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- **Sasaki, Fisako,**
c/o Fukushima Techn. Support Cnt.
Fukushima-shi, Fukushima-ken (JP)
- **Touse, Makoto,**
c/o Fukushima Techn. Support Cnt.
Fukushima-shi, Fukushima-ken (JP)
- **Yashima, Yoshinobu,** c/o Japan Basic
Sendai-shi, Miyagi-ken (JP)

(71) Applicant: **Japan Basic Material Co., Ltd.**
Sendai-shi, Miyagi-ken (JP)

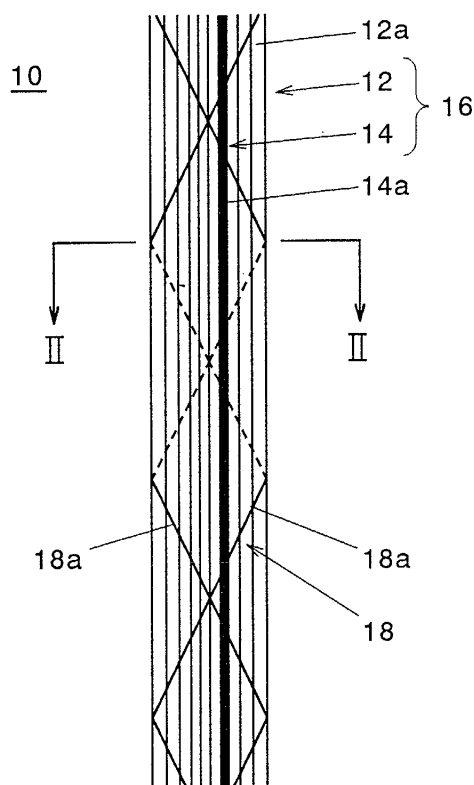
(72) Inventors:
• **Kanno, Youichi,**
c/o Fukushima Techn. Support Cnt.
Fukushima-shi, Fukushima-ken (JP)

(74) Representative: **White, Duncan Rohan**
Edward Evans Barker
Clifford's Inn
Fetter Lane
London EC4A 1BZ (GB)

(54) **Conjugated yarn and fiber reinforced plastic**

(57) A conjugated yarn (10) is provided which is capable of preventing a high-tenacity fiber used therein from being ruptured during a weaving or knitting process. The conjugated yarn (10) includes: core yarns (16) each having a high-tenacity fiber (12) and a reinforcing fiber (14) positioned parallel with the high-tenacity fiber (12) for reinforcing the high-tenacity fiber (12) and a tying yarn (18) bundling the core yarns (16). Also provided is a fiber reinforced plastic of which the strength and safety are improved by the use of the conjugated yarn.

Fig.1



Description

BACKGROUND OF THE INVENTION

5 Field of the Invention

[0001] The present invention relates to a conjugated yarn for use in weaving or knitting of a reinforcing fiber material to be used to ensure the strength of a carbon fiber reinforced plastic (hereinafter referred to as "CFRP") for example, and to a fiber reinforced plastic (hereinafter referred to as "FRP") employing such a conjugated yarn.

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Description of the Related Art

[0002] Various methods have been employed to manufacture CFRP products such as shafts of golf clubs, fishing rods and concrete-reinforcing members. Widely known ones of such methods include, for example, a method (1) comprising the steps of: weaving a fabric with a carbon fiber yarn; allowing the woven fabric to be impregnated with a thermosetting resin to form a prepreg; forming the prepreg into a product shape; and thermosetting the prepreg thus shaped, and a method (2) comprising the steps of: weaving or knitting a preform with a carbon fiber yarn; allowing the preform to be impregnated with a resin matrix; and thermosetting the matrix impregnating the preform.

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[0003] Flexure stress works on such a carbon fiber yarn used in the method (1) or (2) during the weaving or knitting process. If the carbon fiber yarn is ruptured due to such flexure stress, a resulting product cannot ensure a desired strength.

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[0004] It has been a conventional practice to lower the weaving or knitting speed or to coat the carbon fiber yarn with a reinforcing resin in order to prevent rupture of such carbon fiber yarn. However, the prior art still have a problem that a satisfactory rupture-preventive effect cannot be provided.

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[0005] On the other hand, conventional CFRPs involve a problem in terms of safety because they might take dangerous forms when broken. Specifically, though a golf club shaft or ski pole made of metal for example is not ruptured but merely bent when damaged in use, a golf club shaft or ski pole formed of CFRP is ruptured at a damaged portion. Ruptured phases of such broken pieces might hurt the body of the user or a person around the user.

