

July 27, 1943.

H. G. INGERSOLL

2,325,060

NON-SHRINKING YARN

Filed Feb. 25, 1942

2 Sheets-Sheet 1

Fig. 1.

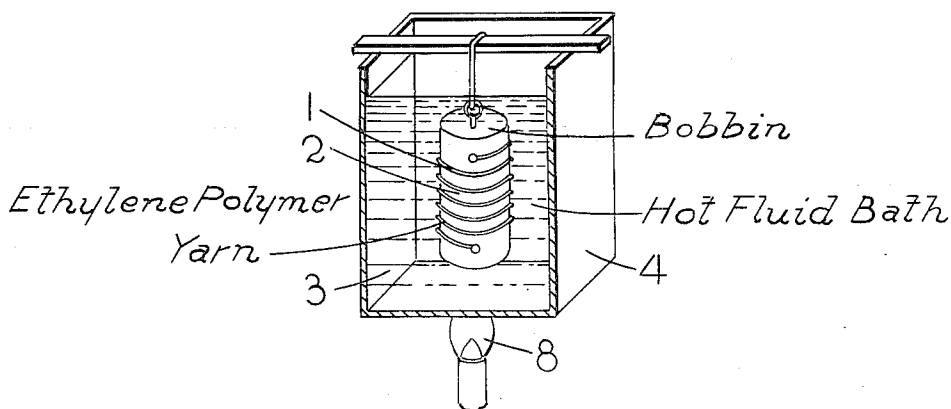


Fig. 2.

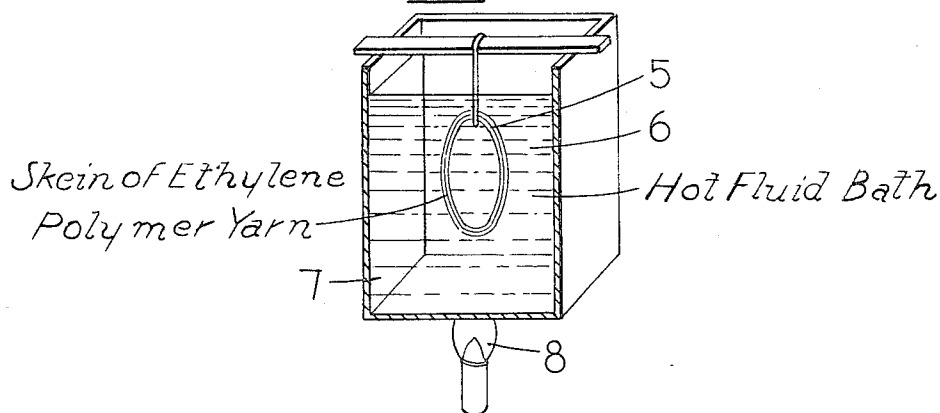
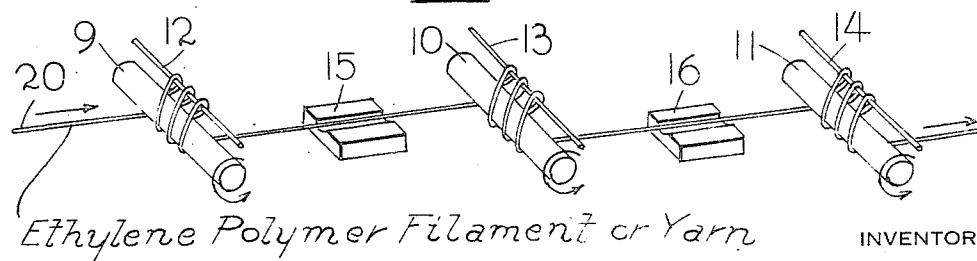


Fig. 3.



INVENTOR.

Henry G. Ingersoll

BY

R. F. Miller

ATTORNEY

July 27, 1943.

H. G. INGERSOLL

2,325,060

NON-SHRINKING YARN

Filed Feb. 25, 1942

2 Sheets-Sheet 2

Fig. 4.

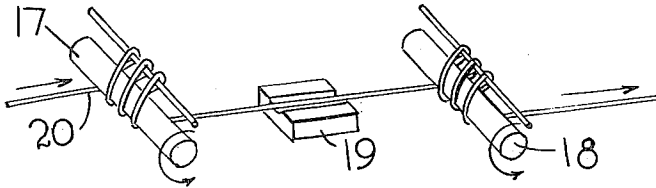


Fig. 5.

