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(54) **Polyacrylonitrile-based carbon fiber and process for producing the same.**

(57) A polyacrylonitrile-based carbon fiber having both high Young's modulus and high tensile strength is disclosed along with a method for producing the same. The fiber is produced by winding an infusibilized polyacrylonitrile fiber onto a stable bobbin, carbonizing the fiber on the bobbin and subjecting the carbonized fiber to a heat treatment in a threadline operation.

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Polyacrylonitrile-based carbon fiber and process for producing the same.

The invention relates to an improved polyacrylonitrile-based carbon fiber and a method for producing the same.

The commercial value of polyacrylonitrile(PAN)-based carbon fibers is well known in the prior art.

Generally, a PAN-based carbon fiber is produced by spinning polyacrylonitrile into a fiber, infusibilizing the fiber by raising it to an elevated temperature in air, and thereafter carbonizing the infusibilized fiber at an elevated temperature in an inert atmosphere under tension in a threadline to produce a carbon fiber.

Commercially, thousands of continuous filaments or fibers are spun simultaneously and collected together to form a green yarn and the yarn is processed subsequently to produce an infusibilized yarn and then a carbon yarn.

The carbonizing operation for the infusibilized yarn is carried out as a threadline operation in order to subject the yarn to tension during the carbonizing step. The carbonizing step can be carried out as a sequence of operations using separate heating units. For example, one heating unit can be used at a temperature of about 1300°C to carbonize the infusibilized yarn initially and another heating unit can be used to carbonize the yarn to a higher temperature and thereby improve the mechanical properties of the carbon yarn.

One of the drawbacks of the prior art processes for commercially producing PAN-based carbon yarns is that the tensile strength of the fibers degrades as the carbonizing processing results in a higher Young's modulus. Table I shows typical properties of commercially available PAN-based carbon fibers.

TABLE I

Commercial Fiber	Young's Mod 10^6 kPa	Tensile Str. 10^3 kPa	Density Mg/M^3
A	227.5	3103	1.74
B	234.4	3103	1.81
C	234.4	3241	1.77
D	268.9	2896	1.67
E	358.5	2482	1.82
F	365.4	2206	1.83
G	393.0	2413	1.81
H	517.1	1862	1.96

In contrast, the instant invention produces a PAN-based carbon yarn having as average fiber properties a Young's modulus of greater than about 344.10^6 kPa and a tensile strength at least one third greater than the commercially available PAN-based carbon fiber having a similar average value of Young's modulus.

In addition, the process according to the invention is simple to implement and can be carried out economically with improved productivity, yielding high quality PAN-based carbon fibers.

The invention in one embodiment is a PAN-based carbon fiber having a Young's modulus of about 386.10^6 kPa and a tensile strength of about 3289.10^3 kPa.

The process of the invention in its broadest embodiment relates to the production of a PAN-based carbon fiber comprising the steps of spinning a polyacrylonitrile fiber, infusibilizing the fiber, and thereafter carbonizing the infusibilized fiber to produce a carbon fiber; and features the improvement of carrying out the carbonizing by winding the infusibilized fibers on to a bobbin which is thermally and mechanically stable at temperatures used to pyrolyze and carbonize the infusibilized fiber and which is chemically compatible with the infusibilized fiber, subjecting the infusibilized fiber on the bobbin to a predetermined first heat treatment in an inert atmosphere to pyrolyze and carbonize the infusibilized fiber, and thereafter subjecting the carbonized fibers to a second heat treatment in an inert atmosphere in a threadline operation.

For commercial operations, the process would be carried out using yarn, a plurality of fibers.

The bobbin for carrying out the process comprises a cylindrical body made of material such as stainless steel, or refractory oxides, or boron nitride, or graphite and preferably has a layer of compressible resilient carbon material such as carbon felt positioned on the outside surface of the cylindrical body to receive the infusibilized fiber and thereby minimize the stress between the cylindrical body and the infusibilized fiber during the treatment. The bobbin can be with or without end flanges. For relatively high winding angles, end flanges are not needed.

Typically, the cylindrical body of the bobbin can have an inside diameter of 7.62 cm and an outside diameter of about 8.89 cm with an overall length of about 27.94 cm.

Preferably, carbon felt has a thickness of from about 0.63 cm to about 1.27 cm thick.

The winding of the infusibilized yarn onto a bobbin can be carried out using a range of winding angles. Preferably a wind angle of at least two degrees should be used and as high as about twenty-three degrees is advantageous. During the heat treatment on the bobbin, the fibers tend to shrink considerably and the use of a high wind angle permits shrinkage without adverse effects on the fibers. Moreover, the use of a high wind angle leads to uniform fiber properties throughout the length of the fiber from the core to the outer winding layer.

The heat treatment of the fibers on the bobbins conveniently allows the bulk heat treatment of a large amount of fibers, at a relatively slow rate of increase in temperature to an elevated final temperature. The surprising advantage of this heat treatment is that both the rate of reduction in nitrogen content of the fibers and the final nitrogen content are much lower as to compared to a heat treatment to the same final temperature using a conventional threadline arrangement. As a result, the subsequent threadline heat treatment can be carried out at a high rate of movement of the yarn through the heating unit even if a considerably elevated temperature is used. This threadline treatment straightens out the fibers and establishes the final fiber mechanical properties.

Generally, the threadline temperature should be at least about 600°C higher than the temperature used for the first heat treatment of the yarn on the bobbin.

Table II shows a typical schedule of temperatures for the first and second heat treatments according to the invention in order to obtain PAN-based carbon fibers having predetermined values for the Young's modulus. The estimated nitrogen content after the first heat treatment is an important criteria for determining the heat of the threadline for any given temperature for the second heat treatment. A high nitrogen content will result in severe fiber damage due to the sudden evolution of the nitrogen from the fiber during a sudden temperature increase for a second heat treatment.

TABLE II

Desired Young's Mod 10^6 kPa	First Heat Treatment °C	Estimated Nitrogen Content %	Second Heat Treatment °C
276	1300	1	1900
345	1500	0.7	2300
414	1700	0.4	2500

Generally, the first heat treatment according to the invention can be carried out at a rate of from about 50°C to about 500°C per hour to a maximum temperature of from about 1300°C to about 1700°C.

Preferably, the first heat treatment is carried out by increasing the temperature at the rate of about 50°C for an hour from room temperature to about 800°C and thereafter increasing the temperature at a rate of 250°C per hour until the predetermined maximum temperature is reached and the maximum temperature is maintained for an additional two hours. The maximum temperature is maintained in order to give all of the fibers on the bobbin the opportunity to reach a temperature equilibrium.

A typical prior art threadline heat treatment at a temperature of 1300°C results in a PAN-based carbon fiber having a nitrogen content of about 4% or more by weight whereas the same heat treatment carried out using the first heat treatment according to the invention results in a PAN-based carbon fiber having a nitrogen content of about 1% by weight. The lower nitrogen content is important for carrying out a second heat treatment using a threadline at a relatively high speed.

