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METHOD OF IMPROVING FILAMENTS OF HYDROLYZED OLEFIN/VINYL ORGANIC ESTER INTERPOLYMERS

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This invention relates to improved hydrolyzed olefin/vinyl organic ester interpolymer filaments and, more particularly, to a new process for improving the properties of filaments derived from hydrolyzed olefin/vinyl organic ester interpolymers.

This invention has as an object the provision of oriented filaments of hydrolyzed ethylene/vinyl organic ester interpolymers which are characterized by improved properties. A further object is the provision of oriented filaments of hydrolyzed ethylene/vinyl organic ester interpolymers which are characterized by improved dye receptivity and increased elongation. A still further object is the production of oriented filaments of hydrolyzed ethylene/vinyl organic ester interpolymers which are markedly more resistant to boiling water than prior art filaments of hydrolyzed ethylene/vinyl organic ester interpolymers. Additional objects will become apparent from an examination of the following description and claims.

These and other objects and advantages are accomplished according to the herein described invention which broadly comprises drawing at a temperature within the range of from 80° C. to 100° C. in a medium containing H_2O a filament of a substantially completely hydrolyzed interpolymer of ethylene with a vinyl ester of a monocarboxylic acid having the general formula

RCOOH

wherein R is of the group consisting of hydrogen atoms and hydrocarbon radicals, said acid being free from unsaturated linkages between acyclic carbon atoms and any carbon atom alpha to the carbon atom in the carboxyl group of said acid being attached to at least one but not more than three carbon atoms, the mol ratio of ethylene to vinyl organic ester prior to hydrolysis having been within the range of from 1/1 and 5/1, and thereafter contacting the resultant stretched filament at a temperature within the range of from 101° C. to 106° C., in a taut condition, with a medium comprising H_2O at a temperature within the range of from 101° C. to 106° C.

A preferred embodiment of this invention comprises drawing, at a temperature within the range of from 90° C. to 100° C. in steam at a temperature within the range of from 90° C. to 100° C., a filament of a substantially completely hydrolyzed interpolymer of ethylene with vinyl acetate, the mol ratio of ethylene to vinyl acetate prior to hydrolysis having been within the range of from 2/1 to 4/1, and thereafter subjecting the

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resultant stretched filament in a taut condition and at a temperature within the range of from 102° C. to 104° C. to steam at a temperature within the range of from 102° C. to 104° C.

The following examples, in which proportions are in parts by weight unless otherwise specified, are given for illustrative purposes and are not intended to place any restrictions on the herein described invention.

Example I

An interpolymer of ethylene and vinyl acetate having a molar ratio of 2.6/1 of ethylene to vinyl acetate was prepared by the controlled addition of ethylene at about 1000 atmospheres pressure and at about 65° C. to vinyl acetate containing a small amount of benzoyl peroxide. The ethylene/vinyl acetate interpolymer was hydrolyzed in a benzene-methanol solution with excess caustic and the interpolymer was isolated and the caustic removed by washing with water. The hydrolyzed ethylene/vinyl acetate interpolymer was dried and filaments prepared by melt spinning the molten polymer in a rod spinner as described in U. S. Patent 2,253,089. The filaments obtained were oriented by drawing in water heated at 98° C., employing a draw ratio of 6:1. The yarn had a tenacity of 4.4 g./d. at 11% elongation and a shrinkage of 52% when immersed for 5 minutes in water heated at approximately 100° C.

When the drawn yarn was wound on a metal bobbin under slight tension and heat treated by subjecting to steam in an autoclave at 104° for 5 minutes, the yarn had a tenacity of 4.4 g./d. at 16% elongation and had a shrinkage of only 8.5% when immersed in boiling water for 5 minutes.

Example II

A melt-spun yarn of a substantially completely hydrolyzed ethylene/vinyl acetate interpolymer having a molar ratio of ethylene-vinyl acetate of 2.8/1 was drawn in steam at 99–100° C. at a draw ratio of 5.3/1 to give an oriented yarn having a tenacity of 3.7 g./d. at 15% elongation and having a shrinkage of 27% when heated in water to 100° C. This yarn was heat treated in steam for about 5 minutes at 103° C. under slight tension. The resulting heat-treated yarn had a tenacity of 3.4 g./d. at 19% elongation and had a shrinkage of only 7% when heated in water at 100° C.

