United States Patent

[11] 3,624,245

[72] Inventor **Lawrence W. Crovatt, Jr.**
Gulf Breeze, Fla.

[21] Appl. No. **14,206**
[22] Filed **Feb. 25, 1970**
[45] Patented **Nov. 30, 1971**

[73] Assignee **Monsanto Company**
St. Louis, Mo.

Continuation-in-part of application Ser. No. 759,210, Sept. 11, 1968, now abandoned, which is a continuation-in-part of application Ser. No. 732,826, May 29, 1968, now abandoned, which is a continuation-in-part of application Ser. No. 674,662, Oct. 11, 1967, now Patent No. 3,388,104, which is a continuation-in-part of application Ser. No. 579,509, Sept. 15, 1966, now abandoned, which is a continuation-in-part of application Ser. No. 422,822, Dec. 31, 1964, now abandoned. This application Feb. 25, 1970, Ser. No. 14,206

The portion of the term of the patent subsequent to June 11, 1985, has been disclaimed.

[54] **HEAT STABILIZED ANTISTATIC POLYAMIDES**
11 Claims, No Drawings

[52] **U.S. Cl.** ..... **260/18 R,** 260/45.7 R, 260/45.75 R, 260/45.95 R, 260/78 R
[51] **Int. Cl.** **C08g 51/58**
[50] **Field of Search** ..... 260/18 N, 45.95, 45.85, 78, 18 R, 45.7, 78 R

[56] **References Cited**

UNITED STATES PATENTS

3,502,613	3/1970	Berger	260/45.8
3,493,633	2/1970	Lange	260/45.95
3,389,119	6/1968	Sherill	260/45.95
3,388,104	6/1968	Crovatt	260/31.4
3,285,855	11/1966	Dexter et al.	260/45.85
3,274,151	9/1966	Settele	260/45.95

Primary Examiner—Donald E. Czaja
Assistant Examiner—Eugene C. Rzucidlo
Attorney—John W. Whisler

ABSTRACT: Tensile strength loss on heating is reduced, in polycarbonamides containing between 0.1 and 20.0 weight percent polyalkoxylated triglyceride of a fatty acid containing from 10 to 30 carbon atoms, by adding from 0.01 to 2.0 weight percent of a sterically hindered phenol.

HEAT STABILIZED ANTISTATIC POLYAMIDES

This is a continuation-in-part of applicant's copending application, Ser. No. 759,210, filed Sept. 11, 1968, which in turn is a continuation-in-part of applicant's Ser. No. 732,826, filed May 29, 1968 both now abandoned which is in turn a continuation-in-part of Ser. No. 674,662 filed Oct. 11, 1967, now U.S. Pat. No. 3,388,104 which application is in turn a continuation-in-part of Ser. No. 579,509 filed Sept. 15, 1966, now abandoned which is in turn a continuation-in-part of Ser. No. 422,822 filed Dec. 31, 1964, now abandoned.

The invention relates to an additive for a polycarbonamide composition having antistatic and antisoil properties, wherein the additive reduces loss of strength upon heating.

U.S. Pat. No. 3,388,104, discloses and claims polycarbonamides having greatly improved permanent antistatic properties, produced by incorporating into the molten polymer prior to a filament formation from 0.1 to 20.0 weight percent of a polyalkoxylated triglyceride of a saturated fatty acid having from 10 to 30 carbon atoms. The disclosure of the above noted application is incorporated herein by reference. Unfortunately, the resulting antistatic filaments tend to lose tensile strength on exposure to elevated temperatures for short periods of time, such as during heat setting of fabrics formed from the yarn. It has been discovered that the loss in tensile strength can be reduced by the further addition of sterically hindered phenols as more fully set forth below.

Accordingly, a primary object of the invention is to provide additives for reducing strength loss upon heating in polycarbonamides containing polyalkoxylated triglycerides. A further object is to provide methods for incorporating such additives into filaments, and to provide for such filaments which retain a greater proportion of their original tensile strength after heating.

Other objects of the invention will in part be obvious and will in part appear hereinafter.

