appearance due to portions of the fabric having dyed to a deeper shade than others. It is believed that

these stripes are caused by variations in the amine end group content of the polyamide forming the yarns from which the fabric is woven or knitted.

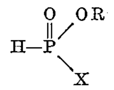
We have now found that the stability of the polyamides to the degradative effects of high temperature can be increased, and in particular that the stripy appearance of polyamide fabrics which have been heat set and then dyed with anionic dyestuffs can be reduced or eliminated, if there are incorporated with the polyamide certain phenols and certain derivatives of phosphorus. Moreover, unlike some stabilising systems which have been proposed for reducing the stripy effect, the stabilsing system of the invention has the advantage of remaining effective even if the fabric is scoured before heat setting. In addition, polyamides stabilised according to our invention may be whiter initially than polyamides not so stablised and on exposure to high temperatures, for example during heat setting, they show less discolouration. Again, our stabilised polyamides show a smaller loss in the proportion of amine end groups on exposure to high temperatures.

Thus the invention is a polyamide with which has been incorporated a phenol stable in the polyamide when molten and a phosphorus compound which is an organic phosphorus compound having the general formula:



(Formula I)

in which $R_1$ represents a hydrogen atom or an aliphatic, cycloaliphatic, aryl or araliphatic radical, $R_2$ and $R_3$, which may be the same or different, represent aliphatic, cycloaliphatic, aryl or araliphatic radicals or, when $R_1$ is not a hydrogen atom, may represent hydrogen atoms, or $R_2$ and $R_3$ together may represent a bivalent radical of the aliphatic, cycloaliphatic, aromatic or araliphatic series which forms with the two oxygen atoms to which it is attached and the phosphorus atom a heterocyclic ring; or a phosphorus compound of the general formula:



(Formula II)

in which R represents a hydrogen atom or an aliphatic, cycloaliphatic, araliphatic or aryl radical, and X represents an aliphatic, cycloaliphatic, araliphatic or aryl radical or the group —OH or, where the phosphorus compound or Formula II is an acid, a salt of the said acid.

The phenol and the phosphorus compound may be incorporated with the polyamide after the polycondensation step. Thus they may be added to the molten polyamide. Alternatively they may be mixed with the solid polyamide, or the solid polyamide in the form of lumps or "chip" may be coated with the ingredients and the polyamide then melted. On the other hand the phenol and the phosphorus compound may be added to the polyamide forming ingredients before the polycondensation step or may be added at some stage during the polycondensation process, and the polycondensation completed by heating. Then phenol may be added together with the phosphorus compound or the two may be added separately and may if desired be added at completely different times.

Because the polyamide of the invention usually has to be melted after incorporation of the phenol, the phenol must be stable in the polyamide when molten. Not all phenols fulfil this condition but those that do may be used in the invention. Particularly suitable, however, are the so-called sterically hindered phenols. A particularly suitable class of sterically hindered phenols comprises those compounds which carry in the para or preferably the ortho position to the phenolic hydroxyl group a group which is attached to the phenol nucleus through a carbon atom of the said group which is a saturated carbon atom and is attached to at least two and preferably to three carbon atoms in addition to the carbon atom of the phenol nucleus. Examples of such groups are sec.-alkyl and especially tert.alkyl groups, for example tert. butyl groups, and cycloalkyl groups, especially cycloalkyl groups carrying an alkyl group on the carbon atom through which they are attached to the phenol nucleus, for example a 1-methyl-1-cyclohexyl group. Specific examples of suitable phenols are

2-α-methylcyclohexyl-4:6-dimethylphenol,
bis-(2-hydroxy-3-α-methylcyclohexyl-5-methylphenyl)-methane,
1,1,3-tris-(2′-methyl-4′-hydroxy-5′-tert.-butylphenyl) butane,
1,1,5,5-tetrakis-(2′-methyl-4′-hydroxy-5′-tert.-butylphenyl)pentane,
2,6-di-tert.-butyl-4-methylphenol,
1,2-bis(2′-hydroxy-3′-tert.-butyl-5′-methylphenyl)ethane,
1,1,5,5-tetrakis(2′-hydroxy-3′-tert.-butyl-5′-methylphenyl)pentane,
bis-(2-hydroxy-3-tert.-butyl-5-ethylphenyl)methane and
2,6-di-tert.-butyl-4-diethylcarbamoylthiomethylphenol.