When the above yarn was set at 100° C. in steam under otherwise identical conditions, the heat-set yarn had a tenacity of 3.7 g./d. at 20% elongation but had a shrinkage of 13% when subjected to water at 100° C.

Example III

A hydrolyzed ethylene/vinyl acetate interpolymer of molar ratio of ethylene/vinyl acetate of approximately 2.4/1 was dissolved in a trichloroethylene-ethanol mixture and filaments obtained by "dry-spinning" the solution. The yarn was oriented by drawing in steam at 99° C. at a draw ratio of 8.11/1 *to* give a yarn having a tenacity of 3.9 g./d. at 12% elongation. The yarn was set in steam at 102° C. to give filaments having a tenacity of 3.8 g./d. at 19% elongation. The heat-set yarn had a shrinkage of 12% when treated in water at 100° C. When the unset or untreated yarn which had not been subjected to the steam treatment was placed in boiling water, the yarn was so water-sensitive that it broke.

The process of this invention is applicable to any filament of a hydrolyzed interpolymer of ethylene with a vinyl ester of an organic acid having the general formula RCOOH, wherein R is of the group consisting of hydrogen atoms and hydrocarbon radicals, said acid being free from unsaturated linkages between acyclic carbon atoms and any carbon atom alpha to the carbon atom in the carboxyl group of said acid being attached to at least one but not more than three carbon atoms, provided the mol ratio of ethylene to vinyl organic ester in said interpolymer prior to hydrolysis was within the range of from 1/1 to 5/1. Included among examples of said interpolymers are interpolymers of ethylene with vinyl formate, with vinyl acetate, with vinyl propionate, with vinyl butyrate, with vinyl stearate, with vinyl benzoate, with vinyl cyclohexanoate, with vinyl isobutyrate, with vinyl palmitate, with vinyl myristate, with vinyl toluate, with vinyl naphthoate and the like. On account of superior products had therewith, I prefer to employ interpolymers of ethylene with a vinyl ester of an organic acid having the general formula $C_nH_{2n+1}COOH$, wherein n is a positive integer within the range of from 1 to 3. Inasmuch as the acid group of the vinyl ester is removed by hydrolysis, it is usually most economical to use an interpolymer of ethylene with vinyl acetate which is the most readily available vinyl ester.

Appreciable effects are had when the mol ratio of ethylene to vinyl organic ester in the interpolymer prior to hydrolysis is as low as 1/1, and also when it is as high as 5/1. However, the filaments obtained according to the process of this invention have markedly superior resistance to hot water and substantially improved dye receptivity when the mol ratio of ethylene to vinyl organic ester in said interpolymer prior to hydrolysis is within the range of from 2/1 to 4/1.

As indicated in Example I, interpolymerization of the vinyl ester with ethylene can be carried out under super-atmospheric pressure in the presence of a peroxygen-type polymerization catalyst. The resulting interpolymer may be hydrolyzed either in a lower aliphatic alcohol solution or aromatic hydrocarbon-alcohol solution by treatment with alkali hydroxide. For preparing filaments the resulting hydrolyzed interpolymer should be at least 80% hydrolyzed and preferably substantially completely hydrolyzed.

The heat stability and water resistance of the fibers had in accordance with this invention are improved if the hydrolyzed ethylene/vinyl ester interpolymer is subjected to an extraction with hot methanol prior to formation of the fibers.

As shown in the examples, the filaments may be obtained by either melt spinning of the hydrolyzed ethylene/vinyl organic ester interpolymer or by spinning from a solution of the interpolymer with subsequent evaporation of the solvent. Suitable solvents are trichloroethylene-ethanol-water mixtures, primary aliphatic alcohols boiling above 75°, primary and secondary aliphatic amines and mixtures of aromatic hydrocarbons with such alcohols and amines.