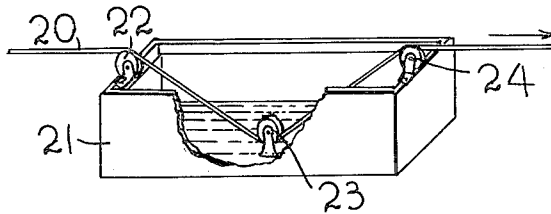


Fig. 6.

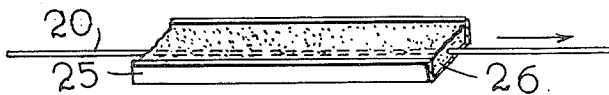
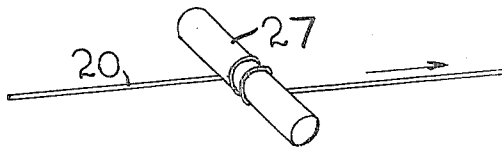


Fig. 7.



INVENTOR.

Henry G. Ingersoll

BY

R. F. Miller

ATTORNEY

UNITED STATES PATENT OFFICE

2,325,060

NONSHRINKING YARN

Henry G. Ingersoll, Wilmington, Del., assignor to
E. I. du Pont de Nemours & Company, Wil-
mington, Del., a corporation of Delaware

Application February 25, 1942, Serial No. 432,369

3 Claims. (Cl. 8—115.5)

This invention relates to filaments from normally solid ethylene polymers and more particularly to the manufacture of filaments of this kind having improved shrinking characteristics.

Fibers and filaments useful in textiles and for other purposes can be obtained by melt extrusion or by other methods from the high molecular weight, normally solid ethylene polymers prepared by polymerizing ethylene under pressure. The filaments thus obtained can be cold drawn, that is permanently elongated under stress in the solid state to yield products of improved strength, which by X-ray diffraction analysis exhibit molecular orientation along the fiber axis. Completely oriented ethylene polymer filaments begin to shrink at 45°–50° C. This shrinkage greatly reduces their tensile strength and leaves them in a highly non-uniform condition. Such shrinkage, for example, warps and distorts fabrics made from such filaments so completely as to materially reduce their utility. Similar shrinkage effects are encountered in the case of filaments obtained from other high molecular weight polymers, such as nylon, vinylidene chloride polymers, and from the vinyl chloride-vinyl acetate interpolymer known as Vinyon. Various stretch-setting processes designed to avoid this difficulty are described in the prior art. Certain of these processes improve to some extent the shrinkage resistance of normally solid ethylene polymer filaments, but none produces the result desired. The previously used method of pre-shrinking, in which relaxed filaments are shrunk by heat treatment, is ineffective in the case of ethylene polymer filaments.

This invention has as an object the manufacture of improved ethylene polymer filaments. A further object is to provide a method for raising the shrinking temperature of these filaments without materially reducing their tenacity and other desirable properties. Further objects will appear hereinafter.

The above objects, generally speaking, are accomplished by maintaining the oriented ethylene polymer filaments at a temperature higher than the desired initial shrinkage temperature, and below the melting point, while allowing no retraction in the direction of orientation, that is in the direction of the length of the filaments, until there is no further reduction in tension, and then heating the filaments in the relaxed condition at a temperature at least as high as the desired initial shrinkage temperature until substantially no further shrinkage occurs.

The thermal conditioning of ethylene polymer

filaments in accordance with the present process consists of two distinct steps or processes: (1) heat-setting, that is maintaining the filaments at constant length during the first heating above the desired initial shrinkage temperature until there is no further reduction in tension, and (2) allowing equilibrium shrinkage, that is relaxing under zero tension during the second heating. The temperature selected for the conditioning depends upon the combination of shrinkage and tensile properties desired in the finished product. Higher temperatures cause a greater reduction in filament strength but also proportionally raise their initial shrinkage temperature. Thus, the initial shrinkage temperature of oriented ethylene polymer filaments can be raised to a temperature not lower than about 40° C. to about 5° C. below the melting point of the polymer by maintaining the filament in the first step at a temperature of from 30° C. to 2° C. below the melting point of the polymer. During this first step the filament is not allowed to retract in the direction of its length and is thus maintained until there is no further reduction in tension. For the second step the filament is heated in a relaxed condition at a temperature above about 40° C. below the melting point of the polymer but not higher than the temperature of the preceding treatment until substantially no further shrinkage occurs.

