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(11) **EP 0 809 795 B9**

(12) **CORRECTED EUROPEAN PATENT SPECIFICATION**

Note: Bibliography reflects the latest situation

(15) Correction information:  
**Corrected version no 1 (W1 B1)**  
**Corrections, see page(s) 3-4**

(48) Corrigendum issued on:  
**17.09.2003 Bulletin 2003/38**

(45) Date of publication and mention  
of the grant of the patent:  
**02.05.2003 Bulletin 2003/18**

(21) Application number: **96903315.8**

(22) Date of filing: **13.02.1996**

(51) Int Cl.7: **G01N 13/00**

(86) International application number:  
**PCT/SE96/00187**

(87) International publication number:  
**WO 96/025655 (22.08.1996 Gazette 1996/38)**

(54) **WETTING INDICATOR FOR COMPOSITES**

BENETZUNGSINDIKATOR FÜR KOMPOSITE

INDICATEUR DE MOUILLAGE POUR DES COMPOSITES

(84) Designated Contracting States:  
**AT BE CH DE DK ES FR GB IT LI NL**

(30) Priority: **13.02.1995 SE 9500513**

(43) Date of publication of application:  
**03.12.1997 Bulletin 1997/49**

(73) Proprietor: **Lönnö, Anders**  
**139 54 Värmdö (SE)**

(72) Inventor: **Lönnö, Anders**  
**139 54 Värmdö (SE)**

(74) Representative: **Hedefält, Dag et al**  
**Försvarets Materielverk**  
**Patentenheten**  
**115 88 Stockholm (SE)**

(56) References cited:  
**US-A- 4 291 079**

- **CHEMICAL ABSTRACTS, Volume 113, No. 23, 3**  
**December 1990, (Columbus, Ohio, USA),**  
**JACKSON P. et al., "Defect Detection in Carbon**  
**Fiber Composite Structures by Magnetic**  
**Resonance Imaging", page 36, Abstract No.**  
**213181y; & J. MATER. SCI. LETT., 1990, 9(10),**  
**1165-1168, (ENG.)**

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## Description

### Technical Field

**[0001]** The invention relates to a composite material comprising indicating means according to the preamble of claim 1 for indicating that a reinforcing material, which is made of fibres and included in a composite material and which does not become translucent or transparent in wetting, has become wetted throughout by the matrix of the composite material while making the composite material. The indicating means can indicate, for instance, that the carbon fibre reinforcement for the material of a hull or the like has been completely wetted throughout by liquid thermosetting plastic in the manufacture of the hull.

### Description of the Prior Art

**[0002]** An object of a composite material can be made by the material, which contains a reinforcement and a matrix that is liquid at certain stages of the manufacture, being supplied to a mould where the object obtains its shape when the matrix sets. Depending on whether the mould is of the type having a cavity or only a surface determining the shape of the object, the shape will be substantially determined by all its surface portions or only the inside or outside of the object. When manufacturing e.g. hulls of reinforced thermosetting plastic, moulds determining only the outer surface of the hull, so-called female moulds, are used in most cases.

**[0003]** One technique of manufacturing hulls is laminating by hand lay-up. The fibre reinforcement consisting of cut-out parts of a fabric or mat is arranged on a layer of liquid plastic which has been rolled on with a roller onto the mould surface. The reinforcement is then worked with a soft roller or brush so as to be impregnated and wetted with plastic. Finally, air and excess plastic are pressed out by means of a metal roller from the layer and the space between the layer and the underlying surface. Moreover, minor inclusions of air that are bound to the surfaces of the reinforcing fibres are removed. Owing to such working, wetting is further improved. The entire surface of each fibre of the reinforcement will then be substantially completely coated with matrix material.

**[0004]** To this first layer, additional layers are applied, as described above for the first layer. For large objects, use can be made of intermediate curings when making the laminate. Otherwise, all the layers can be applied in succession, curing taking place after application of the last layer.

**[0005]** After the application of each layer, it is necessary to make sure that the reinforcement of the layer has been properly wetted throughout. If the composite material should contain inclusions of air or voids, the hull will have an inferior quality with a risk of inferior strength since the composite can delaminate adjacent the inclusions of air and water can diffuse in the inclusions and

cause chemical degradation of the material and cracking by frost. Insufficient wetting also reduces the resistance to compression of the composite, which may cause breaking of the hull.

