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GAS ACTIVATED TREATMENT OF ELASTIC FILAMENTS

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FIG. 1.

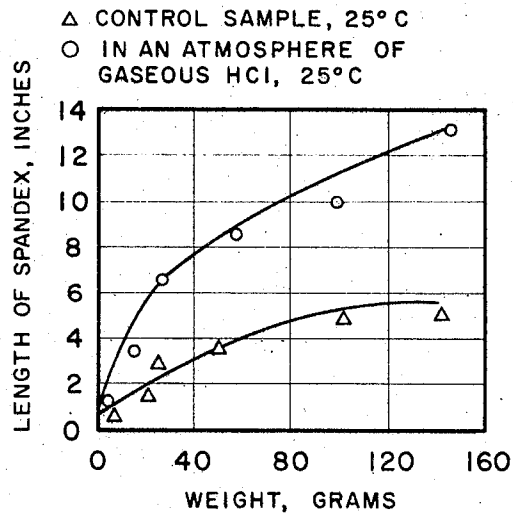
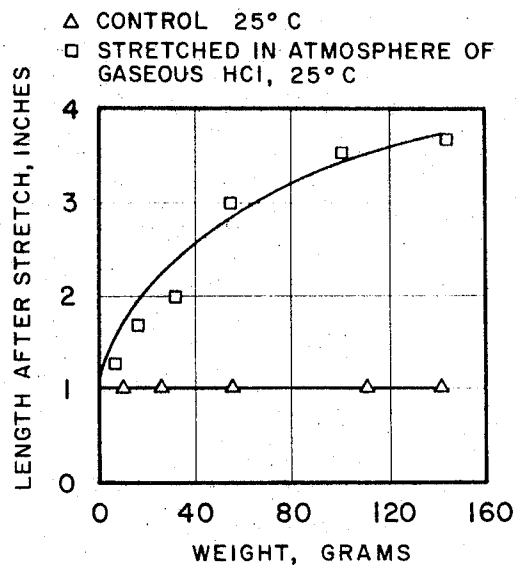


FIG. 2.



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ABSTRACT OF THE DISCLOSURE

The denier of synthetic elastic segmented polyurethane filaments is reduced by the process of stretching the filaments a desired amount, exposing the filaments while in a stretched condition to an atmosphere of an activating gas and then desorbing the gas from the filaments.

The present invention relates to a method for altering the physical characteristics of shaped structures of elastomeric polymers. More particularly, the invention relates to a method for imparting a permanent shape to synthetic elastic filaments.

Since the advent of elastic filaments, such as those composed of segmented polyurethane elastomers, there has been a wide application of these filaments in the manufacture of textile products. Because of the peculiar spinning characteristics involved in the preparation of these filaments, it has been found more advantageous economically to spin large denier filaments and later reduce the denier of such filaments.

Various processes have been employed in the past to reduce the denier of high denier elastomeric filaments, generally referred to as spandex yarn. All of these processes involve stretching the spandex to a predetermined length and subjecting the yarn to a heat treatment to heat set the yarn in its stretched condition. These heat-treatment processes, unless controlled carefully, cause harmful effects which lower the quality of the yarn. Therefore, it would be advantageous to employ a method for reducing the denier of spandex yarn without the application of heat.

It is therefore an object of the present invention to provide a method for permanently reducing the denier of synthetic elastic filaments without heat-setting said filaments.

Another object of the present invention is to affect a permanent change in the size and shape of synthetic elastic filaments such as spandex without subjecting said filaments to the harmful action of high temperatures.

Another object of the present invention is to provide an improved method for altering the physical properties of synthetic elastic filaments.

Another object of the present invention is to provide a method for imparting permanent shapes to synthetic elastic shaped articles.

Other objects and advantages of the invention will become apparent from the description to follow.

The objects of this invention are accomplished by altering the physical characteristics of synthetic elastic filaments composed of a substantially linear segmented polyurethane elastomer which comprises applying tension on the filament in an amount sufficient to reduce the denier thereof to a desired size and treating the filament with a gaseous activator which includes sorption and desorption of said gaseous activator. The filaments may be made to retain other shapes or configurations as, for example, a crimped condition by exposure to a gaseous activator and the subsequent removal of the sorbed gas. Absorption may be carried out under conditions ranging from about 100 to 1000 mm. of Hg and 0° to 50° C.