The objects of the invention are achieved by blending the hindered phenol, polymer, and triglyceride prior to filament formation, i.e., prior to melt spinning. As more fully set forth in my above noted application, the polymeric substances with which this invention is concerned are synthetic high molecular weight fiber-forming polycarbonamides of the general type characterized by the presence of recurring carbonamide groups as an integral part of the polymer chain, and wherein such groups are separated by at least two carbon atoms. They are further characterized by high melting point, pronounced crystallinity and insolubility in most solvents except mineral acids, formic acid and phenols. Upon hydrolysis with strong mineral acids the polymers revert to the reactants from which they were formed.

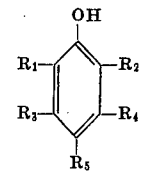
The polyamides of this type are usually made by heating either (a) substantially equimolecular proportions of a diamine and dicarboxylic acid or (b) various amino acids and amide-forming derivatives thereof until the material has polymerized to the fiber-forming stage, which stage is not generally reached until the polyamide has an intrinsic viscosity of at least 0.4, the intrinsic viscosity being defined as:

$$\lim_{C \longrightarrow 0} \left(\frac{\log_e \eta_r}{C} \right)$$

in the preparation of a polyamide, it is usually desirable that the dicarboxylic acid be introduced into the reaction as a preformed salt, i.e., diamine salt. However, this is a matter of convenience only since the dicarboxylic acid and a corresponding molecular quantity of diamine may be in the form of uncombined diacid-diamine when brought into the reaction zone.

The synthetic linear polycarbonamides of this invention may be prepared, spun and drawn under conventional, polyamide-forming production conditions. In addition to the aforedescribed antistatic agents, delusterants, antioxidants, plasticizers, viscosity stabilizers, and other like materials may be used in the preparation of the polyamides of this invention.

According to the invention there is blended into the polycarbonamide-triglyceride system from 0.01 and 2.0 weight percent (based on the weight of the polymer) hindered phenolic materials which are satisfied by the following general formula:



in which at least one of R_1 and R_2 is selected from the class consisting of a branched C_3 to C_8 alkyl radical (a radical containing between three and eight carbon atoms), an aralkyl radical such as benzyl, and a hydroxyaralkyl radical wherein the hydroxyaryl portion contains as a substituent a branched C_3 to C_8 alkyl group attached ortho to the hydroxy group. The preferred hydroxyaralkyl radical is a 3-tert-butyl-2-hydroxybenzyl group, although the hydroxy group can be in the three or four positions if desired. Although the other of R_1 and R_2 can be hydrogen, methyl or ethyl, preferably both of R_1 and R_2 are selected from the class noted above.

R_3, R_4 and R_5 can be hydrogen, alkyl, or other substituents which are chemically inert to the extruded composition under spinning conditions, and substantially inert at 200° C. in air for 2 minutes. The aryl portion of the aralkyl radical (whether or not a phenolic hydroxy group is included therein) can likewise contain such inert further substituents.

The phenols are preferably melted and blended into the polyalkoxylated triglyceride, which is then blended into the molten polycarbonamide just prior to spinning. However, they can be added to the materials which will be reacted to form the polymer, or can be coated onto polymer flake which is to be melted and extruded, or can be separately blended into the molten polymer before or after blending in the polyalkoxylated triglyceride.

EXAMPLE I

This example illustrates the preparation of filaments of the static resistant polyamide disclosed in U.S. Pat. No. 3,388,104, namely, polyhexamethylene diammonium adipate (nylon 66 salt) polyblended with 200 molar polyethoxylated hydrogenated castor oil. These yarns will be used as standard of comparison for strength retention properties with polyamides of the same type modified in accordance with this invention.

