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POLYETHYLENE TEREPHTHALATE MONO-
FILS DRAWN AND HEAT SET FOR USE
AS BRISTLES

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This invention relates to the improvement of synthetic monofilaments for use as bristle material and, more particularly, to a process for improving monofilaments spun from polyethylene terephthalate for use as bristle material.

Monofilaments, i. e., single filaments as contrasted with multifilament yarns, have been prepared from several of the synthetic, organic polymers, particularly from the polyamides (nylon), for instance as described in U. S. Patents 2,226,529, 2,298,868 and 2,341,823. The primary use for these monofilaments is as bristle material for various types of brushes. The nylons are thus far the only synthetic polymers which have found wide usage in the bristle field. This is directly traceable to the fact that the nylons are the only synthetic polymers that have demonstrated a high degree of bristle resilience, a property which is necessary for the satisfactory use of bristles in most brushes.

Bristle resilience has been found to correlate well with the completeness of recovery of a bristle from sharp bending. That is, it has been found that a good judgment of bristle resilience may be obtained without actually fabricating brushes and testing them but simply by observing the completeness of recovery of a bristle from sharp bending. Specifically, bristles exhibiting poor ability to recover well from sharp bending have insufficient bristle resilience for successful utilization in brushes and do not hold their shape well in use with resulting tangling and matting of the bristles.

Natural bristles, for instance, hog bristles, horsehair, etc., exhibit a high degree of bristle resilience. Other synthetic polymers such as those prepared from cellulose acetate, vinyl and vinylidene polymers and copolymers, the polymers from ethylene, etc., are markedly deficient in this property and, as a result, brushes made from these polymers in bristle form do not hold their shape in use. Even with the nylon polyamides for successful utilization as bristle material in the brush field, it is necessary that the polyamide be relatively high in molecular weight and that the monofilaments prepared therefrom be first, oriented, and second, set in hot water or other media having a swelling action on the monofilament, as discussed in further detail in U. S. Patent 2,226,529.

The preparation of filaments from polyethylene terephthalate has been described in Whinfield et al. U. S. Patent 2,465,319. Attempts to convert these filaments into useful bristles following the procedures known in the art for the corresponding conversion of nylon filaments have not been successful. Thus, when polyethylene terephthal-

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ate was spun into a monofilament and stretched in ratios of from 4.0:1 to 4.4:1 and set in boiling water while held to prevent shrinkage, the resulting monofilaments were noticeably deficient in curl-resistance and quite brittle, especially with the more common and more readily prepared medium molecular weight polyesters:

An object of the present invention is to provide an economical and practical process of improving monofilaments spun from polyethylene terephthalate, for use as bristle material. A further object is to provide such a process whereby bristle material exhibiting outstanding recovery from bending is obtained. Other objects will be apparent from the description of the invention given hereinafter.

The above objects are accomplished according to the present invention by drawing a monofilament spun from polyethylene terephthalate, at 55° C. to 180° C. to a total draw of 4.6:1 to 5.2:1 based upon the length of the monofilament before drawing, then heating the drawn monofilament to effect a reduction in its drawn length of 5% to 10% (i. e., relaxing), and finally heating the relaxed monofilament at 150° C. to 250° C. while it is held under tension to prevent shrinkage. For the best bristle material, it is preferred to use monofilaments spun from polyethylene terephthalate having an intrinsic viscosity of at least 0.35 and, to facilitate drawing the monofilament, to carry out the drawing in two steps by first drawing the monofilament at 55° C. to 80° C. to a draw of 3.0:1 to 4.0:1 and then further drawing the monofilament at a higher temperature range of 80° C. to 180° C. to a total draw of 4.6:1 to 5.2:1 based upon the length of the monofilament before drawing.

Surprisingly, it has been found, despite the unsatisfactory results obtained by following the prior art procedures used with success with nylon monofilaments, that polyethylene terephthalate can be processed as set forth above, to flexible, strong, curl-resistant bristle material exhibiting outstanding recovery from bending. Bristles from polyethylene terephthalate processed in this manner, have been found to exhibit extremely high moduli of elasticity (approximately 4 times that of nylon bristles and twice that of natural bristles), thus making possible the manufacture of brushes with small diameter bristles with no sacrifice in brush stiffness. Such small diameter bristles give better "brushiness" to toilet brushes, and in paint brushes they increase the paint holding capacity of the brush and reduce brush marks arising in the painting process. In addition, these bristles are not softened by exposure to high humidity or by contact with water whereas natural bristles lose up to 70% of their stiffness upon wetting. These bristles also are not

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softened by paint solvents and suffer only minor loss in stiffness at slightly elevated temperatures.

"Intrinsic viscosity," or (η), as used throughout this specification is defined by the following equation:

$$[\eta] = C \lim_{C \rightarrow 0} \frac{\ln \eta_{rel}}{C}$$

wherein,

$$\eta_{rel} = \frac{\eta_{solution}}{\eta_{solvent}}$$

$\ln$ represents the natural logarithm, and C is concentration of solute in grams per 100 cc. of solution in a 2/1 by weight mixture of phenol and m-cresol—all measurements being carried out at 25° C.

