

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
4 August 2005 (04.08.2005)

PCT

(10) International Publication Number
WO 2005/070664 A1

(51) International Patent Classification⁷: **B32B 5/28**,
B29C 70/46

European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

(21) International Application Number:
PCT/US2005/000052

(22) International Filing Date: 3 January 2005 (03.01.2005)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
10/757,079 14 January 2004 (14.01.2004) US

(71) Applicant (for all designated States except US): **GENERAL ELECTRIC COMPANY** [US/US]; 1 River Road, Schenectady, NY 12345 (US).

(72) Inventor; and

(75) Inventor/Applicant (for US only): **BIRRELL, Michael, Ian** [GB/GB]; Thistle Dene, 24 High Street, Guilden Morden, Royston, Herts, SG8 0JP (GB).

(74) Agents: **GNIBUS, Michael et al.**; Patent Counsel, Genral Electric Company, 3135 Easton Turnpike (W3C), Fairfield, CT 06828 (US).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),

Declarations under Rule 4.17:

— as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii)) for the following designations AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VC, VN, YU, ZA, ZM, ZW, ARIPO patent (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG)

— as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii)) for the following designations AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VC, VN, YU, ZA, ZM, ZW, ARIPO patent (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG)

Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: MULTILAYER PRODUCT MADE OUT OF A SUBSTRATE AND ON EITHER SIDE AT LEAST ONE COVER LAYER; PROCESS FOR THE MANUFACTURE OF A MULTILAYER PRODUCT AND PAINTED MULTILAYER PRODUCT AND PROCESS FOR PAINTING A MULTILAYER PRODUCT

(57) Abstract: Multilayer product made out of a substrate and at each side at least one cover layer, completely or partly covering the substrate, the substrate being a fibre reinforced thermoplastic product with randomly distributed fibres and with a density of less than 1.2 grams per cm³, preferably less than 1.0 grams per cm³ and the cover layer being a long or continuous fibre reinforced thermoplastic plastic film with the fibres being orientated approximately parallel to one another.



WO 2005/070664 A1

MULTILAYER PRODUCT MADE OUT OF A SUBSTRATE AND ON EITHER SIDE AT LEAST ONE COVER LAYER; PROCESS FOR THE MANUFACTURE OF A MULTILAYER PRODUCT AND PAINTED MULTILAYER PRODUCT AND PROCESS FOR PAINTING A MULTILAYER PRODUCT

BACKGROUND OF THE INVENTION

Glass fibre reinforce products are generally known. They are used for many purposes. One class of glass fibre reinforced products consists of sheet like products with randomly distributed fibres embedded in a thermoplastic resin. Depending on their process of manufacture they can be rather densely packed resulting in sheet with a density of more than 1.00 gram per cm³, usually more than 1.20 grams per cm³ or in loosely packed sheet structures with a density of less than 1.20, usually less than 1.00 grams per cm³.

The present invention deals with products having a substrate made out of the loosely packed sheet structures.

Said loosely packed sheet structures have outstanding strength to weight ratio making them suitable for many applications.

In some applications it is however desirable to improve the stiffness and the surface quality of the known loosely packed structures further.

It is known to improve the surface quality of fibre-reinforced sheet by covering the sheet with a layer or film of a thermoplastic not containing any fibres. Upon further processing of the thus covered sheet, in particular when heating it the fibres of the sheet tend to protrude through the surface of the cover layer thus diminishing the surface quality again.

To increase the mechanical properties of thermoplastic materials reinforced with glass fibres it has been proposed to cover the thermoplastic sheet with layers of materials containing aligned high performance fibres.

SUMMARY OF THE INVENTION

The multilayer product of the invention comprises a substrate in the form of a glass fibre reinforced thermoplastic product with randomly distributed fibres and with a density of less than 1.20 grams per cm³, preferably less than 1.00 grams per cm³ and a cover layer being a long or continuous fibre reinforced thermoplastic plastic film with the long or continuous fibres being orientated approximately parallel to one another.

