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3,654,235

ANTISTATIC POLYCARBONAMIDE FILAMENTS

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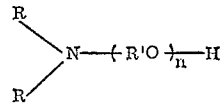
Int. Cl. C08g 20/38
U.S. Cl. 260—78 S 11 Claims

ABSTRACT OF THE DISCLOSURE

Synthetic melt-spun polyamide filaments are provided having uniformly admixed therein, as a separate phase, from about 1% to about 15% by weight of the polyamide of an amine of the structure



wherein each R is an alkyl group, R' is an alkylene group and *n* is an integer of at least 15. Yarns, fibers and fabrics made from these filaments possess permanent antistatic properties, even after numerous launderings.

BACKGROUND OF THE INVENTION

Synthetic polyamide fibers are widely used in the manufacture of textiles. Unfortunately, these fibers are poor conductors of electricity and as a result charges of static electricity are created and accumulated thereon. The accumulation of static charges on fibers is objectionable of the manufacturer during processing of the fibers and particularly to the user of textiles made therefrom; for example, almost everyone has witnessed the effects of the accumulation of static electricity charges on the surface of wearing apparel, carpets, upholstery and the like, constructed from synthetic polyamide fibers.

Several approaches have been attempted in an effort to eliminate or at least to reduce the creation and accumulation of static electricity charges on the surface of polyamide fibers. One approach has been to apply a surface coating to the fibers to render them more conductive. These coating however lack durability or impart an undesirable hand to fabrics. Another approach has been to modify the polyamide structure by introducing hydrophilic monomers into the polyamide molecule. However, this approach tends to adversely affect the physical properties of the fibers.

Yet another approach to providing antistatic fibers has been to admix an antistatic material with the polymer prior to shaping. Various antistatic materials or additives have been used for this purpose, for example: poly(alkylene ethers), such as polyethylene glycols and polyalkoxylated triglycerides, such as polyethoxylated hydrogenated castor oil. Although admixing of the prior art materials with polyamides prior to shaping has rendered the shaped article more antistatic, the shaped articles nevertheless still accumulate noticeable charges of static electricity. In many instances fabrics constructed from fibers containing the prior art materials lose their antistatic properties after the fabric is washed or laundered. Moreover, often a relatively large amount of the material must be used which tends to adversely affect the physical properties of the shaped article.

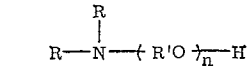
An object of the invention is to provide a linear synthetic polyamide filament or fiber having improved and permanent antistatic properties.

Another object of the invention is to provide fabrics constructed from polyamide filaments or fibers which have

good antistatic properties even after multiple washings or launderings.

SUMMARY OF THE INVENTION

The above objects are attained by providing a melt spun synthetic polyamide filament which contains as a separate phase from about 1% to about 15% by weight, based on the weight of the polyamide, of a tertiary amine of the structure



wherein each R is an alkyl group having at least 8 carbon atoms, R' is an alkylene group having 2 to 4 carbon atoms and *n* is an integer of at least 15.