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[0006] Accordingly, it is a main object of the present invention to provide a conjugated yarn which is prevented from being ruptured during a weaving or knitting process.

[0007] Another object of the present invention is to provide a conjugated yarn with which an FRP having higher strength and safety can be prepared. Yet another object of the present invention is to provide such an FRP having higher strength and safety.

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SUMMARY OF THE INVENTION

[0008] According to a first aspect of the present invention, there is provided a conjugated yarn: comprising core yarns each comprising a high-tenacity fiber and a reinforcing fiber positioned parallel with the high-tenacity fiber for reinforcing the high-tenacity fiber; and a tying yarn bundling the core yarns.

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[0009] Since the high-tenacity fiber (carbon fiber, glass fiber, ceramic fiber or the like) and the reinforcing fiber are bundled with the tying yarn in the conjugated yarn, the high-tenacity fiber is reinforced by the reinforcing fiber during a weaving or knitting process. Therefore, the high-tenacity fiber will not be ruptured during such a process. An FRP employing the conjugated yarn according to the first aspect of the invention exhibits a higher strength as a whole than a conventional one and hence is hard to break because the high-tenacity fiber forming a reinforcing material is reinforced by the reinforcing fiber. When such an FRP is broken, the reinforcing fiber and the tying yarn serve to tie a broken portion to the rest. Accordingly, even if the high-tenacity fiber is ruptured in the broken portion, the FRP is not ruptured as a whole.

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[0010] According to a second aspect of the present invention, there is provided a fiber reinforced plastic comprising a cured product comprising a reinforcing fiber material formed of a conjugated yarn as recited above, and a resin matrix impregnating the reinforcing fiber material.

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[0011] These and other objects, features and attendant advantages of the present invention will become apparent from the following detailed description of the present invention when read in conjunction with the accompanying drawings.

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BRIEF DESCRIPTION OF THE DRAWINGS

[0012]

5 Fig. 1 is a schematic view illustrating one embodiment of the present invention; and
Fig. 2 is an enlarged sectional view taken on line II-II in Fig. 1.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

10 **[0013]** The present invention will now be described in detail with reference to the accompanying drawings.

[0014] A conjugated yarn 10 shown in Fig. 1 as one embodiment of the present invention forms a reinforcing material for CFRPs used to form golf club shafts, fishing rods, ski poles, concrete-reinforcing members, aircraft parts, rocket parts and the like.

15 **[0015]** The conjugated yarn 10 includes core yarns 16 each comprising a high-tenacity fiber 12 and a reinforcing fiber 14, and a tying yarn 18 wound around the core yarns 16.

[0016] The high-tenacity fiber 12 is a strand of carbon monofilaments (i.e., high-tenacity monofilaments, hereinafter the same) 12a having such characteristics as a low elongation, a high elasticity modulus and a high strength. Specific examples of such high-tenacity fibers 12 include Torayca produced by Toray Industries Inc. and GRANOC produced by Nippon Graphite Fiber Co., Ltd.

20 **[0017]** The diameter of each carbon monofilament 12a forming the high-tenacity fiber 12 is not particularly limited but is desirably within a range of from 3 to 15 μ m from the viewpoint of resistance to flexural fatigue. If the diameter of each carbon monofilament 12a is less than 3 μ m, it is possible that carbon monofilament 12a is ruptured during the carbon fiber conjugated yarn making process. If the diameter is more than 15 μ m, carbon monofilament 12a is easy to break when bent.

25 **[0018]** Typical carbon fibers include those of the acrylic type which is obtained through sintering of acrylic fibers and those of the pitch-based type which is obtained through sintering of pitch. The high-tenacity fiber 12 (carbon monofilament 12a) used in this embodiment may be of either type. The high-tenacity fiber 12 may take the form of twisted yarn, untwisted yarn, no twist yarn or the like. From the viewpoint of the balance between formability and strength, the form of untwisted yarn or no twist yarn is desirable.

30 **[0019]** The reinforcing fiber 14 serves as a splint for reinforcing the high-tenacity fiber 12 and comprises a single or plural reinforcing monofilaments 14a to be positioned parallel with the high-tenacity fiber 12. Though there is no particular limitation on the type of a fiber forming the reinforcing fiber 14 (reinforcing monofilament 14a), it is desirable that the reinforcing fiber 14, as a whole, exhibit a higher resistance to flexural fatigue than the high-tenacity fiber 12. Examples of fibers having such a property include titanium fiber, stainless steel fiber, TECHNORA fiber, vinylon fiber, polyamide fiber, polyester fiber, polyvinyl alcohol fiber, polyacrylonitrile fiber, and polyurethane fiber. Use of polyester fiber or polyamide fiber is desirable because they are inexpensive and easy to handle.

