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# ⑫ EUROPEAN PATENT APPLICATION

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## ㊴ Improvement of carbon fiber strength.

㊼ Carbon fibers from pitch are treated with carbonizable resin precursor and carbonized to give an improvement in carbon fiber strength.

# Improvement of Carbon Fiber Strength

## Background of the Invention

The production of carbon fiber from pitch is well known. See, for example, U.S. Patent Nos. 4,005,183 and 4,504,454. It is believed that the maximum tenacity which these fibers are capable of achieving is not attained due in part to defects in the fibers and/or at the fiber surface. The present invention seeks to enhance the fiber tenacity of such fibers.

## Summary of the Invention

This invention provides a method for increasing the tenacity of pitch-based carbon fiber yarn comprising impregnating a pitch-based carbonized or partially carbonized fiber yarn with a carbonizable resin precursor, polymerizing the precursor in situ to form the resin and subjecting the impregnated yarn to a temperature in excess of 1000°C in an inert atmosphere to carbonize the resin.

## Detailed Description of the Invention

The carbon fiber yarn to be strengthened in accordance with the present invention is a pitch-based yarn. This yarn may be prepared by the general procedures described in U.S. Patent No. 4,005,183. Either carbonized or partially carbonized yarn may be employed.

A solution of a carbonizable resin precursor is applied to the yarn. The object is to impregnate the fibers of the yarn with a material which will polymerize or polymerize further to a resinous product which will remain in place and leave a carbon residue within the fiber upon carbonization. Thus, the term "resin precursor" is intended to include unpolymerized or partially polymerized materials. Polymerization or resinification is often facilitated by application of heat. The resin must be capable of being carbonized, the usual temperature of carbonization being above 1000°C. Among suitable carbonizable resin precursors are partially polymerized phenolic condensation products, epoxy resins, furfural, furfuryl alcohol, partially polymerized furfuryl alcohol resin, urea condensation products, acrylic resins, vinyl resins, propylene glycol, etc. A sufficient amount of carbonizable resin precursor must be absorbed by the yarn to provide strengthening. Amounts yielding between about 0.1 and 10% of resin based on the weight of the yarn prior to impregnation have been found satisfactory. Preferably the weight gain is kept below 5%, particularly with partially carbonized fiber because such fibers are less able to absorb the resin precursors.

It is preferred that the resin precursor have a high coking factor, that is, a high percentage of carbon yield when subjected to carbonization. Volatile impregnants which are entirely driven off in the heating step are clearly unsuitable.

The yarn is passed through a bath containing the carbonizable resin precursor. If the resin precursor is furfuryl alcohol, a partially polymerized furfuryl alcohol or combination thereof, it is desirable to incorporate a latent catalyst along with the precursor. These are commercially available and recommended for the purpose of catalyzing the polymerization of the resin precursor at elevated temperatures. One such catalyst is a complex of boron trifluoride and monoethylamine. Another catalyst is maleic anhydride. Use of a latent catalyst permits application of a low viscosity solution to the fiber with subsequent polymerization at the elevated temperatures. If the precursor were to polymerize significantly prior to application, the treating bath would be so viscous as to allow only a coating to be formed. Under such circumstances, the fibers of the yarn would stick to each other and become damaged or adversely affected for use in composites where penetration of matrix medium between the yarn fibers is of utmost importance. Suitable solvents are those which will readily evaporate without leaving any harmful residues. Acetone has been found useful for this purpose.

As mentioned above, the viscosity of the impregnation bath should be sufficiently low as to permit permeation of the resin precursor into the fibers of the yarn, i.e., to fill the voids, cracks and other defects of the fiber. If the bath is too viscous, the yarn itself, rather than the fibers thereof, will entrap such amounts of resin precursor as to cause the fibers to stick to each other. Such fibers often break when attempts are made to separate them from each other. It will be understood that the resin content of the impregnating solution increases with age because partial polymerization is taking place. As this occurs, the viscosity of the bath increases and will influence the degree of fiber permeation.