For a fuller understanding of the nature and objects of the invention, reference should be had to the following detailed description, taken in connection with the accompanying drawings, in which:

Fig. 1 is a graph showing the effect of a first heat treatment according to the invention on the chemical composition of PAN-based fibers;

Fig. 2 is a graph showing the effect of threadline temperature and line speed on the density of recarbonized conventional PAN-based carbon fibers;

Fig. 3 is a graph showing the effect of line speed on threadline temperature on the density of recarbonized conventional PAN-based carbon fibers;

Fig. 4 is a graph comparing the effect of threadline temperature on the density of recarbonized conventional PAN-based carbon fibers and recarbonized PAN-based carbon fibers produced according to the instant invention;

Fig. 5 is a graph showing the effect of threadline temperature and line speed on the tensile strength of recarbonized conventional PAN-based carbon fibers;

Fig. 6 is a graph showing a comparison of the effect of threadline temperature on the tensile strength of both recarbonized conventional PAN-based carbon fibers and recarbonized PAN-based carbon fibers produced according to the instant invention;

Fig. 7 is a graph comparing the effects of threadline temperature and line speed on the Young's modulus of both recarbonized conventional PAN-based carbon fibers and recarbonized PAN-based carbon fibers produced according to the instant invention;

Fig. 8 is a graph showing a comparison of the tensile strength versus Young's modulus for both recarbonized conventional PAN-based carbon fibers and recarbonized PAN-based carbon fibers produced according to the invention;

Fig. 9 is a graph showing a comparison between the tensile strength versus Young's modulus for both recarbonized PAN-based carbon fibers and recarbonized PAN-based carbon fibers produced according to the invention.

In carrying out the invention, certain embodiments have been selected for description in the specification and reference is had to the Fig. 1 to 9.

It is economical in the commercial production of PAN-based carbon yarns to carry out the carbonizing operation in two separate steps. The first step is a carbonizing in a threadline to a temperature of about 1300°C while the second step is a threadline operation at a higher temperature to improve the mechanical properties of the resulting carbon yarn.

Subjecting an infusibilized fiber to a heat treatment results in the release of nitrogen, oxygen, and hydrogen from the fiber. Fig. 1 shows the weight percent of the aforementioned gases and carbon as a result of a first heat treatment in accordance with the invention. The reduction in nitrogen content is particularly important because the loss of nitrogen during a subsequent threadline heat treatment at a higher temperature can result in serious degradation of the fibers.

The tests for Fig. 1 were carried out using a graphite bobbin wrapped with a single layer of graphite felt and the temperature was increased from room temperature to the final temperature at the rate of about 100°C per hour with the final temperature as shown being held for two hours.

In addition to the substantial reduction in nitrogen content, it is significant that the evolution of nitrogen was at a relatively slow rate, particularly in comparison to a threadline operation at 1300°C. It is important that the evolution of nitrogen be at a slow rate so that the escaping gases will not produce flaws and degradation in the quality of the fibers.

Fig. 2 shows the results of a second heat treatment using a threadline operation for fibers which have been subjected to a first heat treatment using a conventional threadline operation at a temperature of about 1300°C. The loss in the density of the carbon fibers for high speeds through the furnace is due to the almost explosive evolution of nitrogen.

Fig. 3 presents the data of Fig. 2 in a different arrangement. From Figs. 2 and 3 it is evident that a threadline heat treatment of a PAN-based fiber which has been subjected to a previous threadline heat treatment has limitation as to the threadline speed and maximum treatment temperature.

Fig. 4 is a comparison in the fiber density after a threadline heat treatment of a fiber which has been subjected to a prior art threadline heat treatment and a fiber which has been subjected to the first heat treatment in accordance with the invention. In both cases, the first heat treatment had a maximum temperature of 1300°C. The line speed the second heat treatment in both cases was maintained at 1829 cm per minute. The evident degradation in fiber density is a result of the rapid evolution of nitrogen. The fiber given a first heat treatment in accordance with the invention has a very low nitrogen content.

Fig. 5 shows the effect of second conventional threadline temperature and line speed on the tensile strength of recarbonized PAN-based carbon fibers which have been subjected to a first conventional threadline treatment. The tensile strength declines rapidly in each case even for relatively slow line speeds as the maximum heat treatment temperature increases.

Fig. 6 shows the tensile strength of fibers after being subjected to a second heat treatment using a conventional threadline. The fiber which has been given a first heat treatment in accordance with the invention is significantly better than the fiber which has been subjected for a first heat treatment in accordance with the prior art. The line speed in all cases was 1219 cm per minute.

Fig. 7 shows the Young's modulus versus maximum temperature for a second heat treatment using a conventional threadline for fibers having a first heat treatment according to the invention and for fibers having a heat treatment according to the prior art. The first heat treatment in all cases had a maximum temperature of 1300°C. The carbon fibers according to the instant invention consistently showed higher value for the Young's modulus even when the line speed for the second heat treatment was ten times greater than the line speed used for the fibers according to the prior art.

Fig. 8 shows the relationship for tensile strength and Young's modulus for fibers according to the instant invention and prior art. In each case, the first heat treatment was carried out using a maximum temperature of 1300°C while the second heat treatments were both convention threadline operations. For both operations, the same threadline speed was used and different temperatures were used to obtain various fiber properties. The data show that for each Young's modulus the tensile strength of the fibers produced by the instant invention is substantially higher than the tensile strength of the fibers produced according to the prior art.

Fig. 9 shows a comparison between the tensile strength and the Young's modulus for fibers prepared according to the instant invention and the prior art. In each case, the maximum temperature used for the first heat treatment was 1300°C and the maximum temperature used in the second heat treatment was 1900°C. The variations in mechanical properties were produced by changes in threadline speed. The carbon fibers according to the invention were overwhelmingly superior to the fibers produced according to the prior art.

Illustrative, non-limiting examples of the practice of the invention are set out below. Numerous other examples can be readily evolved in the ligt of the guiding principles and teachings contained herein. Examples given herein are intended merely to illustrate the invention and not in any sense to limit the manner in which the invention can be practiced. The parts and percentages as cited herein and all through the specification, unless specifically stated otherwise, refer to parts by weight and percentages by weight.

EXAMPLE 1

A PAN-based infusibilized yarn was used. The fibers in the yarn had a composition of 64.0% carbon, 3.9% hydrogen, 6.2% oxygen, and 25.1% nitrogen. The yarn was wound on a bobbin used in commercial production. The yarn was unwound from the bobbin and rotated at 500 revolutions per minute while being unwound at the rate of 1920 cm per minute so that a twist of 0.7 turns per 2.54 cm was established. The twisted yarn was rewound with a tension of 250 grams onto a graphite bobbin having dimensions of 8.89 cm in diameter and 27.94 cm long. The graphite bobbin had a layer of 0.63 cm of graphite felt on the cylindrical portion to receive the yarn. A wind angle of 23 degrees was used and the package pressure was 1.36 kg with a transverse length of 25.4 cm. The rewound yarn amounted to 7163 m of yarn and was in the form of a square-sided package.