As hereinbefore stated, it is essential that the filament should be drawn in a medium comprising water at a temperature within the range of from 80° C. to 100° C. Furthermore, the time of travel of the filament through the drawing medium must be such that said filament is heated to a temperature within said range. While appreciable effects are obtained when drawing is effected at a temperature as low as 80° C., markedly improved filaments are produced when the temperature of the aqueous medium and the filament during the drawing step is within the range of from 90° C. to 100° C. While the medium comprising H_2O in which the drawing of the filament is effected may be a bath of liquid water, said drawing is carried out most readily and conveniently and with the production of filament products having optimum properties when said medium comprises steam. The drawing or orientation of the filament as described above is therefore preferably carried out in steam, or steam and air, at a temperature within the range of from 90° C. to 100° C. Drawing can be conveniently effected by passing the filament from the snubbing roll to the drawing roll through a vertical tube open at both ends and to which steam is admitted. By maintaining a speed differential between the drawing roll and the snubbing roll, the filament is stretched and oriented, the tension on the drawing roll being sufficient to effect stretching but insufficient to cause breaking of the filament. By passing steam in the vertical tube through which the filament is passed during the drawing operation, it may be heated readily to the desired temperature. The use of steam alone usually provides a temperature within the range of from 99° C. to 100° C., while temperatures of from 80° C. to 99° C. are attained by mixing air with the steam before it is introduced into the tube. Such heating prevents local over-heating of the filament and avoids the tendency to form broken filaments. Less preferable, although operable, is the employment of a liquid water bath heated to a temperature within the range of from 80° C. to 100° C. The use of such baths necessitates guides for the filaments and these may bring about breakage of the filaments. Instead of baths of substantially pure liquid water, there may be employed baths of aqueous solutions, e. g., aqueous salt solutions heated to the desired temperature. However, aqueous baths of substantially pure liquid water provide filaments having higher tenacities than are obtained through the employment of baths of aqueous solutions; while highest tenacities are obtained when the medium employed in the drawing operation is steam, either substantially pure or admixed with air. Drawing temperatures above 100° C. cannot be used. Below 80° C., the filament is softened insufficiently for good drawing and lower drawing ratios with lower tenacities (poorer final properties) are obtained.

In general the time of travel of the filament through the drawing medium is 1 to 5 seconds, although usually 1 to 3 seconds are preferred. The time is related to filament size, drawing medium and drawing temperature. With regard to

time of travel, the output of a drawing unit depends on the drawing speed and high speeds may require longer tubes or baths for the heating.

It is to be understood that, during the drawing operation, any draw ratio short of the breaking point of the filament may be employed. However, on account of the superior products thereby obtained, I prefer to employ draw ratios within the range of from 4.5/1 to 8.5/1, i. e. to draw the filament to a length within the range of from 450% to 850% of its original length.

Best results have been obtained by orienting or drawing of the filament which has first been brought into equilibrium with water at room temperature. Filaments containing less than about 2–3% moisture draw more poorly in steam or water than filaments which have been first brought into equilibrium with water at room temperature. It seems probable that equilibrium of the filament with the water cannot be reached rapidly enough during the short time of passage of yarn through the drawing medium.

After the filament has been drawn, and thereby oriented, it must be set. This setting is brought about according to the process of this invention by contacting the drawn filament in taut condition with a medium comprising H_2O at a temperature within the range of from 101° C. to 106° C. Although the medium comprising H_2O may be liquid water at a temperature of from 101° C. to 106° C., it is more convenient to use steam. Furthermore, when said medium is steam, filaments having markedly superior properties result. The heat transfer from steam is better than from liquid water and the filament attains the required temperature within the range of from 101° C. to 106° C. more rapidly and with better control. Equipment adapted for treatment of the filament with steam, e. g., an autoclave, is readily available and when the filament is removed from the steam bath it may be dried quickly. It is preferred that the time of heat treatment in steam should not exceed 20 minutes since heating times in excess of 20 minutes result in degradation of the filaments. In general, optimum results are had when the filament is contacted with steam at from 102° C. to 104° C. for a period of time within the range of from 5 minutes to 20 minutes, although when the filament is treated in the form of thick packages of yarn, sufficient time must be allowed to obtain equilibrium temperature throughout the package.

Setting temperatures in excess of 106° C. are to be avoided since such high temperatures usually cause some degradation of the filament with resulting loss of tenacity and other properties. On the other hand, when setting temperatures of less than 101° C. are employed, the resultant filament is not protected against subsequent shrinkage in boiling water. The subsequent temperature employed within the heat-setting range of from 101° C. to 106° C. may vary with the particular hydrolyzed interpolymer depending upon the molecular weight of said interpolymer and the ratio of ethylene to vinyl organic ester originally present in said interpolymer prior to hydrolysis. The exact setting temperature for maximum properties of any given filament can readily be determined. This determination may be readily carried out by a few preliminary experiments to find the optimum conditions.

The setting or heat treatment in the medium comprising H_2O at a temperature within the range of from 101° C. to 106° C. must be carried out with the filament in a taut condition, i. e., at a fixed length or under a slight tension to prevent shrinkage during the operation. In practice, it is convenient to wind the filament on a heat-resistant bobbin or similar member to maintain said filament at a fixed length during the setting operation.

