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#### **DESCRIPTION KR101189457B1**

Bulletproof material having shear thickening fluid and manufacturing method thereof

## [0001]

The present invention relates to a bulletproof material having a shear thickening fluid and a method for manufacturing the same.

#### [0002]

In general, the material of body armor starts from nylon fibers, and today, aramid-based fibers and ultra-high molecular weight polyethylene (UHMWPE)-based fibers with significantly improved fiber strength are the mainstream. These fibers are manufactured in various forms and are used according to the requirements for protection performance, but the most widely used structure is a unidirectional tape (Uni) in which the fabric form and the fibers are laminated in the 0 degree direction and the 90 degree direction to form one layer. -directional tape: UD). Body armor is used by stacking these materials in multiple layers according to the requirements of the protective power.

#### [0003]

In the form of the fabric used for the body armor, plain weave, Twill, runner weave, etc. are used, and the fabric generally has excellent protection performance against fragmentation bullets, while it is somewhat weak against rear deformation by pistol bullets, and when worn Excellent flexibility.

The one-way tape is somewhat vulnerable to fragmentation bullets and has excellent protection against pistol bullets, but the stiffness of the material suppresses the wearer's activity, and when high protection is required, the thickness of the bulletproof material becomes thicker, causing more activity problems. is becoming

#### [0004]

In general, the fabric is composed of warp and weft yarns, and the fibers used here are woven using different denier (1g per 9000m) depending on the purpose.

There are various weaving types of fabrics, but the plain weave type, which has high flexibility and high friction between yarns and has excellent shock energy absorption, is the most used for personal body armor. In the case of fabric, when the fragmentation bullet collides, the yarn constituting the fabric is pulled-out, absorbing and dispersing the energy of the bullet and stopping it. When the energy of the yarn exceeds the frictional force or the tensile strength of the yarn, the bullet breaks and penetrates the yarn. On the other hand, pistol bullets are generally made of lead and the outside is covered with copper, so when the bullet collides with a bullet, the shape of the bullet changes to a mushroom shape, giving a big impact to the body, which is different from fragment bullets. It has a different bulletproof mechanism. Therefore, fragmentation bullets must block penetration, and pistol bullets must reduce the back face signature (BFS) to mitigate the impact on the human body. Modern body armor requires protection against both high-speed flying fragments and pistol bullets, such as bullets.

## [0005]

Existing fabrics have limitations in preventing high-speed fragmentation bullet penetration and reducing back deformation caused by pistol bullets due to the difficulty of increasing the yarn strength and increasing the friction between the yarns.

Fabric is more effective for body armor because the use of fabric improves the wearer's activity rather than the use of UD material when increasing the protective power.

## [0006]

Basically, when an external impact is applied to a bulletproof material, the kinetic energy must be transferred to the adjacent fiber or fabric layer and the shock must be dispersed to increase the bulletproof performance.

In U.S. Patents 5,776,839, 5,854,143, 3,649,426 and 3,649,426 in order to disperse impact energy by increasing friction between fibers, a technology of dispersing kinetic energy by coating an expandable dry powder (Dilatants) on a fiber or applying it to a fabric to increase friction between fibers However, this technique is bulky, heavy and has relatively limited flexibility.

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It is an object of the present invention, by impregnating a fabric used as a body armor with a shear thickening fluid containing nanoparticles, and by appropriately increasing the friction force between the fibers constituting the bulletproof fabric by the generation of a fluid cluster of nanoparticles during external impact, the impact energy An object of the present invention is to provide a bulletproof material capable of improving bulletproof performance by absorbing and dispersing and a method for manufacturing the same.

Another object of the present invention is, by impregnating a fabric used as a body armor with a shear thickening fluid, while reducing the weight of the body armor, and maintaining the flexibility of the same level as that of the fabric, a ballistic material capable of improving the wearing comfort and a method for manufacturing the same is to provide

In the ballistic material having a shear thickening fluid according to an embodiment of the present invention for achieving the above objects, in the ballistic material comprising a fabric layer, the front portion including the first fabric layer; a central portion including second fabric layers impregnated with the shear thickening fluid; and a rear portion including third fabric layers impregnated with the shear thickening fluid, wherein the amount of impregnation of the shear thickening fluid impregnated in the second fabric layers is the amount of the shear thickening fluid impregnated in the third fabric layers. It is characterized in that it is set differently from the impregnation amount.

As an example related to the present invention, the shear thickening fluid is characterized in that only the edge portions of the second and third fabric layers are impregnated.

As an example related to the present invention, the impregnation amount of the shear thickening fluid impregnated in the second fabric layers is set to be lower than the impregnation amount of the shear thickening fluid impregnated in the third fabric layers.