The filaments of the present invention are made by thoroughly blending or admixing the tertiary amine with the polyamide prior to extrusion thereof into filaments. This may be accomplished, for example, by admixing the tertiary amine with molten polyamide just prior to the spinning thereof. According to a preferred embodiment, sufficient tertiary amine is admixed with the polyamide to provide filaments having as a separate phase between about 3% and about 8%, based on the weight of the polyamide (O.W.P.), of the tertiary amine. The filaments have excellent antistatic properties which are retained even after multiple washings or launderings. Additionally, fabrics constructed from the filaments, such as carpeting, have good aesthetics.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The following examples are given to further illustrate the invention. In the examples fabrics knitted from various yarns identified therein were tested to determine the static build-up on the fabric surfaces and the time, in seconds, required for the dissipation of one-half this build-up, i.e., charge. Prior to the testing, the fabrics were subjected to a specific number of machine launderings wherein after each laundering, using commercially available detergent, namely, Tide XK, the fabrics were tumble dried a total of 5 times and then conditioned a specified period of time at 40% relative humidity of 73° F. More specifically an electric washing machine (Sears Unit) was loaded with the test fabric and sufficient cotton fill fabric to make 4 lbs. total load. One-half cup (125 cc.) of the detergent was added and the unit set to wash for 10 minutes with 16 gallons of warm water (48° C.) and for warm water rinsings. After the washings the fabric was tumbled dried at maximum setting in an electric dryer (Sears Unit). The exhaust air was about 65° C. and the total drying cycle was 45 minutes. After washing, the fabric was subjected to 5 drying cycles. The testing was carried out on a dynamic static tester similar to that described in vol. 40, American Dyestuff Reporter, pp. 164–168 (1951). In brief, the test is carried out by attaching the test fabric to an aluminum cylinder which is rotated at approximately 300 r.p.m. The fabric is then electrostatically charged by allowing it to rub against another similar fabric surface for one minute. Then, while continuing to rotate the cylinder at 300 r.p.m., the period of time (in seconds) for the static charge build-up on the fabric to dissipate to one-half its original value is measured. In these tests the shorter the time required for dissipation of one-half the static charge build-up, i.e., static half-life ($t^{1/2}$), the greater the degree of antistatic property.

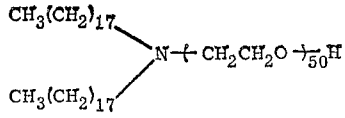
EXAMPLE 1

This example illustrates the preparation of conventional polyhexamethylene adipamide (nylon 66) fiber.

10 stainless steel, high pressure autoclave was added 150 parts of hexamethylene diammonium adipate and 50 parts of water. The autoclave was equipped with stirring means to permit the content to be agitated. The autoclave was purged of oxygen by use of purified nitrogen and the temperature and pressure were slowly raised until values of 243° C. and 250 p.s.i.g. were reached. During this time steam was continuously removed from the autoclave as a condensate. The pressure was then gradually reduced to atmospheric over a 25 minute period. The polymer was then permitted to equilibrate for 30 minutes at 278° C. The finished polymer was melt spun directly from the bottom of the autoclave through a 13-hole spinneret to yield white multifilament yarn. The yarn was drawn at a draw ratio of 4.70:1 and possessed a tenacity of 5.3 grams per denier. The yarn was later converted to knit fabric suitable for static testing.

EXAMPLE 2

Yarn was made acording to the procedure of Example 1, except that 6% O.W.P. of a tertiary amine of the structure



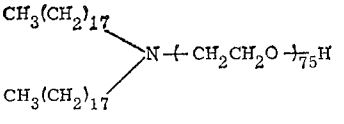
was blended into the nylon melt during the 30 minute equilibrium cycle. Nine knit fabrics were made from the yarn. Following the above described testing procedure each fabric was washed 5, 15, and 25 times and the static build-up and static half-life were determined after each of specified washings and at conditioning periods of 0, 1 and 7 days. The corresponding test results obtained for the nine fabrics were averaged and are given in Table I. For purposes of comparison the fabric of Example 1 was also identically tested.

TABLE I

Conditioning time, days	Static decay half-life, secs.			Static build-up, microamps		
	0	1	7	0	1	7
No of washings:						
5	5	2	2	204	127	32
15	49	16	6	301	255	160
25	60	25	8	307	284	220
	Example 1 fabric					
5	>600	>600	>600			
15	>600	>600	>600			
25	>600	>600	>600			

EXAMPLE 3

Three knit fabrics were prepared according to the procedure of Example 2, except that instead of the tertiary amine used therein 6% O.W.P. of a tertiary amine of the structure



was used. The static half-life of each fabric was determined as in Example 2. The test results obtained for the three fabrics were averaged as in Example 2 and are given in Table II.

