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(54) **Transparent armour**

(57) The invention relates to a transparent armour suitable for providing ballistic protection from an impacting projectile, the armour comprising a plurality of trans-

parent pellets (1) arranged in a layer and embedded in a transparent matrix (2), wherein the ratio of the refractive index of the pellets (1) to the refractive index of the matrix (2) is in the range of 0.9:1 to 1.1:1.

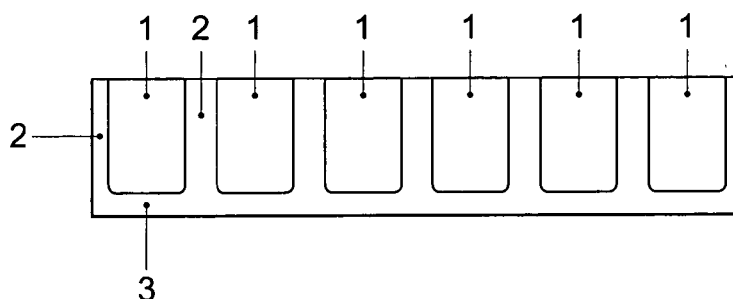


Fig. 1D

Description

[0001] The invention relates to a transparent glass suitable as an armour material.

[0002] Transparent armour with antiballistic properties are usually made of multiple layers of transparent material having a hard frangible face plate backed by one or more transparent tough resilient plates, bonded together by a suitable transparent adhesive layer. Such armour is for instance described in United States Statutory Invention Registration H1567 (application number 667,624). Another laminated transparent armour is described in United States Statutory Invention Registration H1519 (application number 522,788).

[0003] Laminated transparent armour has a high tendency of lateral tearing or bursting upon impact of a bullet or other projectile. Accordingly, it offers limited "multi-hit" protection (protection against impact of a plurality of projectiles). As a result, laminated armour generally needs to be very thick, and therefore rather heavy, to provide a given level of antiballistic protection. Further, the freedom in shaping the laminated armour materials is limited, usually to flat plates. This can make application in transports, for instance military vehicles or armoured cars, problematic. Further, a laminated design may be detrimental to the transparency of the armour. In order to maintain good transparency special precautions may have to be taken during the manufacture of the armour.

[0004] It is an object of the present invention to provide a novel armour which may be used as an alternative to known armour.

[0005] It is in particular an object of the invention to provide a novel transparent armour which is suitable to provide adequate protection against the impact of a projectile, more in particular an armour which provides a good multi-hit protection.

[0006] It is a further object of the invention to provide an armour that is relatively light and/or thin for a given level of antiballistic protection.

[0007] One or more objects which may be solved in accordance with the invention may be derived from the description herein below.

[0008] It has now been found that one or more objects are solved by providing a specific composite armour, making use of a specific combination of a hard material and a more ductile material.

[0009] In particular the inventors have realised that it is possible to provide a transparent armour from pellets of a relatively hard transparent material embedded in a relatively elastic material, provided that these materials are carefully selected upon a specific optical parameter.

[0010] Accordingly the present invention relates to a transparent armour suitable for providing ballistic protection from an impacting projectile, the armour comprising a plurality of transparent pellets arranged in a layer and embedded in a transparent matrix material, wherein the ratio of the refractive index of the pellets to the refractive index of the polymeric material is in the range of 0.9:1 to

1.1:1. In view of better transparency, the ratio is preferably in the range of 0.95:1 to 1.05:1, more preferably in the range of 0.99:1 to 1.01:1.

[0011] Figures 1A, 1B and 1C schematically shows a top view of an armour of the invention.

[0012] Figures 1D, 1E and 1F schematically show cross-sections of armour plates of the invention.

[0013] Figure 2 illustrates how non-matching refractive indices for the pellets and the material surrounding the pellets results in insufficient transparency.

[0014] Figure 3 shows a picture of an armour material of the invention.

[0015] The term "transparent" is generally understood in the art. It will be understood that transparency is to some extent dependent upon the thickness of the armour. In particular a material, such as the armour/pellet/matrix/backing material, is considered transparent if the luminous transmission is 85 % or more and/or the haze is 5 % or less.

[0016] Figure 2 illustrates that a composite material is not transparent, if the refractive indices of the embedded phase (pellets) and the surrounding phase, do not match. Figure 2 shows a number of transparent pellets surrounded by air (also transparent, but having a different refractive index). It is shown that a large part of the characters opposite to the viewing side of the pellets are distorted such that they cannot be read.

