United States Patent

Phillips

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[54] **CONTINUOUS CARBON FIBER TAPES**

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Nov. 6, 1969 Great Britain 54,452/69

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[51] **Int. Cl.** **D03d 15/00**

[58] **Field of Search** .... 117/161 ZB, 161 P, 161 LE, 117/161 LC, 228; 57/140 G; 161/87, 88, 90, 91, 92, 93; 139/383 R, 384 R, 420 R, 420 G; 28/75

[56] **References Cited**

UNITED STATES PATENTS

2,962,386	11/1960	Doll et al.	117/228
3,073,004	1/1963	Zeise	139/420
3,239,403	3/1966	Williams	117/228
3,444,120	5/1969	Boyes	117/161 ZB
3,494,888	2/1970	McElroy	117/161 ZB

FOREIGN PATENTS OR APPLICATIONS

790,216	2/1958	Great Britain	139/420 G

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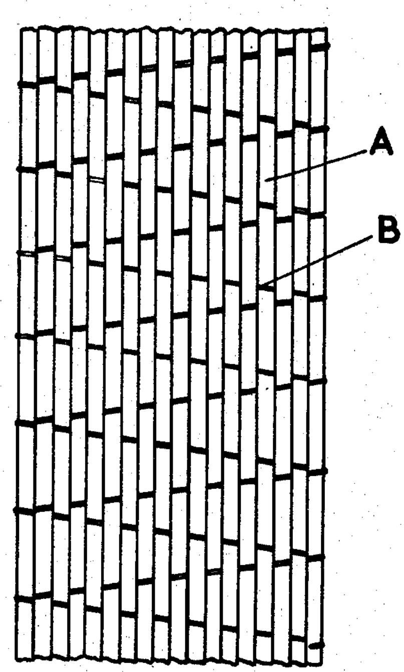
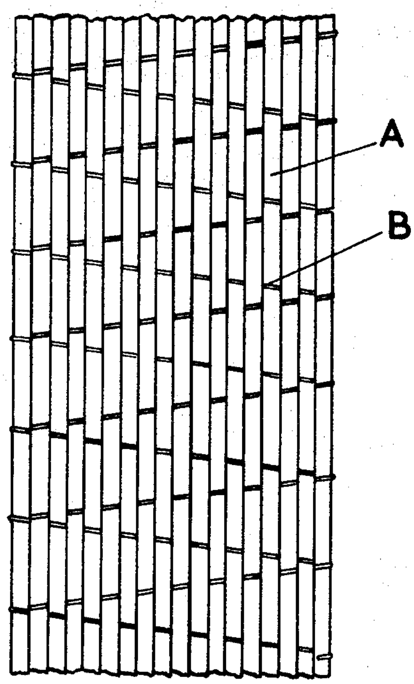
[57] **ABSTRACT**

Tape containing continuous high strength high modulus carbon fibers and optionally also glass fibers suitable for use as pre-impregnated tape in mechanical winding processes is disclosed wherein there is a light cross-weave of 1–10 filaments of fine glass fiber at a frequency of about 10–2 threads per inch.

10 Claims, 1 Drawing Figure

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CONTINUOUS CARBON FIBER TAPES

The present invention relates to tape containing unidirectional carbon fibers which may be resin impregnated and used to produced reinforced plastic articles by applying to or winding on a former followed by curing.

It is well known to produce composite shaped articles by winding a resin pre-impregnated tape upon a former or mandrel of a suitable shape and then to place the former and tape in a mould either without further addition of resin or after further resin has been impregnated into the tape. However, it has been discovered that the parallel alignment of the reinforcing fibers in the tape is not retained in the mould because in the early stages of cure the resin is liquid and under the influence of the hydrostatic pressure in the liquid resin the individual reinforcing fibers in the pre-impregnated tape are forced apart and the phenomenon known as barrelling takes place. This results in misalignment of the reinforcing fibers and may lead to failure to realize the full strength possible of the composite material.

Misalignment of fibers in carbon fiber reinforced articles can cause weakness because the relatively small extension at break of carbon fibers means that in a composite in which the fibers are not properly aligned individual fibers may fail before other fibers in a different orientation are taking an appreciable proportion of the load.

