ABSTRACT OF THE DISCLOSURE

Nylon is rendered more resistant to heat deterioration and better capable of being spun into high tenacity yarn particularly suitable for reinforcing pneumatic tires by having incorporated therein a combination of additives including (1) a small amount of a dissolved stabilizing copper compound; (2) a small amount of a stabilizing halogen compound; and (3) an N-substituted toluene sulfonamide, either the ortho or para isomers thereof or a mixture thereof represented by the structural formulae:

\[
\begin{align*}
\text{CH}_3 &+ \text{CH}_3 \\
\text{SO}_2\text{NHR} &+ \text{SO}_2\text{NHR}
\end{align*}
\]

wherein R is an alkyl radical of 1 to 4 C-atoms including methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl and tertiary-butyl. The sulfonamide is present in an amount of about 0.025-3.0% by weight of the nylon. The nylon is prepared by forming a mixture of a nylon-forming monomeric component and the particular heat stabilizing combination of additives and thereafter heating the resulting mixture at nylon-forming temperatures and pressures for a sufficient time to polymerize the nylon-forming monomeric component to a degree of polymerization represented by a relative viscosity of at least 50. The nylon polymer is worked or shaped into drawn textile filaments by conventional spinning and drawing procedures, the filaments being drawn at least 4.5×.

Cross-reference to related application

The present application is a continuation-in-part application of copending application S.N. 273,830 filed Apr. 18, 1963 (now abandoned).

Background of the invention

The present invention relates to the preparation of polycarbonamides having recurring amide groups as an integral part of the main polymer chain, i.e., nylon, having enhanced resistance to deterioration caused by heat. More particularly, this invention relates to nylon polymer containing additives which enhance the resistance thereof to deterioration caused by sustained application of heat and to a method of making such polymer, as well as to a method of shaping the polymer into textile structures and the like.

Yarns made of nylon have gained wide acceptance in the construction of tires for motor vehicles. In addition to being significantly stronger, an important advantage which nylon yarn enjoys over viscose rayon yarn is that the former can be flaked at elevated temperatures much longer with less loss of strength. This property makes nylon yarn very suitable for reinforcing tires used under conditions wherein the temperature thereof is elevated. Notwithstanding this inherent advantage of nylon, much research has been conducted to further improve the resistance of nylon against heat degradation. Certain chemical additives incorporated in the nylon polymer are known to reduce or inhibit degradation caused by prolonged elevated temperatures.

It has been disclosed in U.S. 2,705,227 that the additive combination of a copper compound and a halogen compound when incorporated in relatively small amounts in nylon increases the resistance of same against being degraded by application of heat. Examples of such copper compounds and halogen compounds which improve the heat stability of nylon are given hereinbelow. It has been found that, generally speaking, increased amounts of copper up to a point proportionally increase the heat stability effect caused by the presence of the copper compound in the nylon. Unfortunately, when nylon containing the copper heat-stabilizing additive is spun into filaments by the melt-spinning technique, a quantitative level of the copper compound above about 15 p.p.m. cannot be steadily maintained in the filaments. When copper is added in greater amounts to the polymer, the amounts of copper present in the melt-spun filaments have been found to be much less than the added amounts. The added copper in excess of that present in the filaments becomes deposited on the surfaces of the spinning equipment. Obviously, it would be desirable to raise the level of the copper compound in the nylon and to maintain same without concomitant deposition of the quantity of the copper compound in excess of that which can be normally maintained in filaments melt spun therewith.

When nylon is used as reinforcing elements in pneumatic tires, the strength of the yarn is a most important physical property. Generally, higher yarn strengths are obtained from nylon with greater molecular weights. Accordingly, in the production of nylon tire yarn the use of additives that would tend to or reduce the molecular weight of the polymer is to be avoided. Mono-functional acid and amines, therefore, are not usually employed in tire yarn polymer since they have the function of limiting the viscosity (and yarn strength) attainable in the polymerization. U.S. 3,113,120 discloses that nylon-6 composition containing copper compounds can show improved aging resistance through the addition therein of certain arylsulfonic acids and derivatives thereof hydrolyzable to the acid. However, such additives behave as chain-terminators, resulting in a lowering of the viscosity of the polymeric product. Of course, this limits the maximum strength of yarn made from the polymeric product.