**[0006]** For high-strength composite materials, a reinforcement consisting of practically merely carbon fibres or aramide fibres or a mixture thereof has recently come into use. The drawback of these materials is that it is difficult to visually form an opinion whether they have become well wetted throughout. To make sure that the wetting has been sufficient, ultrasonic testing and other testing techniques have been applied, which has contributed much to these composites being very expensive. The fact that the manufacture must be particularly precise owing to the lack of easy checking has also contributed to the increased cost.

**[0007]** Document US 4 291 079 A shows a method of manufacturing a noise attenuation structure. In one step during the manufacturing process a perforated sheet is treated with an anti wetting solution containing an indicator, such as a pigment dye visible in natural light or a dye visible under ultra-violet light. The perforated sheet is then visually inspected for traces of the indication which may have bled through the perforation. If traces are found necessary steps are taken. The method described in the document is used with perforated sheets and is not suited to be used during the manufacture of a composite comprising a matrix material of thermosetting plastic and a reinforcement.

### Description of the Invention

#### Technical Problem

**[0008]** The object of the invention is to provide a composite material comprising indicating means as mentioned in the introduction and having the following properties:

- When manufacturing composite materials, it should be easy to make sure whether a reinforcing material has been well wetted throughout. This applies to reinforcing fibres in e.g. high-strength composite materials, the wetting of which has previously been difficult to estimate.
- It should be possible to carry out the inspection in a short time and without expensive and complicated equipment.

#### The Solution

**[0009]** The object is achieved by the composite material having the features as defined in the appended claims.

**[0010]** According to the invention, it is suggested that, intermixed with the reinforcing material, elements are added which have the same wetting properties as the reinforcing material, preferably as fibres in the form of

threads, bundles, flakes, wads or the like of a material which becomes translucent or transparent by a shade of colour that depends on the nature of the material when its surface has been wetted by the matrix material. This indicating material, which preferably should also serve as reinforcement, should be added in an amount that is relatively small, such that the properties of the composite material are not changed to an unacceptable extent, but yet sufficient to obtain a good indication. The amount, which in the preferred embodiment is selected to be 4%, should in normal applications be less than about 5%. The elements added should be uniformly spread in the reinforcing material in such a manner that if they have all become wetted throughout, it can be assumed that the reinforcing material in the areas round the elements has also become wetted. The distances between the elements should not be chosen to be greater than to make these surrounding areas together cover the entire reinforcing material. Mixed reinforcements containing e.g. carbon fibre and glass fibre materials are already available, but the purpose of these reinforcements is to obtain other properties or a less expensive reinforcement. The admixture of glass fibres therefore is much greater, about 50%, as compared with reinforcements according to the present invention.

**[0011]** The reliability of the indication will be improved if the elements have such properties that they will be translucent/transparent only when the adjoining reinforcing material has become completely wetted throughout. These properties can be affected by the choice of the material of the elements and surface treatment.

**[0012]** When the composite material is a reinforced thermosetting plastic intended for hulls, use is often made of ester plastic or epoxy plastic as matrix material. In their liquid state, these materials are transparent in ordinary light. The indicating elements may then consist of certain polymers or glass fibre materials which from being, for instance, white in dry state become translucent or transparent when wetted. They will then let through the colour of the base, which can be the colour of the gel coat or the black colour of the subjacent carbon fibre reinforcement. Of course, a colour of the elements should be selected that is different from that of the base in order to obtain a clear change of colour. For other matrix and indicator materials, it may be necessary to use a light of a different wave range, for instance, the fluorescence from elements that have become wetted can be used for indicating purposes.

**[0013]** Reinforcing materials of carbon fibres often are in the form of a fabric or a stitched so-called multiaxial mat. The warp and weft threads of the fabric consist of flat bundles of a large number of carbon fibres or fibrils. The mat, which is used if a more rigid composite having a higher fibre content is desired, may consist of two plies, each comprising parallel threads of the same type as those used in the fabric. The threads of the various plies are allowed to be oriented in different directions.

When two plies are used, the threads of the second ply are often directed perpendicular to the threads of the first ply. For fixing the threads, seams are made through the plies. A reinforcement of aramide fibres is carried out in a similar manner.

**[0014]** According to the invention, it is further suggested that a fabric or mat comprises, as elements, threads or bundles of the above-mentioned material, which is suitable for indicating. By using such threads of a colour contrasting with that of the reinforcing material, such as a bright colour in the black carbon fibre material, they will be easy to spot in inspection. The threads, which can have the same thickness as the threads of the reinforcing material, are inserted preferably at the same distance from each other in the warp and in the weft as well as in both plies or all plies. This distance should give the elements a spreading in the reinforcing material that, as stated above, is determined by the used materials, the type of composite, the manufacturing technique etc.

