United States Patent [19]

Kunde et al.

[11] **3,725,503**

[45] **Apr. 3, 1973**

[54] **POLYAMIDES WITH DISPERSED OXYALKYATED GRAFTED POLYAMIDES**

[75] Inventors: **Joachim Kunde**, Frankenthal; **Gerhard Ramlow**, Ludwigshafen; **Guenter Buechler**, Heidelberg; **Heinz Pohlemann**, Limburgerhof; **Hans Hendus**, Ludwigshafen, all of Germany

[73] Assignee: **Badische Anilin- & Soda-Fabrik Aktiengesellschaft**, Ludwigshafen/Rhine, Germany

[22] Filed: **June 3, 1971**

[21] Appl. No.: **149,778**

[52] **U.S. Cl.** .....**260/857 TW**, 260/37 N, 260/78 R, 260/857 PG

[51] **Int. Cl.** **C08g 41/04**

[58] **Field of Search** .....260/857 TW, 857 PE

[56] **References Cited**

UNITED STATES PATENTS

3,514,498	5/1970	Okazaki	260/857
3,038,885	6/1962	Best	260/857
3,522,329	7/1970	Okazaki	260/857
3,549,724	12/1970	Okazaki	260/857

FOREIGN PATENTS OR APPLICATIONS

1,110,394	4/1968	Great Britain	260/857
665,018	6/1965	Belgium	260/857

Primary Examiner—Paul Lieberman

Attorney—Johnston, Root, O'Keeffe, Keil, Thompson & Shurtleff

[57] **ABSTRACT**

Filaments or fibers of synthetic linear polyamides containing highly oxyalkylated polyamides. The filaments or fibers are notable for their excellent antistatic properties and their soil-hiding effect.

8 Claims, No Drawings

POLYAMIDES WITH DISPERSED OXYALKYATED GRAFTED POLYAMIDES

This invention relates to filaments or fibers of synthetic linear high molecular weight polyamides containing oxyalkylated polyamides.

There is a great demand, for example in the carpet industry, for fibers and filaments which show a reduced tendency to build up static charges and also exhibit increased brilliance and opacity, which in turn weaken the impression of soiling ("soil-hiding effect")

There have been a number of attempts to improve the antistatic properties of filaments or fibers by applying antistatic agents thereto. However, the stability of such finishes is unsatisfactory, since the agents are generally removed during washing or are dislodged by mechanical influences.

U.S. Pat. No. 3,329,557 reveals a method of incorporating antistatic agents such as polyalkylene glycols in the filaments or fibers. German Published Application DOS 1,494,963 also reveals a method of incorporating oxyalkylated polyamides, in which the ratio of polyamide to alkylene oxide is up to : 4 by weight, in plastics materials such as polyamides. However, the incorporation of polyalkylene glycols or oxyalkylated polyamides of the said relatively low degree of oxyalkylation does not provide the advantages achieved by the present invention, as is demonstrated by comparative tests.

It is an object of the invention to provide filaments or fibers of polyamides showing a greatly reduced tendency to build up static charges and exhibiting a soil-hiding effect.

This object is achieved by filaments or fibers of synthetic linear high molecular weight polyamides having recurring amide groups in the backbone, which filaments or fibers contain, as a separate phase dispersed therein, from 1 to 15 percent by weight of highly oxyalkylated polyamides in which the ratio of synthetic linear polyamide having recurring amide groups in the backbone to 1,2-alkylene oxide of from two to four carbon atoms and chemically combined therewith is from 1 : 10 to 1 : 15 by weight.

By synthetic linear high molecular weight polyamides we mean those having recurring amide groups in the backbone.

By filaments or fibers we means, for example, those obtained by a usual melt-spinning technique followed, if desired, by drawing and having a round or profiled cross-section, for example a trilobate or tetralobate cross-section. Two-component filaments or fibers are also suitable. Other suitable filaments or fibers are those produced from polyamide sheeting by mechanical means, for example by cutting or fibrillating. The filaments or fibers may be texturized, for example by false-twist or stuffer box processes or by means of moving gaseous media.