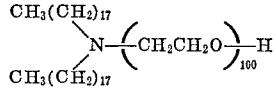
TABLE II

Conditioning time, days	Static half-life, seconds					Static build-up, microamps		
	0	1	3	5	7	0	1	7
No. of washings:								
5	3	2	1	1	1	189	72	224
15	52	12	6	4	4	330	287	255
25	[a] 111	26	21	13	10	300	296	249

[a] Only one fabric was tested after 25 washings and no conditioning.

EXAMPLE 4

Two knit fabrics were prepared and tested in the same manner as the fabrics described in Example 3, except that instead of the tertiary amine used therein 6% O.W.P. of a tertiary amine of the structure



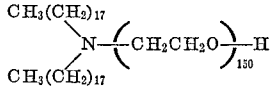
was used. The test results obtained for the two fabrics were averaged as in Example 2 and are given in Table III.

TABLE III

Conditioning time, days	Static half-life, seconds					Static build-up, microamps		
	0	1	3	5	7	0	1	7
No. of washings:								
5	17	11	28	42	47	270	262	296
15	56	21	19	15	17	297	279	262
25		21	31	25	27	293	276	236

EXAMPLE 5

Three knit fabrics were prepared and tested in a manner identical to the fabrics described in Example 3, except that instead of the amine used therein 6% O.W.P. of a tertiary amine of the structure



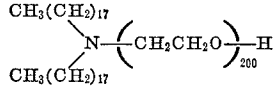
was used. The test results obtained for the three fabrics were averaged as in Example 2 and are given in Table IV.

TABLE IV

Conditioning time, days	Static half-life, seconds					Static build-up, microamps		
	0	1	3	5	7	0	1	7
No. of washings:								
5	10	23	56	86	88	252	269	303
15	51	25	27	19	30	310	286	306
25		37	50	52	51	291	298	287

EXAMPLE 6

Three knit fabrics were prepared and tested in a manner identical to the fabrics described in Example 3, except that instead of the tertiaryamine used therein 6% O.W.P. of a tertiary amine of the structure



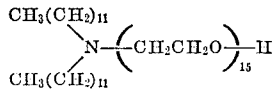
was used. The test results obtained for the three fabrics were averaged as in Example 2 and are given in Table V.

TABLE V

Conditioning time, days	Static half-life, seconds					Static build-u , microamps		
	0	1	3	5	7	0	1	7
No. of washings:								
5	13	52	109	149	161	263	288	313
15	62	35	40	41	47	307	242	333
25		57	80	75	78	300	306	320

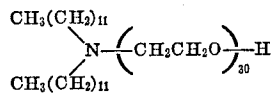
EXAMPLE 7

Nine knit fabrics were prepared and tested in the manner as the fabrics described in Example 2, except that instead of the tertiary amine used therein 6% O.W.P. of a tertiary amine of the structure



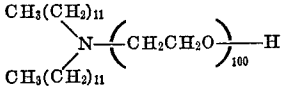
(I)

was used in making three of the nine fabrics; 6% O.W.P. of a tertiary amine of the structure



(II)

was used in making another three of the fabrics; and 6% O.W.P. of a tertiary amine of the structure



(III)

was used in making the other three fabrics. The test results obtained for each of the three groups of three fabrics were averaged as in Example 2 and are given in Table VI.

TABLE VI

Fabric containing amine No.	No. of washings	Conditioning time, days: Static half-life, seconds 0	1	3	5	7	Static build-up, microamps 0	1	7
(I) n=15	5	266	174	115	98	88	316	323	296
(I)	15	264	254	137	115	96	331	334	296
(I)	25	275	201	244	213	169	336	327	336
(II) n=30	5	62	31	17	13	11	287	290	249
(II)	15	90	62	28	19	18	308	326	271
(II)	25	159	73	69	55	42	333	323	321
(III) n=100	5	81	25	31	44	51	329	293	323
(III)	15	274	154	113	81	83	335	335	338

EXAMPLE 8

Three knit fabrics were prepared and tested according to the procedure of Example 2, except that 4% O.W.P. was used instead of 6% O.W.P. and the fabrics were not tested after 25 washings. The test results obtained for each fabric were averaged as in Example 2 and are given in Table VII.