35 **[0020]** In order for the reinforcing fiber 14 to exhibit the CFRP rupture preventive effect, it is desirable that the reinforcing fiber 14 (reinforcing monofilament 14a) be made using a fiber such as to impart the reinforcing fiber 14 with a higher resistance to flexural fatigue and a higher tensile elongation at break than the high-tenacity fiber 12. Examples of fibers having such properties include titanium fiber, stainless steel fiber, TECHNORA fiber, vinylon fiber, polyamide fiber, polyester fiber, polyvinyl alcohol fiber, polyacrylonitrile fiber, and polyurethane fiber.

40 **[0021]** The tying yarn 18 serves to bundle the core yarns 16 (each comprising carbon monofilament 12a and reinforcing monofilament 14a) and comprises a single or plural tying fibers 18a to be wound around the core yarns 16. Though there is no particular limitation on the type of a fiber forming the tying yarn 18 (tying fiber 18a), the tying yarn 18 is desirably formed of a fiber having a superior abrasion resistance because the tying yarn 18 becomes exposed on the outer surface of the carbon fiber conjugated yarn 10. In order for the tying yarn 18 to exhibit the CFRP rupture preventive effect, it is desirable that the tying yarn 18 (tying fiber 18a) be made using a fiber such as to impart the tying yarn 18 with a higher resistance to flexural fatigue and a higher tensile elongation at break than the high-tenacity fiber 12. Examples of fibers having such properties include titanium fiber, stainless steel fiber, TECHNORA fiber, vinylon fiber, polyamide fiber, polyester fiber, polyvinyl alcohol fiber, polyacrylonitrile fiber, and polyurethane fiber.

45 **[0022]** In making the conjugated yarn 10, the high-tenacity fibers 12 and the reinforcing fibers 14 are positioned parallel with each other to form the core yarns 16 first. Subsequently, the tying fiber 18a is wound around the core yarns 16 to cover the same using an Italian-type twisting machine or a twisting machine for covering for example.

50 **[0023]** To prevent torque from working on the conjugated yarn 10, double-covering of the core yarns 16 with tying fibers 18a wound around the core yarns 16 clockwise and counterclockwise is desired. However, single-covering is sufficient to bundle the core yarns 16.

55 **[0024]** In preparing a CFRP (in the form of a golf club shaft, ski pole or fishing rod) using the conjugated yarn 10 there is employed any one of methods including a method (1) comprising the steps of: weaving a fabric (reinforcing

carbon fiber material) with conjugated yarn 10; allowing the woven fabric to be impregnated with a resin matrix to form a prepreg; forming the prepreg into a product shape; and thermosetting the resin matrix forming the prepreg, a method (2) comprising the steps of: weaving or knitting a preform (reinforcing carbon fiber material) with conjugated yarn 10; allowing the preform to be impregnated with a resin matrix; and thermosetting the matrix impregnating the preform.

5 [0025] Though flexure stress works on conjugated yarn 10 during the weaving or knitting step of such a method, the high-tenacity fiber 12 reinforced by the reinforcing fiber 14 is not ruptured due to such stress.

[0026] In the CFRP employing the conjugated yarn 10, the high-tenacity fiber 12 forming the reinforcing material is reinforced by the reinforcing fiber 14. Accordingly, if the reinforcing fiber 14 comprises a fiber having a high resistance to flexural fatigue, the CFRP is improved in strength as a whole. In the case where the CFRP is applied to a golf club shaft for example, the resulting golf club shaft is nery and hence exhibits considerably improved performance.

10 [0027] When the CFRP employing the conjugated yarn 10 is broken, it is possible that the high-tenacity fiber 12 is ruptured in the broken portion. However, the CFRP as a whole can be prevented from being ruptured if the reinforcing fiber 14 and/or the tying fiber 18 are/is formed of a fiber having a high tensile elongation at break.