1,1,3 - tris - (2′-methyl-4′-hydroxy-5′-tert.-butylphenyl) butane and 1,1,5,5-tetrakis-(2′-methyl-4′-hydroxy-5′-tert.-butylphenyl)pentane are particularly suitable.

The organic phosphorus compounds used in the invention and having the above Formula I may be regarded as derivatives of phosphorous acid. Those compounds of the above formula in which $R_1$ is hydrogen are esters of phosphorous acid; those compounds in which $R_1$ is other than hydrogen are phosphonic acids or esters of phosphonic acids depending on whether $R_2$ and $R_3$ represent hydrogen atoms or organic radicals. In the above formula the aliphatic radicals represented by $R_1$, $R_2$ and $R_3$ are preferably alkyl groups, the cycloaliphatic radicals are preferably cycloalkyl groups and the araliphatic radicals are preferably aralkyl groups. As specific examples of such alkyl groups there may be mentioned methyl, ethyl, propyl, butyl or octyl groups; as specific examples of such cycloalkyl groups there may be mentioned cyclopentyl, cyclohexyl, methylcyclopentyl, and methylcyclohexyl groups; as specific examples of aralkyl groups there may be mentioned benzyl and phenylethyl groups; and as specific examples of aryl radicals represented by $R_1$, $R_2$ and $R_3$ there may be mentioned phenyl and naphthyl groups. When $R_2$ and $R_3$ together form a bivalent radical that radical may be, for example, an alkylene radical especially an ethylene or substituted ethylene radical, a 1,2-cycloalkylene radical or an o-phenylene radical. Particularly suitable organic phosphorus compounds of Formula I are the dialkyl esters of phosphorous acid especially those in which the alkyl group has from 1 to 12 carbon atoms. Specific examples of suitable organic phosphorous compounds of Formula I are phenylphosphonic acid, cyclohexylphosphonic acid, dimethyl phosphite, dioctyl phosphite, ethylene phosphite, o-phenylene phosphite, methyl phosphonic acid and dodecyl phosphonic acid.

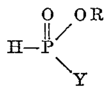
The phosphorus compounds of the above Formula II include phosphorous acid, its salts and its mono-esters, and phosphinic acids, their salts and their esters.

In the above Formula II the aliphatic radicals represented by R or X are preferably alkyl groups, the cycloaliphatic radicals are preferably cycloalkyl groups and the araliphatic radicals are preferably aralkyl groups. As specific examples of such alkyl groups there may be mentioned methyl, ethyl, propyl, butyl or octyl groups; as specific examples of such cycloalkyl groups there may be mentioned cyclopentyl, cyclohexyl, methylcyclopentyl, and methylcyclohexyl groups; as specific examples of aralkyl groups there may be mentioned benzyl and phenylethyl groups; and as specific examples of aryl radicals represented by R or X there may be mentioned phenyl and naphthyl groups.

The salts of those phosphorus compounds of the above Formula II which are acids may be inorganic salts or salts with organic bases. Particularly suitable inorganic salts are ammonium salts and salts with alkali metals or alkaline earth metals, for example sodium, potassium, lithium, calcium and magnesium salts. The organic bases used in forming such salts are preferably organic amines, especially aliphatic amines, including aliphatic diamines, cycloaliphatic amines, and saturated heterocyclic amines. We prefer to use amines of relatively low volability. Suitable amines include hexamethylene diamine, cyclohexylamine, piperidine, morpholine, and N,N′-dimethyl-4,4′-bipiperidyl.

As specific examples of phosphorus compounds of Formula II which may be used in the process of our invention there may be mentioned phosphorous acid, sodium dihydrogen phosphite, phenyl phosphinic acid, sodium phenyl phosphonite, N,N′-dimethyl-4,4′-bipiperidyl phenyl phosphonite and hexamethylenediammonium phenyl phosphonite.