The package was placed horizontally in a graphite tube induction furnace which was purged with nitrogen and fired at the rate of 50°C per hour to 800°C and thereafter temperature was raised at 250°C per hour to 1300°C. The final temperature was maintained for two hours and the package was allowed to cool back to room temperature. As a result of the heat treatment, the package had shrunk longitudinally about 3.81 cm to 5.08 cm from its original 25.4 cm length.

The package was then mounted horizontally on a tension-loaded payoff creel, and the yarn was unwound under a tension of approximately 50 grams, passed through a grooved-reel, tension-controlled drive system maintained at a tension of about 1,825 grams and thereafter through graphite tube electric resistance furnace having a hot zone maintained at a temperature of about 1830°C and 152 cm long. The yarn exiting the furnace was then subjected to a finish treatment in accordance with the prior art and wound onto bobbins made of cardboard in 305 m lengths. Twenty-two samples of the yarn were taken at about 305 m intervals.

The average tensile strength of the resulting fiber was

3447.10^3 kPa with a coefficient of variation of 1.3%. The average Young's modulus for the resulting fiber was about 284.10^6 kPa with a coefficient of variation of 2.9%. The average density of the fibers was 1.766 Mg per cubic meter with a coefficient of variation of 0.6%. The average yield was 2397 m per kg with a coefficient of variation of 2.1%.

The carbon yarn obtained had an excellent appearance and was equivalent in quality to a carbon yarn produced by carbonizing with two separate threadlines in accordance with the prior art.

EXAMPLE 2

Infusibilized yarn as in Example 1 was used in this example. For this example, however, 1432 m on infusibilized yarn was used. As in Example 1, the yarn was wound onto the graphite bobbin having a graphite felt layer.

The same temperature schedule was used for the first heat treatment. The second heat treatment was different in this example for Example 1 in that the furnace temperature was held at 2460°C, the take off tension was 100 grams, the line tension was 1950 grams, the line speed was 2134 cm per minute, and only water was applied to the carbon yarn instead of a finish.

Five samples taken at about equal separations were tested. The fibers had an average tensile strength of 3289.10^3 kPa, an average Young's modulus of 391.10^6 kPa, a density of 1.813 Mg per cubic meter, and a yield of 2549 m per kg. The yarn was excellent in appearance.

EXAMPLE 3

1432 m of carbon yarn produced from the steps of Example 1 were wound on a graphite bobbin having a diameter of 11.43 cm and a length of 17.78 cm. No carbon felt was used and the wind angle was about 0.4°. This package was then loaded horizontally in a graphite tube induction furnace, purged with argon, and fired at the rate of 100°C per hour to a temperature of 2950°C. The final temperature was maintained for two hours and the package was allowed to cool back to room temperature.

The average properties of the fibers so obtained was a tensile strength of 2482.10^3 kPa, Young's modulus of 668.10^6 kPa, density of 2.080 Mg per cubic meter, and a yield of 2832 m per kg.

The reduction in strength over the values obtained from Example 1 indicates that new flaws were introduced during the subsequent thermal processing and handling.

In any event, the carbon fibers of this example constitute a significant improvement over commercially available PAN-based carbon fibers.

I wish it to be understood that I do not desire to be limited to the exact details shown and described, for obvious modifications will occur to a person skilled in the art.

Having thus described the invention, what I claim as new and desired to be secured by Letters Patent, is as follows:

CLAIMS

1. In a method of producing a PAN-based carbon fiber comprising the steps of spinning a polyacrylonitrile fiber, infusibilizing the fiber, and thereafter carbonizing the infusibilized fiber to produce the carbon fiber, the improvement comprises carrying out the carbonizing by winding the infusibilized fiber onto a bobbin which is thermally and mechanically stable at temperatures used to pyrolyze and carbonize the infusibilized fiber and which is chemically compatible with the infusibilized fiber, subjecting the infusibilized fiber on the bobbin to a predetermined first heat treatment in an atmosphere to pyrolyze and carbonize the infusibilized fiber, and thereafter, subjecting the carbonized fiber to a second heat treatment in an inert atmosphere in a threadline operation.

2. The method of Claim 1, wherein the threadline temperature is at least about 600°C higher than the maximum temperature used for the first heat treatment.

3. The method of Claim 1, wherein the first heat treatment is carried out at a rate of from about 50°C to about 500°C per hour to a maximum temperature of from about 1300°C to about 1700°C.

4. The method of Claim 1, wherein the infusibilized fiber is wound onto the bobbin with a wind angle of at least about two degrees.

5. The method of Claim 3, wherein the wind angle is about 23 degrees.

6. The method of Claim 1, further comprising a third heat treatment subsequent to the second heat treatment and having a maximum temperature greater than the maximum temperature of the second heat treatment.

7. A PAN-based carbon fiber having a Young's modulus of about 669.10^6 kPa and a tensile strength of about 2482.10^3 kPa.

8. A PAN-based carbon fiber having a Young's modulus of about 386.10^6 kPa and a tensile strength of about 3289.10^3 kPa.

