

[54] TREATMENT OF GRAPHITE FIBERS 3,687,701 8/1972 Reinhart 117/72 X
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[57] ABSTRACT

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156/242, 180; 264/137

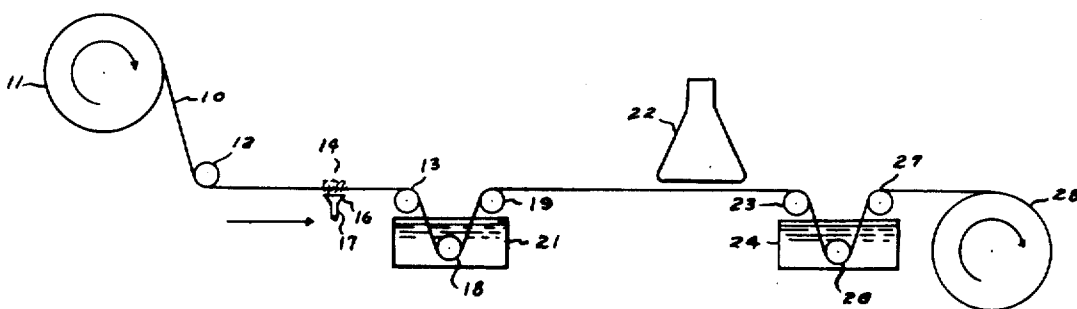
A method of fabricating a composite reinforced with graphite yarn that comprises heating the yarn in an oxidizing atmosphere and then coating the yarn with a thermoplastic polymer. Thereafter, the treated yarn is coated with a thermosetting resin prior to fabrication of composites having greatly enhanced interlaminar shear strength.

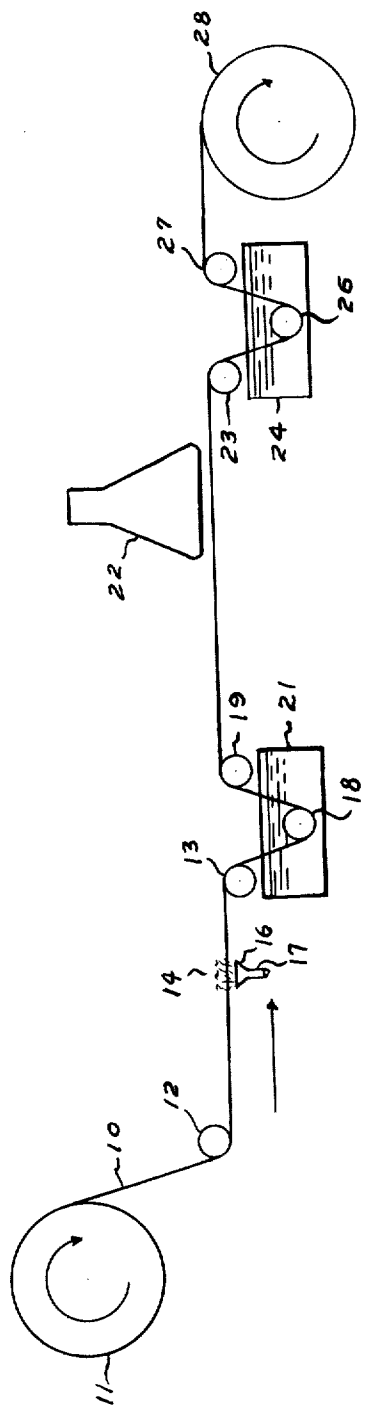
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11 Claims, 1 Drawing Figure





TREATMENT OF GRAPHITE FIBERS

FIELD OF THE INVENTION

This invention relates to the treatment of high modulus graphite fibers. In one aspect it relates to composites which include the treated fibers. In another aspect it relates to a method for fabricating composites.

BACKGROUND OF THE INVENTION

Graphite fibers and yarns derived from a variety of precursors are described in the literature. Examples of precursors that have been used include fibers from cellulosic materials, such as cotton, flax, sisal, and viscose rayon, acrylonitrile polymers, polybenzimidazoles, polyamides, polyimides and the like. The graphite fibers are often prepared by initially heating the precursory fibers in an oxidizing atmosphere at a temperature of about 450° to 575°F followed by carbonization and graphitization steps carried out in an inert atmosphere at elevated temperature. While the properties of the graphite fibers depend to a substantial degree upon the particular precursory fiber employed, they generally have a high tensile strength and high modulus of elasticity.

