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(54) Method for preparation of antibacterial, deodorant polyurethane yarns.

(57) A method for preparation of an antibacterial, deodorant polyurethane yarn. The improvement comprises adding a solution resulting from dissolving a mordenite, a class of antibacterial zeolites, in dimethylformamide to a polyurethane polymer before spinning in a conventional process for preparing the polyurethane yarn. The mordenite is previously prepared, before being dissolved in the dimethylformamide, by being boiled in a strong acid to have a silica/alumina molar ratio in the range of about 12 to 33, then ion-exchanged with an antibacterial metal, such as silver, copper, zinc or the like, thereafter, controlled to have an average particle size in the range of about 0.5 μm to 2.0 μm.

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BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates in general to a method for preparation of polyurethane yarns, and more particularly to a method for preparation of polyurethane yarns which comprises adding a mordenite, a class of antibacterial zeolites, to a polyurethane polymer just before spinning, thereby providing the final polyurethane yarns with improved resistance to fabric weakening, decolorization and foul odor emission due to the propagation of bacteria, and with improved hygroscopicity to give a person comfortable wearing feelings.

Description of the Prior Art

Conventionally, shaped articles, such as yarns and fibers, of polyurethane polymers, that is, spandex polymers, are well known. These types of polymers are widely used for filaments that are incorporated into fabrics of hosiery, swimwear, gymnastic wear, medical fabric articles (bandages and medical protect hosiery), women's underwear and other garments. However, the known polyurethane yarns generally have no resistance to bacteria or mildews and no hygroscopicity. In result, the articles, especially sports garments, made of the known polyurethane yarns, when they are soaked with the perspiration of the human body, hurt a person's feeling together with provision of a good condition for propagation of bacteria, thus causing a foul odor to be emitted therefrom and a bacterial contamination of the human body.

In an effort to solve the above problems, there have been proposed several methods for imparting resistance to bacteria to the polyurethane yarns such as disclosed in U.S. Patent No. 4,837,292 and Japanese Laid-Open Patent Publication No. Sho. 59-26,573. The U.S. patent discloses a method for preparing a polyurethane-urea spandex having polycarbonate soft segments which are derived from poly-(pentane-1,5-carbonate)-diol, poly(hexane-1,6-carbonate)diol, copolymers thereof, or mixtures thereof without using additional antibacterial agent, while the Japanese patent discloses a method wherein a pyridine compound is used for imparting resistance to bacteria to the polyurethane yarns. However, it is known that the methods disclosed in the above patents can not impart desired resistance to bacteria to the polyurethane yarns.

Therefore, the present inventors conducted a series of experiments and found that when the mordenite, a kind of antibacterial, deodorant and hygroscopic zeolite, is evenly dispersed into the polyurethane polymers just before spinning, it is possible to provide a final polyurethane yarn having an excellent resistance to bacteria and foul odor emission, and having a good hygroscopicity together with the unchanged intrinsic properties of the conventional elastic fibers.

SUMMARY OF THE INVENTION

It is a primary object of the present invention to provide a method for preparation of a polyurethane yarn which comprises adding a mordenite, a kind of antibacterial, deodorant and hygroscopic zeolite, to polyurethane polymers just before spinning, thereby providing the resultant polyurethane yarn with an improved resistance to fabric weakening, decolorization and foul odor emission due to the propagation of bacteria, and with improved hygroscopicity.

In an aspect, the present invention provides a method for preparation of an antibacterial, deodorant polyurethane yarn, characterized in that the improvement comprises adding a solution resulting from dissolving a mordenite, a class of antibacterial zeolites, in dimethylformamide to a polyurethane polymer before spinning in a conventional process for preparing the polyurethane yarn, said mordenite being previously prepared, before being dissolved in the dimethylformamide, by being boiled in a strong acid to have a silica/alumina molar ratio in the range of about 12 to 33, then ion-exchanged with an antibacterial metal, such as silver, copper, zinc or the like, thereafter, controlled to have an average particle diameter in the range of about 0.5 μm to 2.0 μm.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Briefly described, the method according to this invention is characterized in that during a process for preparing a polyurethane yarn by (i) pre-polymerizing polytetramethylene ether glycol having a number average molecular weight (Mn) in the range of about 1,000 to 2,500 with an excess of an organic diisocyanate, (ii) chain-extending the isocyanate end-group of the resultant prepolymer with organic