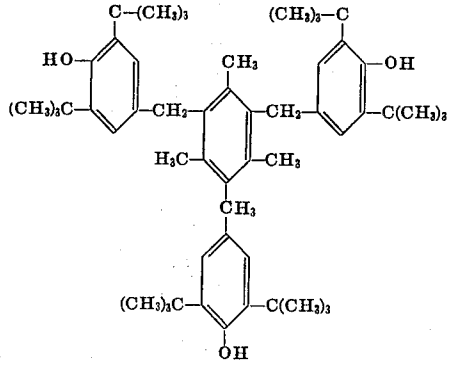
The following materials are added to a stainless steel high-pressure autoclave equipped with a mechanical stirrer: 150 parts of hexamethylene diammonium adipate, 50 parts of water, 50 p.p.m. of manganese added in the form of manganous hypophosphite monohydrate salt, and 10.0 weight percent (based on the weight of unmodified polyamide) of hydrogenated castor oil polyethoxylated with 200 moles of ethylene oxide per mole of the glyceride. The autoclave is then purged of air using purified nitrogen and, while stirring, the temperature in the autoclave is slowly raised until values of 190° to 200° C. are reached. At this point 2.0 weight percent (based on the weight of unmodified polyamide) of titanium dioxide is added. Next the temperature and pressure in the autoclave are raised until 220° C. at 250 p.s.i.g. pressure are reached. The temperature is then further increased while steam condensate is removed until the temperature reaches 243° C. At this point the pressure is slowly reduced over a 25-minute period to atmospheric pressure while the temperature of the molten polymer is raised to 278° C., at which point the polymer melt is allowed to equilibrate for 30 minutes.

The resultant molten polymer is melt extruded through a 14-hole spinneret to yield white multifilament yarn. The yarn is drawn 4.43 times its original length and has a tenacity of

5.69 grams per denier at an ultimate elongation of 24.1 percent. Resistance of this yarn to strength loss upon being exposed to high temperatures is shown in table I.

EXAMPLE II

A batch of polymer is prepared under conditions identical to those employed in example I, except that 0.05 weight percent (based on the weight of unmodified polymer) of the hindered phenol, 1,3,5-trimethyl-2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl) benzene is added to the polymer preparation ingredients. This compound has the following structural formula:



This finished polymer is then melt spun through a 14-hole spinneret to yield white filament yarn. The yarn is drawn 4.61 times its original length and has a tenacity of 4.85 grams per denier at an ultimate elongation of 27.5 percent. Resistance of this yarn to strength loss upon being exposed to high temperatures is shown in table I and comparison made against control yarn of example I.

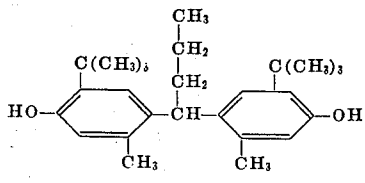
EXAMPLE III

Polymer is prepared by employing procedures and techniques identical to those used in example I, except that 0.5 weight percent (based on the weight of unmodified polymer) of 1,3,5-trimethyl-2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl) benzene is added to the polymer preparation ingredients.

The final polymer thus obtained is melt spun through a 14-hole spinneret to yield a white multifilament yarn. The yarn is drawn 4.50 times its original length and has a tenacity of 4.67 grams per denier at an ultimate break elongation of 29.0 percent. Resistance of this yarn to strength loss upon exposure to elevated temperatures is shown in table I and comparison made against control yarn of example I.

EXAMPLE IV

Polymer is prepared by employing procedures and techniques identical to those used in example I, except that 0.5 weight percent (based on the weight of unmodified polymer) OF 4,4'-butylidenebis(6-tert-butyl-m-cresol) is added to the polymer preparation ingredients. This compound has the following formula:



The final polymer thus obtained is melt spun through a 14-hole spinneret to yield a white multifilament yarn. The yarn is drawn 4.55 times its original length and has a tenacity of 4.32 grams per denier at an ultimate break elongation of 28.0 percent. Resistance of this yarn to strength loss upon exposure to elevated temperatures is shown in table I and comparison made against control yarn of example I.

EXAMPLE V

Polymer is prepared by employing procedures and techniques identical to those used in example I, except that 0.5 weight percent (based on the weight of unmodified polymer) of 2,2'-methylene bis (4-methyl-6-tert-butyl-phenol) is added to the polymer preparation ingredients.