The above-mentioned properties of graphite fibers render them particularly suitable for use as reinforcing materials in the fabrication of composites. Composites prepared by incorporating reinforcing materials in various matrices, particularly thermosetting resins, have in recent years been utilized in many applications, especially in the construction of aerospace components, such as the leading edges of high speed aircraft, nose cones, rocket engine components, and the like. While graphite fibers possessing high tensile strength and high modulus properties are important in providing satisfactory composites, it is equally important that a good bond exists between the fibers and matrix. Otherwise, the composite will have a low interlaminar shear strength that could result in composite failure.

It is an object of this invention, therefore, to provide graphite fibers which possess improved bonding characteristics when incorporated in thermosetting resins.

Another object of the invention is to provide a method for treating graphite fibers so as to improve their adherence to thermosetting resins.

A further object of the invention is to provide composites having an improved interlaminar shear strength.

Still another object of the invention is to provide a method for fabricating composites having an improved interlaminar shear strength.

Other objects and advantages of the invention will become apparent to those skilled in the art upon consideration of the accompanying disclosure and the drawing which is a schematic illustration of apparatus that can be used in practicing the method of this invention.

SUMMARY OF THE INVENTION

Broadly speaking, the present invention resides in a method for treating graphite fibers so as to improve their adherence to thermosetting resins. The method for improving the fiber bonding characteristics comprises the steps of heating the graphite fibers, generally in the form of a yarn, under oxidizing conditions; coating the heated fibers with a solution of a thermoplastic polymer; and heating the coated fibers so as to evaporate solvent therefrom.

In a more specific embodiment of the invention the fibers, treated as described above, are immersed in a solution of a thermosetting resin so as to form prepregged fibers which are then placed in a form or shape appropriate for their intended use. For example, the fibers can be cut to a desired length or they can be wound on a mandrel preparatory to forming a sheet or tape. After precuring the thermosetting resin, the resulting B-staged material is arranged in a mold or press wherein it is heated under pressure to affect a cure. Thereafter, a cured product having a desired configuration and structure, e.g., a laminate, is recovered.

Reference is now made to the drawing which illustrates schematically apparatus suitable for carrying out the method of this invention. As shown in the drawing, a graphite fiber or yarn 10 is pulled from "take-off" reel 11. Any graphite fiber or yarn, such as those mentioned hereinbefore, can be employed. From reel 11 the graphite yarn passes under roller 12 and over roller 13 which are so positioned that the yarn moves substantially in a horizontal plane. While moving from roller 12 to roller 13, the yarn passes through an oxidation zone which, as illustrated, is an oxidizing flame (non-luminous) 14 emanating from flared nozzle 16 of gas burner 17. Any hydrocarbon gas mixed with air can be used to produce the oxidizing flame, but it is generally preferred to use propane or butane or mixtures thereof. In passing through the oxidation zone, the graphite yarn is subjected to a temperature ranging from about 1000° to 4500°F. The speed at which the yarn moves is controlled so that it is present in the oxidation zone and thereby exposed to the high temperature for a period ranging from about 0.10 to 12 seconds. It is to be understood that the higher the temperature the shorter the time period and vice versa. Although it is generally preferred to utilize an oxidizing flame, it is within the scope of the invention to pass the yarn through an induction furnace susceptor in an oxygen-containing atmosphere such as air. When utilizing such a furnace, the length of the susceptor and its temperature are such that the yarn is maintained at a temperature in the above-mentioned range for the indicated period of time. Another type of heating means that can be employed, particularly at lower temperatures, is a tube furnace.