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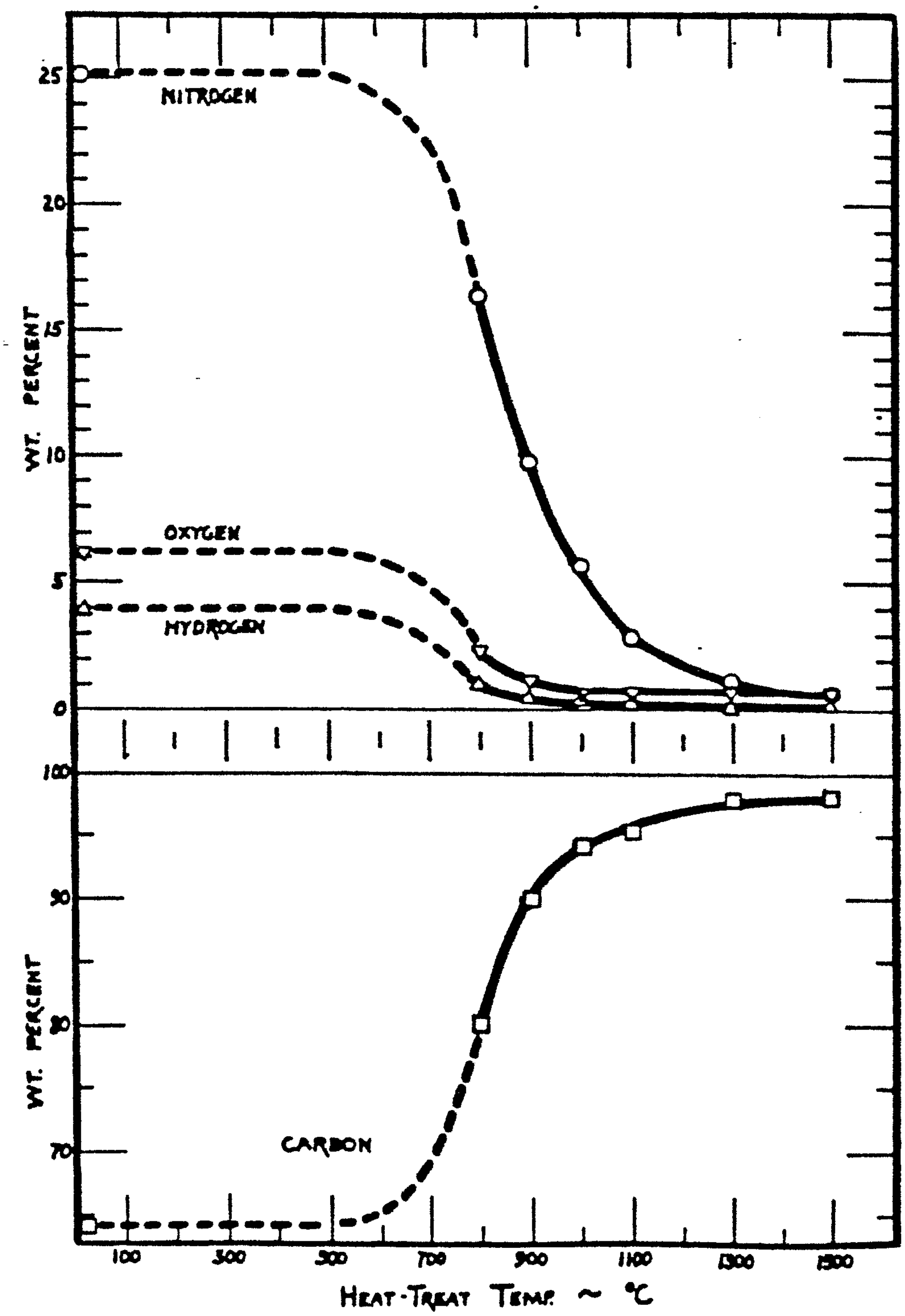
fig-1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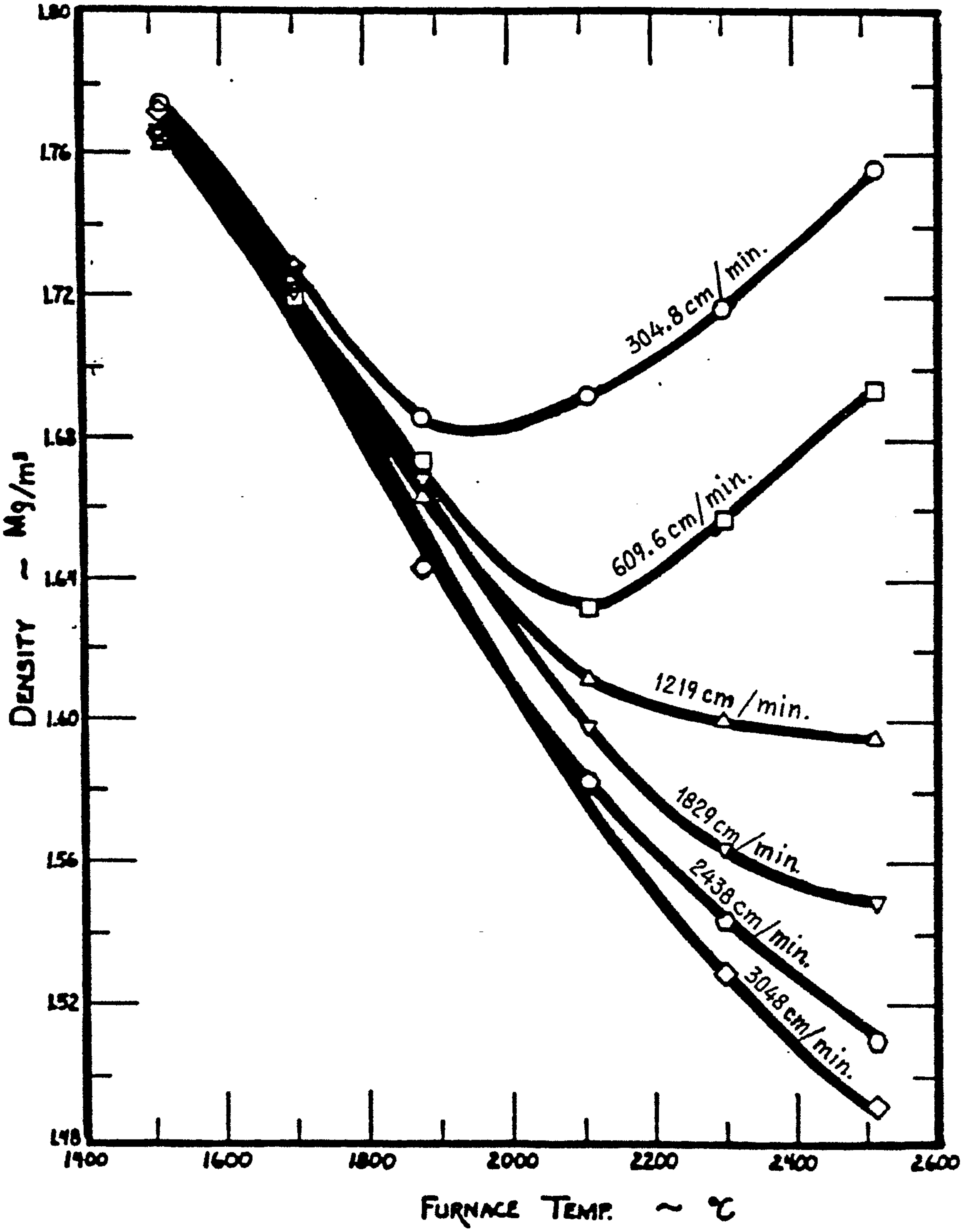
20
15
10
5
0
100
90
80
70
WT. PERCENT
WT. PERCENT
NITROGEN
OXYGEN
HYDROGEN
CARBON
100
300
500
700
900
1100
1300
1500
HEAT-TREAT TEMP. ~ °C