Suitable filament-forming or fiber-forming synthetic linear polyamides are, for example, the polycondensates of lactams of from four to 12 carbon atoms, such as ϵ-caprolactam, octanolactam, dodecanolactam or mixtures thereof, and the polycondensates of salts of diamines and dicarboxylic acids of from four to 12 carbon atoms, such as the salts of adipic acid, suberic acid or sebacic acid with hexamethylene diamine, octamethylene diamine or dodecamethylene diamine, or mixed condensates of the above polyamide-forming

starting materials. Particularly suitable are polycaprolactam and polyhexamethyleneadipamide. The filament-forming or fiber-forming polyamides may contain an excess of basic groups, for example from 50 to 130 milli-equivalents per kilogram, or they may contain sulfonic acid groups or alkali metal sulfonate groups in a proportion of, say, from 50 to 150 milli-equivalents per kilogram.

It is important that highly oxyalkylated polyamides be present in the filaments or fibers during their formation. By highly oxyalkylated polyamides we mean synthetic linear polyamides having recurring amide groups in the backbone and which contain from 10 to 50 times their weight of 1,2-alkylene oxide chemically combined therewith.

The production of the highly oxyalkylated polyamides, which is not claimed in the present specification, is not generally effected directly from the polyamides and the 1,2-alkylene oxides. It may be carried out, for example, by reacting oxyalkylated polyamides showing a low degree of oxyalkylation, i. e. synthetic linear polyamides containing 1,2-alkylene oxide in a ratio of from 1 : 1 to 1 : 4 by weight, with 1,2-alkylene oxides at elevated temperature and pressure, if necessary in the presence of basic oxyalkylation catalysts, such that a polyamide is produced which contains combined 1,2-alkylene oxide in a ratio of from 1 : 10 to 1 : 50 and in particular from 1 : 15 to 1 : 30 by weight. The reaction of the 1,2-alkylene oxides with the synthetic linear polyamides takes place at the NH groups of the polyamides to form chemically combined polyalkylene oxide chains. The said oxyalkylated polyamides may be classified as graft polymers.

Suitable 1,2-alkylene oxide or epoxides are those containing from two to four carbon atoms, such as 1,2-butylene oxide and, in particular, ethylene oxide and/or 1,2propylene oxide.

Suitable polyamides from which the highly oxyalkylated polyamides used as antistatic agents may be prepared are, for example, conventionally produced polycondensates of lactams of from four to 12 carbon atoms, such as caprolactam, octanolactam, dodecanolactam or mixtures thereof; salts of diamines with dicarboxylic acids of from four to 12 carbon atoms, such as salts of adipic acid, suberic acid or sebacic acid with hexamethylene diamine, octamethylene diamine or dodecamethylene diamine; or mixed polyamides derived from the above polyamide forming starting materials. Particularly suitable are polycaprolactam, polyhexamethyleneadipamide and their copolyamides. We have found polyamides having relative viscosities between 1.5 and 2.9 to be particularly suitable. The incorporation of the highly oxyalkylated polyamides may be effected in any conventional manner, for example by thorough distribution in, advantageously, the finished filament-forming polyamide in the molten state, for example by kneading or extrusion techniques. Alfternatively, the highly oxyalkylated polyamides may be added to the polyamide-forming components before or during the manufacture of the polyamides.

The highly oxyalkylated polyamides do not form a homogeneous phase with the filament-forming or fiber-forming polyamides; after the composition has been shaped to filaments or fibers and cooled, the highly ox-

yalkylated polyamides form separate, elongated particles.