The following examples illustrate specific embodiments of the present invention. "Fatigue index" as used in these examples is calculated from the percentage of bristles in a tuft that are not broken or damaged upon severe flexing in an accelerated laboratory test for one hour. The "per cent angle of deformation" retained after sharp bending of a bristle, as used in these examples, is a measure of the recovery or bending resilience of the bristle. It is obtained by wrapping the bristle being tested several complete turns around a mandrel, 0.09 inch in diameter, holding the bristle in this position for four minutes, releasing the bristle, and placing it in water. The per cent angle of deformation remaining after one hour is then determined, utilizing the following formula:

$$\text{Per cent angle of deformation} = \frac{100(\gamma - \alpha)}{\beta - \alpha}$$

wherein

α = The original angle of curvature of the bristle in degrees

β = total angle of curvature in degrees applied to the bristle in being wrapped on the mandrel

γ = the angle of curvature in degrees remaining in the bristle after relaxation

In most instances, since the original angle of curvature of the bristle will be 0° (i. e., the original bristle will be straight), this formula will reduce to

$$\frac{100\gamma}{\beta}$$

Example I

Monofil spun from polyethylene terephthalate of $[\eta] = 0.58$ are oriented by stretching the monofil in water at 80° C. to a ratio of 4.0:1. The resulting oriented monofil is further stretched in contact with water at 95° C. to a ratio of 1.3:1, thus, giving an overall draw ratio of 5.2:1 based upon the length of the monofil before drawing. The monofil is then given several turns around a constant speed roller, passed through steam at 100° C., or boiling water, and finally given several turns around a second constant speed roller which has a speed 90% that of the first roller. In this process the shrinkage or relaxation of the monofil is controlled at 10%, i. e., to 90% of the original drawn length of the monofil. This drawn and relaxed monofil is then wrapped on a reel and set by exposure for 30 minutes to mineral oil at 180° C. The final 7.5 mil bristle exhibits a modulus of elasticity of 1,700,000 lbs./sq. in., a fatigue index of 74%, and the per cent angle of deformation remaining from bending the bristle is 9%.

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In contrast, a 50% angle of deformation remains after bending a polyester monofil prepared from the same batch of polymer by the process methods taught in the art for the nylons (i. e., drawn to a ratio of 5.2:1 and then set in boiling water or steam). Toothbrushes fabricated with this type bristle were wholly unsatisfactory as the bristles in the tufts lost their shape badly on first useage while, on the other hand, toothbrushes fabricated from bristles drawn, relaxed and set by the process of this invention, as described previously, exhibited satisfactory service in average use for several months.

The original unoriented monofil described in this example when drawn to overall ratios of 4.0:1 and 4.4:1 based upon the length of the monofil before drawing, exhibits fatigue indexes of only 40% and 44%, respectively. Other samples of the same monofil drawn to overall ratios greater than 5.2:1, with or without subsequent relaxing, exhibit somewhat better fatigue indexes than the 74% exhibited by the treated monofil of this example but on the other hand, exhibit progressively poorer recovery properties. For example, bristles drawn to overall ratios of 5.5:1 and 6.0:1 and then set in hot oil at 180° C., exhibit fatigue indexes of 92% and 98%, respectively, but the per cent angles of deformation remaining in the bristles after bending are much higher than desired, being 30% and 42%, respectively.

Example II

Monofil spun from the polyethylene terephthalate described in Example I is drawn and relaxed as described in Example I except that the shrinkage is controlled to 5% instead of 10%. The resulting drawn and relaxed monofil is wrapped on a reel and set by exposure to mineral oil at 190° C. for 15 to 20 minutes. The resulting monofil in bristle form exhibits a modulus of elasticity of 2,300,000 lb./sq. in., a fatigue index of 78%, and a 13% angle of deformation remaining in the bristle after bending.

Example III

Monofil spun from polyethylene terephthalate of $[\eta] = 0.61$ is drawn in water at 75° C. to a 3.82:1 ratio and then to a ratio of 1.35:1 in water at 95° C., thus giving an overall draw ratio of 5.15:1 based upon the length of the monofil before drawing. The resulting, oriented monofil is then relaxed to the extent of 7% of its drawn length by the method described in Example I. The resulting drawn and relaxed monofil (6.3 mils in diameter) is wrapped on a reel and set by exposure to mineral oil at 190° C. for 20 minutes. There remains in the bristle after recovery from bending a 7.5% angle of deformation.

Example IV

Monofil spun from polyethylene terephthalate of $[\eta] = 0.62$ is drawn in water at 76.7° C. to a 4.0:1 ratio and then in steam at 100° C. to give an overall ratio of 4.8:1 based upon the length of the monofil before drawing. The resulting oriented monofil is then relaxed to the extent of 10% of its drawn length by the method described in Example I. The resulting drawn and relaxed bristle (6 mils in diameter) is wrapped on a reel and set by exposure to air at 180° C. for 30 minutes. The final bristle exhibits a modulus of elasticity of 1,430,000 lbs./sq. in., a fatigue index of 95%, and an 11% angle of deformation remaining in the bristle after bending.