As the molecular weight of nylon is increased above that indicated by a formic acid relative viscosity of 50 and above, there is a greater tendency than normal to form gel under the polymerization conditions required. This gelatinous thermal degradation product slowly builds up on the walls of the polymerizing and melting apparatus. Gel particles will break off during operation thereof and will be accumulated in a sand filter used at a point just prior to melt-spinning of the filaments, thereby requiring increases in the pressure needed to move the molten polymer therethrough with many attendant problems. Gel particles passing through the filter become manifest in the ultimately drawn yarn as nubs and points of yarn breaking. Obviously, it would be desirable to minimize the accumulation of the gel deposits.

It is an object of the present invention to provide a nylon having improved resistance to heat deterioration. It is another object of the present invention to provide nylon composition made more resistant to heat deterioration by the presence of a combination of additives. It is a further object of the present invention to provide a nylon structure shaped from a nylon composition made more resistant to heat deterioration by the presence of a combination of additives. It is yet another object to provide a method of preparing nylon having extra high molecular weight, less gel causing breakage in the yarn made therefrom, and improved resistance to heat deterioration.
It is still another object to provide a method of preparing a nylon textile yarn resistant to heat deterioration particularly suitable for reinforcing tires and exhibiting improved quality and freedom of breaks.

Summary of invention

The above objects are accomplished by incorporating in nylon, preferably prior to the completion of the polymerization thereof, a particular heat stabilizing combination of additives. The combination comprises a small but heat stabilizing amount of a dissolved copper compound, and a small but heat stabilizing amount of a halogen compound selected from the group consisting of sodium, potassium, magnesium, and ammonium chloride, bromides and iodides, and certain N-substituted toluene sulfonamides. The last named ingredient is present in the polymer in an amount of about 0.025-3.0% by weight of the polymer and is either the ortho- or para- isomers thereof or a mixture of such isomers represented by the structural formulae:

wherein R is an alkyl radical of 1 to 4 C-atoms. The nylon is prepared by forming a mixture of a nylon-forming monomeric component and the particular heat stabilizing combination of additives and thereafter the heating the resulting mixture at nylon-forming temperatures and pressures for a sufficient time to polymerize the nylon-forming component to a degree of polymerization represented by a formic acid relative viscosity of at least 50. The nylon polymer may then be shaped into drawn textile filaments by conventional spinning and drawing procedures, the spun filaments being drawn at least 4.5 times. Not only is the loss of copper compound minimized but also the yarn exhibits a reduction in breakage during drawing attributable to particles of gel in the yarn.

Description of the invention

Nylons useful in the practice of the present invention are defined as long-chain synthetic polymeric carbonamides which have recurring carbonamide groups as an integral part of the main polymer chain and which are capable of being formed into a filament in which the structural elements are orientable in the direction of the axis of the filament. Nylons are of two types, those obtaine

from polymerizing monoaminomonoacrylic acids such as 6-aminocaproic acid and those obtained from polymerizing suitable diamines and dicarboxylic acids such as hexamethylenediamine and adipic acid. Obviously, many other nylon-forming monomeric components can be used to prepare the nylon herein. For examples, 2-pyrrolidone and 11-aminoundecanamide can be condensed into nylon-4 and nylon-11, respectively. Also, hexamethylenediamine and sebacic acid can be polycondensed into nylon-610. The most useful nylons have high molecular weights indicated by a formic acid relative viscosity of 55 or above. The high molecular weight nylons can be formed into textile-grade filaments. Normally, for commercial nylon-66 (prepared by polycondensing the salt of hexamethylenediamine and adipic acid) useful for making the yarn suitable for reinforcing tires the relative viscosity ranges from 30 to 100.