Fig-2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1.68
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1.60
1.56
1.52
1.48
1400
1600
1800
2000
2200
2400
2600
DENSITY ~ Mg/m³
FURNACE TEMP. ~ °C
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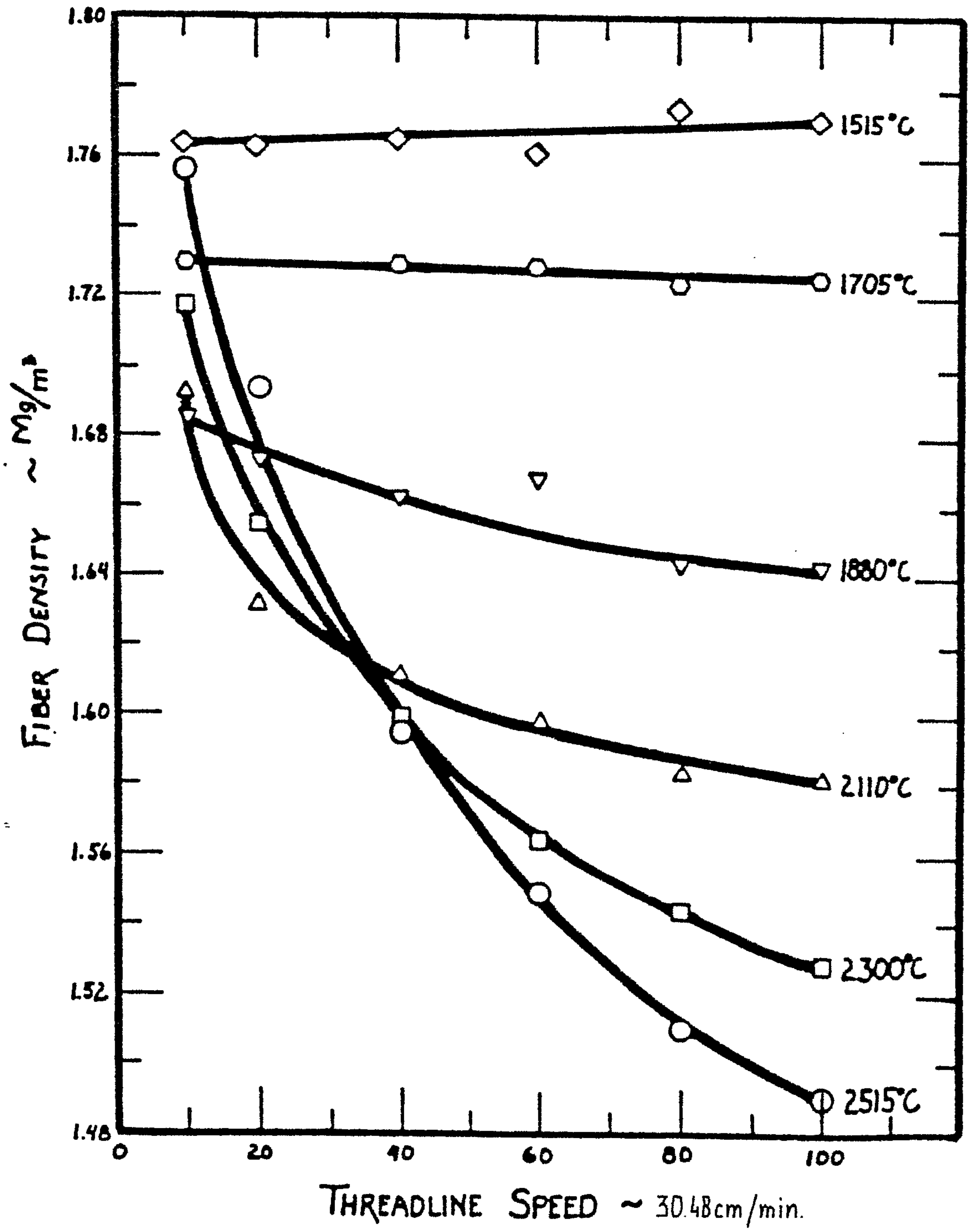
1219 cm/min.
1829 cm/min.
2438 cm/min.
3048 cm/min.

Fig-3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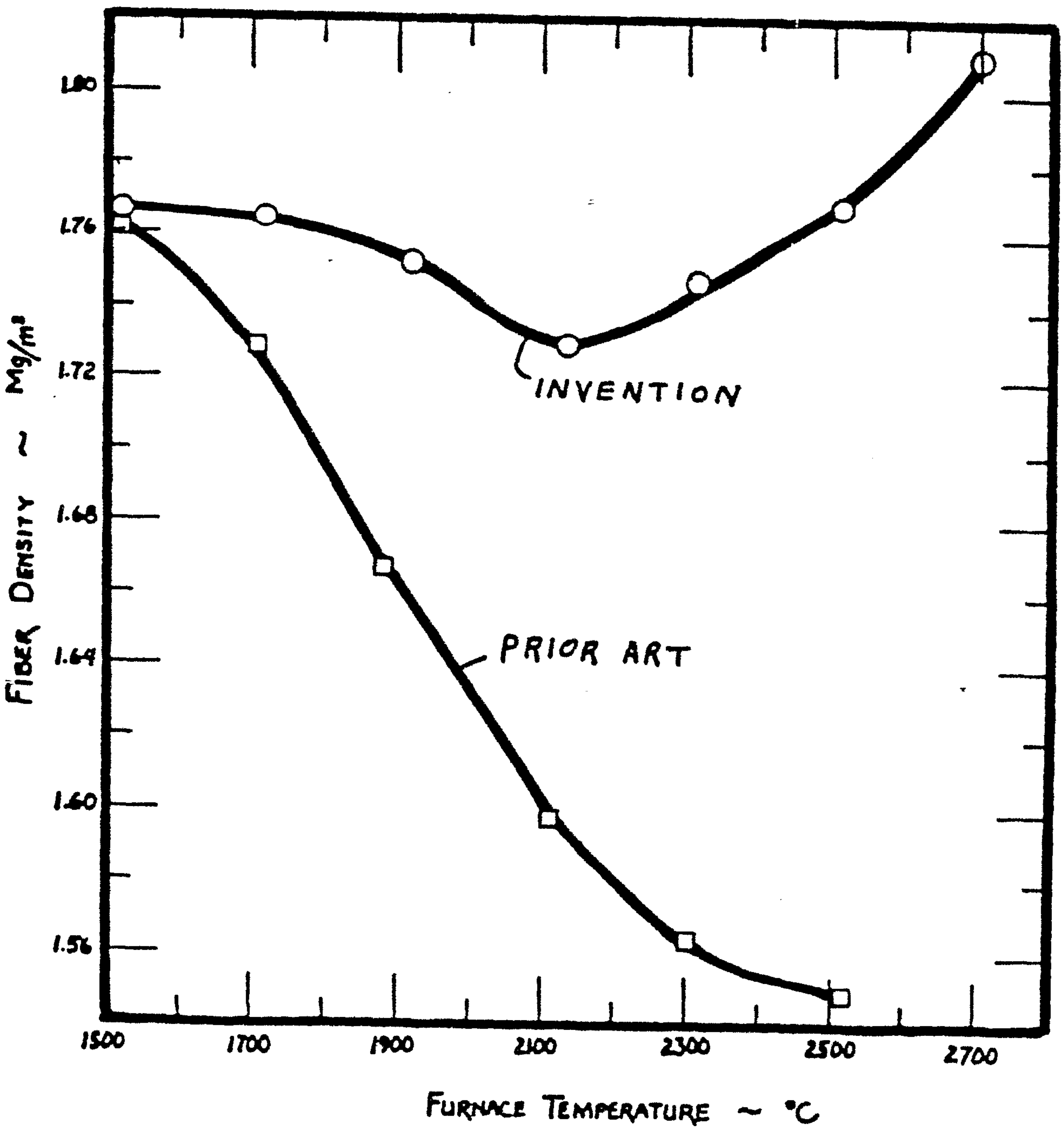
1.76
1.72
1.68
1.64
1.60
1.56
1.52
1.48
FIBER DENSITY ~ Mg/m³
0
20
40
60
80
100
THREADLINE SPEED ~ 30.48cm/min.
1515°C
1705°C
1880°C
2110°C
2300°C
2515°C