In accordance with the present invention, a tape containing unidirectional carbon fiber comprises a plurality of warp members, which include carbon fiber tows, and a continuous weft-thread woven through said warp members at a frequency of between about 10 and 2 threads per inch said weft thread being arranged to maintain the warp members parallel to and contiguous with one another.

Normally the warp members are not individual filaments but aggregations of individual filaments and conveniently a warp member is a tow of carbon fiber of about 10,000 ends or filaments although for particular purposes the number of ends or filaments in any given carbon fiber tow warp member may be any number down to about 500 as may be convenient.

The warp members may be entirely carbon tows or a proportion thereof may be replaced by bundles or tows of glass fiber and up to 90 percent by weight of the total warp may be bundles or tows of glass fiber.

Tows of carbon fiber and tows of glass fiber may alternate as warp members or a plurality of adjacent warp members may be of carbon fibers and/or a plurality of adjacent warp members may be of glass fiber so that the tape has a banded structure wherein the carbon and glass fiber are grouped together in the warp. In an extreme example a single tow of glass fiber or a single tow of carbon fibers may be interposed between two groups of fiber of the opposite type. For example if a tape containing both carbon fiber and glass fiber has to be trimmed at the edges it is more economical to have the edges to be trimmed off entirely of glass fiber because of the cost of carbon fiber, so long as this does not detract from the properties of the finished composite.

Conveniently the tows of glass fiber and tows of carbon fiber are substantially the same size so that the weave of the finally produced tape remains even. The sizes may, however, vary quite markedly if this does not spoil the evenness of the weave of the finally produced tape or permit misalignment of the carbon fibers in a finally produced composite such that an appreciable number of carbon fibers break under strain before substantially all the carbon fibers are loaded.

Preferably the unidirectional carbon fiber tows of the warp members are of high strength high modulus carbon fiber manufactured by one or more of the processes described in the specifications of U.K. Pat. Nos. 1,110,791, 1,148,874, 1,166,251, 1,166,252, 1,168,619, 1,180,441 and U.K. application No. 28881/66 now U.K. Pat. No. 1,193,263.

The carbon fiber tows of this invention include high strength high modulus carbon fiber produced by one or more of the processes described in U.S. Pat. No. 3,412,062.

In U.S. Pat. No. 3,412,062, there is described a method of making carbon fibers having a Young's modulus parallel to the fiber axis of not less than 16×10^6 pounds per square inch comprising the steps of oxidizing an organic polymer fiber by simultaneously heating the fiber in an oxidizing atmosphere at a temperature of from about 200° to 250°C for a time sufficient to permit substantially complete permeation of oxygen throughout the core of the fiber while the fiber is held under longitudinal tension, said tension being sufficient at least to limit shrinkage of the fibers during heating to not more than about 12 percent of the length of the fiber, and carbonizing the fiber by heating the oxidized fiber in a non-oxidizing atmosphere to a temperature of up to about at least 1,000°C. Preferably the organic polymer fiber is polyacrylonitrile.

It is to be noted that the term polyacrylonitrile fibers is used by those skilled in this art to include copolymers or terpolymers of acrylonitrile with other monomers e.g. methyl methacrylate or vinyl acetate, either alone or to which have been added polymers compatible with them for example phenolic resins or Friedel-Crafts condensates. It is in this sense that the term polyacrylonitrile fibers is used throughout said U.S. Pat. No. 3,412,062.

The high temperature carbonizing is performed under vacuum or in a non-oxidizing atmosphere such as hydrogen.

The preliminary low temperature oxidizing step which forms part of said method should not be of too short duration as the fibers are then left with a soft core and upon subsequent high temperature heat treatment holes are formed in the resulting fibers.

In a further embodiment according to said U.S. Pat. No. 3,412,062, a process of producing carbon fibers comprises initially heating fibers of polyacrylonitrile while held under tension in an oxidizing atmosphere at from 200°–250°C for sufficient time to permit substantially complete permeation of oxygen throughout the individual fibers and subsequent further heating of the fibers so formed to a carbonizing temperature of at least 1,000°C under non-oxidizing conditions.

The duration of the initial heating required will depend to a large extent on the diameter of the fibers concerned but for a temperature of 220°C complete oxygen permeation of the fibers takes place after heating for about 24 hours for 2½ denier fibers and after about 50 hours for 4½ denier fibers.

The fibers are tensioned so that longitudinal shrinkage which normally takes place during this initial heating is reduced, eliminated or is such as to cause the fibers to elongate.