The term "relative viscosity" as used in this specification is the ratio of absolute viscosity at 25° C. (in centipoises) of the solution of nylon in 90% formic acid (10% by weight and 90% formic acid) to the absolute viscosity at 25° C. (in centipoises) of the 90% formic acid. An 8.4% (by weight) solution of the nylon dissolved in 90% formic acid is used in this determination. The absolute viscosities of this 8.4% nylon solution and of the 90% formic acid are determined at 25° C. in the conventional manner and the relative viscosity calculated as the ratio of the two. Since the additives described herein find their best utility in nylon for tire reinforcement, nylons of high molecular weight and a relative viscosity of at least 50 are preferred. However, the relative viscosity may be between 50 and 100, as above stated.

The copper compound in the combination of additives is incorporated in nylon in dissolved form; i.e., it is distributed uniformly throughout the nylon and does not include undissolved copper powder that real copper reacts with and dissolves in the nylon material are useful. Among the copper compounds are the cuprous and cupric salts of organic or inorganic acids. Copper salts of alkanolic acids such as acetic, butyric, lauric, palmitic, and stearic acids are preferred. Other organic salts of copper useful herein include copper citrate, copper lactate, copper oleate, copper oxalate, copper tartrate, copper benzoate, copper salicylate and others. Only relatively small amounts of the copper compound are required to be present in the nylon to render it more resistant to degradation caused by heat. The amount of dissolved copper compound, expressed in terms of copper by weight of nylon is usually 0.001-0.3%, although lesser amounts and greater amounts of copper compound can be employed. When the nylon is melt-spun into filaments, experience has shown that amounts of the copper compound in excess of 15 p.p.m. do not provide proportionally increased stabilization against heat degradation as would be expected because the excess copper compound is removed between polymer formation and filament formation by deposition of the copper compound on the surfaces of the filament-forming apparatus. Quite surprisingly, amounts of copper compound can be employed in nylon filament forming in considerable excess of 15 p.p.m. as copper when the combination of additives is employed without the ordinary copper loss occurring between polymer formation and filament formation. The increased amounts of copper compound provide greater stability against heat degradation to the nylon. The ability of the nylon to retain amounts of copper is attributed to presence in the nylon of the aryl sulfonamide in the combination of heat stabilizing additives, because without the presence of the aryl sulfonamide copper in excess of 15 p.p.m. will be lost in significant amounts during melt spinning of the nylon into filaments.

Sodium and potassium bromides and iodides are the preferred halogen compounds for use in the present combination of additives. Alkali metal bromides and iodides also can be used. Other halogen compounds which are included are: hydrogen halide acids; other metal halides such as magnesium chloride; and ammonium halides such as ammonium chloride, bromide and iodide. The amount of halogen compound, based upon the weight of polyamide, is usually about 0.1-5.0%, although lesser amounts and greater amounts of halogen compound can be employed.

The third and essential ingredient in the combination of additives is an N-substituted toluene sulfonamide that is chemically inert to the nylon. That is, the toluene sulfonamide must not react with the nylon-forming monomeric material or the nylon polymer to become a part of the nylon polymer chain. Although the toluene sulfonamides are compatible when blended with the nylon, they should not react to form an integral part of the molecule either in the center portion of the chain or as chain linking or chain terminating agents. Therefore, aryl sulfonamides that hydrolyze to form the corresponding sulfonic acids are to be avoided since the acids would be available during polymerization to restrict and level the degree to which the nylon material can be crosslinked. It is quite important that the sulfonamide have an N-substituent since sulfonamides having no N-substituent do not provide the overall improvement in regard to copper retention and reduction in breakage of yarns and fila-
ments; but, nevertheless their presence in small amounts are not detrimental as long as a sufficient amount of the N-substituted toluene sulfonamide additive is employed. A preferred sulfonamide is a mixture of ortho- and para-

N-ethyl toluene sulfonamide made and sold by Monsanto Company under the name “Santizier-8” which includes a minor amount (9–13%) of o- and p-toluene sulfonam-

des. The presence of such latter amides does not detract from the beneficial results obtained through the use of the combination of additives of the present invention.