[0017] Figure 3 shows an armour according to the invention. This armour is transparent as the characters are not visually distorted and are clearly readable through the armour.

[0018] Besides transparency, mechanical properties of the matrix material (usually a polymer or composition comprising a polymer) embedding the pellets are relevant. The material is generally chosen such that it is sufficiently strong (after curing) that it is dimensionally stable during normal use. Preferably (after curing) the matrix preferably meets one or more of the following criteria:

- shrinkage (compared to uncured resin): 0.3 % or less, in particular 0.15-0.3 %.
- elongation until rupture: at least 100 %, in particular 175-500 %
- tensile strength: at least 2 MPa, in particular 2-20 MPa.
- tear strength: at least 0.2 MPa, in particular 0.2-2 MPa.
- hardness: at least Shore A 50, in particular Shore A 50 - 95.
- Glassy (dynamic, 1 Hz) Young's modulus: about 2700 MPa.
- Rubber (dynamic, 1 Hz) Young's modulus: about 4.5 MPa.
- glass transition temperature about 15 to about 25 °C.
- a relaxation curve as measured by the method described in "C van 't Hof, Mechanical Characterization and Modeling of Curing Thermosets, PhD thesis Delft University of Technology, 2005, essentially cor-

responding to the curve shown in Figure 4.

[0019] Tear strength may be determined according to ISO 34, Hardness according to ISO 868, parameters obtainable by a tensile test according to ISO 35.

[0020] It is desirable that the material is relatively elastic (compared to the pellets), to prevent the material from excessive cracking. The skilled person is aware of desirable values for such properties. Further, it is desirable that the matrix adheres well to the pellets, for improved multi-hit capability and thus improved armour performance of the product.

[0021] The inventors have found that it is particularly advantageous with respect to improving the multi-hit capacity of the armour by providing the armour with a visco-elastic material. For improving multi-hit capacity, the visco-elastic relaxation time, preferably should be in the range of 10^{-9} - 10^{-1} [s].

[0022] The matrix material may in particular comprise one or more transparent polymers selected from the group consisting of acrylonitrile-butadiene-styrene; acetal resins; cellulose derivatives, in particular such cellulose esters, such as cellulose acetate, cellulose butyrate, cellulose propionate, cellulose triacetate and alkyl celluloses, such as ethyl cellulose; acrylics, allyl resins; polyethers, in particular such chlorinated polyethers; fluoroplastics; transparent melamines; polyamides (nylon); parylene polymers; phenolics; phenoxy resins; polybutylene, polycarbonates; polyesters; polyethylenes; polypropylenes; polyphenylenes; polystyrenes, transparent polyurethanes; polysulphones; polyvinyl alcohols; polyvinyl fluorides; polyvinyl butyrals; polyvinylidene chlorides, silicones; styrene acrylonitrile; styrene butadiene; including copolymers of any of these.

[0023] Preferably the matrix comprises a polymer selected from the group consisting of transparent polyurethanes, transparent silicones and transparent polycarbonates. Particularly good results have been achieved with a transparent polyurethane, in particular with respect to transparency, (visco)-elastic properties and/or adherence to the pellets, in particular with glass pellets.

[0024] Suitable resins for providing a matrix in an armour of the invention are commercially available. Examples thereof include: Castable transparent Polyurethane resin (PUR, such as ClearFlex hardness Shore A between 50 and 90, manufacturer Smooth-On, 2000 Saint John Street, Easton, PA 18042); MB International 438 PU; MB International Poly A80; Permapur RD 3505; Simula: SIM 2025, SIM 2003. Such resins form a suitable matrix upon curing.

[0025] For an improved antiballistic property, the hardness of the matrix, after curing, such as a cured polyurethane resin, is preferably relatively high. Usually the hardness is at least 50 Shore A, in particular at least 60 Shore A, preferably at least 70 Shore A.

[0026] Generally the hardness of the matrix (after curing) is chosen such that the risk of cracking of the matrix

during impact of a projectile is sufficiently low. Usually the hardness is 25 Shore D or less, preferably .20 Shore D, in particular 95 Shore A or less.

[0027] Optionally, the matrix comprises one or more additives in order to alter a mechanical property, adherence to the pellets, transparency and/or the refractive index. In particular a refractive index modifier may be included to match the refractive index more closely with the refractive index of the pellets. Examples of such modifier include organic or inorganic nano-particles, such as ceramic, metallic or polymeric nanoparticles. A suitable inorganic nanoparticulate material is e.g. described in WO 01/04050. Herein inorganic fillers are described that have been subjected to an ion exchange with a modifier, which modifier comprises at least two ionic groups, which groups are separated from each other by at least four atoms.