The highly oxyalkylated polyamides impart excellent antistatic properties to the filaments or fibers. When the filaments are treated with hot aqueous liquors, for example during dyeing or washing, at temperatures between 90° and 110°C, some of the particles of highly oxyalkylated polyamides embedded in the filaments or fibers are dissolved out leaving cavities. These filaments or fibers show excellent brilliance and opacity, which in turn weakens the impression of soiling and significantly improves the soil-hiding effect over known filaments. The good antistatic properties of the filaments or fibers of the invention are surprisingly retained after several washes.

The proportion of highly oxyalkylated polyamides in the filaments or fibers is conveniently from 1 to 15 percent by weight. The proportion of said highly oxyalkylated polyamides in the non-extracted filaments or fibers is conveniently from 2 to 15 percent by weight and preferably from 3 to 10 percent by weight, whilst the proportion thereof in the extracted filaments or fibers is conveniently from 1 to 8 percent by weight and preferably from 1 to 5 percent by weight. It is possible, if desired, to incorporate larger proportions of oxyalkylated polyamides, but this entails certain changes in the properties of the filaments.

Suprisingly, the filaments or fibers of the invention prepared with the addition of highly oxyalkylated polyamides show a significantly better soil-hiding effect than filaments or fibers prepared with the addition of polyalkylene glycols or oxyalkylated polyamides showing a low degree of oxyalkylation, i. e. polyamides containing not more than four times their weight of 1,2-alkylene oxide. One would have expected the effect to have approached that of polyalkylene glycols when polyamides are increasingly oxyalkylated.

The filaments or fibers of the invention show, after extraction, a charge of less than 300 volts at 35 percent relative humidity and virtually no measurable charge at all at a relative humidity of 65 percent, whilst filaments in which polyethylene oxide having a molecular weight of 20,000 has been incorporated show, after extraction, values of more than 900 volts and 200 volts respectively. Unmodified filaments show charges of about 2,500 and 1,000 volts respectively.

The filaments of the invention may contain other additives such as pigments, e. g. titanium dioxide, or light stabilizers and heat stabilizers. They are suitable, for example, for the manufacture of textiles such as woven, knitted or non-woven fabrics and, in particular, carpets.

For the purpose of measuring the electrostatic charges, strands of yarn are made. The strands are extracted for 1 hour in boiling water and then stored at two different relative humidities (35 percent and 65 percent) for 2 days. After adjusting the humidity to ambient conditions, the filaments are drawn through an insulated brass eyelet under the respective atmospheric conditions until the maximum charge is reached. The charge on the filaments is then transferred to a metal plate connected to a voltmeter, which in turn indicates a voltage corresponding to the charge.

Assessment of the soil-hiding effect is carried out by observing the brightness of filaments or fibers under an optical microscope with light directed from the side, after the said filaments or fibers have been extracted for 1 hour with boiling water. Unmodified filaments appear dark, whilst the modified filaments show various degrees of brightness according to the effect of the additive.

In the following Examples the parts and percentages are by weight. The relative viscosities given ($\eta_{rel.}$) are measured in 1 percent w/w solution in 98 percent sulfuric acid at 20°C.

EXAMPLE 1

In a twin worm extruder, 5 parts of a highly oxyalkylated polycaprolactam containing chemically combined ethylene oxide in a proportion equal to 20 times the weight of polycaprolactam are mixed into 95 parts of a conventionally prepared polycaprolactam ($\eta_{rel.}$ = 2.7) at 240°C. The mixture is then granulated and the resulting granules are melt-spun to filaments and then drawn to form a 1,200/67 denier yarn, the draw ratio being 1 : 3.36. A strand is extracted in boiling water for 1 hour.

EXAMPLE 2

7.5 parts of a highly oxyalkylated polycaprolactam consisting of 1 part of polycaprolactam ($\eta_{rel.}$ = 2.4) and 25 parts of chemically combined ethylene oxide are mixed into 92.5 parts of polyhexamethyleneadipamide ($\eta_{rel.}$ = 2.7) in a twin worm kneader. A yarn is spun from the resulting granules and drawn at a draw ratio of 1 : 3.28. It has a weight of 40/10 denier and is extracted as described in Example 1.