Upon removal of the yarn from the bath, excess surface fluid is gently removed as by padding with an absorbent material to avoid damaging the yarn. Exposure of the yarn to air at room temperature for extended periods allows solvents from the impregnating solution to evaporate and the resin precursor to partially cure. Alternatively, this may be achieved by slowly heating the yarn from room temperature to final polymerization temperatures. In any event, the yarn must be heated to completely polymerize the impregnant. Conditions for such polymerization are well known in the art. In general, the yarn will be heated to temperatures in the range of about 100 to 200°C for periods of at least five minutes. Following this polymerization, the yarn is subjected to carbonization conditions, namely, treatment in an inert atmosphere, e.g., nitrogen argon, etc., at temperatures of above 1000°C until the resin has carbonized.

## Testing Procedures

Tenacity, elongation and modulus (T/E/M) are measured according to ASTM D-3379-75.

The following examples are submitted to illustrate the invention and are not intended as limiting. In each case, the pitch-based yarn was impregnated by passage through a bath containing the resin precursor.

The yarn contained 496 filaments each having a diameter of about 10 microns. The carbonized yarn (at 1600°C) had an initial modulus of about 900 to 1000 grams per denier (gpd).

## Example 1

Carbon fiber yarn was impregnated with furfuryl alcohol containing 1% latent catalyst (commercially available complex of boron trifluoride and monoethylamine ($BF_3$.MEA). The fibers were heated at 4°C/min. to 150°C and held at 150°C for 32 minutes to polymerize the furfuryl alcohol. After polymerization the fibers were found to have gained 1.45% of their original weight. The fibers were then carbonized at 1584°C. An 11% improvement in tensile strength over the control fiber resulted (T/E/M impregnated fiber: 14.6gpd/1.22%/1055gpd, T/E/M control fiber: 13.2gpd/1.17%/988 gpd).

## Example 2

Carbon fiber yarn was impregnated with the solution used in Example 1. The solution had been aged for 22 days. The furfuryl alcohol was polymerized under the same conditions as in Example 1. After polymerization, the fibers were found to have gained 8.7% of their original weight. The fibers were then recarbonized at 1584°C. A 22% improvement in tensile strength over the control fiber resulted (T/E/M impregnated fiber: 16.1gpd/1.25%/997gpd, T/E/M control fiber: 13.2gpd/1.17%/988gpd).

## Example 3

Carbon fiber yarn was impregnated using a 90/10% by wt. mixture of furfuryl alcohol and furfural modified furfuryl alcohol resin with 2% of the latent catalyst of Example 1. The fibers were heated at 4°C/min. to 120°C and held at 120°C for 32 minutes to polymerize the furfuryl alcohol/resin. After polymerization, the fibers were found to have gained 3.2% of their original weight. The fibers were then recarbonized at 1600°C. A 29% improvement in tensile strength over the control fiber resulted (T/E/M impregnated fiber: 14.2gpd/1.23%/1025gpd, T/E/M control fiber: 11.0gpd/.95%/1081gpd).

## Example 4

Carbon fiber yarn was impregnated using a 90/10% by wt. mixture of furfuryl alcohol and furfural modified furfuryl alcohol resin with 2% of the latent catalyst of Example 1. The fibers were heated at 4°C/min to 120° and held at 120°C for 32 minutes to polymerize the furfural modified resin. After polymerization, the fibers were found to have gained 6.1% of their original weight. The fibers were then recarbonized at 1600°C. A 24% improvement in tensile strength over the control fiber resulted (T/E/M impregnated fiber: 15.1gpd/1.18%/1148gpd, T/E/M control fiber: 12.2gpd/1.023%/1095gpd).

## Example 5

Carbon fiber yarn was impregnated using a 10% by wt. solution of furfural modified furfuryl alcohol resin dissolved in acetone. The fibers were then heated at 4°C/min to 120°C and held at 120°C for 32 minutes. The resulting weight gain was 7.7% of their original weight. The fibers were recarbonized at 1600°C. A 12% improvement in tensile strength over the control fiber resulted (T/E/M impregnated fiber: 15.0gpd/1.41%/945, T/E/M control fiber: 13.4gpd/1.34%/868gpd).

## Example 6 - Comparative Example

Carbon fiber yarn was impregnated using acetone containing 5% of the latent catalyst of Example 1. The fibers were then heated to 4°C/min to 120°C. and held at 120°C for 32 minutes. The resulting weight gain was less than 1%. The fibers were then recarbonized at 1600°C. No increase in strength resulted (T/E/M impregnated fiber:

13.7gpd/1.13%/1131gpd, T/E/M control fiber: 14.2gpd/1.07%/1272gpd). This example shows treatment with a non-resin forming medium did not result in strength improvement.