In contrast, a 29% angle of deformation remains after bending a polyester monofil prepared from the same batch of polymer by the process methods taught in the art for the nylons, (i. e., drawn to a ratio of 4.8:1 and then set in boiling water).

It will be understood that the above examples are merely illustrative and that the invention, in its broader phase, comprises drawing a monofil spun from polyethylene terephthalate at 55° C. to 180° C. to a total draw of 4.6:1 to 5.2:1 based upon the length of the monofil before drawing, then heating the drawn monofil in a relaxed condition until it shrinks 5% to 10% of its original drawn length, and finally heating the monofil at 150° C. to 250° C. while it is held under tension to prevent shrinkage.

Even in its broader phase, the present invention is quite definite and relatively specific as it must necessarily be to obtain the improved bristle material herein described. So far as known, this process is only applicable to polyethylene terephthalate. The intrinsic viscosity of the polymer is not a sharply critical factor but, in general, for the most acceptable bristle material a polymer having an intrinsic viscosity of at least 0.35 should be used. As the intrinsic viscosity of the polymer increases, the bristles prepared therefrom increase in fatigue index. Polymers exhibiting an intrinsic viscosity of 0.75 or greater have been found to be particularly outstanding in the fatigue indexes exhibited by the bristles prepared therefrom according to the process of this invention. Specifically, it has been found that polymer of intrinsic viscosity of at least 0.75 is capable of producing bristles exhibiting fatigue indexes of essentially 100° when measured in the manner previously described in this specification.

The drawing step is, despite the elevated temperature used, "a cold drawing" which effects orientation of the monofil. That is, the maximum temperature during the drawing is well below the fairly sharp melting point of the polymer. It is important that the monofil be drawn to a total draw of 4.6:1 to 5.2:1 based upon the length of the monofil before drawing to obtain the improved bristle material. It is not a serious factor in so far as properties of the treated monofil are concerned, whether the drawing is carried out in one or two steps or whether any of the heating steps are carried out on wet or dry monofil, including the presence of other non-solvents for the polymer other than water or steam, which may or may not be swelling agents for the polymer.

As a matter of facilitating the drawing of the monofil, it may be desirable to carry this out in two steps although this is not necessary. When the drawing is carried out in two steps, it is preferred to first draw the monofil in the temperature range of about 55° C. to 80° C. to a draw of around 3.0:1 to 4.0:1 and then, in a second step at a higher temperature range of about 80° C. on up to 180° C., to finish off the drawing up to a total draw of 4.6:1 to 5.2:1 based upon the length of the monofil before drawing.

The second important step of the invention is to heat the drawn monofil to effect a reduction in its drawn length of 5% to 10%. It is quite immaterial within reason how this heating is carried out always provided that the temperature and duration of heating is sufficient to effect the specified reduction. It will be obvious that no such extreme temperature should be used

as would incur any danger of actually melting the monofil.

The third important step of the invention is to heat the monofil at a temperature of 150° C. to 250° C. while it is held under sufficient tension to prevent shrinkage. The duration of the heating is not important providing the monofil is brought up to the specified temperature range. While this may be accomplished in quite short periods of time, heating the monofil longer than necessary does no harm and it is preferred to heat it for a period of 5 minutes up to as much as one-half hour or more to be sure the heat treatment has been adequate. Any means of holding the monofil to prevent it from shrinking during the heat treatment, may be used but the monofil must be prevented from shrinking.

The outstanding advantage of the present invention is that it provides a process of improving polyethylene terephthalate monofil to the point where they are practical for use as bristle material for toilet brushes, paintbrushes, and the like, thus providing the first acceptable synthetic bristle material other than nylon for this purpose. A further advantage is that the invention is relatively simple and economical to carry out as it does not involve any difficult manipulative operations or costly equipment.

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 the invention is not limited to the specific embodiments thereof except as defined in the appended claims.

The invention claimed is:

1. Process of improving a monofil spun from polyethylene terephthalate, for use as bristle material, which process comprises drawing said monofil at 55° C. to 180° C. to a total draw of 4.6:1 to 5.2:1 based upon the length of said monofil before drawing, heating said drawn monofil in a relaxed condition until it shrinks 5% to 10% of its original drawn length, and thereafter heating said monofil to 150° C. to 250° C. while held under tension to prevent shrinkage.

2. Process of improving a monofil spun from polyethylene terephthalate having an intrinsic viscosity of at least 0.35, for use as bristle material, which process comprises drawing said monofil at 55° C. to 80° C. to a draw of 3.0:1 to 4.0:1 based upon the length of said monofil before drawing, further drawing said monofil at 80° C. to 180° C. to a total draw of 4.6:1 to 5.2:1 based upon the length of said monofil before drawing, heating said drawn monofil in a relaxed condition until it shrinks 5% to 10% of its original drawn length, and thereafter heating said monofil to 150° C. to 250° C. while held under tension to prevent shrinkage.

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