The low shrinkage in boiling water (5% to 10%) of the filaments obtained in accordance with this invention as compared to the shrinkage of from 15% to 60% of hydrolyzed ethylene vinyl organic ester interpolymer filaments obtained by prior art drawing procedures permits the use of the filaments in fabrics when conventional dyeing, laundering or other operations are carried out at elevated temperatures. The filaments as obtained by the process of this invention have improved dye receptivity and increased elongation. Said filaments are particularly useful in the production of fabrics such as hosiery, filter cloths, battery separators, tents and the like.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that I do not limit myself to the specific embodiments thereof except as defined in the appended claims.

Having described the present invention, the following is claimed as new and useful:

1. The process for obtaining an improved hydrolyzed ethylene/vinyl organic ester interpolymer filament, which comprises drawing at a temperature within the range of from 80° C. to 100° C. in a medium containing H_2O at a temperature within the range of from 80° C. to 100° C., a filament of a hydrolyzed interpolymer of ethylene with a vinyl ester of a monocarboxylic acid having the general formula RCOOH, wherein R is of the group consisting of hydrogen atoms and hydrocarbon radicals, said acid being free from unsaturated linkages between acyclic carbon atoms and any carbon atom alpha to the carbon atom in the carboxyl group of said acid being attached to at least one but not more than three carbon atoms, the mol ratio of ethylene to vinyl organic ester in said interpolymer prior to hydrolysis having been within the range of from 1/1 to 5/1, and thereafter heating the resultant stretched filament at a temperature within the range of from 101° C. to 106° C. in a taut condition in contact with a medium comprising H_2O at a temperature within the range of from 101° C. to 106° C.

2. The process for obtaining an improved hydrolyzed ethylene/vinyl organic ester interpolymer filament, which comprises drawing at a temperature within the range of from 90° C. to 100° C. in a medium comprising H_2O at a temperature within the range of from 90° C. to 100° C., a filament of a hydrolyzed interpolymer of ethylene with a vinyl ester of a monocarboxylic acid having the general formula $C_nH_{2n+1}COOH$, wherein n is a positive integer within the range of from 1 to 3, the mol ratio of ethylene to vinyl organic ester in said interpolymer prior to hydrolysis having been within the range of from 1/1 to 5/1, and thereafter heating the resultant stretched filament at a temperature within the range of from 101° C. to 106° C. in a taut condition in contact with a medium comprising H_2O at a temperature within the range of from 101° C. to 106° C.

3. The process for obtaining an improved hydrolyzed ethylene/vinyl acetate interpolymer filament, which comprises drawing for a period of

from 1 to 5 seconds in a medium comprising steam at a temperature within the range of from 90° C. to 100° C., a filament of a substantially completely hydrolyzed interpolymer of ethylene with vinyl acetate, the mol ratio of ethylene to vinyl acetate in said interpolymer prior to hydrolysis having been within the range of from 1/1 to 5/1, and thereafter contacting the resultant stretched filament in a taut condition for a period of from 5 to 20 minutes with a medium comprising steam at a temperature within the range of from 101° C. to 106° C.

4. The process for obtaining an improved hydrolyzed ethylene/vinyl acetate interpolymer filament, which comprises drawing for a period of from 1 to 5 seconds in steam at a temperature within the range of from 90° C. to 100° C., a filament of a substantially completely hydrolyzed interpolymer of ethylene with vinyl acetate, the mol ratio of ethylene to vinyl acetate in said interpolymer prior to hydrolysis having been within the range of from 1/1 to 5/1, and thereafter contacting the resultant stretched filament in a taut condition for a period of from 5 to 20 minutes with steam at a temperature within the range of from 102° C. to 104° C.

5. The process for obtaining an improved hydrolyzed ethylene/vinyl acetate interpolymer filament, which comprises drawing for a period of from 1 to 5 seconds in steam at a temperature within the range of from 90° C. to 100° C., a filament of a substantially completely hydrolyzed interpolymer of ethylene with vinyl acetate, the mol ratio of ethylene to vinyl acetate in said interpolymer prior to hydrolysis having been within the range of from 2/1 to 4/1, and thereafter contacting the resultant stretched filament in a taut condition for a period of from 5 to 20 minutes with steam at a temperature within the range of from 102° C. to 104° C.

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