The product of the invention has an optimum combination of good mechanical properties and surface quality. Of importance is further that its coefficient of thermal expansion (CTE) is very low. For products of the invention where the substrate is covered at each side with several cover layers wherein the orientation of the long or continuous fibres in each adjacent cover layer is different it is possible to obtain a product that for practical purposes can be considered as isotropic.

The thermoplastic material in the substrate and in the cover layer can be the same or can be different. The thermoplastic can be chosen among all known thermoplastic materials.

The product of the invention can be shaped by heating the multilayer product and pressing it or vacuum consolidating it in a mould having the desired shape.

It can be painted with or without an intermediate surface treatment such as applying a primer, flame treatment and the like.

DETAILED DESCRIPTION OF THE INVENTION

The multilayer product of the invention comprises a substrate that is provided at each side with at least one cover layer.

The substrate is formed by a glass fibre reinforced thermoplastic product with randomly distributed fibres and with a density of less than 1.20, preferably less than 1.00 gram per cm³.

The cover layer is formed by a long or continuous fibre reinforced thermoplastic film, the fibres being oriented approximately parallel to one another within each layer.

THE SUBSTRATE

Substrates of the kind described above are well-known and commercially available products. They can be manufactured in various ways. They can be made by a process similar to paper making wherein the reinforcing fibres and the thermoplastic material are mixed together into an aqueous solution, subsequently the water is removed by vacuum. The so obtained sheet like product is dried and is heated and finally pressed whereby the thermoplastic material softens and keeps the fibres together upon cooling. A description of this process can be found in US 4,734,321.

In another process for making suitable substrates reinforcing fibres and fibres of a thermoplastic material are admixed and the obtained structure is needed. The needed structure is heated and finally pressed to an intermediate product. This process is described for instance in WO 02/076711.

The content of reinforcing fibres in the substrate can vary within a broad range. The content of reinforcing fibres varies usually between 20 to 90 % by weight.

The fibres have an average length of about 7 to 200 millimetres.

The substrates have a low density and are air permeable. The substrate usually has a thickness of between 1 to 10 millimetres.

THE COVER LAYER

The cover layer or cover layers is/are formed by a long or continuous fibre reinforced thermoplastic film or prepreg with the long or continuous fibres being orientated approximately parallel to another. Such films are commercially available.

The films can be made for example drawing a plurality of continuous filaments through a melt of a thermoplastic polymer with a relatively low melt viscosity while keeping the filaments aligned along the direction of the draw under tension. Such a process has been described for instance in EP A- 0 056 703. The average length of the long fibres is over 100 millimetres. The fibres are individually embedded in the

thermoplastic material. The thickness of the film varies between about 0.1 and 1.0 millimetres.

THE REINFORCING FIBERS

The material of the reinforcing fibres in the substrate and in the cover layer can be the same or can be different. The fibres can be made out of glass (all types of glass are suitable), carbon, synthetic materials, mineral or natural materials.

THE THERMOPLASTIC MATERIAL

The thermoplastic material of the substrate and of the cover layer can be the same or can be different. They should however be selected so that the substrate and the cover layer bond together upon heating them under pressure and at elevated temperatures. Suitable thermoplastic materials are for example polyolefins, polycarbonates, vinyl aromatic homopolymers, vinyl aromatic compounds containing copolymers, vinyl aromatic compounds containing graft copolymers or vinyl aromatic compounds containing block copolymers, thermoplastic polyesters, thermoplastic polyurethanes, polyetherimides; polyphenylene sulfide, polyphenylene ethers, polyamides or blends of thermoplastic materials comprising at least one of the mentioned thermoplastic materials.

