PROCESS FOR PRODUCING FIBROUS GRAPHITE

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9 Claims

ABSTRACT OF THE DISCLOSURE

A refractory carbonaceous yarn characterized by its high tensile strength and modulus of elasticity is provided. The process for producing such a yarn comprises heating the starting carbonaceous yarn to a temperature sufficient to cause its plastic flow and longitudinally stretching the heated yarn by subjecting it to a tensile force until an elongation of at least 1% of the original length of the yarn has been obtained while heating the elongated yarn to graphitizing temperatures and cooling the permanently so-elongated yarn.

This application is a continuation-in-part of application Ser. No. 157,259, filed Dec. 5, 1961, now abandoned.

The present invention relates to an improved process for the production of filaments or yarn from carbonized polymeric fibrous materials and to the filaments and yarn so produced.

It is known to subject to graphitizing temperatures cellulosic fibrous material such as cloth, felt, braids, yarns, knits and weaves by subjecting them to a controlled heating schedule which comprises a slow heating stage at a temperature of from 100° C. to 300° C. at a rate of increase of up to 50° C. per hour, followed by a second heating stage from 300° C. to 400° C. in which the temperature is increased at a rate of up to 10° C. per hour, then heating to cause the temperature to increase at a rate of up to 100° C. per hour at temperatures up to 900° C. From 900° C. until the treatment is complete, at around 3000° C., rapid heating rates of up to 3000° C. per hour may be employed.

The individual monofilaments of the thus treated or graphitized material have a tensile strength of up to 100,000 pounds per square inch. While the individual filaments possess such strength, the yarns made from a plurality of the same filaments and treated under the same conditions have a tensile strength of only approximately 15,000 pounds per square inch.

When it is considered that during the described process the individual filaments within the twisted yarn undoubtedly undergo unequal shrinkage, this discrepancy in strength is not surprising. With unequal shrinkage from filament to filament, unequal residual strains are bound to exist. When a yarn is stressed uniformly, the shorter filaments are the first to be strained. The elongation prior to breaking in a manufactured graphite filament has been found to be less than 1% at room temperature, and the shorter filaments break before the strain can be distributed equally throughout the yarn.

The principal object of the present invention is to provide a method of producing a high temperature refractory filament or yarn from a carbonized polymeric filament or yarn, the produced material having improved physical properties such as an increased Young's modulus and an improved tensile strength.

Another object of the present invention is to provide a method of increasing the Young's modulus and tensile strength of the individual monofilaments which make up a length of graphite yarn.

Still another object of the present invention is to provide a graphite yarn having a tensile strength more comparable with the tensile strength of the individual monofilaments which make up the yarn.

These objects are achieved by heating a carbonaceous polymeric filament or yarn to a temperature high enough to cause the filament or the individual monofilaments forming the yarn to reach a degree of plasticity which allows them to be stretched, when the yarn is subjected to a tensile force, while in such a plastic condition and to remain permanently stretched after cooling of the filament or yarn. The heating and stretching is done in an atmosphere which protects the material from being oxidized. An inert atmosphere, such as argon, has been found very suitable for this purpose.

Accordingly, the present invention provides a process for producing an improved high temperature refractory filament or yarn which comprises heating a carbonaceous polymeric filament or yarn to a temperature sufficient to permit plastic flow and longitudinally stretching the heated filament or yarn by subjecting said heated filament or yarn to a tensile force until an elongation of at least 1% of the original length of the filament or yarn has been obtained. While in the case of yarn, a significant improvement is shown after a stretch of only 1%, in the case of an individual monofilament a stretch of the order of about 10% is required before significant improvements in the properties are clearly in evidence.

The present invention also provides an improved high temperature refractory yarn of cellulosic origin formed of a plurality of monofilaments having a Young's modulus of more than 10×10^6 lbs./in.^2 and a breaking strength of more than 12×10^4 lbs./in.^2. By utilizing the optimum process conditions a yarn of cellulosic origin has been produced wherein the individual monofilaments have a Young's modulus of the order of 55×10^6 lbs./in.^2 and a breaking strength of the order of 36.5×10^4 lbs./in.^2.