Fig-4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1.76
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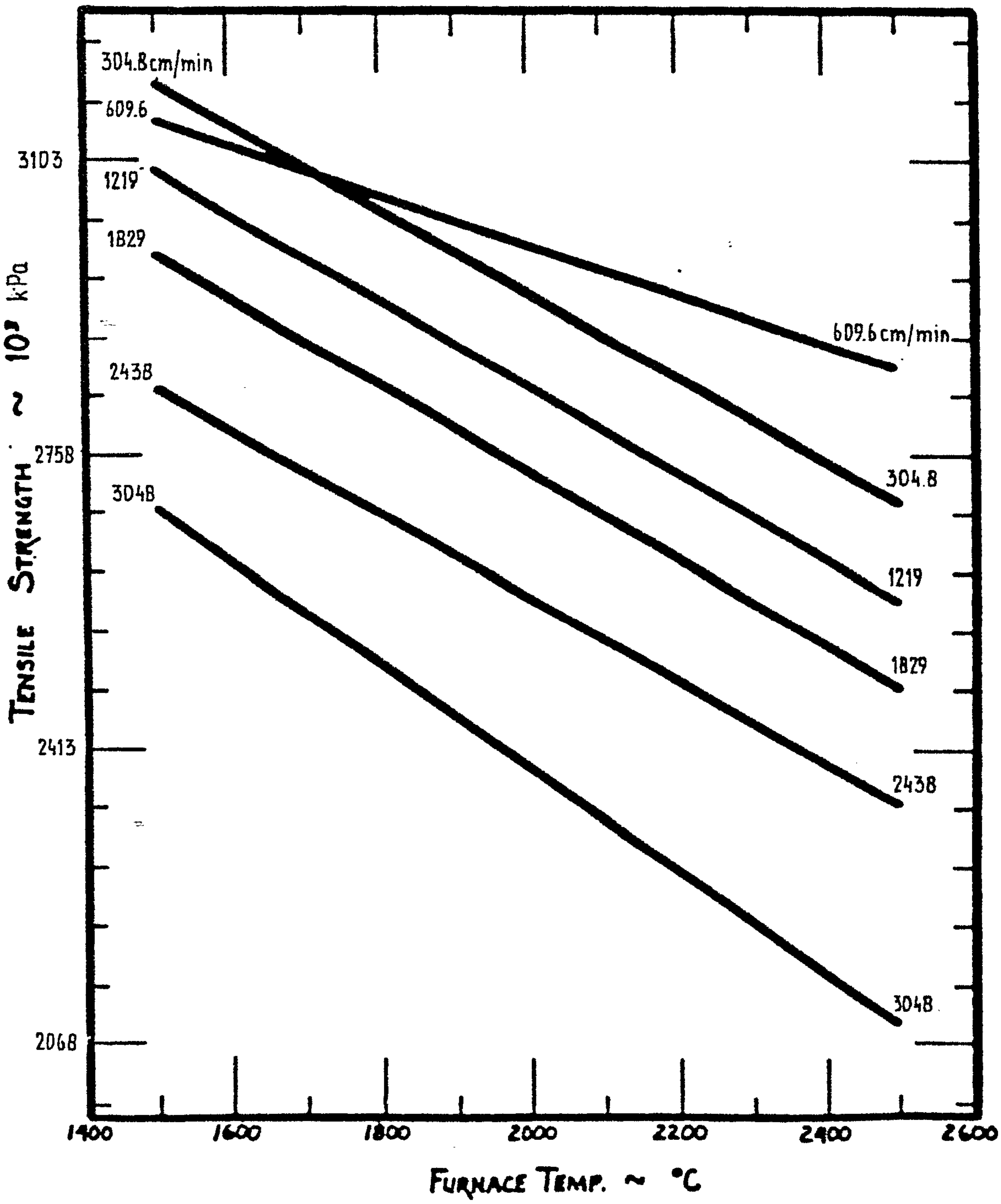
1500
1700
1900
2100
2300
2500
2700
INVENTION
PRIOR ART
FIBER DENSITY ~ Mg/m³
FURNACE TEMPERATURE ~ °C

Fig-5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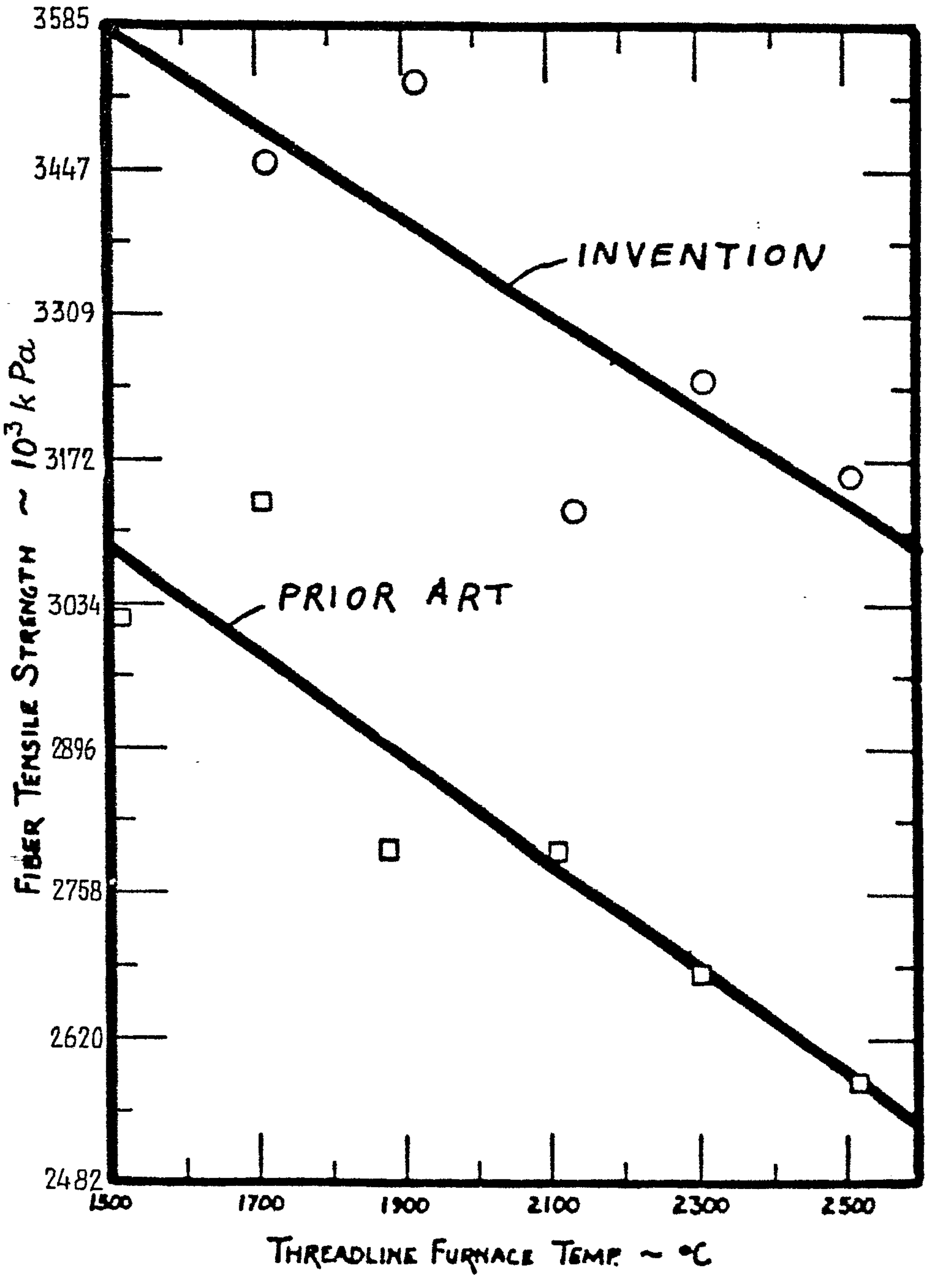
609.6
1219
1829
2438
3048
609.6cm/min
304.8
1219
1829
2438
3048
3103
2758
2413
2068
TENSILE STRENGTH ~ 10³ kPa
1400
1600
1800
2000
2200
2400
2600
FURNACE TEMP. ~ °C