PROCESS FOR MAKING THE MULTILAYER PRODUCT

The manufacture of the multilayer product of the invention is relatively simple. On both sides of the substrate as defined in the claims are applied one or more layers of the film. To prevent distortions of the multilayer product of the invention it is simplest to apply on each side of the substrate the same number of films and with a balanced orientation. When using more than one layer of the film the film is usually applied such that the direction of the long or continuous fibres of each subsequent layer differs from the orientation of the previous layer. This is normally as a 0°/90° lay-up but may also be uni-directional or quasi isotropic lay-up depending on the application. The substrate and the film are heated together under pressure at a temperature to assure good bonding between the substrate and the film or prepreg

layer. During this process or in a subsequent step the multilayer product may be moulded into the desired three dimensionally shaped forms by pressing or vacuum consolidating it in a properly shaped mould. It is also possible to subject the substrate to a treatment under heat and pressure prior to applying the film cover layer.

PAINTING THE MULTILAYER PRODUCT

The multilayer product may be painted with one or more paint layers. To obtain an optimal surface quality and good adherence of the paint layers a pre-treatment of the surface of the multilayer product may be advisable. Such pre-treatment may consist for example of the application of suitable primer layer and or surface flame treatment.

USE OF PRODUCT INVENTION

The products of the invention can be used in many applications. Due to their low density, great stiffness, low CTE and good surface quality they are ideally suited for use as body panels for the automotive industry or outdoor vehicles.

CLAIMS

1. Multilayer product made out of a substrate and at each side at least one cover layer, completely or partly covering the substrate, the substrate being a fibre reinforced thermoplastic product with randomly distributed fibres and with a density of less than 1.2 grams per cm³, preferably less than 1.0 grams per cm³ and the cover layer being a long or continuous fibre reinforced thermoplastic with the fibres being orientated approximately parallel to one another within each balanced layer.
2. Multilayer product of claim 1 with a substrate with fibres having an average length of between about 7 and 200 millimetres.
3. Multilayer product of claim 1 with a cover layer having long or continuous fibres with an average length of at least 100 millimetres.
4. Multilayer product of claim 1 with a cover layer with long or continuous fibres, which are each individually embedded in the thermoplastic material.
5. Multilayer product of claim 1 with a plastic material in the substrate and in the cover layer which may be the same or different and that is chosen among the following thermoplastic materials: polyolefins, polycarbonates, vinyl aromatic homopolymers, vinyl aromatic compounds containing copolymers, vinyl aromatic compounds containing graft copolymers or vinyl aromatic compounds containing blockcopolymers, thermoplastic polyesters, thermoplastic polyurethanes, polyetherimides; polyphenylene sulfide, polyphenylene ethers, polyamides or blends of thermoplastic materials comprising at least one of the mentioned thermoplastic materials.
6. Multilayer product of claim 1 with a substrate with a thickness between 1.0 and 10.0 millimetres.
7. Multilayer products of claim 1 with cover layers with a thickness of between 0.1 and 5 millimetres.

8. Multilayer products of claim 1 wherein the thermoplastic material of the substrate and the cover layer comprise compatible thermoplastic material.
9. Multilayer product of claim 1 with on each side of the substrate at least two cover layers, the long fibres of at least two cover layers on each side of the substrate having a different orientation of the long or continuous fibres.
10. Multilayer product of claim 1 with fibres in the substrate, which have been made out of any of the following materials: glass; carbon; synthetic materials, mineral or natural fibres.
11. Multilayer product of claim 1 with long fibres, which have been made out of any of the following materials: glass; carbon; synthetic materials, mineral or natural fibres.
12. Process for the manufacture of a multilayer product by covering a substrate at each side at least partly with at least one film or prepreg layer, the substrate being a fibre reinforced thermoplastic product with randomly distributed fibres and with a density of less than 1.2 grams per cm³, preferably less than 1.0 grams per cm³ and the cover layer being a long or continuous fibre reinforced thermoplastic with the fibres being orientated approximately parallel to one another within each layer.
13. Process of claim 12 comprising at least one additional step of heating the multilayer product covered with the cover layers under pressure in a mould corresponding with the desired shape of the product at a temperature above the glass transition temperature of the thermoplastic material in the substrate.
14. Process of claim 15 comprising the step to heat the substrate under pressure before applying the cover layers.
15. Painted multilayer product made out of a substrate and at each side at least one cover layer, the substrate being a fibre reinforced thermoplastic product with randomly distributed fibres and with a density less than 1.2 grams per cm³, preferably less than 1.0 grams per cm³ and the cover layer or layers being a long or continuous fibre reinforced thermoplastic with the fibres being orientated approximately parallel