In order that the degree of orientation achieved by the process of the invention be fully illustrated, reference will be had to the drawing, the figures of which are electron micrographs of unstretched and stretched filaments.

More specifically, FIGURE 1 is an electron micrograph having a magnification factor of 93,000 of a thin slice of an unstretched rayon filament which has been subjected to graphitizing temperatures. The plane of the slice is parallel to the filament axis. The "grain" of this structure is parallel to the filament axis, but the orientation is not very pronounced.

FIGURE 2 is an electron micrograph having a magnification factor of 138,000 of a thin slice of a rayon filament which has been subjected to a graphitizing temperature and stretched by the process of the invention. The plane of the slice is parallel to the filament axis. The "grain" of this structure is also parallel to the filament axis and as compared to FIGURE 1, the orientation is very pronounced. The filament of FIGURE 2 had a Young's modulus of 55×10^6 lbs./in.^2. The significance of this high degree of orientation will be fully discussed hereinafter.

For convenience sake the bulk of the disclosure hereinafter will be directed to the treatment made up a plurality of filaments and the yarn so produced. It will be appreciated that the disclosed process is equally applicable to the treatment of a monofilament.

The expression "carbonaceous yarn" is intended to cover a yarn which has already been graphitized in a separate operation and is thereafter subjected to the process of the present invention, as well as a "carbon yarn" which is a yarn having been carbonized by being heated up to a carbonizing temperature but below graph-
lizing temperatures and which is therefore simultaneously treated to higher temperatures which are commonly recognized as graphitizing and stretched by the process of the present invention.

The yarns suitable for use in the process of the present invention include carbon and graphite yarns produced by carbonizing polymeric, fibrous materials such as polyacrylonitrile, polyvinyl alcohol, and natural and preferably regenerated cellulose. The sample treatment at which the monofilaments of the yarn show a significant degree of plasticity varies according to the nature and origin of the yarn; with yarns of cellulose origin it has been observed that stretching under a tensile force begins at a temperature in the vicinity of the maximum temperature of the previous heat-treatment to which the material has been subjected. For example, stretching of a carbon yarn under load will begin at approximately 1200°C, whereas no stretching of a pre-graphitized yarn will take place at a temperature much below 2300°C. However, significant stretching of the carbon yarn will not begin at a temperature of less than 1500°C and a minimum temperature of 2500°C is necessary to obtain significant stretching of the pre-graphitized yarn. In addition, the closer the temperature at which the stretching is done is to the maximum temperature to which the material was previously subjected, the longer the time required at a given temperature within the indicated range to achieve the same improvement in properties. The maximum temperature at which the process of the present invention may be carried out is not critical. It should be kept below the temperature of vaporization of graphite, i.e., approximately 3600°C.

The present invention will now be further described in the following examples.

**EXAMPLE I**

A high temperature induction furnace was constructed for stretching carbonaceous yarns at elevated temperatures according to the process of the present invention. It consisted of a hollow, cylindrical graphite susceptor which was inductively heated by a conventional induction coil, a graphite support rod positioned across the top of the susceptor for mounting the sample, and a system for providing an inert atmosphere in the hot zone of the assembly. A carbon yarn sample (single ply, 697 denier with 720 filaments per ply of regenerated cellulose which had previously been carbonized at a maximum temperature of 1300°C, was doubled over and passed through the apparatus. The yarn was joined together at the two ends and a weight was attached thereto which thereby put the sample under tension. The susceptor was heated by gradually increasing the power and the yarn was, accordingly, heated by radiation from the susceptor. When the temperature within the hot zone reached about 1200°C the yarn began to stretch. The amount of stretch was measured by means of a cathetometer. The final temperature achieved was between 2800°C and 2830°C. The sample was maintained at this maximum temperature for 25 minutes. The sample was then cooled to room temperature, removed from the apparatus and measured for any change in physical properties.

Four experiments were carried out with four identical yarns in each case. The only difference was in the weight of the load attached to the sample, which was 50 gm., 400 gm., 800 gm. and 1400 gm., respectively. Stretching or elongation of the samples increased with increasing load attached to the yarn.