We prefer that the phosphorus compound is a compound of Formula II or a compound of Formula I in which $R_1$ represents a hydrogen atom, or, where the said phosphorus compound is an acid, a salt of the said acid. Such preferred compounds may be represented collectively by the formula—



$$\mathrm{H{-}P({=}O)(OR)Y}$$

(Formula III)

in which Y represents an aliphatic, cycloaliphatic araliphatic or aryl radical, or the group —OR, and R has the same meaning as in Formula II, provided that where such compounds are acids the preferred compounds include the salts of the said acids.

The amount of the phenol incorporated with the polyamide may fall within the range 0.01% to 10% by weight of the polyamide but is preferably within the range 0.01% to 2% by weight, and the amount of the phosphorus compound so incorporated normally falls within the range 0.01% to 2% by weight of the polyamide.

When the phenol or the organic phosphorus compound is added to the polyamide forming components or to the partly formed polymer during polycondensation the addition may be made together with other adjuvants, for example viscosity stabilisers (for example acetic acid), light stabilisers (for example manganese compounds) or delustrants (for example titanium dioxide).

The polyamides of our invention may be obtained in fibrous form by melting, spinning the molten material and drawing the resulting filaments in known manner. Particularly suitable polyamides of our invention are those in which the polyamide is polyhexamethylene adipamide.

The invention is illustrated but not limited by the following examples in which the parts and percentages are by weight. In the examples the b-chromaticity is the ratio of the percent reflected blue light to the sum of the percent reflected blue, green and red light and is similar to the z-trichromatic coefficient of the International Commission on Illumination System (Handbook of Colorimetry, A. C. Hardy, The Technology Press, Cambridge, Mass., U.S.A.).

## EXAMPLE 1

6.6-nylon polymer chip containing 2% of titanium dioxide, 56 parts per million of manganese (added as the acetate) and 0.5 mole percent of acetic acid was coated with 0.2% of the phenol and 0.1% of the organic phosphorus derivative set out in the following table and the chip melted and spun at 290° C. into a yarn of 10 filaments which was doubled, drawn and twisted to a total denier of 70. Yarn was also spun from polymer chip which had not been coated. The yarns were heated at 220° C. for 30 seconds. The b-chromaticity of the yarns was measured before and after heating using a Colormaster Mark 5 Colorimeter. The amine end group concentration in the yarn was determined before and after heating by titration of a solution in phenol and methanol with N/20 hydrochloric acid.

The results are given in the following Table I.

TABLE I

| No. | Phenol | Organic phosphorus compound | Before test: b-Chromaticity | Before test: Amine end group conc., g./equivs. $10^6$ g. | After test: b-Chromaticity | After test: Amine end group conc., g./equivs. $10^6$ g. | Loss of b-Chromaticity | Loss of amine end groups, g./equivs. $10^6$ g. |
|---|---|---|---|---|---|---|---|---|
| 1 | None | None | .316 | 41.5 | .279 | 27.5 | .037 | 14.0 |
| 2 | 1,1,3-tris(2′-methyl-4′-hydroxy-5′-tert.-butylphenyl) butane. | Dimethyl phosphite | .319 | 33.2 | .312 | 25.5 | .007 | 7.7 |
| 3 | 1,1,5,5-tetrakis-(2′-methyl-4′-hydroxy-5′-tert.-butylphenyl) pentane. | Cyclohexyl phosphonic acid. | .318 | 37.0 | .308 | 31.25 | 0.10 | 5.75 |

NOTE.—The loss of b-chromaticity is a measure of discolouration.