fig-6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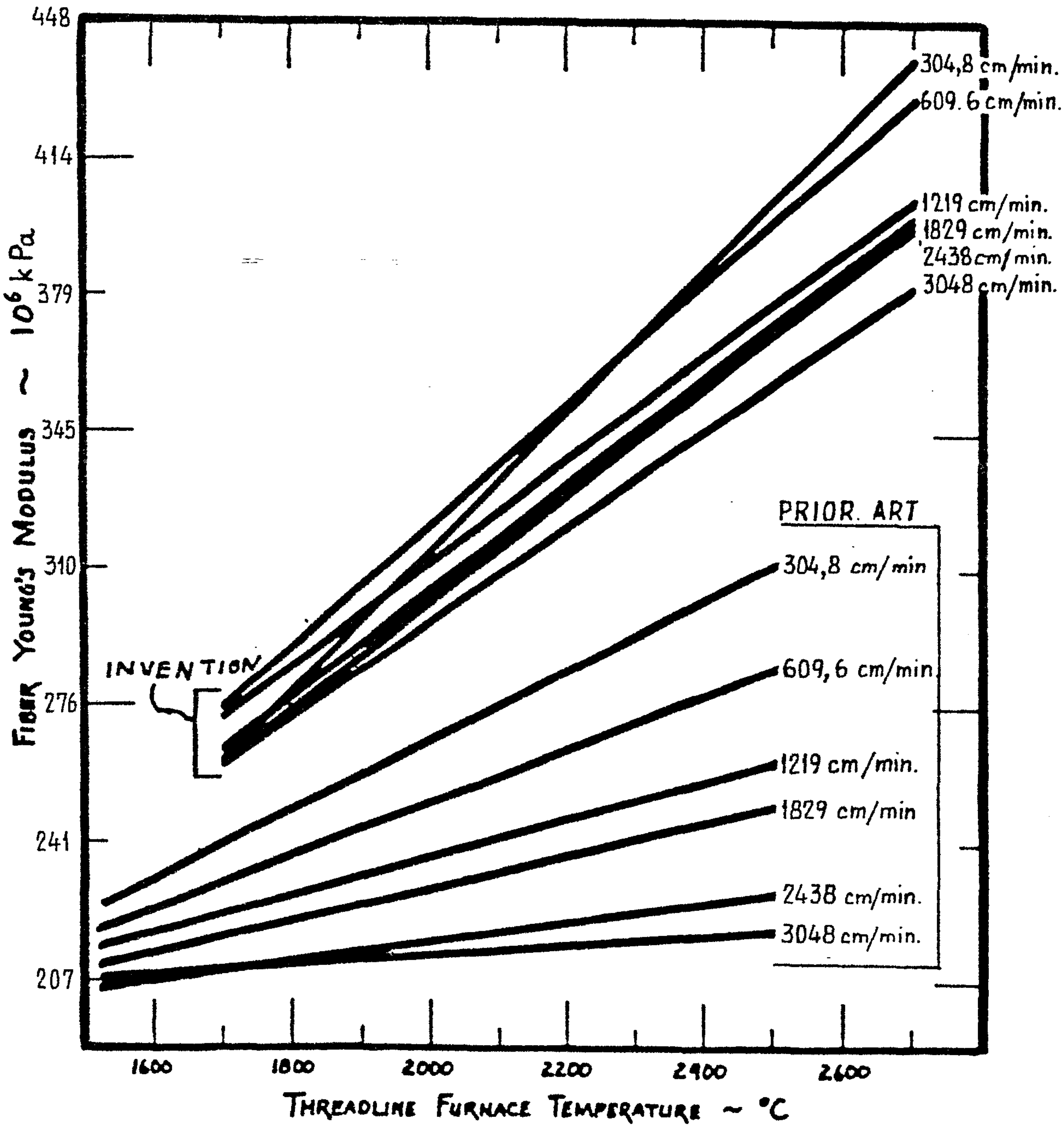
FIBER TENSILE STRENGTH ~ 10^3 k Pa
INVENTION
PRIOR ART
1500
1700
1900
2100
2300
2500
THREADLINE FURNACE TEMP. ~ °C