The combination of additives can be incorporated in the nylon in various ways. One preferred way is to admix the ingredients of the combination of additives with the nylon-forming monomer component prior to completing the polycondensation. However, incorporation of the additive together or separately into the nylon-forming reac-
tants at any time during the condensation can be made. Addition of the heat stabilizing agents can be made to molten nylon or to the surface of nylon flake followed by homogenization by extrusion.

The nylon polymer having the combination of heat stabilizing agents incorporated therein can be shaped or worked into various forms. For example, the nylon can be melt-spun into yarns, bristles, films and the like. Espe-

cially useful are tire yarns made from the polymer. Arti-
cles can be molded from the nylon; and the surfaces can be coated with the nylon.

For a more detailed description of the present invention, reference is made to the following specific examples. The examples are intended merely to be illustrative and not limiting. In the examples all parts and percentages are by weight unless otherwise indicated.

**EXAMPLE I**

A 50% aqueous solution of the adipic acid salt of hexa-
methyleneediamine by weight was prepared. Cuprous acetate was added to the solution in an amount to provide 45 p.p.m. copper in the ultimate nylon polymer. Also, potassium iodide was added to the solution to provide 165 p.p.m. potassium in the ultimate nylon polymer. Nylon polymer was made from the resulting solution in conventional continuous polymerization and water removing unit employing an evaporator, reactor, flasher and finisher in that order. The molten nylon polymer exiting from the flasher was pumped through a standard spinning unit containing sand and then through 210 orifices in a setup to form a bundle of filaments having a drawn denier of 1260. The filaments were drawn 5.4X to produce a marketable yarn for use in reinforcing pneumatic tires.

The yarn was analyzed for copper. It was found that the yarn contained initially 40 p.p.m. copper; and as spinning progressed the copper content in the yarn dropped quickly to 15 p.p.m., this concentration being maintained until a new spinning pack was employed.

Two ends of the yarn were twisted 10 Z-turns per inch and then ply twisted 10-turns per inch. This is a nor-
mal geige cord construction for reinforcing tires. The geige cord was subjected to certain conditions to deter-
mine its behavior with respect to deterioration caused by heat and flexing. The data obtained are compared with data obtained by running the same tests on similar cord prepared from yarn containing the combination of heat stabilizing additives of the present invention. The com-

parative data are listed in Table 1 below and the various tests are described below.

**EXAMPLE II**

Nylon tire cord was prepared as in the above example except that cuprous acetate and potassium iodide were added in amounts to provide 80 p.p.m. copper and 45 p.p.m. potassium and that N-ethyl-p-toluene sulfonamide was added to provide a 0.5% concentration of this latter material in the ultimate nylon polymer. The yarn was analyzed for copper. It was found that the yarn contained

80 p.p.m. copper. This level of copper in the yarn was maintained constantly even though the spinning pack was not changed for two weeks. This shows that the presence of the aryl sulfonamide permits the maintenance of a high level of copper compound in the melt-spun nylon yarn without significant loss thereafter between polymer formation and extrusion of the polymer into filaments which normally occurs in the absence of the aryl sulfonamide. The thermal stabilities of the cord of this example and the cord of the above example were compared.