## EXAMPLE 2

5,240 parts of nylon 6.6 salt (hexamethylene diammonium adipate), 2,500 parts of distilled water, 22.7 parts of 26.4% aqueous acetic acid solution, 1.1 parts of manganese acetate tetrahydrate and 9.04 parts of phenyl phosphinic acid were heated in an autoclave to a temperature of about 215° C. and pressure of 250 lb. per square inch. The heating was continued and the pressure maintained at 250 lbs. per square inch by bleeding off steam. At a temperature of 220° C., 226 parts of a 40% aqueous dispersion of titanium dioxide in water was added via a lock. When a temperature of 240° C. was reached, the pressure was gradually reduced to atmospheric during 60 minutes after which time the temperature had risen to about 270° C. As soon as atmospheric pressure was reached a stream of nitrogen was passed through the autoclave and 9.04 g. of 1,1,3-tris-(2′-methyl-4′-hydroxy-5′-tert.butylphenyl) butane was added. After 10 minutes agitation the polymer was extruded from the autoclave under nitrogen pressure as a ribbon and quenched with water. The polymer ribbon was then chipped. The polymer chips were melted and spun at 290° C. into a yarn of 10 filaments which was doubled, drawn and twisted to a total denier of 100. Yarn was also spun from polymer chip which had been made from nylon 6.6 salt as described above but without any addition of phenyl phosphinic acid or 1,1,3-tris-(2′-methyl-4′-hydroxy-5′-tert.butylphenyl) butane. The yarns were heated at 220° C. from 30 seconds. The b-chromaticity of the yarns was measured before and after heating using a Colormaster Mark 5 Colorimeter. The amine end group concentration in the yarn was determined before and after heating by titration of a solution in phenol and methanol with N/20 hydrochloric acid. The results are given in Table 2 following Example 3.

## EXAMPLE 3

A polymer was made as in Example 2 excepting that, in place of phenyl phosphinic acid, 3.34 parts of phosphorous acid were added and 2.26 parts of 1,1,3-tris-(2′-methyl-4′-hydroxy-5′-tert.butylphenyl) butane were added with the nylon 6.6 salt instead of later in the polymerisation. The polymer chip was melted and spun at 290° C. into a yarn of 9 filaments. Four strands were plied together and drawn and twisted to a total denier of 108. Yarn was also spun in the same way from polymer chip made without any addition of phosphorous acid or 1,1,3-tris - (2′ - methyl-4′-hydroxy-5′-tert.butylphenyl) butane. The yarns were heated at 220° C. for 30 seconds. The change in b-chromaticity and the loss of amine end group were determined as in Example 2.

The results are given in the following Table 2.

TABLE 2

| Additives | b-Chromaticity: Before test | b-Chromaticity: After test | b-Chromaticity: Loss | Percentage loss of amine end groups |
|---|---|---|---|---|
| Example 2: | | | | |
| None | .3145 | .2801 | .0344 | 33.3 |
| Phenyl phosphinic acid and 1,1,3-tris-(2′-methyl-4′-hydroxy-5′-tert.butylphenyl) butane | .3219 | .3061 | .0158 | 22.6 |
| Example 3: | | | | |
| None | .3201 | .2836 | .0365 | 39.1 |
| Phosphorous acid and 1,1,3-tris-(2′-methyl-4′-hydroxy-5′-tert.butylphenyl) butane | .3236 | .3127 | .0109 | 17.6 |

NOTE.—The loss of b-chromaticity is a measure of discolouration.

## EXAMPLE 4

A polymer was made as in Example 2 except that in place of phenyl phosphinic acid, 13.56 parts of dioctyl phosphite were added.

## EXAMPLE 5

A polymer was made as in Example 2 except that in place of phenyl phosphinic acid, 4.52 parts of cyclohexylphosphonic acid were added.

## EXAMPLE 6

A polymer was made as in Example 5 except that the addition of 1,1,3-tris-(2′-methyl-4′-hydroxy-5′-tert.butylphenyl) butane was omitted.

## EXAMPLE 7

A polymer was made as in Example 5 except that in the place of 1,1,3-tris(2′-methyl-4′-hydroxy-5′-tert.butylphenyl)butane, 9.04 g. 1,1,5,5 - tetrakis(2′ - methyl-4′-hydroxy-5′-tert.butylphenyl)pentane was added.

## EXAMPLE 8

A polymer was made as in Example 5 except that in place of 1,1,3, - tris-(2′-methyl-4′-hydroxy-5′-tert.butylphenyl)butane, 9.04 g. of bis(2-hydroxy-3-tert.butyl-5-ethylphenyl)methane was added.

The polymers from Examples 4 to 8 inclusive were melt spun and the yarn drawn and tested as in Example 2. The results are given in the following Table 3.