[0028] The pellets may be made of any transparent material, in particular any transparent glass or ceramic, suitable for use in anti-ballistic armour. Usually the vickers hardness of the material is at least 400 kg/mm². Preferably the glass/ceramic has a Vickers hardness of at least 500 kg/mm². In particular, the glass may be selected from the group consisting of transparent silicates, such as transparent fused quartz, transparent borosilicate glass, transparent aluminium oxide, transparent magnesium aluminium oxide (spinel), transparent sapphire, transparent aluminium oxynitride (ALON) glass

[0029] Preferred pellets include pellets made of glass or fused quartz up to level B6 EN 1063 (7.62x51 mm Ball), spinel (up to level B7 EN 1063 (7.62x51 AP)), sapphire (up to level B7 EN 1063 (7.62x51 AP)) and aluminomoxynitride (from level B7 EN 1063 (7.62x51 AP) and higher).

[0030] From an antiballistic viewpoint, spinel and sapphire have particularly good properties, but these materials are still very expensive. The glass up to level B6 on the other hand is relatively cheap, yet provides sufficient hardness for adequate antiballistic properties, especially for use in relatively low thread applications. Fused SiO₂, is on the one hand relatively cheap compared to spinel and sapphire, yet generally provide improved protection against the impact of projectiles compared to regular glasses.

[0031] Suitable glass/ceramic material for providing the pellets are commercially available or can be made by glass manufactures upon request by specifying the desired refractive index and mechanical properties. If desired the refractive index can be altered by adding a refractive index altering additive, such as a specific metal oxides (for instance PbO, BaO, Li₂O, B₂O₃, ZnO).

[0032] Regarding the design of the armour, in particular with respect to shape of the pellets and the orientation of the pellets in the matrix, it is noted that it has been suggested in the prior art to provide non-transparent armour comprising pellets of a hard material embedded in an elastic material. In principle any such design may be applied to the present armour, provided that transparen-

cy is maintained. Figures 1A, 1B and 1C schematically show two armour plates of the invention (in top view). In principle, the pellets 1 - embedded in matrix 2 - may be arranged in any other way. Good results with respect to anti-ballistic protection, have in particular been achieved with an arrangement as shown in Figure 1B or 1C, where-

[0033] Figures 1D-1F schematically show cross-sections of an armour of the invention. The geometry of the pellets is preferably substantially cylindrical, in particular substantially round cylindrical, more in particular substantially round circular cylindrical (Figure 1D), substantially oval (Figure 1E) or substantially spherical (Figure 1F). Such a geometry is considered advantageous because of the presence of relatively large space for the matrix between the pellets, also if the pellets are arranged relatively close to each other, even if they are arranged that they even touch adjacent pellets. Such pellet geometry allows a high degree of freedom with respect to the shape of the armour. Accordingly, such geometry of the pellets is in particular preferred for three-dimensionally shaped armour, such as an armour with a curved surface. Substantially oval or substantially spherical pellets are highly preferred in view of one or both of these advantages.

[0034] Cylindrical pellets are preferably arranged such that an end of the cylinder is substantially parallel to the surface plane of the armour and the curved surface of the cylinder is substantially perpendicular to the surface plane of the armour. This is considered advantageous for improved transparency, a favourable distribution of matrix material between the pellets and/or the design of a three-dimensionally shaped armour.

[0035] The dimensions of the pellets are generally chosen based on the desired weight and thickness of the armour on one hand and the desired anti-ballistic properties on the other. The dimensions of the pellets are usually in the range of 1-50 mm.

[0036] A relatively large height (i.e. the dimension in the direction perpendicular to the surface plane of the armour) is generally desired for improved antiballistic properties in general. The dimensions in the plane of the surface is preferably relatively low for an improved multi-hit capacity. Usually, the height of the pellets is at least 1 mm, preferably at least 3 mm. Usually the height is up to 50 mm.

[0037] Preferably, the diameter of the pellets (the largest dimension in parallel to the plane of the layer in which the pellets are positioned) is at least 10 mm. Usually the diameter is up to 50 mm.

[0038] Usually, it is sufficient to provide the pellets in a single layer of pellets which are directly bound and retained in the desired form by the matrix such that the pellets are bound in a plurality of adjacent rows.