It could be seen that a measurable amount of elongation had taken place even under very small loads. Some of the elongation was reversible as it was due to the thermal expansion of the fibers while the remaining position of the elongation was permanent as it was due to an actual stretching or lengthening of the fibers themselves. Any elongation which occurred beyond the purely heat-treatment-induced elongation is called stress-induced elongation, or "stretching" and is permanent in nature. It is only the stress-induced elongation which accounts for the improvement of the properties under discussion as reported in Table 1.

As a result of the permanent stretch applied to these samples, marked increases were found in strength and Young's modulus, measured on individual filaments. Individual filaments were tested in tension at room temperature with an Instron testing machine. For each stretched sample, at least 10 measurements of strength and Young's modulus were made. The average cross-sectional area of individual filaments for each yarn sample were obtained by direct measurements of at least twenty representative individual filaments taken from the yarn sample. Results of these measurements are shown in Table 1 below. The average cross-sectional area, Young's modulus and breaking strength of the individual filaments of the initial carbon yarn samples were also measured and are shown in Table 1. For comparison purposes, the properties of a graphite filament produced by the known heating schedule previously mentioned are also listed in Table 1. It should be understood that the percent elongation given in the table for the monofilaments is substantially equal to the percent elongation occurred in the yarn upon stretching. The actual percentage figures in Table 1 represent the inverse ratio of the cross sections of the filaments before and after stretching, and this figure closely approximates the percent elongation.

<table>
<thead>
<tr>
<th>Load applied (g)</th>
<th>Stress (p.s.i.)</th>
<th>Average cross-sectional area (cm.²)</th>
<th>Percent elongation</th>
<th>Young's modulus (10¹⁵ dynes/cm²)</th>
<th>Breaking strength (10⁻¹⁰ dynes/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Initial 2,800°C</td>
<td>A²</td>
<td>30%</td>
<td>10,000</td>
<td>4.0</td>
</tr>
<tr>
<td>40</td>
<td>6,000</td>
<td>5,000</td>
<td>50%</td>
<td>30,000</td>
<td>6.0</td>
</tr>
<tr>
<td>3,000</td>
<td>21,000</td>
<td>10,000</td>
<td>70%</td>
<td>12,000</td>
<td>9.0</td>
</tr>
<tr>
<td>1,400</td>
<td>21,000</td>
<td>21,000</td>
<td>25%</td>
<td>22,000</td>
<td>18.0</td>
</tr>
</tbody>
</table>

*Range.

Since the yarn sample heated under a load of 50 gm. was found to stretch only very slightly, this sample showed properties which are substantially equivalent to the properties to be expected from a yarn sample heated under zero load. Comparison of the properties of the sample heated under a load of 1400 gm. with that of the 50 gm. sample, shows that the effect of stretching the yarn under a load of 1400 gm. was to produce nearly a 6-fold increase in Young's modulus and a 3½-fold increase in breaking strength of individual filaments taken from the yarn. It should be pointed out that there is no absolute limit on the amount stretch which may be imparted to a filament or yarn by the process of the invention other than a practical one, i.e., the stress employed to impart the stretch must not exceed the stress which the material can withstand at each given point in time.

The explanation for the remarkable changes in properties lies first in the fact that one result of the stretching was the partial alignment of graphic or graphic-like layers into positions characterized by preferred orientation of layers parallel to the filament axis. That this effect had even for very small elongations was reversible as it was due to the thermal expansion of the fibers while the remaining position of the elongation was permanent as it was due to an actual stretching or lengthening of the fibers themselves. Any elongation which occurred beyond the purely heat-treatment-induced elongation is called stress-induced elongation, or "stretching" and is permanent in nature. It is only the stress-induced elongation which accounts for the improvement of the properties under discussion as reported in Table 1.
The cause of this is known to be the high Young's modulus of crystallites measured along the layers as compared to the modulus measured normal to the layers.

Secondly, with regard to the increase in strength of stretched filaments compared to unstretched filaments, there are several probable causes:

1. The preferential orientation of layers parallel to the filament axis makes it difficult to propagate incipient cracks within the filament in directions transverse to the axis. This is because cracks can more easily propagate between graphitic layers than across, or through, the layers. Cracks transverse to the axis tend to be propagated by an applied tension, whereas cracks parallel to the axis are not propagated by an applied tension, and are hence ineffective in producing fracture.