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depending upon the rate of absorption desired. It was found that increased pressure and temperature produce a more rapid rate of absorption of the gas up to an equilibrium point. Removal of the gas can be accomplished by such methods as exposing the treated sample to vacuum, heat, or a water bath. Preferably the absorption is conducted under substantially anhydrous conditions.

The gaseous activators which may be employed with the present invention must be strong enough as Lewis acids to complex with the basic units comprising the synthetic elastic filaments. Such activators include the hydrogen halides, boron trifluoride, sulfur dioxide, and chlorine. Hydrogen chloride is the preferred activating gas, however, because of its faster absorption and desorption rate and comparative ease of handling in a continuous process.

The process of this invention is not limited to any specific type of segmented polyurethane elastomer. Such elastomers are generally prepared by a process which comprises reacting a polymeric diol with an organic diisocyanate and thereafter extending with a compound containing two active hydrogen atoms. The diols may be a polyether glycol such as polyalkylene ether glycols, polyalkylenearylene ether glycols, polyalkylene etherthioether glycols, and the like, or polyester glycols including polyester glycols derived from caprolactone, either with or without internal extension. The diisocyanates employed are generally arylene diisocyanates and it has been found preferred to employ a para oriented symmetrical aromatic diisocyanate. The chain-extending agent is a compound having two active hydrogen atoms as determined by the test described in J. Am. Chem. Soc. 49, 3181 (1927). Such compounds may be diols or diamines. Ordinarily, the diamines are preferred. The reactants used in preparing such polyurethane elastomers, including the glycol, the organic diisocyanate, and the chain-extending agent, are all well known in the art. See for example, U.S. Patent 2,871,227 to Walter and 3,115,384 to Cacella et al.

In accordance with the present invention, the process may be conducted in conjunction with a spinning process which is employed to produce continuous spandex filaments. The spandex filaments usually are received from the drying rolls and advanced through a sorption chamber filled with the gaseous activator. Preferably, the chamber should be maintained at approximately room temperature to provide uniform treating conditions and handling convenience although substantially higher or lower temperatures may be employed with somewhat less favorable results. It is desirable to maintain a pressure on the chamber of about 200 to 800 mm. of Hg but almost any pressure range may be employed where found to be convenient or practical. Thereafter, the spandex filament containing the gas absorbed in the sorption chamber is washed in a neutral or slightly basic water bath to remove the gas. Another effective method for removing the gas is by heating to above about 50° C. Higher temperatures may be employed, but precautions should be taken against heat degradation of the filament properties.

Yarns treated in accordance with the process of this invention exhibit permanent changes in size or configuration and improved physical properties such as tenacity and modulus. It is thought that the gaseous activator disrupts the hydrogen bonds between the urethane and/or urea groups to form a complex therewith which permits molecular flow or shifting of these groups to relieve stress imposed by tension or pressure on the filamentary structure. The complex formation is reversible and therefore the filamentary structure will assume permanently the

shape possessed at the time the gaseous activator is removed.

This invention can be further illustrated by the following examples which are intended to be illustrative only.

EXAMPLE I

In the preparation of sample yarn for illustrating certain aspects of the invention, 3990 grams of a polyester diol having a molecular weight of 2838 prepared from 3 moles of polycaprolactone of molecular weight 830 internally extended with 348 grams of tolylene diisocyanate, was dissolved in dimethylformamide with 735 grams p,p'-methylene-di(phenyl isocyanate) to form a prepolymer solution having a solids content of about 65 percent. A second solution was prepared by adding 30.1 grams of ethylenediamine to 8370 grams of dimethylformamide. The first solution was added to the second solution with agitation while maintaining the temperature at 45° C. After 2510 grams of the first solution had been added, the addition was stopped and the solution had a Brookfield viscosity of 37,000 centipoises at 25° C. and contained approximately 15.0 percent solids. The resulting dope was filtered and wet-spun by extrusion through a 15-hole, 5.5-mil hole-size spinneret. The coagulating bath contained 75 percent H₂O and 25 percent solvent and was maintained at a temperature of 80° C. The filament bundle was drawn from the bath, washed substantially solvent free in a hot water bath, and dried on heated rolls at 135° C.