TABLE VII

Conditioning time, days	No. of washings	Static half-life, seconds 0	1	3	5	7	Static build-up, microamps 7
No. of washings:							
5		25	8	5	3	3	324
15		------	53	53	25	22	298

The above examples illustrate the excellent antistatic properties of the filaments of the present invention. The data indicates that the best results are obtained when the filaments contain the distearylamine having 50 or 75 ethoxy units. In Tables II and III the data shows that fabrics knitted from filaments containing these distearylamines possess an extremely short static decay half-life, even after multiple washings. The above results show that the filaments are relatively good conductors of electricity and retain their conductivity after multiple washings, i.e., are permanently antistatic.

In the following examples fabrics were prepared and tested in the same manner as the fabrics described in Example 2, except that different antistatic agents were used in preparing the fabric yarns.

EXAMPLE 9

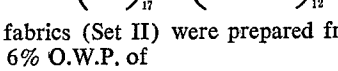
In this example six test fabrics were prepared from filaments containing 6% O.W.P. of the compound described in U.S. Pat. 3,388,104, issued June 11, 1968 to L. W. Crovatt, Jr., i.e., polyethoxylated hydrogenated castor oil containing 200 ethoxy units. The test results obtained for the fabrics were averaged as in Example 2 and are given in Table VIII

TABLE VIII

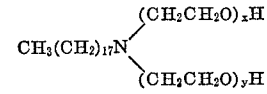
Conditioning time, days	Static half-life, seconds 0	1	7	Static build-up, microamps 0	1	7
No. of washings:						
5	55	49	67	306	295	313
15	120	74	62	322	314	333
25	143	99	92	314	296	320

EXAMPLE 10

In this example six test fabrics were prepared, three fabrics (Set I) were prepared from filaments containing 6% O.W.P. of



and three fabrics (Set II) were prepared from filaments containing 6% O.W.P. of



($x+y=35$). Each of the indicated additives contain the optimum amount of ethoxy units. Attempts to put more of these units into the respective molecules resulted in an additive/nylon blend which could not be melt spun into filaments under the specified conditions employed. The test results obtained for the fabrics were averaged as in Example 2 and are given in Table IX.

TABLE IX

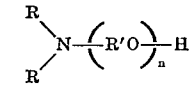
5 machine washings:	Static half-life, seconds [1]
Set I	24
Set II	89

[1] Conditioning time was one hour.

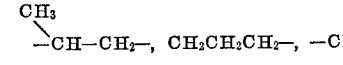
A comparison of the results given in Tables VIII and IX with those given in Table I shows that the filaments of the present invention have a substantially shorter static half-life and less static build-up than filaments, illustrated in Example 9.

The filaments of the present invention have exceptional antistatic properties which are permanent in nature, as evidenced by the foregoing examples, and which permit for the manufacture of static resistant fabrics heretofore unattainable.

In general, tertiary amines which may be used in practicing the invention are those of the structure



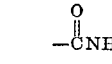
The R's are each alkyl groups in which the total number of carbon atoms present in both groups is at least about 16. Preferably each of the alkyl groups contains at least 8 carbon atoms. When the amine contains less than about 16 carbon atoms, they do not impart significant antistatic properties to the resulting filaments. Although the invention has been demonstrated with amines containing R groups having 12 and 18 carbon atoms, it is contemplated that the alkyl group may contain as many as 30 carbon atoms or more. Preferably the alkyl groups are straight-chained although the groups may be branched-chained, if desired. In the above structure R' is an alkylene group containing from 2 to 4 carbon atoms, i.e., $-CH_2CH_2-$,



and the like and n is an integer having a value of at least 15. At n values of less than 15 the amines do not blend satisfactorily with the polyamide and as a result the spinnability of polymer containing such amines is unacceptable. On the other hand the n value may be 200 or higher, e.g., 450, without noticeably affecting the properties of the resulting filaments. In order to attain tertiary

amines having high n values it may be necessary to employ chain extending agents such as 2,2-bis(4-hydroxyphenyl)propane.