2. Flaws in the structure of the filament, such as internal voids or pits on the external surface of the filament, produce stress concentrations at their extremities when a tension is applied to the filament. In the example of surface pits, if the radius of curvature at the bottom of the pit is small, the stress concentration will be correspondingly large, and when the applied tension becomes sufficiently large a crack leading to ultimate fracture can develop. The stretching of the filament would cause the radius of curvature at the bottom of the surface pit to increase, and thereby reduce its effectiveness as a stress-concentrator.

3. When a carbon filament is cooled to room temperature from the maximum heat-treatment temperature used in its manufacture or preparation prior to tensile testing, internal stresses are produced due to unequal thermal contractions in adjacent regions within the filament. The cause for these unequal thermal contractions is the difference in thermal expansion coefficient of crystallites measured parallel to the layers and measured normal to the layers. If adjacent crystallites are oriented in different relations to the filament axis, then unequal thermal contractions will occur and produce internal stresses. These internal stresses, when added to the externally applied tensile stress, will lead to premature fracture. Since the stretching process tends to orient crystallites with their layers parallel to the axis of the filament, there is a reduction in the induction of internal stresses during cooling and hence an increase in strength.

**EXAMPLE II**

Using the apparatus described in Example I, and under the same conditions of temperature and time, experiments were carried out with a yarn (single ply, 506 denier with 720 filaments per ply) of a regenerated cellulose origin which had been previously subjected to a graphitizing temperature of 2800°C. A load of 1000 gm. was attached to the yarn sample. While for the carbon yarns of Example I stretching under load had begun at approximately 1200°C, i.e., near the maximum carbonization temperature of the yarns, it was found that no significant stretching of this yarn occurred until approximately 2500°C. which was near the previous graphitizing temperature. At 2500°C the amount of stretching which occurred was very slight. Only after raising the temperature to 2800°C did appreciable stretching occur. The amount of stretching that occurred as a result of the increase in temperature from 2500°C to 2800°C was similar to that which occurred in the corresponding samples which had been subjected to their respective graphitizing temperatures as a result of the same increase in temperature from 2500°C to 2800°C. Therefore the total elongation of the samples treated previously at graphitizing temperatures was much less than that of samples not treated at such high temperatures.

The results of these experiments are shown in Table 2 below. The individual filaments of the samples were measured in the same manner as described in Example I.

| TABLE 2 Properties of filaments from yarns previously treated at graphitizing temperatures stretched under tensile loads during heating to a temperature of 2800°C: |
| Load applied, (g.) | 1000 |
| Average cross section area, 10⁻² cm.² | 50.3 |
| Percent elongation | 16 |
| Young's modulus, 10⁶ lb./in.² | 13.6 |
| Breaking strength, 10⁶ lb./in.² | 12.8 |

It is clear from this second series of experiments that, although the previously high temperature treated yarns do not benefit from heating under load as much as the yarns which have only been partially carbonized, their individual filaments still show a definite improvement in Young's modulus and breaking strength over the filaments of prior art graphite yarns.

**EXAMPLE III**

A single ply 206 denier graphite yarn consisting of 720 filaments having approximately 2 twists per inch was tested and found to have an effective yarn tenacity of .81 gram per denier: (corresponding to an actual effective breaking load of 167 grams). Based on actual tensile strength tests on individual filaments, the theoretical maximum tenacity of this yarn is calculated to be 7.15 grams/denier. A span of this yarn corresponding to a free length of 0.9 inch was mounted in a small jig constructed from parts machined from structural graphite. The mechanical design of the jig was such that a tensile load of a known amount could be applied to the yarn sample by means of a fixed weight and the amount of elongation taking place over the sample length could be limited to a predetermined amount by means of a support rod having a calibrated thread under the weight. The entire assembly, was installed within a 4 inch diameter graphite tube which could be heated electrically to graphitizing temperatures. After flooding the interior of the graphite tube with argon, the tube and assembly with the yarn sample supporting a tensile load of 40 grams (corresponding to 2 gram/denier) was heated rapidly to 2800°C and held at that temperature for approximately 5 minutes and the tube furnace was then allowed to cool rapidly. In the case of one sample, the total stretch was limited to 1% of its free span length. Examination of the cooled testing assembly showed that the yarn sample had reached a plastic stage at a temperature of about 2200°C and had been permanently stretched. The effective strength of the thus treated yarn was found to be 1.18 grams/denier. In a second experiment under these same conditions with another sample of the same size of yarn a total elongation of 2% was allowed to take place. The effective strength of this yarn was found to be 1.23 grams/denier.