<table>
<thead>
<tr>
<th>TABLE 1</th>
<th>Physical Properties of Cords</th>
<th>Ext. I</th>
<th>Ext. II</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) Initial Strength, lbs.</td>
<td>13.8</td>
<td>13.8</td>
<td></td>
</tr>
<tr>
<td>(2) Stress after heat exposure, lbs.</td>
<td>13.0</td>
<td>13.9</td>
<td></td>
</tr>
<tr>
<td>(3) Stress loss after heat exposure, percent</td>
<td>11.7</td>
<td>11.1</td>
<td></td>
</tr>
<tr>
<td>(4) Stress after dipped-hot stretched, lbs.</td>
<td>10.1</td>
<td>10.0</td>
<td></td>
</tr>
<tr>
<td>(5) Strength loss after dipped-hot stretched, percent</td>
<td>11.2</td>
<td>12.0</td>
<td></td>
</tr>
<tr>
<td>(6) Stress after dipped-hot stretched and relaxed, lbs.</td>
<td>13.2</td>
<td>13.9</td>
<td></td>
</tr>
<tr>
<td>(7) Stress loss after dipped-hot stretched and relaxed percent</td>
<td>11.2</td>
<td>11.6</td>
<td></td>
</tr>
<tr>
<td>(8) Tenax Vibrator life, min.</td>
<td>885</td>
<td>1,195</td>
<td></td>
</tr>
</tbody>
</table>

In the above table the initial breaking strengths (1) of each 10 x 10 cord were measured in the conventional manner. The cords were subjected to comparative tests indicating expected performance of the cords as reinforcing elements in pneumatic tires. In the first test samples of each cord under no tension were placed in an oven at 200° C. for eight hours. The breaking strengths (2) of the cords after being exposed to such heat were measured. It was observed that the strength loss of the nylon cord containing the combination of heat stabilizing additives (Example II) was only 11%, whereas the strength loss of the nylon cord containing the prior art additives (Example I) was 21%.

In a second test, the cords were dipped and hot stretched in a conventional manner for preparing nylon tire cords. Specifically, the cords were passed through a liquid bath containing a mixture of NaCl and conventional resorcinol-

formaldehyde potentially resinous material. The bath con-

tained 10% solids and was at room temperature. The cords picked up about 3% by weight of the solids. There-

after, the cords were dried by being run through a heat-

ing chamber at 180° C; the time of exposure to the heat was 8 seconds. The immersed cords were given a 14% continuous stretch at 205° C. with the hot stretch being imposed for 14 seconds. The breaking strengths (4) of the cords after being hot dipped and stretched were measured. It was observed that the strength loss of the nylon cord containing the instant combination of heat stabilizing additives was only 2%, whereas the strength loss of the nylon cord containing the prior art additives was 11%.

In a third test, the cords which had been dipped and hot stretched in the second test were heated free of tension at 121° C. for 5 minutes. The breaking strengths (6) of the cords after being relaxed were measured. It was ob-

served that the strength loss of the nylon cord containing the instant combination of heat stabilizing additives was only 1.6%, whereas the strength loss of the nylon cord containing the prior art additives was 7%.

In a fourth test, the cords were evaluated for their ability to withstand prolonged flexing at elevated tem-

peratures, A Goodrich Cord Tension Vibrator was em-

ployed. The cords were secured to a plate at one of their ends. At their free ends six-pound weights were suspended. In this manner the cords were rapidly flexed at 200° C. by vibration of the plate. The elapsed times at which the cords broke were recorded. It was found that the nylon cord containing the combination of additives of the present invention broke after being subjected to the hot tension vibration for 1496 minutes, whereas the comparative cord broke after only 834 minutes.
EXAMPLE III

A 50% by weight aqueous solution of the adipic acid salt of hexamethylene diamine was prepared. Cuprous acetate was added to the solution in an amount to provide 80 parts per million (p.p.m.) copper in the ultimate nylon polymer. Potassium iodide was added to the solution to provide 475 p.p.m. potassium in the ultimate nylon polymer. To this solution Santitizer-8 (SN-8) was added in an amount equivalent to 1% by weight based on dry polymer. The composition of SN-8 was as follows:

87.91%—mixture of 40% N-ethyl-o-toluene sulfonamide and 60% N-ethyl-p-toluene sulfonamide.
9.86%—mixture of 40% o-toluene sulfonamide and 60% p-toluene sulfonamide.
(Note—percent is by weight.)