Further improvements in the characteristics of the fibers produced are achieved if, subsequent to carbonizing to about 1,000°C the fibers are further heat treated to above 2,000°C in a non-oxidizing atmosphere.

The tensioning of fibers may also be maintained during the subsequent carbonizing and/or heat treatment.

For further details, please refer to the examples of said U.S. Pat. No. 3,412,062.

The weft is intended to prevent the phenomenon of barrelling described above and maintain the fibers in alignment and the material used is selected to be sufficiently strong to achieve this end although it must also be selected to be compatible with the unidirectional carbon fiber used as reinforcement, with the plastic to be reinforced, and with any additive thereto.

The weft thread may be of continuous carbon fiber but this is not in general successful. Advantageously the weft thread is glass fiber and it has been found that between **1** and **10** ends or filaments of fine glass fiber is preferred.

An embodiment of the invention is illustrated in the accompanying drawing in which A represents warp members which may be tows of carbon fiber or a mixture of tows of carbon fiber and tows of glass fiber as described above and B represents the continuous weft thread, which is woven at a frequency of between about 10 and 2 threads per inch and which is between 1 and 10 filaments of fine glass fiber. More particularly, as shown in said drawing, B represents the continuous weft thread, which is continuously woven throughout the length of said warp members and zigzaggedly crossing said warp members at an oblique angle at a frequency of between about 10 and 2 threads per inch.

The tape may be woven by the well known means of the weaving art and preferably prior to the weaving process the carbon fiber tows are treated by the process of dressing described in U.K. Pat. Application Nos. 52,653/67 and 4,711/68, now issued as a single U.K. Pat. No. 1,195,219 which discloses a dressing for facilitating the handling and processing of carbon fibers comprising a dilute solution of not more than 35 percent by weight of resin in a volatile organic non-aqueous solvent.

The resin may comprise an epoxy, phenolic, Friedel-Crafts, polyimide or polyester resin.

Suitable solvents are acetone, ethyl acetate, methyl ethyl ketone and chlorinated hydrocarbons such as ethylene dichloride and 1.2 dichloroethane.

In one example it was found that a solution of 1–5 percent by weight of epoxy resin in acetone formed a satisfactory dressing.

Examples of epoxy resins which have been used are Araldite (Registered Trade Mark) LY 558 and Shell (Registered Trade Mark) Epikote 828. Other epoxy resins may be used, it being desirable that they should have a high viscosity and that brittle resins be avoided. Low viscosity resins of the cycloaliphatic type, such as a cyclopentadiene based resin, may be blended with other more viscous resins in order to obtain the overall required viscosity.

It a further example it was found that a solution of 5–20 percent by weight of polyester resin in methyl ethyl ketone formed a satisfactory dressing.

It was also found that either a hot or cold setting polyester resin was satisfactory, e.g. Bakelite (Registered Trade Mark) S.R. 17449 resin an unsaturated polyester made from a glycol, a dicarboxylic acid and maleic anhydride has been found satisfactory.

Also, according to the present invention a process for rendering carbon fibers readily handleable comprises impregnating the fibers with a dressing comprising a weak solution of resin, such as an epoxy, phenolic, Friedel-Crafts, polyimide or polyester resin in a volatile organic non-aqueous solvent, and allowing the solvent to evaporate, evaporation of the solvent leaving the carbon fibers in a close knit handleable form.

It is to be noted that the term Friedel-Crafts resin means a resin formed from an aromatic compound with an aromatic linking agent which has two chloromethyl or methoxymethyl groups attached to an aromatic nucleus by means of a polycondensation reaction involving the nuclear hydrogen atoms and may be aided by the presence of a small amount of Friedel-Craft type catalyst such as stannic chloride.

Once the tape is obtained it may then be impregnated with an appropriate resin and converted to a pre-impregnated tape suitable for use as described above.

Such a process lends itself to the continuous production of thin carbon fiber reinforced composite material. In an example of such a process a continuous supply of carbon fibers, as from a process in which carbon fibers are produced continuously, are drawn in turn through a bath containing said dressing, a drying region in which surplus dressing drains from the fiber and that remaining on the fibers is dried, a second bath containing a heat catalyzed polyester resin in which the fibers are immersed and between a pair of rollers between which the composite material comprising the fibers, dressing which has been softened by the polyester resin and the resin are flattened to a tape like form. The resin content of the tape may subsequently be cured by the application of heat.