EXAMPLE 3

95 parts of hexamethylenediamine adipate (AH salt), 25 parts of water and 5 parts of highly oxyalkylated polycaprolactam from 1 part of polycaprolactam ($\eta_{rel.}$ = 2.4) and 18 parts of ethylene oxide chemically combined therewith in 20 parts of water are heated in an autoclave at 280°C, the pressure being held at 18 atmospheres by bleeding off steam. The pressure is than allowed to fall to atmospheric over 1 hour and condensation is continued for a further 45 minutes at 280°C in a stream of nitrogen. The resulting polycondensate is melt-spun and drawn at a ratio of 1 : 3.2 to form a 210/30 denier yarn. A strand is extracted in the manner described in Example 1.

EXAMPLE 4

Example 1 is repeated except that the additive used is a highly oxyalkylated polyamide from 1 part of a mixed polyamide consisting of 40 percent by weight of polycaprolactam and 60 percent by weight of polyhexamethyleneadipamide and 20 parts of chemically combined ethylene oxide.

COMPARATIVE EXAMPLE I

Example 1 is repeated except that the additive used is 5 parts of the reaction product of 1 part of caprolactam with 4 parts of chemically combined ethylene oxide as proposed in German Published Application DOS 1,494,963.

COMPARATIVE EXAMPLE II

Example 1 is repeated except that the additive used is 5 parts of

a. a polyethylene oxide having a molecular weight of 9,500,

b. a polyethylene oxide having a molecular weight of 18,000 or

c. a polyethylene oxide having a molecular weight of 36,000, as proposed in U.S. Pat. No. 3,329,557.

The effects achieved as regards reduction in static build-up and increase in brightness or brilliance are demonstrated in the following Table. Brightness is rated in grades 1 to 5 (5 = very good).

Example	Electrostatic Charge in Volts reached at a relative humidity of		Brightness
	35%	65%	
I	200	0	5
2	150	0	5
3	200	0	5
4	250	0	5
I	500	50	1
II*a*	900	150	2
II*b*	1500	450	3
II*c*	1400	450	2
Unmodified polycaprolactam	2300	1200	1

The above Table shows that the filaments or fibers of the invention, as prepared in Examples 1 to 4, are significantly superior to filaments of unmodified polyamides and are also considerably better, as regards antistatic properties and brightness, than filaments or fibers produced according to U.S. Pat. No. 3,329,557 or German Published application DOS 1,494,963 comprising the nearest prior art.

We claim:

1. Filaments or fibers of synthetic linear high molecular weight polyamides having recurring amide groups in the backbone, which filaments or fibers contain, as a separate phase dispersed therein, from 1 to 15 percent by weight of highly oxyalkylated grafter polyamides in which synthetic linear polyamide having recurring amide groups in the backbone is grafted with 1,2-alkylene oxide of from two to four carbon atoms and in which the ratio of the polyamide and the chemically bonded alkylene oxide is from 1 : 15 to 1 : 50 by weight.

2. Filaments or fibers as claimed in claim 1, wherein the said ratio of synthetic linear polyamide to chemically combined 1,2-alkylene oxide is from 1 : 15 to 1 : 30 by weight.

3. Filaments or fibers as claimed in claim 1, containing 3 to 10 percent by weight of the said highly oxyalkylated polyamides.

4. Filaments or fibers as claimed in claim 1, containing highly oxyalkylated polyamides prepared with ethylene oxide.

5. Filaments or fibers as claimed in claim 1, containing, after extraction with water, cavities and from 1 to 8 percent by weight of said highly oxyalkylated polyamides.

6. Filaments or fibers as claimed in claim 1, containing, after extraction with water, cavities and from 1 to 5 percent by weight of said highly oxyalkylated polyamides.

7. Filaments or fibers as claimed in claim 1, composed of polycaprolactam.

8. Filaments or fibers as claimed in claim 1, composed of polyhexamethyleneadipamide.

* * * * *