In an embodiment of the invention a majority of said pellets is in direct contact with at least four adjacent pellets

in the same layer to provide mutual lateral confinement there between, said pellets each have a substantially regular geometric form. Such embodiment is schematically shown in Figures 1A and 1B. Such design is in generally also described for non-transparent armour in WO99/60327, the contents of which with respect to the design of the pellets and the arranging of the pellets in the armour is incorporated herein by reference.

[0039] In particular with respect to improved multi-hit properties the present inventors have realised that it may be advantageous to arrange the pellets such that the majority of the pellets do not touch most of the surrounding pellets. This is schematically shown in Figure 1C. It is noted though that the general arrangement of the pellets relatively to each other may be different, for instance as shown in Figure 1A, but with the difference that in this embodiment the majority of the pellets not touching the surrounding pellets. Accordingly, in a preferred embodiment at least the majority of the pellets is in direct contact with less than four adjacent pellets, preferably at least the majority is in direct contact with less than three adjacent pellets, more preferably at least the majority is in direct contact with one or zero adjacent pellets.

[0040] An armour of the invention may be provided with a backing layer 3, at the rear side of the armour (taken from the side from which the threat by impacting projectiles is expected). In principle, the backing layer may be a separate transparent plate bonded to the layer comprising the pellets, e.g. as described in the above identified prior art. However, it has been advantageous to provide a backing layer forming an integral part with the matrix, as shown in Figures 1D, 1E and 1F. Thus, the backing layer 3 and matrix 2 form a visually homogenous (monolithic) structure, rather than a laminate.

[0041] This may be advantageous with respect to improved transparency. Further, such structure has improved integrity of the armour (as opposed to a laminated structure wherein the backing layer may delaminate relatively easily from the remainder of the armour and/or a pellet may relatively easily be partially or fully forced out of the matrix, especially upon impact by a projectile). Further, it is considered that a monolithic structure allows or facilitates repair of an armour of the invention after an impact by a projectile.

[0042] If present, the backing layer usually has a thickness of at least 5 mm, preferably at least 10 mm. The upper limit is chosen depending upon the maximum desired thickness of the armour and/or the desired antiballistic properties. Usually a thickness of 60 mm or less is sufficient.

[0043] The matrix and backing layer are usually formed of the same class of materials (such as both polyurethanes, both silicones or both polycarbonates). The mechanical properties need not be the same. In particular one may provide the armour with a monolithic structure comprising the matrix embedding the pellets and the backing layer wherein the matrix is softer and/or more elastic than the backing layer and/or wherein the backing

layer is stronger and stiffer than the matrix. (See also below, where the manufacture of an armour is described.)

[0044] An armour of the invention may in particular be a substantially flat or curved. In particular it may be a (flat) window, a (curved) windshield, a visor, a screen, a canopy or a dome.

[0045] The armour is in particular suitable for use (as a window/screen) in a vehicle, visor or counter. Accordingly the invention also relates to a transport or counter of the invention. Preferred transports included, military vehicles, in particular logistic military vehicles, and cars in general.

[0046] The invention further relates to a method for manufacturing an armour according to the invention, comprising

- positioning the pellets in a layer in a mould
- filling the space between the pellets with a reaction mixture for forming the polymeric material; and
- curing the reaction mixture, thereby forming the polymeric material.

[0047] Suitable reaction mixtures for providing the transparent matrix are known in the art (see e.g. above). They typically comprise a castable polymer and/or liquid polymerisable compound and - if desired - one or more additives for initiating the curing and/or providing cross-links (such as a multifunctional polymerisable compound). Preferred examples include polyurethane resins, such as Clearflex 50, Clearflex 75, Clearflex 90 and combinations thereof. In particular, good results have been achieved with Clearflex 75.

[0048] If desired, a backing layer is provided together with the matrix. Preferably a reaction mixture for providing the backing layer comprise a curable polymer and/or polymerisable compound and - if desired - one or more additives for initiating the curing and/or providing cross-links (such as a multifunctional polymerisable compound, which may also be referred to as a curing agent). If present, the reaction mixture for the backing layer is cured simultaneously with the reaction mixture for the matrix. Thus, a single structure (a monolith) is obtained of the backing layer and the matrix, which may be directly chemically bound together, especially in case the same class of curable polymer and/or polymerisable compound are used for the backing layer and the matrix (such as both reaction mixtures for providing a polyurethane). Thus, no adhesive is required to bind matrix and backing layer and an improved integrity of the matrix and backing layer, or even the armour in general, may be accomplished.