## Example 7

Carbon fiber yarn was impregnated using propylene glycol containing 5% of the latent catalyst of Example 1. The fibers were then heated at 4°C/min to 200°C and held at 200°C for 32 minutes. A resin was formed from propylene glycol under these conditions. The resulting weight gain was less than 1%. The fibers were then recarbonized at 1600°C. A 10% improvement in tensile strength over the control fiber resulted (T/E/M impregnated fiber: 13.2gpd/ 1.05%/1133gpd, T/E/M control fiber: 12.0gpd/.947%/1141gpd).

## Example 8

Partially carbonized yarn (heated to 1000°C) was impregnated with furfuryl alcohol containing 2% of the latent catalyst of Example 1 which had been aged 72 hours. The fibers were heated at 4°C/min to 120°C and held at 120°C for 32 minutes to polymerize the furfuryl alcohol. The resulting weight gain was less than 1%. The fibers were then carbonized at 1599°C. A 24.5% improvement in tensile strength over the control fiber resulted. (T/E/M impregnated fiber: 14.5gpd/1.18%/1083gpd, T/E/M control fiber: 11.6gpd/97%/1080gpd).

## Example 9

Carbon fiber was impregnated with furfural containing 2% of the catalyst of Example 1. The fibers were heated at 4°C/min to 120°C and held at 120°C for 32 minutes to polymerize the furfural. After polymerization, the fibers were found to have gained 0.1% of their orginal weight (weight gain from dipping was 3%). The fibers were then recarbonized at 1600°C. A 14% improvement in tensile strength over the control fiber resulted (T/E/M impregnated fiber: 13.8gpd/1.06%/1194gpd, T/E/M control fiber: 12.2gpd/1.023%/1095gpd).

## Example 10

Carbon fiber was impregnated using a 95/5% by wt. mixture of furfuryl alcohol and furfural modified furfuryl alcohol resin with 5% maleic anhydride added as a latent catalyst. The fibers were heated at 4°C/min to 120°C and held at 120°C for 32 minutes to polymerize the furfuryl alcohol/resin. After polymerization, the fibers were found to have gained 6.1% of their original weight (weight gain after dipping was 160%). The fibers were then recarbonized at 1594°C. A 20% improvement in tensile strength over the control fiber resulted (T/E/M impregnated fiber: 14.6gpd/1.17%/1155gpd, T/E/M control fiber: 12.2gpd/1.02%/1087gpd).

## Claims

1. A method for improving the tenacity of pitch-based carbon fiber comprising impregnating pitch-based carbon fiber yarn or partially carbonized yarn with a carbonizable resin precursor, polymerizing the precursor in situ to form the resin and subjecting the impregnated yarn to a temperature in excess of 1000°C in an inert atmosphere to carbonize the resin.

2. The method of claim 1 wherein the precursor is furfuryl alcohol.

3. The method of claim 1 wherein the precursor is partially polymerized furfuryl alcohol.

4. The method of claim 1 wherein a sufficient amount of precursor has been absorbed by the yarn to provide a weight gain after polymerization of between 0.1% and 10% based on the weight of the yarn prior to impregnation.

5. The method of claim 1 wherein a latent catalyst is employed to catalyze polymerization of the precursor.

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# EUROPEAN SEARCH REPORT

Application number
EP 87 30 5466

## DOCUMENTS CONSIDERED TO BE RELEVANT

| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | CLASSIFICATION OF THE APPLICATION (Int. Cl.4) |
|---|---|---|---|
| X | US-A-3 908 061 (BYRNE)<br>* Column 4, lines 23-68; claims * | 1 | D 01 F 11/10 |
| X | US-A-4 115 528 (CHRISTNER)<br>* Column 1, line 63 - column 4, line 59; claims * | 1-5 | |

TECHNICAL FIELDS SEARCHED (Int. Cl.4)
D 01 F

The present search report has been drawn up for all claims

| Place of search | Date of completion of the search | Examiner |
|---|---|---|
| THE HAGUE | 22-09-1987 | HELLEMANS W.J.R. |

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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