A sample of the yarn was suspended on a Worden fused quartz spring in a gaseous sorption apparatus. The system was evacuated to 0.5 mm. of Hg. After one hour the system was filled to atmospheric pressure with anhydrous hydrogen chloride (HCl) gas at 25° C. The increase in weight of the spandex sample was followed by the elongation of the spring.

Spandex yarn rapidly absorbed HCl under these conditions up to about 12% by weight. The detailed results were as follows:

Time, sec.	Wt., mg.	Wt. gain,* mg.	Wt. gain, percent
0	58.55	-----	-----
80	63.85	5.30	9.05
135	64.60	6.05	10.3
190	65.15	6.60	11.3
315	65.55	7.00	12.0
980	65.65	7.10	12.15
1,920	65.65	7.10	12.15
2,400	65.65	7.10	12.15

*Wt. gain compared to original weight.

EXAMPLE II

Upon completion of Example I the sorption apparatus was evacuated to 0.5 mm. of Hg at 25° C. The spandex lost most of its sorbed HCl as shown below.

Time, sec.	Wt., mg.	Wt. gain,* mg.	Wt. gain, percent
0	65.65	7.10	12.15
180	61.75	3.20	5.1
360	60.35	1.80	3.1
600	59.75	1.20	2.1
1,200	59.75	1.20	2.1

*Wt. gain compared to original weight.

EXAMPLE III

After Example II had been completed the sorption apparatus was heated to 54° C. The spandex lost essentially all of its sorbed HCl as indicated in the table below.

Time, sec.	Wt., mg.	Wt. gain,* mg.	Wt. gain, percent
120	59.10	0.55	0.9
600	58.60	0.05	0.1

*Wt. gain compared to original weight.

The same sample of spandex yarn was resubjected to the sorption-desorption procedure. The results obtained were essentially identical to those obtained with the first experiments.

EXAMPLE IV

A sample of spandex yarn was mounted in the sorption apparatus as described in Example I. The system was evacuated to one mm. of Hg. After one hour, HCl gas was passed into the apparatus until the pressure was 286 mm. of Hg. This pressure was maintained by passing additional HCl into the system as needed. The spandex was therefore exposed to HCl at a partial pressure of 286 mm. of Hg. The spandex absorbed only about 7 percent by weight of HCl under these conditions. The following results were obtained.

Time, sec.	Wt. of sample, mg.	Wt. gain, mg.	Wt. gain, percent
0	105.85	-----	-----
15	108.70	2.85	2.7
30	110.65	4.80	4.9
180	112.10	6.25	5.9
1,320	113.33	7.50	7.1

The pressure of HCl gas was increased to 366 mm. of Hg. Within three minutes the yarn sorbed to equilibrium at this pressure. The data are shown below.

Time, sec.	Wt. of sample, mg.	Wt. gain, mg.	Wt. gain, percent
15	114.65	8.80	8.3
180	115.20	9.35	8.9
3,600	115.30	9.45	9.0

The pressure of HCl was increased to 744 mm. of Hg. The spandex yarn sorbed HCl to a weight gain of about 12%.

The sorption apparatus was subjected to evacuation until the pressure of HCl was reduced to 286 mm. of Hg. After three minutes the spandex retained only 6.1 percent weight gain of HCl. This value agrees reasonably well with the value of 7 percent weight gain found by approaching this HCl pressure from the low side. Thus, it can be concluded that the amount of sorbed gas is dependent upon the pressure employed in the chamber during exposure.