To obtain the optimum combination of shrinkage and tensile properties the first stage of the thermal conditioning is conducted at the maximum temperature that will not cause filament injury, that is slightly below the melting point of the polymer and is continued until there is no further reduction in the residual shrinkage of the relaxed filament. Usually this temperature is 2° to 5° C. below the melting point of the polymer. During the second stage the temperature employed is usually 10° to 20° C. below the melting point of the polymer.

The exact time and temperature limits for both stages of the conditioning treatment can be determined by simple test in any particular instance. That is, stage (1) of the conditioning is completed when the residual shrinkage, that is the tension on the filaments held against retraction, is at a minimum, and stage (2) is completed when the relaxed filaments show no more shrinkage. The time and temperature limits are interdependent and are influenced also by the grade and orientation of the filaments, the heating means used, and the type of conditioning process, that is whether batch or continuous.

At temperatures of 95° to 108° C. contact times of the order of one second suffice for both stages. In the batch process it is best to use immersion times of 5 minutes or thereabouts because of the additional heat capacity of the bobbin and cake.

By residual shrinkage is meant the loss of length upon exposure of the relaxed filament to elevated temperatures.

The requirement of minimum filament tension in the first stage of the process corresponds to minimum residual shrinkage. For example, when the change in tension during heating at constant length is measured by a dynamic method wherein the oriented filaments traveling between rolls positively driven at the same speed are heated by a copper block to 100° C. and tensions for various heating times at this temperature are determined by varying the speed, it is found that the tension increases rapidly to a maximum, then decreases asymptotically to a constant minimum value after the filaments have been heated for about 0.64 second. This asymptotic tension value is the final minimum value, as evidenced by the fact that it is substantially maintained continuously when the filaments are held at 100° C. for 15 minutes. This value also corresponds to the minimum residual shrinkage desired since minimum shrinkage properties are attained when short samples of the filaments are held at constant length at 100° C. for about 1 second.

Various heating means are applicable. Any type of fluid bath may be used provided that the fluid does not soften the filaments or injure them mechanically or chemically. For the first stage in batch process conditioning, it is convenient to hold the filaments at constant length on a bobbin. In the second stage it is suspended in the heating medium in skein form. The filaments can be conditioned continuously by running them over three consecutive separator rolls. The first two run at exactly the same speed, corresponding to the first stage in the conditioning process. The second stage is accomplished by running the third roll slowly enough to allow equilibrium relaxation between the last two rolls. Heated rolls, a heated pin, a hot metal surface or a hot powder or fluid bath placed between the rolls provide satisfactory heating.

The filaments or fibers of ethylene polymer to which this process is applied can be prepared by extrusion of the polymer in a fluid condition. Illustrative processes are described in United States patents, 2,210,774 and 2,219,700. Before conditioning treatment, the filaments or fibers must be completely oriented, as by drawing to the greatest extent possible without breakage.

The ethylene polymers useful in the practice of this invention must be capable of remaining in an oriented condition when allowed to relax freely at room temperature and in addition the oriented polymer should show marked shrinkage when relaxed at elevated temperatures. These polymers can be obtained by heating ethylene alone or in admixture with another polymerizable unsaturated compound under a pressure above 500 atmospheres and preferably above 1000 atmospheres and at temperatures of from 100° to 400° C., and preferably from 150° to 250° C. as described in United States patents, 2,153,553, 2,188,465, and 2,200,429, or in contact with water and a per-compound catalyst at temperatures in the range of 40° to 350° C. and at superatmospheric pressures in excess of 3 atmospheres. The polymers of ethylene alone are normally solid, correspond in composition substantially to

(CH₂)_x, and show a crystalline pattern by X-ray diffraction analysis. The physical properties of the polymers of ethylene with other polymerizable organic compounds vary depending upon the composition of the polymer and the nature of the organic compound polymerized with the ethylene.

The melting point of the ethylene polymer, as defined herein, is the temperature of zero tensile strength and can be accurately and conveniently determined by measuring the tensile strength at several temperatures near the melting point. The temperature of zero tensile strength is particularly significant to thermal conditioning since it is closely associated with the highest permissible setting temperatures. Usually fairly similar results are obtained by other melting point determinations such as by the ball and ring method described in United States Patent 2,210,771 or by the temperature of sticking to a heated copper block.

This invention will be better understood in connection with the accompanying drawings in which:

Fig. 1 is an elevational view of apparatus that can be used in the batch treatment of the yarn during the first stage of the process;

Fig. 2 is a similar view of apparatus for treating the yarn in the second stage of the process;

Fig. 3 is a diagrammatic view in perspective of mechanism suitable for carrying out the invention in a continuous manner;

Fig. 4 is a similar view of a modified apparatus; and

Figs. 5 to 7 are perspective views of heating means for the yarn which can replace that used in Figs. 3 and 4.