Polyhexamethylene adipamide (nylon-66) was prepared from the resultant solution in a conventional manner in a continuous polymerization and water-removing unit employing an evaporator, reactor, flasher, and finisher in that order. The molten nylon-66 polymer containing SN-8 exiting from the finisher was pumped through a standard spinning pack containing sand and then through a 210 orifice spinneret to form a bundle of filaments having an optimum drawn denier of 1260. The filaments were drawn in a drawtwist operation at a draw ratio of 5.48. The yarn was analyzed for copper. It was found that the yarn contained 80 p.p.m. copper. This level of copper in the yarn was maintained constantly even though the spinning pack was not changed for two weeks. This shows that the presence of above-described mixture of N-substituted toluene sulfonamides maintains the maintenance of a high level of copper compound in the meltspun yarn without significant loss thereof between polymer formation and extrusion of the polymer into filaments which normally occur in the absence of the N-substituted toluene sulfonamide. In addition, it is to be noted that the presence of the unsubstituted toluene sulfonamide does not detract from the copper retaining property of the N-substituted toluene sulfonamide.

The physical properties of two samples of resulting polymer and yarn are shown in Table 2 in which these properties are summarized.

EXAMPLE IV

The procedure of Example III was repeated utilizing the same amounts of identical materials with the exception that for SN-8 there was substituted the equivalent amount of p-toluene sulfonic acid (PTSA). The PTSA was added to the mixture in the mono-hydrate form.

The PTSA mono-hydrate employed in the test is indicated by its manufacturing, Nesse Chemical Co., to conform to the following specifications:

Melting point .......... 101° C. minimum.

Analytical:

Sulfuric acid .......... 0.5% maximum.
Dinitro sulfones .......... 0.5% maximum.
-p-toluene sulfonic acid .......... 88.5% minimum (anhydrous basis).

Water ................ 10.5-13.5%.

The same processing conditions were used in the preparation of the PTSA-containing polymer as were employed in the polymer containing SN-8. Two samples of the PTSA polymer were run. Four hours run of yarn between the baths was cut to waste to avoid any contamination of either due to forward mixing holdup in the process. The molten nylon-66 polymer exiting from the spinneret was in each case pumped through a standard spinning pack containing sand and then through a 210 orifice spinneret to form a bundle of filaments having an ultimate drawn denier of 1260 at a draw ratio of 5.48. The yarn was analyzed for copper. It was found that the yarn contained initially 60 p.p.m. copper; and as spinning progressed the copper content in the yarn quickly dropped to 0.5 p.p.m. In the first sample of polymer the filaments were drawn in a drawtwist operation at a draw ratio of 5.48 as in the case of the yarn containing SN-8. The performance level attained at the indicated draw ratio was so poor, i.e., 417 breaks per pound of yarn, that it was necessary in the second batch of polymer to reduce the draw ratio of 5.07. This lower draw ratio resulted in a higher denier yarn. At this draw ratio a performance level in the drawtwist operation approximating that of the yarn containing SN-8 was obtained. The drop in the draw ratio, however, while raising the performance level of the PTSA yarn, caused a drop in the yarn strength and machine productivity.

In each of the samples, the polymer containing PTSA had a slight yellow-green cast to it in thefinisher and this color was carried through to the final yarn product. Under the same processing conditions in the finisher the relative viscosity of the polymer containing PTSA dropped over 10 units when compared with the polymer containing SN-8. Analysis of end groups in the yarn showed that the PTSA caused a heavy over-balance of the acid end groups, indicating that the PTSA behaved as a chain terminating agent.

EXAMPLE V

In order to determine the dyeing properties of the respective yarns prepared under Examples III and IV above, a knitted fabric was prepared in which one-half of the fabric was made up of yarn prepared under Ex. III and the other half of the fabric was composed of yarn prepared in the second batch as indicated in Ex. IV. The fabric was scoured to remove finish and was saturation vat dyed using Anthraquinone Blue SWF (a dye still produced by E. I. du Pont de Nemours and Company). The dyed article was dried in the standard manner. The SN-8 containing yarn exhibits a much darker color indicating a greater depth of dyeing than for the PTSA containing yarn.