After passing over roller 13, the thermally treated yarn is guided by rollers 18 and 19 through tank 21 containing a bath of a solution of a thermoplastic polymer. While thermoplastic polymers in general can be employed, it is usually preferred to use a polyhydroxy ether, polyphenylene oxide, polysulfone, polyarylsulfone, polycarbonate or polyamide. Suitable solvents for such polymers are well known in the art and include acetone, methyl ethyl ketone, Carbitol (diethylene glycol ethyl ether), butyl Carbitol (diethylene glycol butyl ether), Cellosolve (glycol ethyl ether), Cellosolve acetate (hydroxyethyl acetate), butyl Cellosolve (glycol butyl ether), dimethylformamide, dimethylsulfoxide, dimethylacetamide, dioxane, ethoxy triglycol, mesityl oxide, tetrahydrofuran, benzene, toluene, xylenes, butanol, tetrachloroethane, methylene chloride, ethylene chloride, and the like.

The solution in tank 21 contains about 0.5 to 25, preferably 0.75 to 12, weight percent of the thermoplastic polymer, based on the total weight of the solution. The amount of polymer coated on the graphite yarn depends upon the polymer concentration of the

bath and the period of time during which the yarn is immersed in the bath. The yarn-solution contact time in turn depends upon the speed at which the yarn moves through the bath and the length of the path that the yarn travels in the bath. Since the speed at which the yarn moves is determined by the time during which it is in contact with oxidizing flame 14, in the final analysis the amount of polymer coating is controlled by varying the polymer concentration and the length of the path of travel in the bath. In general, these variables are so controlled that the amount of thermoplastic polymer coating on the graphite yarn is in the range of about 5 to 30 percent by weight of the yarn.

After leaving tank 21, the yarn is passed through a heating zone wherein the solvent is evaporated. As depicted in the drawing, an infrared lamp 22, positioned a short distance above the coated fiber, provides a source of heat for the heating zone. However, it will be apparent to those skilled in the art that other heating means, e.g., a hot air gun, can be utilized. The temperature of the heating zone is sufficient to cause evaporation of solvent contained in the thermoplastic polymer coating, and will necessarily vary with the particular solvent used in preparing the polymeric coating bath in tank 21. However, the temperature is usually no greater than about 180°F. Furthermore, when using solvents having boiling points below room temperature, the heating zone may be omitted, the solvent being permitted to evaporate under ambient conditions.

After traveling through the heating zone, the graphite yarn, now coated with a dried thermoplastic polymer, passes over roller 23 into tank 24. Contained in tank 24 is a solution of a thermosetting resin which will subsequently function as the matrix in fabricating composites. Any suitable thermosetting resin, of which there are many described in the literature, can be utilized. Examples of such suitable resins or polymers include polyepoxides, such as the condensation products of bisphenol A (4,4'-isopropylidene phenol) and epichlorohydrin; phenolic resins prepared by reaction of phenol and formaldehyde; polyimide resins formed by the condensation of an aromatic tetrabasic acid anhydride and an aromatic diamine; polybenzimidazole resins formed by the reaction of an aromatic tetraamine with an aromatic diacid; pyrrone resins formed by the condensation of an aromatic dianhydride and an aromatic tetraamine; and the like. Solvents for a particular thermosetting resin are well known and include alcohols such as propanol and butanol, ketones such as acetone and methyl ethyl ketone, dimethylformamide, dimethylsulfoxide, N-methylpyrrolidone, dimethylacetamide, and the like. The solution in tank 24 contains in the range of about 30 to 80 percent by weight of the thermosetting resin.

The coated yarn is guided through tank 24 containing the thermosetting resin solution by means of rollers 26 and 27. In its passage through the solution, the coated yarn picks up in the range of about 25 to 60 weight percent of the resin, based upon the weight of the coated yarn. As in the case of the thermoplastic polymer coating operation, the amount of thermosetting resin "pick up" is controlled by varying the resin concentration and the length of the path of travel in the resin solution. Thus, these variables are so adjusted that the amount of resin deposited on the coated yarn is in the aforementioned range.

After leaving tank 24, the graphite yarn, coated with successive layers of a thermoplastic polymer and a thermosetting resin, is wound onto "take-up" mandrel or drum 28. The yarn is wound on the mandrel under tension with filaments parallel to each other and in a single layer. The mandrel is rotated at a speed such that the yarn will move through flame 14 at a desired rate. After completion of the winding operation, solvent is allowed to evaporate from the prepreg yarn. This can be accomplished by exposing the yarn to the atmosphere at room temperature for an extended period of time, e.g., for about 8 to 24 hours, or until the yarn is slightly tacky to non-tacky. It is also within the scope of the invention to heat the mandrel, as with an internal heater, so as to evaporate the solvent. When the drying method is used, the prepreg yarn is usually heated at a temperature ranging from about 100° to 150°F for a period of about 15 minutes to 1 hour.