In carrying out the invention as a batch process the yarn 1, secured at constant length on the bobbin 2, is immersed in the hot fluid bath 3 contained in the vessel 4. The bobbin is then withdrawn from the fluid bath, the yarn cooled, and after being formed into the skein 5 it is suspended in a second hot fluid bath 6 contained in the vessel 7. The baths 3 and 6 can be heated by any suitable means, for example, electrically or by the flame 8.

In the apparatus shown in Figs. 3 and 4 for continuously conditioning the yarn, the yarn passes over draw roll-separator roll combinations referred to herein as separator rolls composed of the rolls 9, 10 and 11 with the spaced guide rolls 12, 13 and 14. The rolls 9 and 10 run at exactly the same speed and the yarn thereby held at constant length while heat is applied by means of a hot block 15, the treatment of the yarn between these first two rolls being that of stage 1. The separator roll 11 is driven at less speed and runs slowly enough to allow equilibrium relaxation during the heating of the yarn by the hot block 16 which is the heating at the second stage of the process.

Alternatively, several wraps of the yarn are passed over a heated separator roll 17 which completes the first stage of the process. The roll 18 then takes up the yarn at a rate which is slow enough to allow the equilibrium relaxation which is produced at the temperature of the heating block 19.

In Figs. 5 to 7 are shown different means for heating the yarn which can replace the hot blocks of Figs. 3 and 4. In Fig. 5 the yarn 20 passes into a hot fluid bath contained in a vessel 21 provided with grooved wheels 22, 23 and 24 for guiding the yarn into and out of the bath. In Fig. 6

the numeral 25 indicates a trough containing heated sand 26 through which the yarn passes. In Fig. 7 the yarn passes a few turns over a heated pin 27.

The examples which follow are illustrative of the practice of this invention.

EXAMPLE I

Fully oriented 5-filament yarn having a denier of 90 made from an ethylene polymer having a molecular weight of 20,000 and a melting point of 110° C. is wound upon a metal bobbin. Both yarn ends are tied securely and the bobbin is immersed for 5 minutes in a sodium chloride-water bath held at 108° C. (stage 1). The bobbin is then cooled and the yarn removed and skeined. The skein is suspended in a 90° C. water bath for 5 minutes and allowed to relax completely (stage 2). This treatment remarkably improves the shrinkage characteristics of the yarn without substantial decrease in its tenacity, as summarized in Table I. Tenacities here are given in grams per denier based upon the original dimensions of the yarn (o. d.).

Table I

	Shrinkage at 90° C.	Initial shrinkage at about—	Tenacity (g./d.-o.d.)	Elonga- tion
	Percent	°C.		Percent
Original.....	38	40	3.2	10
Stage 1.....	6	70	2.9	27
Stages 1 and 2.....	0	95	2.2	40

EXAMPLE II

Fully oriented yarn having a denier of 92 and a filament count of 5 made from an ethylene polymer having a molecular weight of 9,000 and a melting point of approximately 100° C. is wound upon a metal bobbin. Both yarn ends are tied to prevent contraction and the bobbin immersed for 5 minutes in a water bath held at 95° C. (stage 1). The bobbin is cooled and the yarn rewound in skein form. This skein is then placed in a water bath held at 90° C. to allow equilibrium relaxation, and removed after 5 minutes. This procedure raises the initial shrinkage temperature of the yarn about 52° C. without unduly reducing the tenacity. The results obtained are shown in the following table.

Table II

	Shrinkage at 90° C.	Initial shrinkage at about—	Tenacity (g./d.-o.d.)	Elonga- tion
	Per cent	°C.		Per cent
Original.....	34	40	1.7	14
Stage 1.....	16	70	1.6	30
Stages 1 and 2.....	0	92	1.1	57

The methods given in the examples can be varied considerably with regard to the particular manipulations used. For example, in applying a continuous process to stage 1, tenacities are improved by actually drawing the filament to slightly less than break elongation instead of merely holding it at constant length. Or, starting with unoriented filaments, hot drawing with long contact times, that is, slow rates of draw, produces a setting action which in this instance must still necessarily occur after the filament has been oriented. It is also possible to combine both steps of the process into one step procedurally but the actual physical changes must be stepwise. For example, passing several wraps of

the filament around a heated separator roll would accomplish stage 1 of the process. The filament can then be taken over a hot surface for the second stage heating and allowed to relax completely before being wound up.