[0049] Curing may be accomplished in any manner suitable for curing the reaction mixture. Suitable curing techniques are known in polymer technology, with preferably Room Temperature-curing, low shrinkage, low exothermic and/or long potlife. Desired mechanical properties, such as (visco-)elasticity, stiffness, strength, hard-

ness and/or toughness may be imparted to the matrix/backing layer by selecting a specific ratio for the ingredients of the reaction mixtures, in particular the ratio of curable polymer to curing agent.

[0050] In order to obtain a transparent armour it is preferred that care is taken that gas bubbles (such as air bubbles) are removed from the reaction mixture after filling the space and before curing the reaction mixture. This can be done by sonication or by applying a vacuum to the mould after filling it. Preferably a reaction mixture is used with a relatively low viscosity, in order to facilitate such removal and/or to facilitate adequate filling of the spaces between the pellets.

[0051] The invention will now be illustrated by the following examples

Example 1

Construction of transparent armour plate

[0052] The pellets (10 mm diameter and 18 mm high borosilicate glass pellets were placed as a layer into a flat mould. The PUR reaction mixture Clearflex 50 (available from Smooth-on, USA) was poured into the mould filling the gaps between the pellets. By placing the mould in a vacuum (< 10 mbar), the expanding air bubbles were allowed to escape from the casting and a pore free (crystal clear transparent) PUR is obtained. After curing, a 40 mm back layer of Clearflex 75 (A : B = 100:175) was poured directly on top of the layer surrounding the pellets. The vacuum procedure was repeated also for the back layer.

Transparency test

[0053] As shown in Figure 3, the material of the invention shows very good transparency.

Ballistic test

[0054] The armour was shot at twice with 7,62x51 mm Ball projectiles. The shots (impact velocities of 827 en 829 m/s) were at a distance of 47 mm from each other. Both impacts did not perforate the transparent armour. The damaged area of each shot had a diameter of approx. 60 mm and the total damaged area was approx. 50 cm².

[0055] A comparable laminated transparent armour was subjected to the same test. The damaged area was approx. 500 cm² per impact with a comparable type of glass with a comparable thickness and mass.

Claims

1. Transparent armour suitable for providing ballistic protection from an impacting projectile, the armour comprising a plurality of transparent pellets arranged

- in a layer and embedded in a transparent matrix, wherein the ratio of the refractive index of the pellets to the refractive index of the matrix is in the range of 0.9:1 to 1.1:1.
2. Armour according to claim 1, wherein the ratio is in the range of 0.95:1 to 1.05:1, preferably in the range of 0.99:1 to 1.01:1.
 3. Armour according to claim 1 or 2, wherein the matrix comprises a transparent visco-elastic polymer.
 4. Armour according to any one of the preceding claims, wherein the matrix comprises a polymer selected from the group consisting of transparent acrylonitrile-butadiene-styrenes, transparent acetal resins, transparent cellulose derivatives, transparent acrylics, transparent allyl resins, transparent polyethers, transparent fluoroplastics, transparent melamines, transparent polyamides, transparent parylene polymers, transparent phenolics, transparent phenoxy resins, transparent polybutylene, transparent polycarbonates, transparent polyesters, transparent polyethylenes, transparent polypropylenes, transparent polyphenylenes, transparent polystyrenes, transparent polyurethanes, transparent polysulphones, transparent polyvinyl alcohols, transparent polyvinyl fluorides, transparent polyvinyl butyral, transparent polyvinylidene chlorides, transparent silicones, transparent styrene acrylonitrile and transparent styrene butadiene, preferably from the group consisting of transparent polyurethanes, transparent silicones and transparent polycarbonates, more preferably from transparent polyurethanes.
 5. Armour according to any one of the preceding claims, wherein the pellets are selected from substantially round cylindrical pellets and substantially spherical pellets.
 6. Armour according to any one of the preceding claims, wherein the pellets have a refractive index in the range of 1.47-1.52.
 7. Armour according to any one of the preceding claims, wherein the pellets comprise a material selected from the group consisting of transparent silicates, such as transparent fused quartz, transparent borosilicate glass, transparent aluminium oxide, transparent magnesium aluminium oxide, transparent sapphire and transparent aluminium oxynitride glass.
 8. Armour according to any one of the preceding claims, wherein the armour comprises a backing layer, preferably a backing layer comprising a polymer of the same class as the matrix.
 9. Armour according to claim 8, wherein the backing layer and the matrix together forming a monolithic structure.
 10. Armour according to any one of the preceding claims, wherein the dimensions of the pellets are in the range of 1-50 mm.
 11. Armour according to any one of the preceding claims, wherein at least the majority of the pellets is in direct contact with less than four adjacent pellets, preferably at least the majority is in direct contact with less than three adjacent pellets, more preferably at least the majority is in direct contact with zero adjacent pellets.
 12. Armour according to any one of the preceding claims, wherein the armour is a window, screen, windscreen, visor, canopy or dome.
 13. Transport or counter comprising an armour according to any one of the preceding claims.
 14. Method for manufacturing an armour according to any one of the claims 1-11, comprising
 - positioning the pellets in a layer in a mould
 - filling the space between the pellets with a reaction mixture for forming the polymeric material; and
 - curing the reaction mixture, thereby forming the polymeric material.
 15. Method according to claim 13, wherein gas bubbles are removed from the reaction mixture after filling the space and before curing the reaction mixture.