The final polymer thus obtained is melt spun through a 14-hole spinneret to yield a white multifilament yarn. The yarn is drawn 4.51 times its original length and has a tenacity of 4.23 grams per denier at an ultimate break elongation of 27.1 percent. Resistance of this yarn to strength loss upon exposure to elevated temperatures is shown in table I and comparison made against control yarn of example I.

EXAMPLE VI

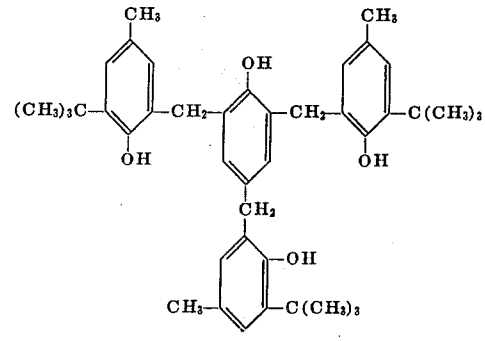
Polymer is prepared by employing techniques and procedures identical to those employed in example I, except that 0.1 weight percent (based on the weight of the unmodified polymer) of 2,2'-methylene bis (4-methyl-6-tert-butyl phenol) is added to the polymer preparation ingredients.

The final polymer is spun through a 14-hole spinneret to yield a white multifilament yarn. The yarn is drawn 4.51 times its original length and has a tenacity of 4.24 grams per denier and an ultimate break elongation of 27.1 percent.

Testing of the yarns prepared in the foregoing examples is conducted by determining the amount of strength loss on elevated temperature exposure.

EXAMPLE VII

A batch of polymer is prepared under conditions identical to those employed in example I, except that 0.1 weight percent (based on the weight of unmodified polymer) of hindered phenolic compound 2,4,6-tris(3-tert-butyl-5-methyl-2-hydroxybenzyl) phenol is added to the polymer ingredients. The structure of this phenol is as follows:



The finished polymer is melt spun through a 14-hole spinneret to yield a white multifilament yarn. The yarn is drawn 4.4 times its original length having a tenacity of 4.80 grams per denier at ultimate break elongation of 30.0 percent.

Strength retention of this yarn after exposure to 200° C. for 5 minutes is shown in table 1.

TABLE 1

	% Tensile Strength Retained After 5 Mins. 200° C. Exposure
I (control)	47.3
II (test)	56.7
III (test)	100.0
IV (test)	94.2
V (test)	79.5
VI (test)	52.3
VII (test)	75.0

TABLE 2

Example	% Tensile Strength Retained After 5 Mins. Exposure At 220° C.
VIII (control)	45.0
IX (test)	90.0
X (test)	88.0

EXAMPLE VIII

This example illustrates the preparation of filaments of static resistant poly-ε-caproamide (nylon 6) polyblended with 200 molar polyethoxylated hydrogenated castor oil. These yarns are used as standard of comparison for heat stability properties with polyamides of the same type, modified in accordance with this intention.

The following materials are added to a stainless steel autoclave, equipped with a mechanical stirrer:

130 parts of ε-caprolactam, 5 parts of water, 10 p.p.m. of manganese (added in the form of manganous hypophosphite-monohydrate salt), and 10.0 weight percent (based on weight of unmodified polyamide) of 200 molar polyethoxylated hydrogenated castor oil (glyceride ester). The autoclave is then purged of air using purified nitrogen and with stirring, the temperature in the autoclave is slowly raised until values of 190°–200° C. are reached. At this point 0.3 weight of percent (based on the weight of unmodified polyamide) of titanium dioxide is added. The temperature and pressure in the autoclave are then raised to 220° C. and 250 p.s.i.g. with removal of steam condensate. Further temperature increase to 243° C. is carried out at which point the pressure is gradually lowered over a 25-minute period to atmospheric pressure while the melt temperature continues to increase to 280° C. The polymer melt is then allowed to equilibrate in the molten state for 30 minutes during which time the temperature is lowered to 240° C.