**[0015]** When indicating threads, which become translucent or transparent when wetted, are inserted in both the warp and the weft and in the two plies of the mat, spots arise where the threads intersect, i.e. parts of the built-up layer which, when wetted, become translucent or transparent throughout the layer. If more than two plies are used in a mat, the indicating threads are arranged in the additional plies, such that they extend in the above-mentioned spots or restricted parts. In this manner, indication is obtained throughout the layer. As a result, it is possible to make sure that the layer has been wetted throughout its thickness, not only in its uppermost ply.

**[0016]** If the layers include a reinforcing fabric or mat having threads or bundles in one ply only, the reinforcement is usually laid with the threads oriented in different directions in the layers. In the intersection of indicating threads, spots for indicating in two layers will be obtained.

**[0017]** The invention is not restricted to manufacture by simple hand lay-up. It can also be used in vacuum infusion using a transparent coating foil and for preimpregnated reinforcing materials, the wetting being checked before manufacturing the composite object.

#### Advantages

#### **[0018]**

- According to the invention, it is possible to have a quality control of e.g. high-strength composite materials with reinforcement of carbon fibres and aramides. The appearance of these materials does not change when wetted, and therefore it has previously been necessary to use time-consuming and expensive techniques.
- The composite material according to the invention causes an indication in depth throughout the layer

last applied, in some cases throughout the thickness of the entire applied material.

- The inspection can be carried out more systematically since a checked pattern or the like is available for assistance.
- It is possible to avoid expensive preparation of the carbon fibre material, which is often regarded as necessary for complete wetting, such as preimpregnation and subsequent cold storage to prevent the curing of the impregnation.

#### Description of the Drawing

**[0019]** A preferred embodiment will be further described with reference to the accompanying drawing, which shows a reinforcing material in the form of a fabric containing elements according to the invention.

#### The Preferred Embodiment

**[0020]** The Figure illustrates a portion of a plain weave fabric 1 to be used as reinforcement in a composite. The fabric, which is of standard type with the exception of the inserted indicating elements which will be described below, comprises bundles of the same type for both the warp 2 and the weft 3 of the fabric. The bundles are of an ordinary kind and are elongate in cross-section having a height which is small in relation to the length and consist of a large number of parallel longitudinal fibres of fibrils of carbon fibre. Instead of every twenty-fifth carbon fibre bundle in warp as well as weft, indicating elements 4 in the form of bundles of glass fibres are inserted. In the preferred embodiment, these bundles are of a cross-section corresponding to that of the carbon fibre bundles so as to prevent the thickness of the fabric from **[deletion(s)]** being irregular. The ratio 4% of the amount of indicating material, glass fibres, to the amount of reinforcing material, carbon fibres and glass fibres, has been selected empirically. In other types of fabrics, other ratios can be selected. If narrower bundles of glass fibres are used, the ratio can, of course, be reduced to, for instance, 2.5% which in respect of strength is more favourable, or the distance between the glass fibre bundles can be reduced at the same ratio. This ratio should not be so great that the reinforcement is impaired in an impermissible manner. Also the manufacturing technique is of importance. If, for instance, during application, the layers are worked more between the bundles than on the bundles, the ratio can be decreased without the risk of error in indication being unacceptable.

**[0021]** The manufacture of composite is carried out in the same manner whether the reinforcing material comprises elements according to the invention or not. However, the inspection after application of each layer is effected more systematically by making sure that all the fibre glass threads and especially their intersections have changed from the original colour to a colour which depends on, inter alia, the base of the previously applied

layer.