EXAMPLE V

Several 5-inch lengths of spandex yarn were mounted stretched to 20 inches on a glass rod. The rod was placed in a sorption vessel which was subsequently evacuated to 0.5 mm. of Hg. After one hour the system was filled to atmospheric pressure with anhydrous HCl gas. After 15 minutes the system was again evacuated to 0.5 mm. of Hg for one hour. The yarn was washed in water to remove the last traces of HCl. The samples when removed from rod were 16 inches in length had a decreased denier and increased tenacity. Results of physical testing were as follows:

Sample	Denier	Ultimate tenacity, g./d.	Ultimate elong., percent
1	314	0.93	248
2	310	0.88	240
3	318	0.78	233
Untreated	902	0.68	571

EXAMPLE VI

Several samples prepared as described in Example V were examined after being placed unrestrained in boiling water for 15 minutes. The average denier of these samples was 345 before and 471 after the treatment.

EXAMPLE VII

Several samples of spandex yarn were treated as follows. A one-inch sample was mounted in the sorption apparatus to support a certain weight and the extension of the yarn as a function of this weight was measured in air at 25° C. The vessel was then evacuated to 0.5 mm. of Hg and after one hour the system was slowly filled to atmospheric pressure with anhydrous HCl gas. The

weight-supporting yarn began to elongate, rapidly reaching a maximum value depending on the supported weight. For example, a sample of yarn supporting 100 grams stretched to 4.5 inches in air, but in an atmosphere of HCl stretched to 10 inches. Additional results are shown by the curves plotted in FIGURE 1. These data illustrate that the yarn stretches more readily when exposed to the gaseous activator.

After about 15 seconds exposure the sorption vessel was again evacuated to 0.5 mm. of Hg for one hour to desorb HCl. Upon removal from the apparatus the yarn was washed in water to remove residual HCl. These samples thus stretched in an atmosphere of HCl assumed a new increased length depending on the supported weight. For example, the sample subject to HCl sorption-desorption while supporting 100 grams was 3.5 times its original length after removal of the weight. The results for several samples are shown by the curves plotted in FIGURE 2.

EXAMPLE VIII

Several yards of spandex yarn were coiled onto two glass rods of 1/8 inch diameter. Each rod was put into a sorption vessel which was subsequently evacuated to 0.5 mm. of Hg. After one hour the first vessel was filled with gaseous HCl to atmospheric pressure. After 15 minutes this vessel was evacuated to 0.5 mm. for one hour and both samples were subsequently washed in water. The second vessel was at no time exposed to HCl.

The spandex yarn that was exposed to HCl retained the coiled shape after removal from the rod. However, the sample from the second vessel showed no sign of coil retention.

EXAMPLE IX

A sample of the HCl-treated spandex yarn of Example V was tested according to standard procedures. The following results were obtained.

Sample	Denier	Ultimate tenacity, g./d.	Ultimate elong., percent	Secant modulus at 150% stretch, g./d.
Untreated.....	920	0.66	560	0.07
HCl-treated.....	350	1.03	345	0.16

It will be apparent from the foregoing illustrative examples to those skilled in the art that the present invention may be employed to alter the shape and physical properties of synthetic elastic filaments. Further it will be

apparent that improved properties other than those enumerated can be obtained from the practice of the invention set forth or the modification and changes thereto which will be obvious from the disclosure made herein.

We claim:

1. A process for permanently reducing the denier of synthetic elastic segmented polyurethane filaments which comprises attenuating said filaments, exposing said filaments to an atmosphere of an activating gas and then desorbing said gas from said filaments.
2. The process of claim 1 in which the activating gas is a hydrogen halide.
3. The process of claim 1 in which the activating gas is boron trifluoride.
4. The process of claim 1 in which the activating gas is sulfur dioxide.
5. The process of claim 1 in which the filaments are stretched from 2 to 7 times original length prior to exposure to the activating gas whereby the denier of said filaments is permanently reduced upon desorption of said gas.
6. The process of claim 2 in which the activating gas is hydrogen chloride.
7. A process for permanently reducing the denier of a synthetic elastic filament composed of a substantially linear segmented polyurethane elastomer which comprises applying tension to said filaments sufficient to reduce the denier a predetermined amount, exposing the filament to an atmosphere of an activating gas while under said tension wherein gas is absorbed by said filament, and thereafter desorbing said gas from the filaments.
8. The process of claim 7 in which the activating gas is a hydrogen halide.
9. The process of claim 8 in which the hydrogen halide is hydrogen chloride.

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