15 [0028] That is, if the tensile elongation at break of the reinforcing fiber 14 and/or the tying fiber 18 is higher than that of the high-tenacity fiber 12, the high-tenacity fiber 12 is ruptured first, followed by the occurrence of rupture of the reinforcing fiber 14 and/or the tying fiber 18, provided an equal breaking energy is applied. Actually, however, the breaking energy is attenuated upon rupture of the high-tenacity fiber 12 and, hence, the possibility that rupture of the reinforcing fiber 14 and/or the tying fiber 18 is reached is low. For this reason the reinforcing fiber 14 and/or the tying fiber 18 play(s) the role of tying the broken portion to the rest, thereby preventing the whole CFRP from being ruptured in many cases. Accordingly, there is no fear that the ruptured phases of any broken piece hurts a human body.

20 [0029] The inventor of the present invention conducted the following test to verify the effect of the present invention.

Test Method

25 [0030] There were provided a high-tenacity fiber consisting of a carbon fiber (67Tex, 1000f, 1.6% elongation), a comparative yarn comprising the high-tenacity fiber bundled with a vinylon fiber (30d), and a conjugated yarn comprising the high-tenacity fiber, a stainless steel fiber (40 μ m , number of fibers = 4) positioned parallel with the high-tenacity fiber, and the vinylon fiber (30d) bundling the high-tenacity fiber and the stainless steel fiber. Three types of test samples (first to third test samples) each comprising 11 test pieces were woven using the high-tenacity fiber, comparative yarn and conjugated yarn, respectively, as weft and a cotton yarn as warp. Each of the test samples (11 test pieces of the three types) was subjected to a flexural test.

30 [0031] Each test sample was of plain weave and was sized about 3.5 cm in the warp direction x about 18 cm in the weft direction, and the number of weft yarns of each test sample was 50.

35 Test Results

[0032] The test results were as shown in Tables 1 and 2. It was found from the graph of Table 1 that: the first test sample employing only the high-tenacity fiber (carbon fiber) as weft did not exhibit a sufficient flexural strength; the flexural strength of the second test sample employing the comparative yarn was still insufficient; and the third test sample employing the conjugated yarn 10 exhibited a very high flexural strength.

40 [0033] It can be predicted from the test results that a fabric employing the high-tenacity fiber (carbon fiber) only might be ruptured during the weaving process or the like, whereas a fabric employing the conjugated yarn can solve the problem of rupture because the flexural strength of this fabric is remarkably enhanced.

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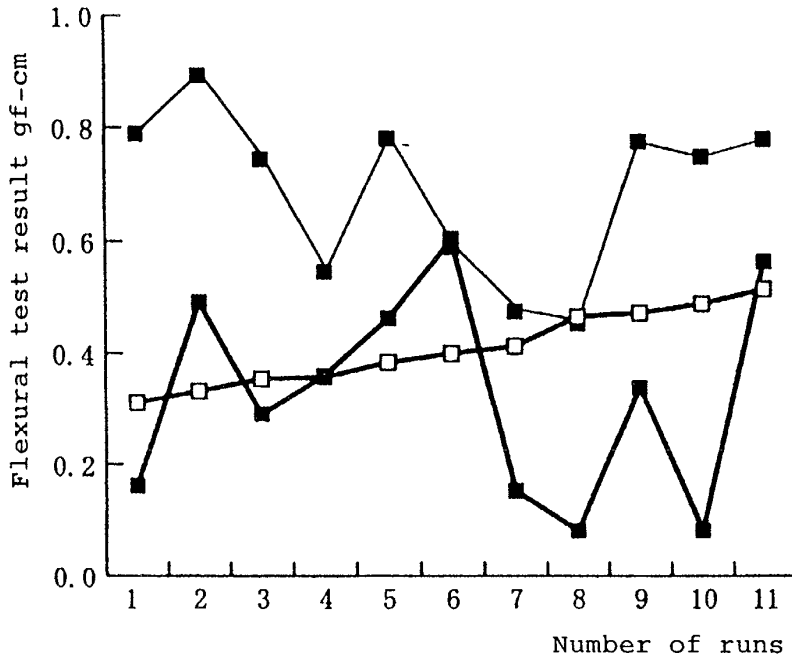
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Table 1

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- First test sample (carbon fiber)
- Second test sample (carbon fiber+vinylon fiber)
- Third test sample (carbon fiber+stainless steel fiber + vinylon fiber)

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Measuring instrument: FLEXURAL TESTER manufactured by KATOTECH CO., LTD.
 Conditions varied: Curvature = ± 2.5/cm
 Flexing rate = 0.5cm/sec
 Measuring environment: 20°C 65%