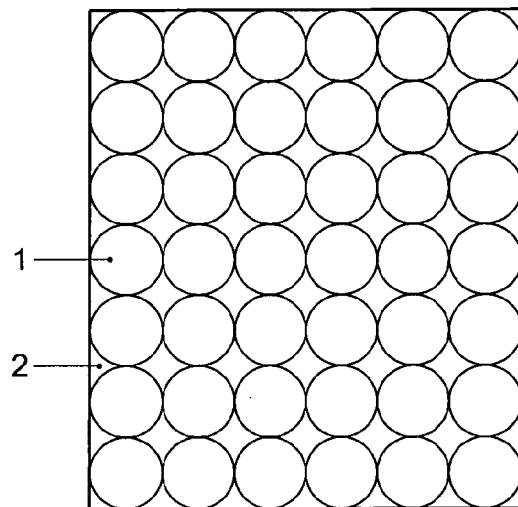


Fig. 1A

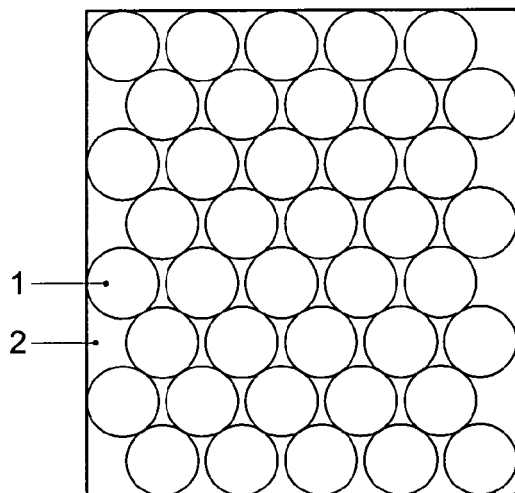


Fig. 1B

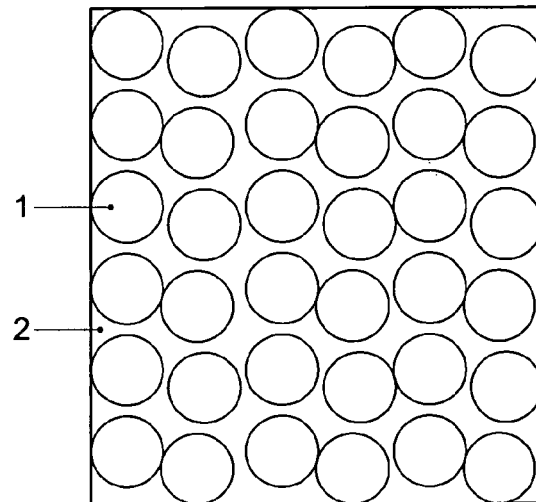


Fig. 1C

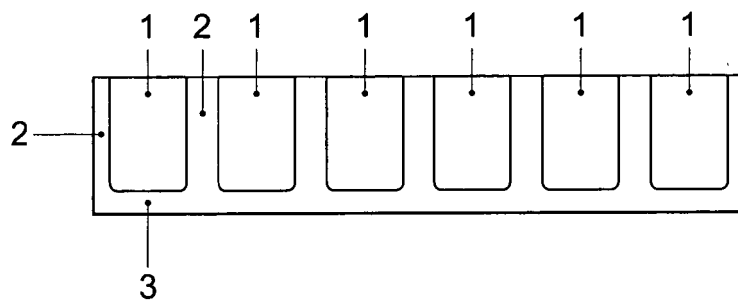


Fig. 1D

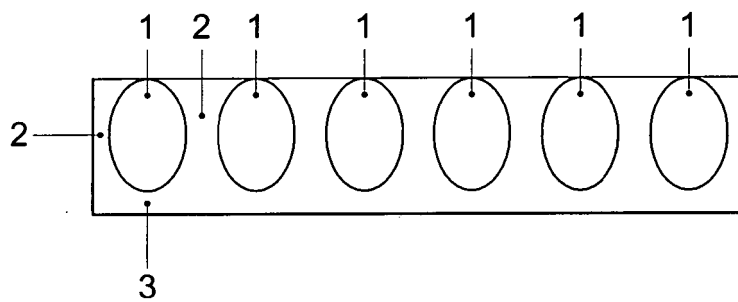


Fig. 1E

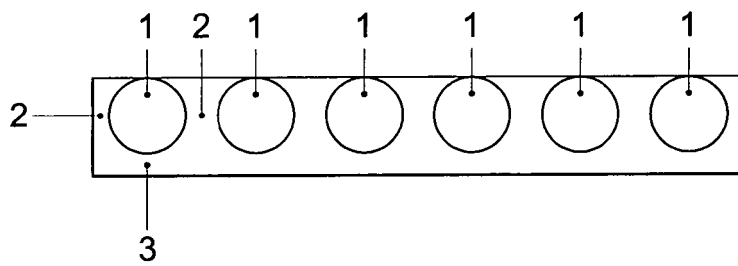


Fig. 1F

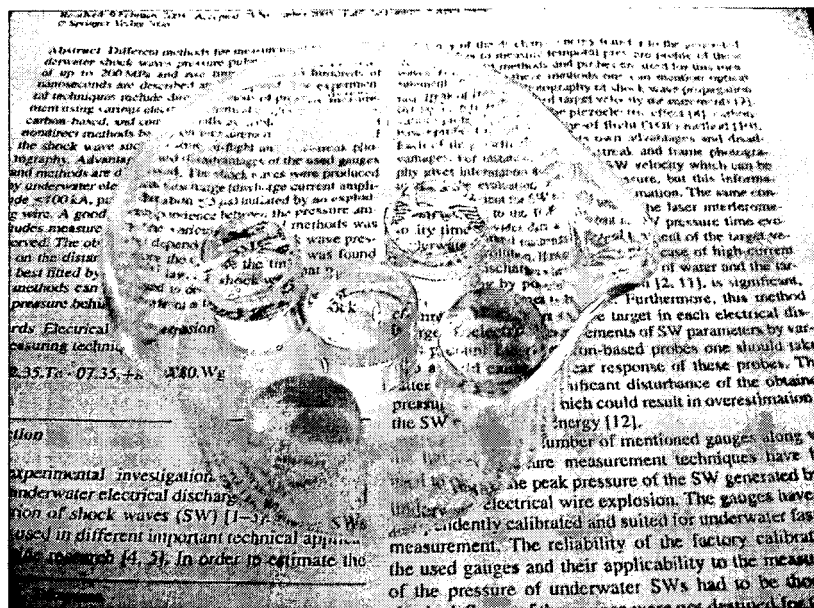


Fig. 2

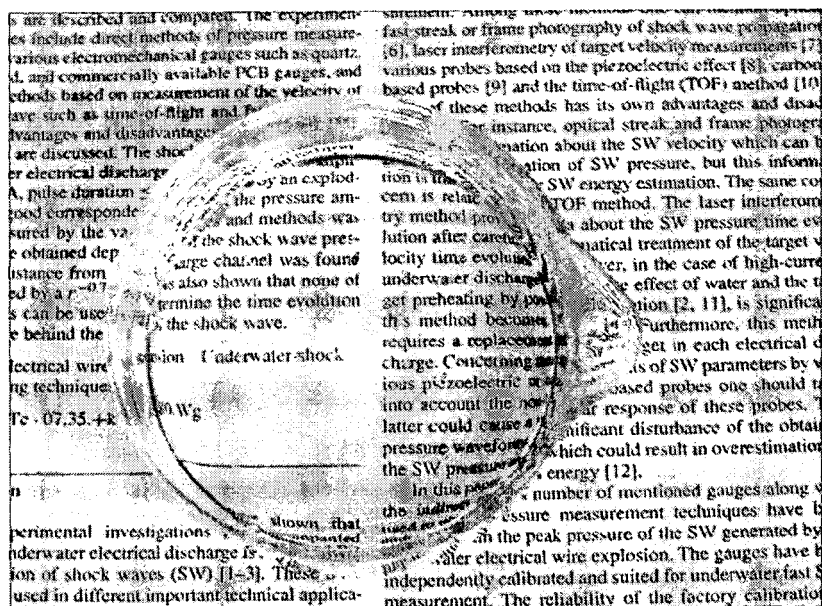


Fig. 3

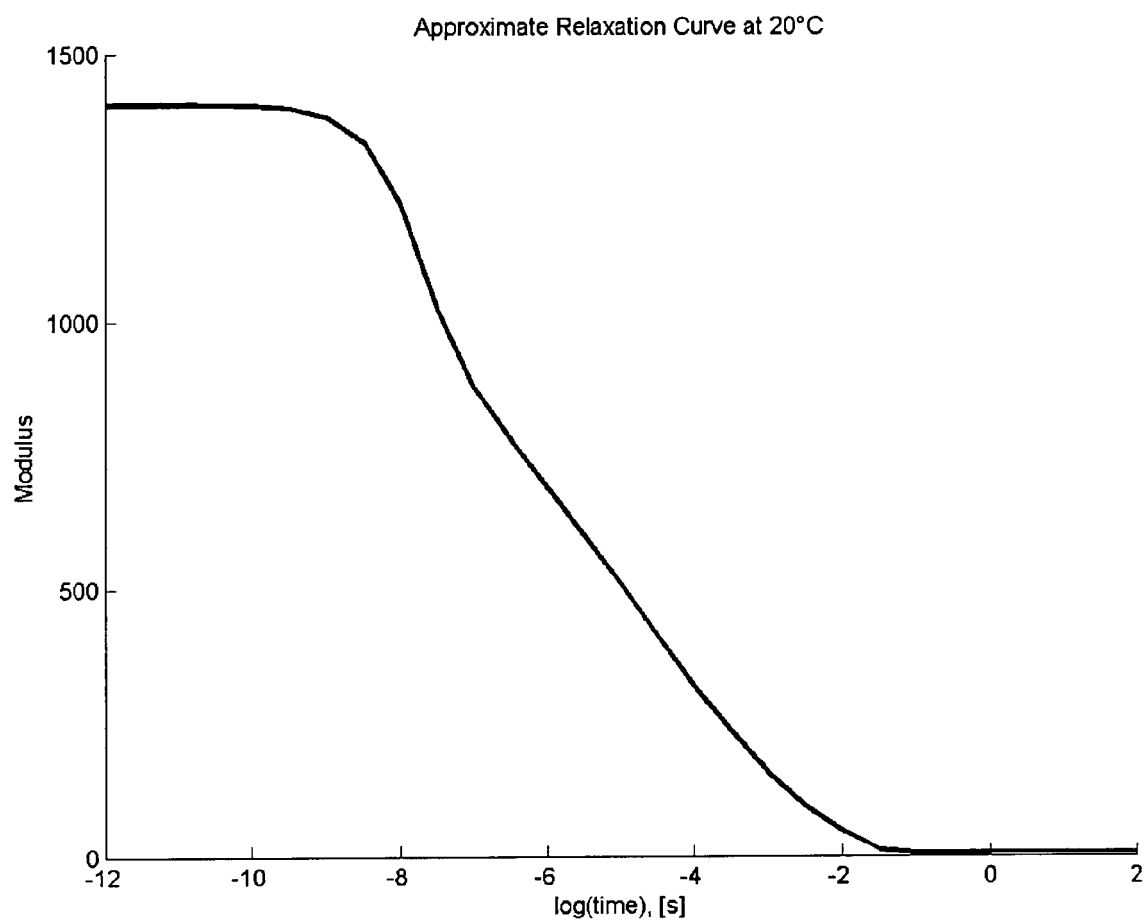


Fig. 4



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 06 07 6944

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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
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The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of the search 13 April 2007	Examiner GEX-COLLET, A
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EPO FORM 1503 03.82 (P04C01)



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Application Number
EP 06 07 6944

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The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of the search 13 April 2007	Examiner GEX-COLLET, A
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			

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

EP 06 07 6944

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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13-04-2007

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