#### Claims

1. A composite material comprising a matrix material of thermosetting plastic, a reinforcement (1), comprising a fabric or mat comprising a warp and a weft and a ply, respectively, which each comprises mutually parallel threads or fibre bundles, which have different orientations in warp and weft and, where appropriate, two adjoining mat plies, respectively, and which do not become translucent/transparent when wetted by the matrix, for instance, fibre bundles of carbon fibres or aramide, and indicating means, indicating that the reinforcement has been wetted by the matrix material, **characterised in that** the indicating means consists of indicating threads/bundles (4) which become translucent/transparent when wetted by the matrix, that said indicating threads/bundles are inserted, in at least the warp or weft of the fabric or one of the plies of the mat, in parallel with the associated reinforcing threads/bundles, and that the volume of the indicating threads/bundles is so small in relation to the volume of the reinforcing threads/bundles that the properties of the composite are not affected to an unacceptable extent.
2. The composite material as claimed in claim 1, **characterised in that** the indicating threads/bundles (4) are adapted to become translucent/transparent only when the adjoining reinforcing threads/ bundles have become wetted throughout.
3. The composite material as claimed in any one of the preceding claims, **characterised in that** the indicating threads/bundles (4) are uniformly distributed across the reinforcement.
4. The composite material as claimed in any one of the preceding claims, **characterised in that** the indicating threads/bundles (4) are made of a material which also serves as reinforcement, e.g. glass fibres or polymer.
5. The composite material as claimed in any one of the preceding claims, **characterised in that** the volume of the indicating threads/bundles amounts to a maximum of about 5% of the total volume of reinforcement, preferably 4%.
6. The composite material as claimed in any one of the preceding claims, **characterised in that** indicating threads/bundles are included in both the warp and weft of the fabric, and that the fabric is so arranged that the indicating threads/bundles form intersections which, when

wetted, become translucent/ transparent throughout the fabric.

7. The composite material as claimed in any one of claims 1 - 5, **characterised in that** the mat comprises two plies, and that indicating threads/bundles are inserted in each ply and that the mat is so arranged that the indicating threads/bundles form intersections which, when wetted, become translucent/ transparent throughout the mat.

8. The composite material as claimed in any one of claims 1 - 5, **characterised in that** the reinforcement comprises two adjoining single ply mats, each of different orientation and having indicating threads/bundles and that the mats are so arranged that the indicating threads/bundles form intersections which, when wetted, become translucent/ transparent throughout the mats.

### Revendications

1. Matériau composite comprenant un matériau de matrice en matière plastique thermodurcissable ; un renforcement (1) constitué d'un tissu ou d'une natte comprenant respectivement une chaîne, une trame et des plis, qui comprennent chacun des faisceaux de fils ou de fibres mutuellement parallèles ayant des orientations de chaîne et de trame différentes et, lorsque cela est approprié, deux plis de natte respectivement adjacents, et qui ne deviennent pas translucides/transparents lorsque par exemple des faisceaux de fibres de carbone ou d'aramide sont mouillés par la matrice ; et des moyens d'indication indiquant que le renforcement a été mouillé par le matériau de matrice,

#### **caractérisé en ce que**

les moyens d'indication sont constitués par des fils/faisceaux d'indication (4) qui deviennent translucides/transparents lorsqu'ils sont mouillés par la matrice, ces fils/faisceaux d'indication étant introduits au moins dans la chaîne ou dans la trame du tissu ou dans l'un des plis de la natte, en parallèle avec les fils/faisceaux de renforcement associés ; et le volume des fils/faisceaux d'indication est si petit, par rapport au volume des fils/faisceaux de renforcement, que les propriétés du composite ne sont pas affectées à un point inacceptable.

2. Matériau composite selon la revendication 1, **caractérisé en ce que** les fils/faisceaux d'indication (4) sont conçus pour ne devenir translucides/transparents que lorsque les fils/faisceaux de renforcement adjacents ont été complètement mouillés.

3. Matériau composite selon l'une quelconque des re-

vendications précédentes,

#### **caractérisé en ce que**

les fils/faisceaux d'indication (4) sont uniformément répartis en travers du renforcement.

4. Matériau composite selon l'une quelconque des revendications précédentes,

#### **caractérisé en ce que**

les fils/faisceaux d'indication (4) sont réalisés dans un matériau qui sert également de renforcement, comme par exemple des fibres de verre ou de polymère.

5. Matériau composite selon l'une quelconque des revendications précédentes,

#### **caractérisé en ce que**

le volume des fils/faisceaux d'indication s'élève à un maximum d'environ 5 % du volume total du renforcement, et se situe de préférence à 4 %.

6. Matériau composite selon l'une quelconque des revendications précédentes,

#### **caractérisé en ce que**

les fils/faisceaux d'indication sont inclus à la fois dans la chaîne et dans la trame du tissu ; et le tissu est disposé de façon que les fils/faisceaux d'indication forment des intersections qui, lorsqu'elles sont mouillées, deviennent translucides/transparents dans tout le tissu.

7. Matériau composite selon l'une quelconque des revendications 1 à 5,

#### **caractérisé en ce que**

la natte comprend deux plis ; les fils/faisceaux d'indication sont insérés dans chaque pli ; et la natte est disposée de façon que les fils/faisceaux d'indication forment des intersections qui, lorsqu'elles sont mouillées, deviennent translucides/transparents dans toute la natte.