In one example a non-continuous process for producing a plastics composite material 80 grams of 10,00 filament tow carbon fibers of 7 microns diameter of the type disclosed in British Pat. No. 1,110,791 and having an ultimate tensile strength of 280×10^3 lg/sq in. and a Young's modulus of 55×10^6 lb/sq in. were supported in a glass fiber cloth cradle or sling and dipped into a tank containing 3 liters of polyester resin solution comprising 1 part by weight of Bakelite (Registered Trade Mark) S.R. 17,449 polyester resin and 4 parts by weight of methyl ethyl ketone.

After immersion for 30 seconds, the cradle supporting the fibers was removed from the solution and the surplus solution allowed to drain off. The fibers, with residual dressing adhering to them, were then suspended vertically for 2 hours at room temperature until dry. The resulting clumped fibers were then incorporated as a reinforcement in a matrix comprising 100 parts by weight S.R. 17,449 polyester resin, 2 parts peroxide catalyst and 2 parts cobalt naphthenate, the fibers comprising approximately 40 percent by volume of the resulting composite formed when curing of the resin was complete.

The tape of the present invention may be used advantageously when it is desired to tension the unidirection carbon fibers while the moulding process is being carried out. This has the advantage that individual carbon fibers are aligned substantially parallel during the curing process and also helps to ensure that the load of the composite finally produced is evenly distributed among the carbon fibers. This is important in view of the relatively small extension at break of carbon fibers which means that in a composite in which fibers are not properly aligned individual fibers may fail before other fibers in a different fibers in a different orientation are taking an appreciable share of the load.

I claim:

1. A pre-impregnation tape comprising a plurality of warp members parallel to and contiguous with one another selected from the group consisting of tow of glass fiber and tow of unidirectional carbon fibers, at least 10 percent by weight of said warp members consisting of said tow of carbon fibers, and a continuous weft thread continuously woven through said warp members at a frequency of between about 10 and 2 threads per inch, said weft thread being selected from the group consisting of continuous glass fiber and continuous carbon fiber.

2. A tape as claimed in claim 1 wherein the warp members are composed entirely of carbon fiber tow.

3. A tape as claimed in claim 1 wherein the carbon fiber tow include high modulus carbon fiber having a Young's modulus parallel to the fiber axis of not less than 16×10^6 pounds per square inch.

4. A tape as claimed in claim 1 wherein the weft thread comprises between 1 and 10 filaments of glass fiber.

5. A tape as claimed in claim 1 wherein the carbon fiber tows have a surface dressing comprising a resin selected from the group consisting of epoxy, phenolic, Friedel-Crafts, polyimide and polyester resin.

6. A tape as claimed in claim 1 and impregnated with resin.

7. A pre-impregnation tape comprising a plurality of warp members parallel to and contiguous with one another selected from the group consisting of tow of glass fiber and tow of unidirectional carbon fibers, at least 10 percent by weight of said warp members consisting of said tow of carbon fibers, and a continuous weft thread continuously woven throughout the length of said warp members and zigzaggedly crossing said warp members at an oblique angle at a frequency of between about 10 and 2 threads per inch, said weft thread being selected from the group consisting of continuous glass fiber and continuous carbon fiber.

8. A method of preparing a cured tape comprising immersing carbon fiber in a dressing solution of not more than 35 percent by weight of resin in a volatile organic non-aqueous solvent and drying to remove said solvent in order to provide a dressing on said carbon fiber, preparing a plurality of warp members from tow of glass fiber and tow of unidirectional carbon fiber comprising said dressed carbon fiber, at least 10 percent by weight of said warp members consisting of tow of carbon fibers, and weaving a continuous weft thread through said warp members and continuously throughout the length thereof at a frequency of between about

10 and about 2 threads per inch whereby said warp members are maintained parallel to and contiguous with one another during curing of said tape, said weft thread being selected from the group consisting of continuous glass fiber and continuous carbon fiber, and curing said tape.

9. A method as claimed in claim **8** wherein the solvent is selected from the group consisting of acetone, ethyl acetate,

methyl ethyl ketone, ethylene dichloride and 1,2-dichloroethane.

10. A method as claimed in claim **8** wherein the dressing solution comprises a 1–5 percent by weight of epoxy resin in acetone.

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