to one another within each layer, provided at least on one side with at least one paint layer.

16. Painted multilayer product of claim 17 with a primer layer between the outer cover layer and the paint layer or layers.

17. Process for painting a multilayer product made out of a substrate and at each side at least one cover layer, the substrate being a glass fibre reinforced thermoplastic product with randomly distributed fibres and with a density less than 1.2 grams per cm^3 , preferably less than 1.0 grams per cm^3 and the cover layer being a long or continuous fibre reinforced thermoplastic plastic film with the fibres being orientated approximately parallel to one another, by optionally providing the surface to be painted by a primer and by optionally giving the surface to be painted a surface treatment followed by application of one or more paint layers.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US2005/000052

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 B32B5/28 B29C70/46

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 B32B B29C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 931 358 A (WAHL ET AL) 5 June 1990 (1990-06-05) abstract column 1, line 27 - column 3, line 8; claims; examples	1-17
A	EP 0 259 121 A (TORAY INDUSTRIES, INC) 9 March 1988 (1988-03-09) figures; examples	1-17
A	EP 0 434 846 A (UBE-NITTO KASEI CO. LTD; JAPAN GMT CO., LTD) 3 July 1991 (1991-07-03) claims; figure 1; examples	1-17
	----- -/--	

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

° Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

7 April 2005

Date of mailing of the international search report

19/04/2005

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Hutton, D

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US2005/000052

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 02/076711 A (QUADRANT PLASTIC COMPOSITES AG; DITTMAR, HARRI) 3 October 2002 (2002-10-03) cited in the application the whole document	1-17
A	EP 0 697 275 A (BASF AKTIENGESELLSCHAFT) 21 February 1996 (1996-02-21) the whole document	1-17

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US2005/000052

Patent document cited in search report	A	Publication date	Patent family member(s)	Publication date
US 4931358	A	05-06-1990	DE 3741669 A1	22-06-1989
			DE 3872689 D1	13-08-1992
			EP 0323571 A2	12-07-1989
			ES 2033404 T3	16-03-1993
			JP 1279931 A	10-11-1989
EP 0259121	A	09-03-1988	JP 1844606 C	25-05-1994
			JP 3080621 B	25-12-1991
			JP 63060743 A	16-03-1988
			DE 3768589 D1	18-04-1991
			EP 0259121 A2	09-03-1988
			KR 9510575 B1	20-09-1995
			US 4770929 A	13-09-1988
EP 0434846	A	03-07-1991	DE 69022566 D1	26-10-1995
			DE 69022566 T2	22-02-1996
			EP 0434846 A1	03-07-1991
			ES 2080146 T3	01-02-1996
			WO 9100796 A1	24-01-1991
			JP 6002348 B	12-01-1994
			US 5540986 A	30-07-1996
WO 02076711	A	03-10-2002	DE 10114553 A1	26-09-2002
			WO 02076711 A1	03-10-2002
			EP 1372940 A1	02-01-2004
			US 2004112501 A1	17-06-2004
EP 0697275	A	21-02-1996	DE 4429599 A1	22-02-1996
			AT 179929 T	15-05-1999
			DE 59505888 D1	17-06-1999
			EP 0697275 A2	21-02-1996
			ES 2132476 T3	16-08-1999