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Table 2

Test Results			
	First test sample	Second test sample	Third test sample
Strength/weight ratio	1	1.3	1.7
Average (gf-cm)	0.326	0.409	0.688
Standard error	0.057	0.020	0.044
Median	0.339	0.400	0.749

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Table 2 (continued)

Test Results			
	First test sample	Second test sample	Third test sample
Mode	#N/A	#N/A	#N/A
Standard deviation	0.190	0.068	0.146
Dispersion	0.036	0.005	0.021
Kurtosis	- 1.453	- 1.334	- 1.071
Degree of distorsion	0.048	0.187	- 0.567
Range	0.523	0.203	0.439
Minimum	0.081	0.312	0.453
Maximum	0.604	0.515	0.892
Total	3.586	4.495	7.568
Number of samples	11	11	11

[0034] While the tying yarn 18 is wound around the core yarns 16 in the foregoing embodiment, the tying yarn 18 may be braided around the core yarns 16 using a braider (for example a braider manufactured by KOKUBU TEKKO CO., LTD.).

[0035] The high-tenacity fiber 12 may be any fiber which has a low resistance to flexural fatigue but exhibits a high tenacity or any fiber which will take a dangerous broken form but exhibits a high tenacity, for example, glass fiber or ceramic fiber.

[0036] It is possible that at least one of the high-tenacity fiber 12, reinforcing fiber 14 and tying yarn 18 may comprise at least two types of fibers.

[0037] The conjugated yarn of the present invention may be used as a reinforcing material for fiber reinforced concrete (FRC).

[0038] According to the present invention, it is possible to prevent rupture of the high-tenacity fiber during a weaving or knitting process. Thus, weaving or knitting at a higher speed becomes possible, whereby the productivity of a reinforcing fiber material or an FRP can be improved remarkably.

[0039] Since the high-tenacity fiber forming such a reinforcing fiber material is reinforced by the reinforcing fiber, an FRP employing the reinforcing fiber material has an enhanced strength as a whole.

[0040] When the FRP employing the conjugated yarn of the present invention is broken, it is possible that the high-tenacity fiber is ruptured in the broken portion. However, the FRP as a whole can be prevented from being ruptured because the reinforcing fiber and/or the tying fiber play(s) the role of tying the broken portion to the rest. Accordingly, there is no fear that the ruptured phases of any broken piece hurts a human body and, hence, the FRP offers remarkably improved safety.

[0041] While only presently preferred embodiments of the present invention have been described in detail,- as will be apparent for those skilled in the art, certain changes and modifications can be made in embodiments without departing from the spirit and scope of the present invention as defined by the following claims.

Claims

1. A conjugated yarn comprising: core yarns each comprising a high-tenacity fiber and a reinforcing fiber positioned parallel with the high-tenacity fiber for reinforcing the high-tenacity fiber; and a tying yarn bundling the core yarns.
2. The conjugated yarn according to claim 1, wherein the high-tenacity fiber comprises a plurality of high-tenacity monofilaments.
3. The conjugated yarn according to claim 1 or 2, wherein the reinforcing fiber comprises a plurality of reinforcing monofilaments.
4. The conjugated yarn according to any one of claims 1 to 3, wherein the reinforcing fiber has a higher resistance to flexural fatigue than the high-tenacity fiber.

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5. The conjugated yarn according to any one of claims 1 to 4, wherein the reinforcing fiber has a higher tensile elongation at break than the high-tenacity fiber.

5 6. The conjugated yarn according to any one of claims 1 to 5, wherein the tying yarn has a higher tensile elongation at break than the high-tenacity fiber.

7. The conjugated yarn according to any one of claims 1 to 6, wherein the tying yarn is wound around the core yarns.

10 8. The conjugated yarn according to any one of claims 1 to 6, wherein the tying yarn is braided around the core yarns.

9. The conjugated yarn according to any one of claims 1 to 8, wherein the high-tenacity fiber comprises a carbon fiber.

10. The conjugated yarn according to any one of claims 1 to 9, wherein the high-tenacity fiber comprises a glass fiber.

15 11. The conjugated yarn according to any one of claims 1 to 10, wherein the high-tenacity fiber comprises a ceramic fiber.

20 12. A fiber reinforced plastic comprising a cured product comprising a reinforcing fiber material formed of a conjugated yarn as recited in any one of claims 1 to 11, and a resin matrix impregnating the reinforcing fiber material.