Crimped fibers can be obtained by combining a crimping operation with the first step of the present process, for example, by using a mandrel of suitable shape. The crimped fibers have a high degree of crimp and are valuable as artificial wool since they are highly elastic and are unaffected by moisture. Degree of crimp refers to the ratio of straightened length to crimped length.

The ethylene polymers mentioned herein are intended to include any of the polymers which are solid at ordinary temperatures, which contain the ethylene constituent in substantial proportions, and which are obtained by polymerizing ethylene alone or in admixture with at least one other polymerizable unsaturated organic compound such as other mono-olefins (propylene or butylene); dichloroethylenes such as 1,2-dichloroethylene, 2-chloropropene; tetrafluoroethylene; vinyl ethers, ketones and ester, and other vinyl compounds such as methyl vinyl ether, methyl and ethyl vinyl ketones, vinyl chloroacetate, vinyl propionate, N-vinyl phthalimide, vinyl thiolacetate; stilbene; styrene; acrylic and methacrylic acids, their esters, amides, and imides; esters of maleic and fumaric acids; and esters of itaconic acid.

The ethylene polymers used in the practice of this invention can, if desired, be blended with such modifiers as dyes, plasticizers, fillers and the like.

The usefulness of ethylene polymer filaments is markedly increased by the present process since shrinkage does not occur at temperatures lower than 15° or 20° C. below the melting point. Thus, the fibers and filaments obtained in accordance with this invention are useful for tapered or cylindrical bristles which are used, for example, in rotary brushes for cleaning filter screens, and in brushes for use in plating and pickling baths. Likewise, the filaments are useful as surgical sutures which can be readily sterilized by chemical means and are inert to water, and to body fluids and tissues. The filaments are also useful as fishing leaders and their property of floating on water makes them of special value as dry-fly leaders. Many types of useful screen which are highly durable can be fabricated from these filaments. The filaments are also useful in the fabrication of such articles as fish nets, hair nets, and dental floss. They can also be used as fibers in currency paper, as corrosion resistant packing, as elastic fibers, as wrappings for heat and electrical insulation, as windings for baseballs and golf balls, and as cords for reinforced rubber articles.

The ethylene polymer filaments are also valuable in the manufacture of yarns, metallized yarns, braided cords, ropes, and coated, impregnated, laminated, or composite fabrics. The filaments or yarns can be used alone or in admixture with other textiles such as cotton, silk, rayon, or wool and the composite material fabricated into textile fabrics such as by knitting, weaving or felting.

In making felted fabrics or artificial felt, heat is applied to the oriented fiber and the resulting shrinkage produces a felting or interlocking action. An artificial leather may be made by felting and fusing the fabric.

Fabrics comprising the ethylene polymer filaments of this invention, because of their water resistance, durability, and elasticity, find many industrial applications, for example, in making awnings, tents, sail cloth, Holland cloth, lamp shades, flags, parachutes, gloves, camera bellows, aeroplane fabrics, filter cloths, corrosion resistant packings and gaskets, aprons for trade, laboratory and surgical uses, diaphragms for gas meters and the like, balloon fabrics, blankets, garters, foundation garments, belting, hosiery, helmets, suspenders, brassières, jackets, artificial fur, composite fabrics, carpets, rugs, 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.

I claim:

1. A process for raising the shrinking temperature of oriented ethylene polymer filaments selected from the class of fibers, yarns, and the like which comprises maintaining the filaments at a temperature of from 30° C. to 2° C. below the melting point of the polymer while preventing

retraction in the direction of the length of the filaments and then heating the filaments in relaxed condition at a temperature above about 40° C. below the melting point of the polymer; but not higher than the temperature of the preceding treatment.

2. A process for raising the shrinking temperature of oriented ethylene polymer filaments comprising fibers, yarns, and the like to a temperature not lower than about 40° C. to about 5° C. below the melting point of the polymer, said process comprising maintaining the filaments at a temperature of from 30° C. to 2° C. below the melting point of the polymer while preventing retraction in the direction of the length of the filaments and then heating the filaments in relaxed condition at a temperature at least as high as the temperature of said first mentioned shrinking, but not higher than the temperature of the preceding treatment.

3. An ethylene polymer filament which does not shrink when heated to temperatures lower than 40° C. to 5° C. below the melting point of the polymer, and which is obtained by the process defined in claim 2.

HENRY G. INGERSOLL.