Upon completion of the drying step, the prepreg yarn is slit from the mandrel as a sheet. The sheet can then, if desired, be cut to form a plurality of plies of tape, or it can be separated into multiple strands. The prepreg yarn in the form of tape or strands is then cured under pressure to form a composite of a desired shape. For example, in fabricating a laminate, a plurality of plies of tape are stacked in a press or mold and heated to a temperature in the range of about 175° to 450°F under a pressure of about 100 to 1000 psi for a period of about 1 to 8 hours. During the curing operation any residual solvent that may be present is released from the press or mold. After cooling, generally while under pressure, the laminate is removed from the press or mold. The edges of the laminate are then trimmed so as to provide a smooth uniform product. Subsequent to the curing operation, it is often desirable to postcure the laminate by heating it in the absence of oxygen to an elevated temperature over an extended period of time, e.g., to a temperature ranging from 300° to 750°F over a period of from about 12 to 72 hours. Thus, the postcuring can be conducted in a furnace in the presence of an inert gas, such as nitrogen, argon or helium. It is to be understood that the actual curing procedure to be followed will depend upon the particular thermosetting resin employed. In many instances a supplier of resins recommends curing conditions that should be used.

A more complete understanding of the invention can be obtained by referring to the following illustrative examples which are not intended, however, to be unduly limitative of the invention.

EXAMPLE I

A series of runs was conducted in which a graphite yarn was treated in accordance with the method of this invention after which the treated yarn was coated with a thermosetting resin and used in the fabrication of laminates. Apparatus similar to that shown in the drawing was utilized in carrying out the runs.

In carrying out the runs, a graphite yarn derived from a cellulosic precursor was pulled through the nonluminous or oxidizing portion of a propane-generated flame. The graphite yarn was a product of Union Carbide sold under the trademark Thornel 50. The yarn was sized with polyvinyl alcohol and had a modulus of elasticity of 50×10^6 psi. The temperature of the flame was about 4000°F, and the width of the flame was about 1 inch. The yarn was pulled at the rate of 4 feet

per minute so that the yarn was in contact with the flame for about 1.25 seconds. Thereafter, the heated yarn was passed into and through a bath of a solution of a thermoplastic polymer. After emerging from the bath, the yarn coated with the thermoplastic polymer, was passed under an infrared lamp, thereby causing evaporation of solvent. The coated yarn was next pulled through a bath of a solution containing 60 weight percent of a thermosetting resin. The thermosetting resin utilized was an epoxy resin, a product of Union Carbide identified by the symbol ERL 2256, composed of a mixture of a diglycidylether of biphenol A diluted with 37.5 weight percent bis 2,3-epoxycyclopentyl ether and containing as the hardener a mixture of m-phenylene diamine and dimethylaniline. Upon emergence from this bath, the yarn coated with successive layers of a thermoplastic polymer and the thermosetting resin was wound on a mandrel to form a monolayer of a prepreg tape.

After exposure overnight to the atmosphere at room

temperature, solvent had evaporated, leaving a slightly tacky prepreg tape. The tape was then slit and stripped from the mandrel and cut into individual pieces corresponding to mold dimensions ($2\frac{1}{4} \times 2\frac{1}{4}$ inches). In each run 10 plies of the tape were stacked in a steel mold and molded according to the recommendations of the supplier of the thermosetting resin. Thus, the mold was first heated at 180°F for 2 hours followed by heating at 300°F for 4 hours. The mold was cooled to room temperature between the heating periods, and was maintained at a pressure of 100 psi during the period. The laminate was removed from the mold and tested to determine its flexural properties and interlaminar shear strength. Control runs were also carried out in which the graphite yarn was merely passed through the thermosetting resin solution prior to fabrication of laminates. The composition of the solutions of thermoplastic polymers and the results of the tests are shown below in Table I.