Fig-7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414
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345
310
276
241
207
FIBER YOUNG'S MODULUS ~ 10^6 kPa
1600
1800
2000
2200
2400
2600
THREADLINE FURNACE TEMPERATURE ~ °C
INVENTION
304,8 cm/min.
609.6 cm/min.
1219 cm/min.
1829 cm/min.
2438 cm/min.
3048 cm/min.
PRIOR. ART
304,8 cm/min
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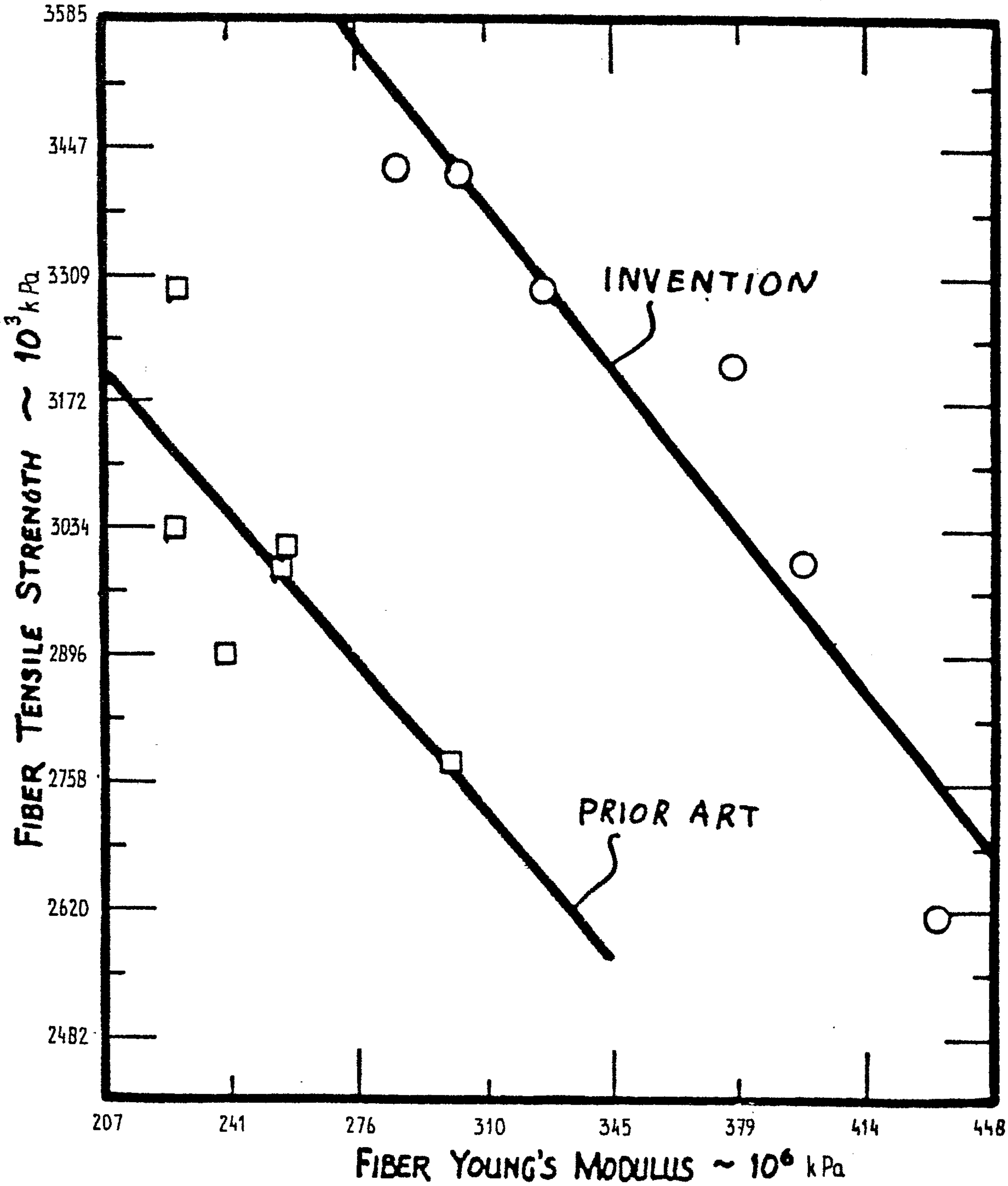
1219 cm/min.
1829 cm/min
2438 cm/min.
3048 cm/min.

Fig-8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FIBER TENSILE STRENGTH ~ 10³ kPa
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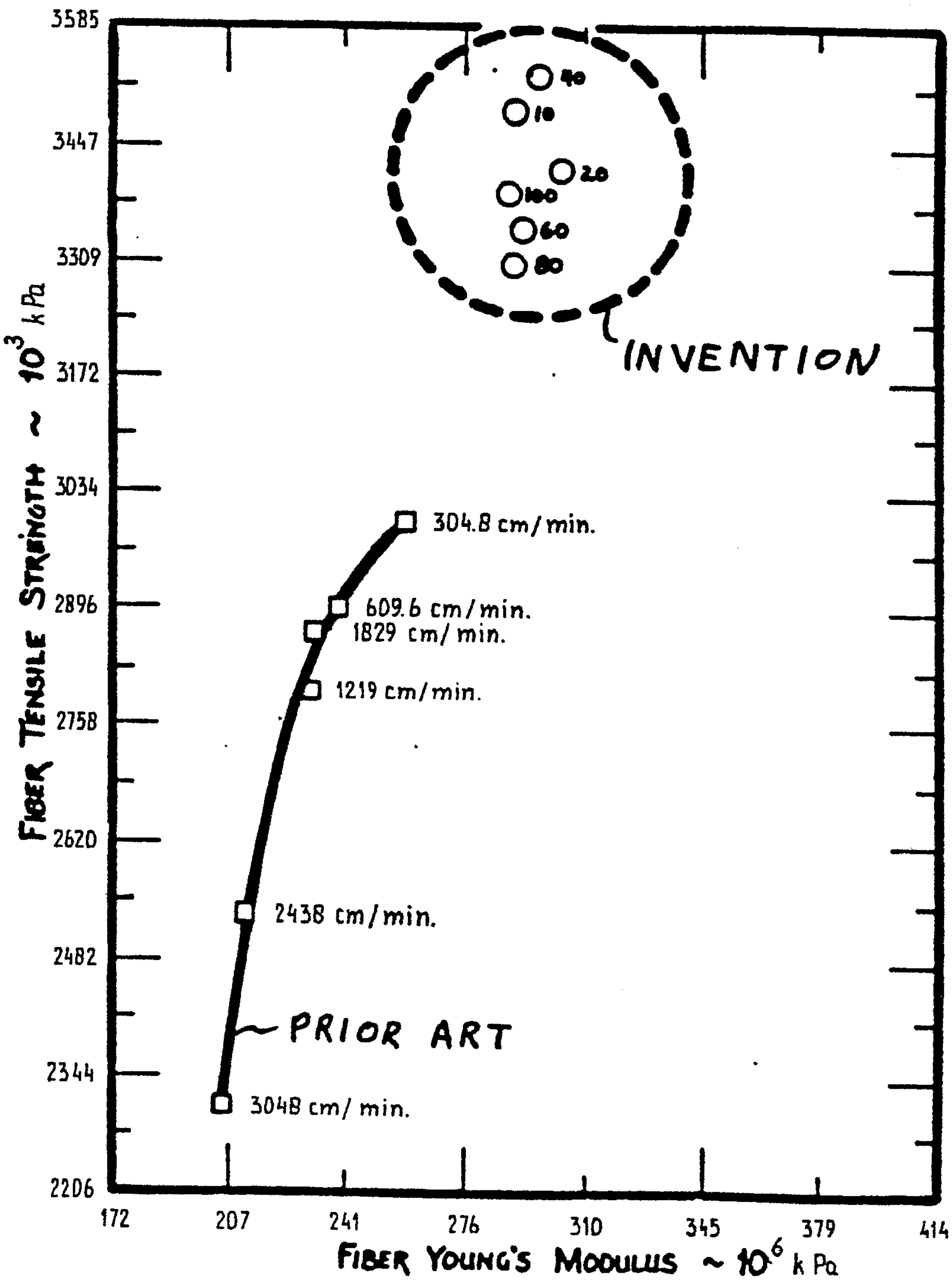
414
448
FIBER YOUNG'S MODULUS ~ 10⁶ kPa
INVENTION
PRIOR ART

fig-9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2344
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FIBER TENSILE STRENGTH ~ 10³ kPa
172
207
241
276
310
345
379
414
FIBER YOUNG'S MODULUS ~ 10⁶ kPa
40
10
20
100
60
80
INVENTION
304.8 cm/min.
609.6 cm/min.
1829 cm/min.
1219 cm/min.
2438 cm/min.
PRIOR ART
3048 cm/min.