diamines in the presence of a catalyst and (iii) end-capping the prepolymer with organic monoamines. The resultant polyurethane polymer just before being spun is mixed with a mordenite, a class of zeolites. The amount of mordenite is 0.5 to 2.5 parts by weight based on the weight of the final polyurethane yarn. Before addition to the polymer, the mordenite is previously boiled in a strong acid to have a silica/alumina molar ratio in the range of about 12 to 33, then ion-exchanged with antibacterial metals, such as silver, copper, zinc and etc., thereafter, controlled to have an average particle diameter in the range of about 0.5 μm to 2.0 μm. The resultant mordenites have the formula (I)

$$M_{x/n}\,[(AlO_2)_x(SiO_2)_y]\,ZH_2O \qquad (I)$$

wherein M is a metal having n atomic valences, x + y are the number of tetrahedrons per unit lattice and z is the molar number of water molecule.

The zeolite, that is, the mordenite, having the formula (I) is a porous material having a very large specific surface so that it has an excellent affinity to a polar material such as moisture, thus being widely used as an absorbent. The zeolite comprises silica-alumina as an essential ingredient and is a crystal wherein TO_4 (T = Si, Al) tetrahedrons are three-dimensionally crystallized sharing the oxygen atoms with each other.

In the lattice structure of the zeolite having the formula (I), the oxygen atoms are shared in the two tetrahedrons as described above so that the lattice of the zeolite has negative electricity, thereby causing the ion exchange capacity thereof to keep the balance with the cation. The zeolite having the above-mentioned structure is ion-exchanged with an antibacterial metal, such as silver, copper or zinc, such that the antibacterial metal ion is stably bonded to the zeolite and evenly distributed therein. In result, the zeolite ion-exchanged with the antibacterial metal shows excellent antibacterial property as a result of high activity on bacteria of fungi. Therefore, in case of using such antibacterial zeolite for sterilization, the zeolite shows an improved resistance to bacteria because the antibacterial ion of silver, copper or zinc has an active site in the structure of zeolite and has a wide contact surface by virtue of the large specific surface thereof as described above. In addition, the zeolite retains the resistance to bacteria for a suprisingly long time because as aforementioned the antibacterial metal is stably bonded thereto such that the elution amount of the metal ion is negligible. On the other hand, the zeolite has an excellent ion exchanging capacity so that there is no problem in the ion exchange thereof with the antibacterial metals.

It is conventionally known that in case of an ion exchange of a sodium zeolite for achievement of antibacterial property, it is preferred to add silver ions in a range of 0.01 to 0.04 % by weight based on the weight of anhydrated zeolite, copper ions in a range of 0.03 to 10 % by weight or zinc ions in a range of 0.04 to 14 % by weight to the zeolite. In case of using the mordenite as a zeolite, the mordenite generally shows more excellent resistance to various acids and alkalis in proportion to the increase of the silica/alumina ratio. However, in order to increase the silica/alumina ratio, it is required to continue the reaction for a substantially long time and this causes the commercial productivity to be reduced. In result, it is known that in using for fabrics the mordenite having a silica/alumina ratio in the range of 12 to 33 exhibits a good resistance to chemicals and bacteria or mildews.

When the antibacterial zeolite is added to the polyurethane polymers, it amounts to preferably 0.5 to 2.5 parts by weight based on the weight of the final polyurethane yarn. If the zeolite amounts to less than 0.5 parts by weight, it has no desired resistance to the bacteria, while if it amounts to more than 2.5 parts by weight, it is not commercially-valuable because it does not show much more improvement of the resistance to the bacteria than amounting to 2.5 parts by weight.

In accordance with this invention, the method for preparation of the antibacterial, deodorant polyurethane yarns is characterized in that during a conventional process for preparing the polyurethane yarns, a synthetic mordenite, which is previously boiled in a strong acid to have a silica/alumina molar ratio in the range of about 12 to 33, then ion-exchanged with an antibacterial metal, such as silver, copper, zinc or the like, thereafter, controlled to have an average particle diameter in the range of about 0.5 μm to 2.0 μm, is added to the polyurethane polymer just before being spun.