The resultant molten polymer is melt spun through a 14-hole spinneret to yield white yarn. The yarn is drawn 4.00 times its original length having a tenacity of 5.5 grams per denier at ultimate elongation of 30.0 percent.

Strength retention of this yarn after exposure to 200° C. for 5 minutes is given in table 2.

EXAMPLE IX

This batch of polymer is prepared under the same conditions as described in example VIII, except that 0.5 weight percent (based on the weight of unmodified polymer) of 1,3,5-trimethyl-2,4,6-tris-(3,5-di-tert-butyl-4-hydroxybenzyl) benzene is added to the polymer preparation ingredients.

The polymer obtained is melt spun through a 14-hole spinneret to yield white yarn. The yarn is then drawn 4.00 times its original length having a tenacity of 5.7 grams per denier at ultimate elongation of 29.1 percent.

Strength retention of this yarn after exposure to 200° C. for 5 minutes is related in table 2.

EXAMPLE X

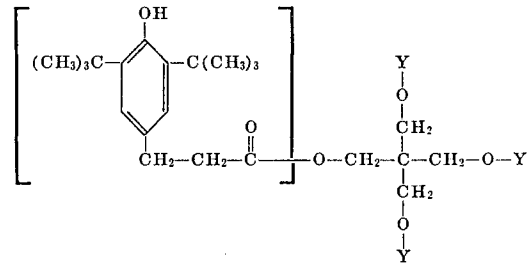
Polymer is prepared by employing procedure and techniques identical to those used in example VIII, except that 0.5 weight percent (based on the weight of unmodified polymer) of 4,4'-butylidenebis-(6-tert-butyl-mucresol) was added to the polymer ingredients.

The polymer obtained is melt spun through a 14-hole spinneret to yield white yarn. The yarn is then drawn 4.00 times its original length having a tenacity of 5.6 grams per denier at ultimate elongation of 30.0 percent.

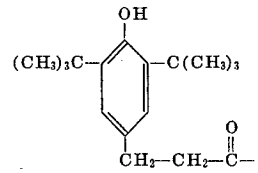
Strength retention of this yarn after exposure to 200° C. for 5 minutes is related in table 2.

EXAMPLE XI

Polymer was prepared by employing procedure and techniques identical to those used in example I, except that 0.05 weight percent, based on the weight of unmodified polymer (o.w.p.) of the tetra-ester of pentaerythritol with 3-(3',5'-ditert. butyl-4'-hydroxyphenyl)propionic acid was dissolved in the polyethoxylated hydrogenated castor oil and then the polyethoxylated hydrogenated castor oil containing said ester dissolved therein was added to the polymer preparation ingredients. The ester has the following structural formula:



wherein Y is



The finished polymer thus obtained was melt spun through a 14-hole spinneret to yield a white multifilament yarn. The yarn was drawn 4.50 times its original length and had a tenacity of 3.86 grams per denier at an ultimate break elongation of 21.0 percent. Resistance of this yarn to strength loss upon exposure to elevated temperatures was determined and is given in table 3.

EXAMPLE XII

Polymer was prepared by employing the procedure and techniques of example XI, except that 0.1 weight percent o.w.p. of the ester used in example XI was dissolved in the polyethoxylated, hydrogenated castor oil. The resulting yarn was drawn 4.50 times its original length and had a tenacity of 4.54 grams per denier at an ultimate break elongation of 29.1 percent. Resistance of this yarn to strength loss upon exposure to elevated temperatures was determined and is given in table 3.

EXAMPLE XIII

Polymer was prepared in the same manner as in example XI, except that 0.2 weight percent o.w.p. of the ester used in example XI was dissolved in the polyethoxylated, hydrogenated castor oil. The resulting yarn was drawn 4.50 times its original

length and had a tenacity of 4.39 grams per denier at an ultimate break elongation of 26.2 percent. Resistance of this yarn to strength loss upon exposure to elevated temperatures was determined and is given in table 3.