TABLE I

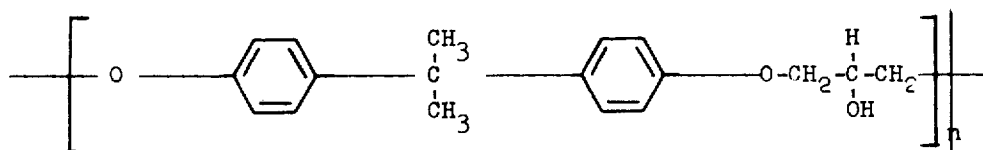
Run No.	Thermoplastic Polymer Solution	Volume % Yarn ⁽¹⁾	Flexural Modulus, $\times 10^6$, psi ⁽²⁾	Flexural Strength, $\times 10^3$, psi ⁽²⁾	Interlaminar Shear Strength, $\times 10^3$, psi ⁽²⁾
1	Control	66.1	19.8	110.7	3.8
2	Control	64.7	20.6	110.2	3.8
3	0.91 wt % polyhydroxy ether (PHE) in Cellosolve ⁽³⁾	64.5	19.3	127.1	7.1
4	0.80 wt % PHE in Cellosolve acetate	64.4	19.5	110.6	6.9
5	3.45 wt % PHE in Cellosolve	64.3	19.2	104.7	6.2
6	3.3 wt % PHE in Cellosolve acetate	62.2	19.0	101.6	6.4
7	11.4 wt % polyphenylene oxide (PPO) ⁽⁴⁾ in benzene	61.7	19.6	99.3	6.8
8	2.3 wt % PPO in benzene	62.0	20.0	111.2	7.5

(1) Volume % yarn was determined by a resin dissolution technique devised by Kuhbender "Determining Fiber Content of Graphite Yarn-Epoxy Resin Composites", University of Dayton Technical Memorandum No. UDRI-TM-66-103 (Jan. 1966).

(2) Flexural modulus and strength and interlaminar shear strength were determined, using the procedures of the Federal Test Specification L-P406b as a general guide. Flexural specimens were tested with a span to depth ratio of 20 to 1. Interlaminar shear specimens were tested at a span to depth ratio of 4 to 1.

(3) A product of Union Carbide having the following structure formula:

Table I—Continued



in which n has a value such that the polymer has a molecular weight of about 35,000.

- (4) A product of General Electric designated as poly(2,6-diphenyl-1,4-phenylene oxide).

EXAMPLE II

Another series of runs was carried out as described in Example I except that the graphite yarn used (Thornel 50) was water sized. The compositions of the thermoplastic solutions and the results of the runs are set forth below in Table II.

TABLE II

Run No.	Thermoplastic Polymer Solution	Volume % Yarn	Flexural Modulus, $\times 10^2$, psi	Flexural Strength $\times 10^3$, psi	Interlaminar Shear Strength, $\times 10^3$, psi
9	Control	64.6	18.2	109.6	3.8
10	0.91 wt % PHE in Cellosolve	65.2	19.6	100.1	5.0
11	2.3 wt % PPO in benzene	57.0	18.5	90.7	7.7

EXAMPLE III

Two runs were carried out as described in Example I except that the graphite yarn used (Thornel 80) had a modulus of elasticity of 80×10^6 psi. The yarn was sized with polyvinyl alcohol. The composition of the thermoplastic solution and the results of the runs are recorded below in Table III.

TABLE III

Run No.	Thermoplastic Polymer Solution	Volume % Yarn	Flexural Modulus $\times 10^6$, psi	Flexural Strength $\times 10^3$, psi	Interlaminar Shear Strength, $\times 10^3$, psi
12	Control	60	28.0	125.0	2.8
13	2 wt % PHE In 37.5% Cellosolve acetate and 62.5% methyl ethyl ketone	59.3	28.7	121.0	6.3

EXAMPLE IV

Other runs were carried out according to the procedure of this invention as described in Example I except that in certain runs the heating step was omitted and in other runs the step of applying the thermoplastic polymer coating was omitted. The results obtained demonstrated that no beneficial effects resulted from the use of only one of the steps. In other words it was found that both of the steps are required in order to improve the interlaminar shear strength of the composites.