TABLE 3

| Example | b-Chromaticity | | | Percentage loss of amine end groups |
|---|---|---|---|---|
| | Before test | After test | Loss | |
| 4 | .3254 | .3178 | .0076 | 21.9 |
| 5 | .3205 | .3018 | .0187 | 23.0 |
| 6 | .3212 | .2925 | .0287 | 29.5 |
| 7 | .3200 | .3043 | .0157 | 18.3 |
| 8 | .3195 | .3039 | .0156 | 22.2 |

NOTE.—The loss of b-chromaticity is a measure of discolouration.

## EXAMPLE 9

131 parts of nylon 6.6 salt, 80 parts of water, 0.226 parts of 2,6 - di - tert.butyl-4-diethylthiocarbamoyl thiomethyl phenol and 0.113 part of dimethyl phosphite were heated in an autoclave to a temperature of about 215° C. and pressure of 250 lb. per square inch gauge. The heating was continued and the pressure maintained at 250 lb. per square inch gauge by bleeding off steam for 60 minutes (temperature about 240° C.). The pressure was then gradually reduced to atmospheric during 90 minutes after which time the temperature had risen to about 270° C. Polymerisation was continued by heating at atmospheric pressure for a further 30 minutes the temperature rising to approximately 270° C. The autoclave was cooled, the polymer removed and chipped. The polymer chips were melted and spun at 290° C. into a yarn of 15 filaments which was doubled, drawn and twisted to a total denier of 90. Yarn was also spun from polymer chip which had been made from nylon 6.6 salt without any additives. The yarns were tested as in Example 2 and the results are given in the following Table 4.

TABLE 4

| Additives | b-Chromaticity | | | Percentage of amine end groups lost |
|---|---|---|---|---|
| | Before test | After test | Loss | |
| None | .2980 | .2540 | .0440 | 29.3 |
| 2,6-di tert. butyl-4-diethyl aminothiocarbamoylthiomethylphenol and dimethyl phosphite | .3124 | .3018 | .0106 | 18.6 |

NOTE.—The loss of b-chromaticity is a measure of discoloration.

## EXAMPLE 10

Samples of the yarns from Example 3 were taken before and after heating at 220° C. for 30 seconds and were dyed with Solway Blue BN 150. The dyed hanks of yarn were examined using a Colourmaster Mark 5 Colorimeter. The difference in the b-chromaticity of the dyed yarns is given below in Table 5 following Example 12.

## EXAMPLE 11

A polymer was prepared as the polymer of Example 3, excepting that 13.56 g. of dioctyl phosphite were added in place of the phosphorous acid. A yarn was made as in Example 3 and was heated at 220° C. for 30 seconds. Samples of the yarn taken before and after heating were dyed with Solway Blue BN 150. The difference between the b-chromaticity of the dyed yarns is given below in Table 5 following Example 12.

## EXAMPLE 12

The polymer prepared in Example 7 was melt spun into a yarn of 9 filaments. Four strands were plied together and drawn and twisted to a total denier of 108. The yarn was heated at 220° C. for 30 seconds and samples of the yarn taken before and after heating were dyed with Solway Blue BN 150. The difference between the b-chromaticity of the dyed yarns is given below in Table 5.

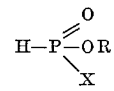
TABLE 5

| Ex. | Additives | Loss in b-Chromaticity of yarn on heating (measured after dyeing with Solway Blue BN 150) |
|---|---|---|
| | None | 0.1337 |
| 10 | Phosphorous acid and 1,1,3-tris(2′-methyl-4′-hydroxy-5′-tert. butylphenyl)butane. | 0.0559<br>0.0559 |
| 11 | Dioctyl phosphite and 1,1,3-tris(2′-methyl-4′-hydroxy-5′-tert. butylphenyl)butane. | 0.0449 |
| 12 | Cyclohexylphosphonic acid and 1,1,5,5-tetrakis(2′-methyl-4′-hydroxy-5′-tert. butylphenyl)pentane. | 0.0631 |

NOTE.—The loss in b-chromaticity in this case is a measure of the loss on heating of the dyeing potential of the yarn for anionic dyestuffs.