The physical properties of yarns obtained in Examples III-V above are summarized in the following table:

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>1</th>
<th>2</th>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight percent of Additive</td>
<td>12</td>
<td>12</td>
<td>12</td>
<td>12</td>
</tr>
<tr>
<td>Impact Resistance Gm./Cm./Den.</td>
<td>10.4</td>
<td>10.4</td>
<td>10.4</td>
<td>10.4</td>
</tr>
<tr>
<td>Drawtwist Performance (Breaks per Round)</td>
<td>211</td>
<td>211</td>
<td>211</td>
<td>211</td>
</tr>
<tr>
<td>Draw Ratio</td>
<td>5.48</td>
<td>5.48</td>
<td>5.48</td>
<td>5.48</td>
</tr>
<tr>
<td>Yarn Color</td>
<td>(1)</td>
<td>(1)</td>
<td>(1)</td>
<td>(1)</td>
</tr>
<tr>
<td>Whiteness (percent)</td>
<td>94</td>
<td>94</td>
<td>94</td>
<td>94</td>
</tr>
<tr>
<td>Relative Viscosity</td>
<td>67.5</td>
<td>67.5</td>
<td>67.5</td>
<td>67.5</td>
</tr>
<tr>
<td>NH₃×10³ Gm. Eqv./Gm.</td>
<td>26</td>
<td>26</td>
<td>26</td>
<td>26</td>
</tr>
<tr>
<td>COOH×10² Um. Eqv./Gm.</td>
<td>74</td>
<td>74</td>
<td>74</td>
<td>74</td>
</tr>
</tbody>
</table>

1 Normal. 2 Yellow-Green. 3 Mini Color Master Model 3 employed for test. The data obtained for PTSA fell outside limits of graph. Lab Conditions: 75°F. 8°F.
The yarns of Tests A, B and F were heated in a 180° C. oven for 16 hours. The percentages of strength retained after such exposure were determined. It was found that Test A yarn with no toluene sulfonic compound retained only 75.7% of its original strength whereas Test B yarn with SN-8 retained 81.1% of its strength and Test F yarn with SN-3 retained 87.6% of its strength.

Likewise, similarly excellent results are obtained when polymer, yarn, and tire cord are prepared from nylon-6, nylon-610 and when other N-substituted toluene sulfonamides and copper compounds and halogen compounds are employed in the combination of heat stabilizing additives.

Thus, it is seen that the present invention provides numerous advantages. Among these is the improved resistance against heat deterioration imparted to nylon yarn by the sustained presence of high amounts of copper compounds therein. By the use of the additives herein nylon yarn resists degradation caused by heat, as well as by flex stress. Hence, nylon yarn containing the heat stabilizing additives is notably useful in reinforcing pneumatic tires and other rubber products flexed to a great extent during employment thereof, particularly at elevated temperatures. The nylon can be polymerized to a high degree of polymerization without the normally occurring buildup of gel in the polymerization and spinning apparatus which would tend to stop off causing a high incidence of breaks in the threadline and spin pack pressure buildup. In the present invention, high tenacity yarn made of relatively high molecular weight nylon can be melt spun with fewer breaks in the molecularly drawn filaments at higher draw ratios.

As many different embodiments of this invention can be made without departing from the spirit and scope thereof, it is to be understood that the invention is not limited to the above-disclosed specific embodiments except as defined in the following claims.