The following example and comparative examples are merely intended to illustrate the present invention in further detail and should by no means be considered to be limitative of the invention.

EXAMPLE 1

1,000 parts by weight of polytetramethylene ether glycol having a molecular weight of 2,000 were mixed with 4,4'-diphenylmethane diisocyanate of 250 parts by weight based on the total weight of the polytetramethylene ether glycol to provide a mixture which was then heated at a temperature of 80 °C for

90 minutes under a nitrogen atmosphere to be polymerized, thereby producing a prepolymer.

Thereafter, the prepolymer was dissolved in 1,000 parts by weight of dimethylformamide and was allowed to cool to 3 °C, then the polymer solution was slowly mixed with a solution which had been prepared by dissolving a chain extender consisting of 29.6 parts by weight of 1,2-propylene diamine, a class of linear type diamines, and 6.8 parts by weight of 1,3-cyclohexylene diamine, a class of ring type diamines, in 1,000 parts by weight of dimethylformamide. The resultant polymer solution had a viscosity of 3,500 poise.

The resultant polymer solution (3,500 poise viscosity) was then slowly mixed with a solution resulting from dissolving 6.1 parts by weight of monoethanol amine in 250 parts by weight of dimethylformamide. In result, a polymer solution having a viscosity of 3,200 poise was produced. Thereafter, a solution, which had been prepared by dissolving 5 parts by weight of acetic anhydride in 250 parts by weight of dimethylformamide, was added to the resultant polymer solution (3,200 poise viscosity) to stabilize the viscosity of the polymer. At this time, this polymerization was carried out at a temperature less than 25 °C.

After the polymerization, the resultant polymer was mixed with a solution which had been prepared by dissolving 25 parts by weight of a pentaerythritol phosphite compound for imparting a good color fastness to light and to harmful gas of the final polyurethane yarn and 4.1 parts by weight of mordenite as an antibacterial compound in 600 parts by weight of dimethylformamide, respectively. As a result the solids content of the resultant polymer was controlled to be 30 %. It had a viscosity of 2,900 poise. Here, before dissolution in the dimethylformamide, the mordenite was previously prepared by being boiled by hydrochloric acid, a class of strong acids, to have a silica/alumina molar ratio of 22, then ion-exchanged with silver, a class of antibacterial metals, to be impregnated with 0.04 % silver ions, thereafter, controlled to have an average particle size of 1.0 μm.

The resultant polymer solution (30 % solids) was subjected to dry spinning in a conventional manner into 70-denier/7-filament yarn at a predetermined spinning speed, treated with a conventional finishing agent and wound onto a conventional cardboard tube. The characteristics, such as strength, elongation, resistance to bacteria and the like, of the final polyurethane yarn were measured and are given in Tables 1 and 2.

COMPARATIVE EXAMPLE 1

The procedure of Example 1 was repeated, substituting a silica/alumina molar ratio of 8.5 of the mordenite for the ratio of 22. The characteristics of the final polyurethane yarn are given in Tables 1 and 2.

COMPARATIVE EXAMPLE 2

The procedure of Example 1 was repeated, substituting a silcia/alumina molar ratio of 40 of the mordenite for the ratio of 22. The characteristics of the final polyurethane yarn are given in Tables 1 and 2.

COMPARATIVE EXAMPLE 3

The procedure of Example 1 was repeated, substituting a mordenite having no silver ion for the mordenite having 0.04 % silver ions. The characteristics of the final polyurethane yarn are given in Tables 1 and 2.

COMPARATIVE EXMAMPLE 4

The procedure of Example 1 was repeated, substituting a mordenite having an average particle size of 3.0 μm for the mordenite having the size of 1.0 μm. The characteristics of the final polyurethane yarn are given in Tables 1 and 2.

COMPARATIVE EXAMPLE 5

The procedure of Example 1 was repeated, adding no mordenite. The characteristics of the final polyurethane yarn are given in Tables 1 and 2.