It will be appreciated from a study of the above figures that untreated graphitized yarn of the prior art has effective strength of only 11% of the theoretical. An elongation of 1% of the graphitized yarn by the process of the present invention results in an effective strength equal to 15% of theoretical or approximately a 50% increase. A 2% elongation results in an effective strength of 17% of theoretical. While an elongation of at least 1% of the original length of the yarn is necessary to improve the strength of the yarn, there is practically no upper limit for the elongation. It is obvious from Tables 1 and 2 above, that the strength of the yarns increases with increasing elongation of the yarn. This example shows the improvement in the treated yarn, obtained by relieving unequal filament-to-filament stresses in said yarn and orienting the crystallites in the graphitic layers in a direction parallel to the longitudinal axis of each monofilament with the resulting improved properties of the individual filaments of the yarn.
EXAMPLE IV

Another experiment was performed in which a sample of carbon yarn, which had not been previously subjected to graphitizing temperatures, was stretched under a load of 1300 gm. in the conditions described in Example I. The resulting stretched and graphitized yarn was cooled to room temperature, and then subjected a second time to the same heating schedule under the same 1300 gm. load. In the second treatment, no detectable stretching occurred until a temperature of 2800° C. was reached. This experiment points up an obvious benefit of the stretching process of the present invention, namely, that stretching of yarns under high loads at high temperature renders them totally resistant to creep under loads equal to or less than that used in the stretching treatment at all temperatures below the maximum temperature attained during the treatment. This property of resistance to creep is of great importance in structural applications at high temperatures, such as when carbon yarns are used in filament wound structures as the primary load-bearing material.

What is claimed is:

1. A process for producing an improved high temperature refractory yarn which comprises heating in a protective atmosphere a carbonaceous yarn in graphite form up to a temperature sufficient to permit plastic flow and longitudinally stretching the heated yarn by subjecting said heated yarn to a tensile force until an elongation of at least 1% of the original length of the yarn has been obtained, and cooling the permanently elongated yarn.

2. A process for producing an improved high temperature refractory yarn which comprises heating a carbonaceous yarn in a carbonized form in a protective atmosphere to a graphitizing temperature sufficient to permit plastic flow and longitudinally stretching the heated yarn by subjecting said heated yarn to a tensile force until an elongation of at least 1% of the original length of the yarn has been obtained, and cooling the permanently elongated yarn.

3. The process of claim 2 wherein said heating is done in an argon atmosphere.

4. A process as claimed in claim 1, in which the graphite yarn is of cellulosic origin and heated to a temperature of at least about 2500° C.

5. A process as claimed in claim 4 wherein said heating is done in an argon atmosphere.

6. A process as claimed in claim 1, in which the carbonaceous yarn is provided by subjecting to a graphitizing environment a yarn selected from the group consisting of polyacrylonitrile, polyvinyl alcohol and natural and regenerated cellulose.

7. A process for producing an improved high temperature refractory monofilament which comprises heating a carbonaceous monofilament in graphite form to a temperature sufficient to permit plastic flow and longitudinally stretching the heated monofilament by subjecting said monofilament to a tensile force until an elongation of at least about 10% of the original length of the monofilament has been obtained, and cooling the permanently elongated monofilament.

8. A process as claimed in claim 2 in which the carbonaceous yarn is provided by subjecting to a carbonizing environment a yarn selected from the group consisting of polyacrylonitrile, polyvinyl alcohol and natural and regenerated cellulose.

9. A process for producing an improved high temperature refractory monofilament which comprises heating a carbonaceous monofilament in a carbonized form to a graphitizing temperature sufficient to permit plastic flow and longitudinally stretching the heated monofilament by subjecting said monofilament to a tensile force until an elongation of at least about 10% of the original length of the monofilament has been obtained, and cooling the permanently elongated monofilament.

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EDWARD J. MEROS, Primary Examiner.

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