8. Matériau composite selon l'une quelconque des revendications 1 à 5,

#### **caractérisé en ce que**

le renforcement comprend deux nattes à un seul pli adjacentes, présentant chacune une orientation différente et comportant des fils/faisceaux d'indication ; et les nattes sont disposées de façon que les fils/faisceaux d'indication forment des intersections qui, lorsqu'elles sont mouillées, deviennent translucides/transparents dans toutes les nattes.

### Patentansprüche

1. Verbundmaterial, enthaltend ein Matrixmaterial aus hitzehärtendem Kunststoff, eine Verstärkung (1),

- enthaltend ein Gewebe oder eine Matte, mit Kett- und Schussfäden bzw. ein Schichtmaterial (ply), von denen jedes zueinander parallele Fäden oder Faserbündel enthält, die in der Kette und im Schuss verschiedene Orientierungen haben bzw., falls zutreffend, zwei angrenzende Mattenschichten, und die nicht durchscheinend/durchsichtig werden, wenn sie durch die Matrix benetzt werden, z.B. Faserbündel aus Kohlefasern oder Aramid, und Indikatormittel, die anzeigen, dass die Verstärkung durch das Matrixmaterial benetzt wurde, **dadurch gekennzeichnet, dass** die Indikatormittel aus Indikator-Fäden/Bündeln (4) bestehen, die durchscheinend/durchsichtig werden, wenn sie durch die Matrix benetzt werden, dass die Indikator-Fäden/Bündel zumindest in der Kette oder im Schuss des Gewebes oder in einer der Schichten der Matte, parallel zu den zugeordneten Verstärkungs-Fäden/Bündeln eingefügt sind, und dass das Volumen der Indikator-Fäden/Bündel im Verhältnis zu dem Volumen der Verstärkungs-Fäden/Bündel so klein ist, dass die Eigenschaften des Verbundmaterials nicht in einem unzulässigen Ausmaß beeinträchtigt werden.
2. Verbundmaterial nach Anspruch 1, **dadurch gekennzeichnet, dass** die Indikator-Fäden/Bündel (4) nur dann durchscheinend/durchsichtig werden, wenn die angrenzenden Verstärkungs-Fäden/Bündel vollständig benetzt sind.
3. Verbundmaterial nach einem der vorhergehenden Ansprüche, **dadurch gekennzeichnet, dass** die Indikator-Fäden/Bündel (4) gleichmäßig über die Verstärkung verteilt sind.
4. Verbundmaterial nach einem der vorhergehenden Ansprüche, **dadurch gekennzeichnet, dass** die Indikator-Fäden/Bündel (4) aus einem Material hergestellt sind, das auch als Verstärkung dient, z.B. aus Glasfasern oder Polymeren.
5. Verbundmaterial nach einem der vorhergehenden Ansprüche, **dadurch gekennzeichnet, dass** das Volumen der Indikator-Fäden/Bündel maximal etwa 5% des Gesamtvolumens der Verstärkung, vorzugsweise 4%, beträgt.
6. Verbundmaterial nach einem der vorhergehenden Ansprüche, **dadurch gekennzeichnet, dass** die Indikator-Fäden/Bündel sowohl in der Kette als auch im Schuss des Gewebes eingeschlossen sind und dass das Gewebe so angeordnet ist, dass die Indikator-Fäden/Bündel Kreuzungspunkte bilden, die, wenn sie benetzt werden, durch das gesamte Gewebe durchscheinend/durchsichtig werden.
7. Verbundmaterial nach einem der Ansprüche 1 bis 5, **dadurch gekennzeichnet, dass** die Matte zwei Schichten enthält und dass Indikator-Fäden/Bündel in jede Schicht eingefügt sind und dass die Matte so angeordnet ist, dass die Indikator-Fäden/Bündel Kreuzungspunkte bilden, die, wenn sie benetzt sind, durch die gesamte Matte durchscheinend/durchsichtig werden.
8. Verbundmaterial nach einem der Ansprüche 1 bis 5, **dadurch gekennzeichnet, dass** die Verstärkung zwei angrenzende einschichtige Matten mit unterschiedlicher Orientierung enthält, welche Indikator-Fäden/Bündel enthalten, und dass die Matten so angeordnet sind, dass die Indikator-Fäden/Bündel Kreuzungspunkte bilden, die, wenn sie benetzt sind, durch die gesamten Matten durchscheinend/durchsichtig werden.