COMPARATIVE EXAMPLE 6

The procedure of Example 1 was repeated, adding the mordenite in an amount of 0.4 parts by weight based on the weight of the final polyurethane yarn. The characteristics of the final polyurethane yarn are

given in Tables 1 and 2.

COMPARATIVE EXAMPLE 7

The procedure of Example 1 was repeated, adding the mordenite in an amount of 3.0 parts by weight based on the weight of the final polyurethane yarn. The characteristics of the final polyurethane yarn are given in Tables 1 and 2.

TABLE 1

(a comparison of characteristics among the final polyurethane yarns of the Example 1 and the Comparative Examples 1 to 7)

Properties / Section	Strength (g/de)	Elongation(%)	Elastic Recovery(%)	300% Modulus	Spinning Property
Example 1	1.35	605	78	0.35	Good
Com.Exam. 1	1.35	605	78	0.35	Good
Com.Exam. 2	1.35	605	78	0.35	Good
Com.Exam. 3	1.35	605	78	0.35	Good
Com.Exam. 4	1.15	590	72	0.30	Bad
Com.Exam. 5	1.35	605	78	0.35	Good
Com.Exam. 6	1.35	605	78	0.35	Good
Com.Exam. 7	1.00	520	65	0.28	Bad

TABLE 2

(A comparison of the resistance to bacteria among the final polyurethane yarns of the Example 1 and the Comparative Examples 1 to 7)

Properties / Section	Reduction Rate of Bacteria Depending Upon Washing Times (%)			
	0 Time	5 Times	10 Times	20 Times
Example 1	99.99	99.80	98.80	97.00
Com.Exam. 1	97.00	96.80	95.70	94.00
Com.Exam. 2	96.40	96.00	95.10	93.00
Com.Exam. 3	51.30	49.70	48.20	40.00
Com.Exam. 4	99.99	99.30	98.00	96.00
Com.Exam. 5	40.20	35.00	33.55	25.00
Com.Exam. 6	61.00	60.20	59.70	57.00
Com.Exam. 7	99.99	99.80	98.90	97.00

In Table 2, the resistance to bacteria of the fabrics were measured by a shake flask method using Staphylococcus aureus (American Type Culture Collection No. 6538), a class of test bacteria, and the fabric before the test of antibacterial activity were washed in a home laundry washing machine set under the following condition, then naturally dried after the dehydration.

a) Laundry detergent:	nonionic sythetic detergent (10 grams/5 lit. water)
b) Washing time:	5 minutes
c) Dehydration time:	1 minute
d) Rewashing time:	8 minutes
e) Dehydration time:	2 minutes

Claims

1. A method for preparation of an antibacterial, deodorant polyurethane yarn, **characterized in that** the improvement comprises:

   adding a solution resulting from dissolving a mordenite, a class of antibacterial zeolites, in dimethylformamide to a polyurethane polymer before spinning in a conventional process for preparing the polyurethane yarn, said mordenite being previously prepared before dissolution in the dimethylformamide, by being boiled in a strong acid to have a predetermined silica/alumina molar ratio, then ion-exchanged with an antibacterial metal, such as silver, copper, zinc or the like.

2. The method according to Claim 1, wherein said silica/alumina molar ratio of the mordenite is in the range of about 12 to 33.

3. The method according to Claim 1, wherein said mordenite added to the polyurethane polymer amounts to the range of about 0.5 to 2.5 parts by weight based on the weight of the polyurethane yarn.

4. The method according to Claim 1, wherein said mordenite has an average particle size in the range of about 0.5 μm to 2.0 μm.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 92 11 1236

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	US-A-4 775 585 (ZENJI HAGIWARA ET AL.) * claims *	1-4	D01F6/70 D01F1/10
P,X	PATENT ABSTRACTS OF JAPAN vol. 15, no. 474 (C-890)3 December 1991 & JP-A-32 05 436 (TORAY IND INC) 6 September 1991 * abstract *	1-4	
A	DATABASE WPIL Section Ch, Week 8910, Derwent Publications Ltd., London, GB; Class A, AN 89-072714 & JP-A-1 024 861 (SHINAGAWA NENRYO KK ET AL.) 26 January 1989 * abstract *	1-4	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

D01F

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	19 OCTOBER 1992	TARRIDA TORRELL J.B.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
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