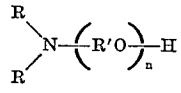
The tertiary amines are easily prepared by reacting a dialkyl secondary amine with the desired amount of alkylene oxide under alkoxylation conditions. The tertiary amines may be blended with any polymer which is compatible therewith. Of particular interest are the linear synthetic fiber-forming polyamides, i.e., polymers consisting essentially of recurring units of the structure



which are separated from one another by at least two carbon atoms. These polyamides are well known in the art and are in general formed by reacting substantially equimolar amounts of diamines and dicarboxylic acids, various amino acids, amide-forming derivatives of these diamines and acids or combinations thereof. Representative examples of these polyamides are the saturated aliphatic polycarbonamide and include polyhexamethylene adipamide, polycaprolactam and the like. The polyamide filaments of the present invention may contain in addition to the tertiary amine delustrants, antioxidants, brighteners, viscosity stabilizers, plasticizers and the like.

We claim:

1. A static resistant melt spun synthetic saturated aliphatic polycarbonamide filament containing as a separate phase from 1% to 15% by weight, based on the weight of the polyamide, of an amine of the structure



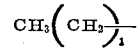
wherein each R is an alkyl group having at least 8 carbon atoms, R′ is an alkylene group having 2 to 4 carbon atoms and n is an integer between 15 and 450.

2. The filament of claim **1** wherein said polycarbonamide is polyhexamethylene adipamide.

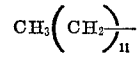
3. The filament of claim **1** wherein said polycarbonamide is polycaprolactam.

4. The filament of claim **1** wherein R′ is $-CH_2CH_2-$.

5. The filament of claim **4** wherein each R is



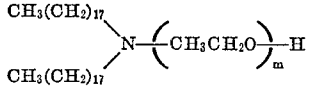
6. The filament of claim **4** wherein each R is



7. The filament of claim **4** wherein each R is an alkyl group having from 12 to 30 carbon atoms.

8. The filament of claim **4** wherein n is between about 30 and about 200.

9. A static resistant melt spun polyhexamethylene adipamide filament containing between about 2% and 8% by weight, based on the weight of polyhexamethylene adipamide, of an amine of the structure



wherein m is in integer between about 30 and 200.

10. The filament of claim **9** wherein m is between about 35 and 100.

11. The filament of claim **9** wherein m is between about 50 and 75.

References Cited

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HAROLD D. ANDERSON, Primary Examiner

U.S. Cl. X.R.

57—140 R; 260—78 R, 78 A, 78 L, Dig. 19

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,654,235 Dated April 4, 1972

Inventor(s) Lawrence W. Crovatt, Jr. and Dennis J. Durant

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

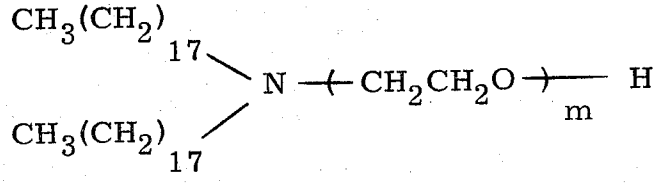
Column 2, line 44, "of" should have been --at--.

Column 7, line 21, "polycarbonamide" should have been --polycarbonamides--.

Column 8, line 6, the formula in Claim 5 should read as follows:

$$CH_3(CH_2)_{17}$$

Column 8, lines 20 through 24, the formula in Claim 9 should read as follows:



Signed and sealed this 1st day of August 1972.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents

FORM PO-1050 (10-69)

USCOMM-DC 60376-P69
* U.S. GOVERNMENT PRINTING OFFICE : 1969 O—366-334