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Fig. 1

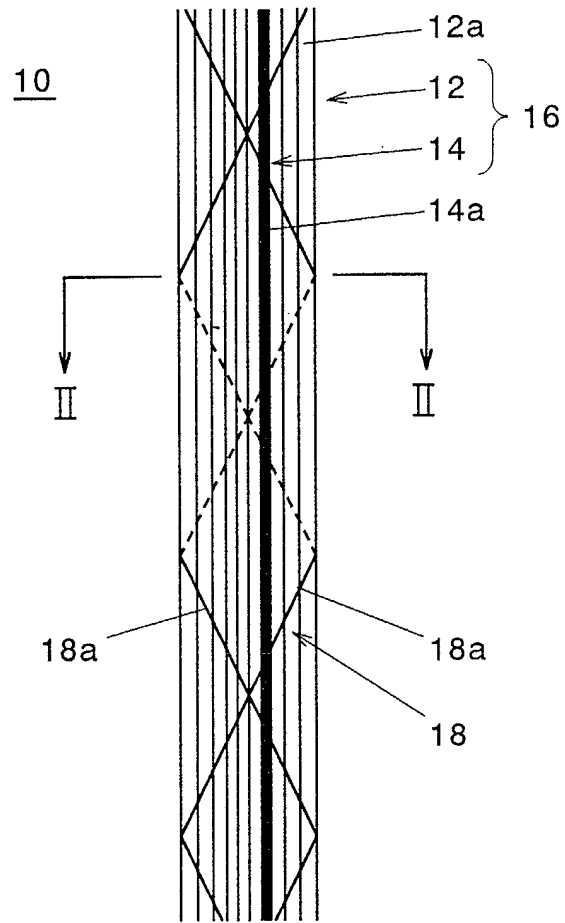
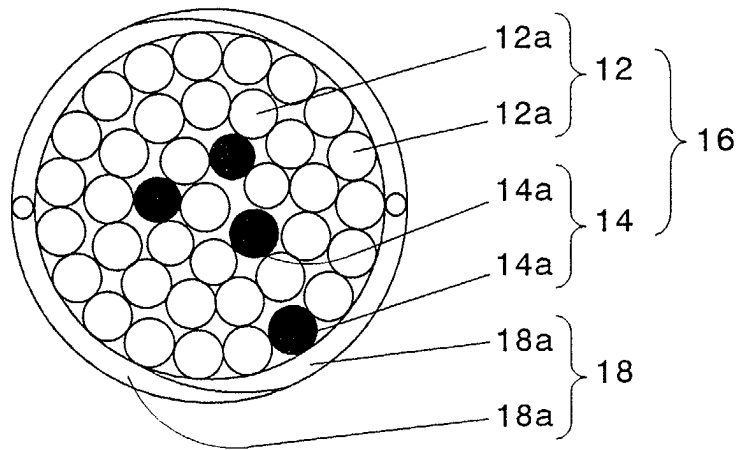


Fig.2

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European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 02 25 7156

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.7)
X	GB 2 105 247 A (COURTAULDS PLC) 23 March 1983 (1983-03-23)	1-7,9-12	D02G3/44 D02G3/38
Y	* claims 1-7; examples 1,2 * ---	8	
X	GB 2 021 660 A (TBA INDUSTRIAL PRODUCTS LTD) 5 December 1979 (1979-12-05) * claims 1-3,7 * ---	1,3-7,9,10	
X	US 4 299 884 A (PAYEN PIERRE) 10 November 1981 (1981-11-10) * claim 1; figure 1 * ---	1	
X	PATENT ABSTRACTS OF JAPAN vol. 1996, no. 01, 31 January 1996 (1996-01-31) & JP 07 243140 A (TORAY IND INC), 19 September 1995 (1995-09-19) * abstract * ---	1,12	
Y	FR 2 576 045 A (COUSIN FRERES SA) 18 July 1986 (1986-07-18) * claim 1; figure 1 * -----	8	
			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
			D02G D07B
The present search report has been drawn up for all claims			
Place of search		Date of completion of the search	Examiner
THE HAGUE		13 March 2003	D'Souza, J
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

EPC FORM 1503.03.82 (P04G01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 02 25 7156

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
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13-03-2003

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
GB 2105247	A	23-03-1983	NONE	
GB 2021660	A	05-12-1979	NONE	
US 4299884	A	10-11-1981	FR 2446336 A1 DE 3000273 A1	08-08-1980 24-07-1980
JP 07243140	A	19-09-1995	NONE	
FR 2576045	A	18-07-1986	FR 2576045 A1	18-07-1986

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