EXAMPLE XIV

Polymer was prepared by employing the procedure and techniques of example XI, except that 0.5 weight percent o.w.p. of the ester used in example XI was dissolved in the polyethoxylated, hydrogenated castor oil. The resulting yarn was drawn 4.27 times its original length and had a tenacity of 4.03 at an ultimate break elongation of 32.0 percent. Resistance of this yarn to strength loss upon exposure to elevated temperatures was determined and is given in table 3.

TABLE 3

Example	% Tensile Strength Retained After 5 Mins. 200° C. Exposure
(control)	47.3
XI (test)	68.1
XII (test)	72.1
XIII (test)	71.6
XIV (test)	91.8

Addition of more than 2.0 percent of the phenol is generally undesirable because of discoloration of the resulting yarn.

What is claimed is:

1. A fiber-forming synthetic linear polycarbonamide having recurring amide groups as an integral part of the main polymer chain, and wherein said groups are separated by at least two carbon atoms, said polycarbonamide containing:

A. from 0.1 to about 20.0 weight percent, based on the weight of said polycarbonamide, of a polyalkoxylated triglyceride of saturated fatty acid having 10 to 30 carbon atoms, wherein the polyalkoxy portion has a molecular weight of between about 2,000 and 22,000; and

B. from 0.01 to 2.0 weight percent of a phenol selected from the group consisting of 1,3,5-trimethyl-2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl)-benzene, 4,4'-butylidenebis(6-tert-butyl-m-cresol), 2,2'-methylenebis(4-methyl-6-tert-butyl-phenol), 2,4,6-tris(3-tert-butyl-5-methyl-2-hydroxy-benzyl)-phenol and pentaerythritol tetra(3,5-di-tert-butyl-4-hydroxy-phenyl)propionate.

2. A fiber-forming synthetic linear polycarbonamide as defined in claim 1, wherein said polyalkoxylated glyceride is polyalkoxylated hydrogenated castor oil.

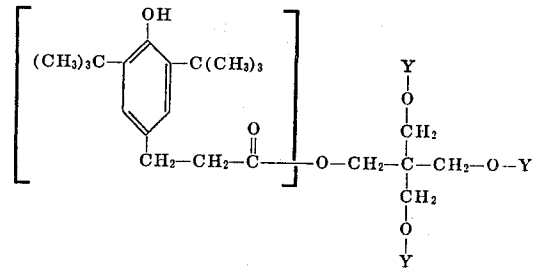
3. A fiber-forming synthetic linear polycarbonamide as defined in claim 2, wherein said polyalkoxylated hydrogenated castor oil is present in an amount of from 1.0 to 15.0 weight percent, based on the weight of said polycarbonamide.

4. The fiber-forming synthetic linear polycarbonamide as set forth in claim 3, wherein said polycarbonamide is polyhexamethylene adipamide.

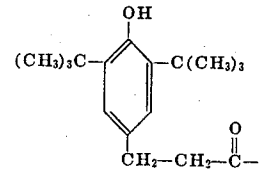
5. A textile fiber comprising the polycarbonamide as defined in claim 1.

6. A textile fiber comprising the polycarbonamide as defined in claim 3.

7. A fiber-forming synthetic linear polycarbonamide having recurring amide groups as an integral part of the main polymer chain, wherein said groups are separated from one another by at least two carbon atoms, and containing incorporated therein from 0.1 to 20 percent by weight, based on the weight of said polycarbonamide, of a polyalkoxylated triglyceride of a saturated fatty acid having 10 to 30 carbon atoms, wherein the polyalkoxy portion has a molecular weight of between about 2,000 and 20,000, and containing dissolved therein between about 0.01 to 2 percent by weight, based on the weight of said polycarbonamide, of the compound of the structure:



wherein Y is



8. The polycarbonamide as defined in claim 7 wherein said polyalkoxylated triglyceride is polyethoxylated hydrogenated castor oil.

9. The polycarbonamide as defined in claim 8 wherein said castor oil is present in an amount between about 1.0 and 15 percent by weight, based on the weight of said polycarbonamide.

10. The polycarbonamide of claim 9, wherein said polycarbonamide is polyhexamethylene adipamide.

11. A textile fiber comprising the polycarbonamide of claim 7.

* * * * *