What is claimed is:

1. A polycarbonamide composition resistant to heat deterioration having recurring amide groups as an integral part of the polymer chain and a fumaric acid relative viscosity of at least 50 and having incorporated therein:
   (a) a stabilizing amount of a dissolved copper compound,
   (b) a stabilizing amount of a halogen compound selected from the group consisting of sodium, potas-

From the above data it is seen that p-toluene sulfonic acid is not desirable as a nylon-66 tire yarn additive in that its presence causes a reduction in relative viscosity and in tensile and impact properties. A deterioration in draw-twist performance is also to be noted. N-ethyl p-toluene sulfonamide is the most desirable tire yarn additive in regard to tenacity and viscosity retention and draw-twist performance as related to breaks and wraps occurrences. The mixture of o- and p-toluene sulfonamide is the least desirable of the sulfonamides tested. Furthermore, the mixture of non-N-substituted sulfonamides and N-substituted sulfonamides gives responses generally in direct accordance with percentage of the N-substituted sulfonamide employed.

<table>
<thead>
<tr>
<th>Test</th>
<th>Additive</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight and Type of Additive</td>
<td>None</td>
<td>1% SN-8</td>
<td>1% PTSA</td>
<td>1% SN-9</td>
<td>0.17% SN-9</td>
<td>1% SN-3</td>
<td></td>
</tr>
<tr>
<td>Relative Viscosity</td>
<td>65.3</td>
<td>64.9</td>
<td>48.4</td>
<td>58.3</td>
<td>65.9</td>
<td>63.5</td>
<td></td>
</tr>
<tr>
<td>Cyclone Degradation Products as P.P.M.</td>
<td>75</td>
<td>75</td>
<td>75</td>
<td>75</td>
<td>75</td>
<td>75</td>
<td></td>
</tr>
<tr>
<td>Pyridine</td>
<td>10</td>
<td>12</td>
<td>29</td>
<td>29</td>
<td>10</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Pounds of Drawn Yarn</td>
<td>280</td>
<td>276</td>
<td>618</td>
<td>405</td>
<td>676</td>
<td>638</td>
<td></td>
</tr>
<tr>
<td>Breaks/pound</td>
<td>0.003</td>
<td>0.00</td>
<td>0.108</td>
<td>0.108</td>
<td>0.083</td>
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<td>Impact Resistance, gin. em.</td>
<td>8.9</td>
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</table>
| Ammonium magnesium and ammonium chlorides, bromides and iodides; and (c) an N-substituted toluene sulfonamide, either the ortho- or para-isomers thereof or a mixture thereof represented by the structural formulae:

\[
\text{CH}_2
\]

\[
\text{SO}_{2}\text{NR}
\]

\[
\text{CH}_2
\]

\[
\text{SO}_{2}\text{NR}
\]

wherein R is an alkyl radical of 1 to 4 C-atoms and the sulfonamide being present in an amount of about 0.025 to 3.0 percent by weight of polycarbonamide.
2. A drawn polycarbonamide textile structure suitable for reinforcing pneumatic tires, having recurring amide groups as an integral part of the polymer chain and a formic acid relative viscosity of at least 50 and made resistant to heat deterioration having incorporated therein:
   (a) a stabilizing amount of a dissolved copper compound;
   (b) a stabilizing amount of a halogen compound selected from the group consisting of sodium, potassium, magnesium and ammonium chlorides, bromides and iodides; and
   (c) in an amount of from about 0.025 to about 3.0%, by weight, of the polycarbonamide, an N-substituted toluene sulfoanamide, either the ortho- or para-isomers thereof or a mixture thereof represented by the structural formulae:

   \[
   \text{CH}_3 \text{SO}_2\text{NHR} \quad \text{and} \quad \text{CH}_1 \text{SO}_2\text{NHR}
   \]

   wherein R is an alkyl radical of 1 to 4 C-atoms.

3. The structure of claim 2, wherein the polycarbonamide is substantially polyhexamethylene adipamide.

4. The structure of claim 2, wherein the polycarbonamide is substantially polymeric 6-aminocaproic acid.

References Cited

UNITED STATES PATENTS

2,705,227 2/1955 Stamatoff 260—45.75
3,113,120 12/1963 Papero 260—42

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