I claim:

**1.** A synthetic linear fiber-forming polyamide composition delustered with titanium dioxide and containing as stabilizers from 0.01 to 10% by weight of the said polyamide, a sterically hindered phenol carrying in the ortho or para position to the phenolic hydroxyl group a group which is attached to the phenol nucleus by a carbon atom of the group which is a saturated carbon atom and is attached to at least two carbon atoms in addition to the carbon atom of the phenol nucleus, said group being selected from the class consisting of tertiary butyl and 1-methyl-1-cyclohexyl groups, and from 0.01% to 2% by weight of a phosphinic acid compound selected from the group consisting of compounds of the formula:



$$H-\underset{X}{\overset{O}{P}}-OR$$

wherein R is hydrogen and X is an aryl radical and the ammonium, alkali metal, alkaline earth metal, aliphatic amine, aliphatic diamine, cycloaliphatic amine or saturated heterocyclic amine salts thereof.

**2.** The polyamide of claim **1** wherein the phenol is 2-α-methylcyclohexyl-4,6-dimethylphenol.

**3.** The polyamide of claim **1** wherein the phenol is bis (2 - hydroxy - 3 - α - methylcyclohexyl - 5-methylphenyl) methane.

**4.** The polyamide of claim **1** wherein the phenol is bis (2-methyl-4-hydroxy-5-tert. butylphenyl) sulphide.

**5.** The polyamide of claim **1** in which the phenol is 1,1,3 - tris - (2′ - methyl-4′-hydroxy-5′-tert.butylphenyl) butane.

**6.** The polyamide of claim **1** in which the phenol is 1,1,5,5 - tetrakis - (2′ - methyl - 4′ - hydroxy - 5′ - tert. butylphenyl)pentane.

**7.** The polyamide of claim **6** wherein the polyamide is polyhexamethylenediammonium adipate and the phosphinic acid compound is sodium phenylphosphonite.

**8.** The polyamide of claim **2** wherein the polyamide is polyhexamethylene diammonium adipate and the phosphinic acid compound is sodium phenylphosphonite.

**9.** The polyamide of claim **3** wherein the polyamide is polyhexamethylene diammonium adipate and the phosphinic acid compound is sodium phenylphosphonite.

**10.** The polyamide of claim **4** wherein the polyamide is polyhexamethylene diammonium adipate and the phosphinic acid compound is sodium phenylphosphonite.

**11.** A synthetic linear fiber-forming polyhexamethylene diammonium adipate composition delustered with titanium dioxide and containing as a stabilizer in combination from 0.01% to 10% by weight of the said polyhexamethylene diammonium adipate of 1,1,3-tris(2′-methyl-4′-hydroxy-5′-tert. butylphenyl)butane and from 0.01% to 2% by weight of sodium phenylphosphonite.

**12.** The polyamide composition of claim **1** wherein the polyamide is polyhexamethylene diammonium adipate.

**13.** The polyamide composition of claim **1** wherein the phosphinic acid compound is phenyl phosphinic acid.

**14.** The polyamide composition of claim **5** wherein the polyamide is polyhexamethylene diammonium adipate, the phosphinic acid compound is phenyl phosphinic acid, and the phenol is 1,1,3-tri-(2′-methyl-4′-hydroxy-5′-tert.-butylphenyl) butane.

**15.** The polyamide composition of claim **1** wherein the phosphonous acid compound is sodium phenylphosphonite.

**References Cited**

UNITED STATES PATENTS

| | | | |
|---|---|---|---|
| 3,196,185 | 7/1965 | Ranson | 260—619 |
| 3,210,428 | 10/1965 | Guest et al. | 260—619 |
| 3,228,898 | 1/1966 | Illing et al. | 260—45.7 |
| 3,260,697 | 7/1966 | Babler | 260—45.95 |
| 3,374,288 | 3/1968 | Lange | 260—45.9 |

FOREIGN PATENTS

| | | |
|---|---|---|
| 890,437 | 2/1962 | Great Britain. |

OTHER REFERENCES

Gefter, E. L.: Organo Phosphorus Monomers and Polymers, Tech. Services Inc., Glen Ridge, N.J., 1962.

Kosolopoff: Organic Phosphorus Compounds, 1950. Wiley and Sons, pp. 4 and 5.

HOSEA E. TAYLOR, Jr., Primary Examiner

U.S. Cl. X.R.

8—133, 134, 178; 260—45.7, 45.8, 45.9, 45.95