From the data shown in the foregoing examples, it is seen that the method of this invention makes it possible to fabricate composites having interlaminar shear strengths that are from 2 to 3 times greater than those

prepared with untreated high modulus graphite fibers.

Modifications of the present invention will become apparent to those skilled in the art after considering the foregoing disclosure. Such modifications clearly come within the spirit and scope of the invention.

I claim:

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1. A method for treating graphite yarn which comprises heating the yarn in air at a temperature in the range of 1000° to 4500°F for a period ranging from about 0.10 to 12 seconds; passing the heated yarn through a solution of a thermoplastic polymer, thereby coating the yarn with the polymer; and evaporating solvent from the coating on the graphite yarn.

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2. A method according to claim 1 in which the yarn is passed through an oxidizing gas flame.

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3. The method according to claim 2 in which the gas flame is a propane-generated flame.

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4. The method according to claim 1 in which the solution contains in the range of about 0.5 to 25 weight percent of thermoplastic polymer.

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5. The method according to claim 4 in which the amount of thermoplastic polymer coated on the graphite yarn is in the range of about 5 to 30 percent by weight of the yarn.

6. The method according to claim 5 in which the thermoplastic polymer is selected from the group consisting of a polyhydroxy ether, a polyphenylene oxide,

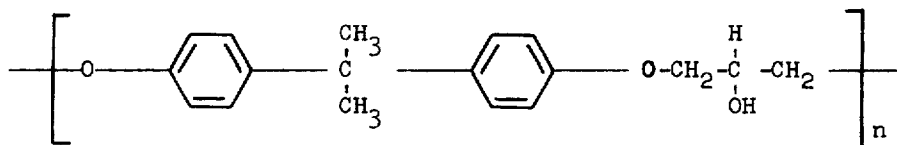
a polysulfone, a polyarylsulfone, a polycarbonate and a polyamide.

7. A method for fabricating a composite reinforced with graphite yarn which comprises heating the yarn in 1000° at a temperature in the range of 100° to 4500°F for a period ranging from about 0.10 to 12 seconds; passing the heated yarn through a solution of a thermoplastic polymer, thereby coating the yarn with the polymer; evaporating solvent from the coating on the graphite yarn; passing the coated yarn through a solution of a thermosetting resin; thereby coating the thermoplastic polymer coated yarn with thermosetting

upon the weight of the thermoplastic polymer coated yarn.

9. The method according to claim 8 in which the thermoplastic polymer is selected from the group consisting of a polyhydroxy ether, a polyphenylene oxide, a polysulfone, a polyarylsulfone, a polycarbonate and a polyamide and the thermosetting resin is selected from the group consisting of an epoxy resin, a phenolic resin, a polyimide resin, a polybenzimidazole resin, and a pyrrone resin.

10. The method according to claim 9 in which the thermoplastic polymer is a polyhydroxy ether having the following structural formula:



resin; evaporating solvent from the coated yarn; and molding portions of the coated yarn under heat and pressure to form a composite.

8. A method according to claim 7 in which the first mentioned solution contains in the range of about 0.5 to 25 weight percent of thermoplastic polymer; the amount of thermoplastic polymer coated on the graphite yarn is in the range of about 5 to 30 percent by weight of the yarn; the second mentioned solution contains in the range of about 30 to 80 weight percent of thermosetting resin; and the amount of thermosetting resin coated on the thermoplastic polymer coated yarn is in the range of about 25 to 60 weight percent, based

wherein n has a value such that the polymer has a molecular weight of about 35,000; the thermosetting resin is an epoxy resin; and stacked plies of the coated yarn are molded at a temperature in the range of about 175° to 450°F under a pressure of about 100 to 1000 psi for a period of about 1 to 8 hours.

11. The method according to claim 9 in which the thermoplastic polymer is poly(2,6-diphenyl-1,4-phenylene oxide); the thermosetting resin is an epoxy resin; stacked plies of the coated yarn are molded at a temperature in the range of about 175° to 450°F under a pressure of about 100 to 1000 psi for a period of about 1 to 8 hours.

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