As an example related to the present invention, the amount of impregnation of the shear thickening fluid impregnated in the second fabric layers is 7%, and the amount of impregnation of the shear thickening fluid impregnated in the third fabric layers is 20% characterized in that do

As an example related to the present invention, the first to third fabric layers are characterized in that they include any one of aramid fibers, polyethylene fibers, polypropylene fibers, xylon fibers, nylon fibers, glass fibers, and carbon fibers.

As an example related to the present invention, the shear thickening fluid includes silica sol, and the dispersion medium of the shear thickening fluid includes polyethylene glycol.

As an example related to the present invention, the shear thickening fluid is a fluid containing inorganic nanoparticles dispersed in an organic solvent, and the inorganic nanoparticles include silicon oxide, aluminum oxide, calcium carbonate, natural mineral particles, or a mixture thereof. Including, the organic solvent is characterized in that it comprises at least one or more of methanol, ethanol, ethylene glycol and polyethylene glycol.

The method for manufacturing a bulletproof material having a shear thickening fluid according to an embodiment of the present invention for achieving the above objects, a front part, a central part, a rear part including a plurality of fabric layers by cutting the fabrics and stacking the cut fabrics, respectively A method of manufacturing a bulletproof material comprising: impregnating the first fabric layers included in the central portion with a shear thickening fluid; and impregnating the second fabric layers included in the rear part with a shear thickening fluid, wherein the amount of impregnation of the shear thickening fluid impregnated in the first fabric layers is the shear impregnated in the second fabric layers. It is characterized in that it is set differently from the impregnation amount of the thickening fluid.

Ballistic material and its manufacturing method according to an embodiment of the present invention, by impregnating the fabric used as a body armor with a shear thickening fluid containing nanoparticles, the fibers constituting the ballistic fabric by the generation of a fluid cluster of nanoparticles upon external impact It has the effect of improving the bulletproof performance by absorbing and dispersing the impact energy by appropriately increasing the friction force between them.

The bulletproof material and its manufacturing method according to an embodiment of the present invention, by impregnating the fabric used as the body armor with a shear thickening fluid, reduce the weight of the body armor, and maintain the flexibility of the same level as that of the fabric to improve the fit There are possible effects.

## [0019]

1 is a configuration diagram showing a bulletproof material according to an embodiment of the present invention.

2 is a view showing a first laminate (front part) of the bulletproof material according to an embodiment of the present invention.

Figure 3 is a view showing a second laminate (central portion) of the bulletproof material according to an embodiment of the present invention.

4 is a view showing a third laminate (rear part) of the bulletproof material according to an embodiment of the present invention.

## [0020]

In the following, by impregnating the fabric used as body armor with a shear thickening fluid containing nanoparticles, the frictional force between the fibers constituting the bulletproof fabric is appropriately increased by the generation of a fluid cluster of nanoparticles during external impact to absorb and disperse the impact energy. 1 to Figure 1 to a bulletproof material and its

manufacturing method according to an embodiment of the present invention that can improve the ballistic performance, reduce the weight of the body armor, and maintain the flexibility of the same level as that of the fabric to improve the wearing comfort 4 will be described in detail.

#### [0021]

In particular, the technical task of body armor requires protection of the above two bullets at the same time as the requirement to protect fragments or pistol bullets alone, and in the case of fragmentation bullets, high-speed fragmentation protection is required.

On the other hand, the protective part was previously limited mainly to the torso, but recently, as the protection of not only the body but also the neck, shoulders, flanks, and cysts is required, the weight of the body armor gradually increases and the volume and thickness become thicker, which impedes the activity. Therefore, in addition to weight reduction, it is also required to improve convenience and wearability when worn.

#### [0022]

Currently, body armor must protect against high-speed fragmentation projectiles of 500 to 600 m/s or level III-A required by the National Institute of Justice (NIJ) standard, that is, 9mm FMJ and .44 magnum bullets.

The conventional fabric form is excellent in defense against fragmentation bullets, but is weak in resistance to rear deformation by pistol bullets.

However, the latter material becomes too stiff when it becomes thick, which greatly reduces the convenience of the wearer.

Therefore, in order to solve this problem, the present invention is to treat the fabric with a shear thickening fluid to satisfy the protective performance, and to maintain flexibility while being lighter.

In order to defend against fragmentation or pistol bullets, optimal conditions for shear thickening fluid and optimal design of bulletproof materials must be resolved.

## [0023]

Even in the amount of impregnation of the shear thickening fluid, if the impregnation amount is too high, the frictional force between fibers increases too much, and on the contrary, the fibers break and the protective force decreases.

Therefore, the present invention is impregnated with a shear thickening fluid in the fabric used as a body armor to appropriately increase the friction force between the fibers constituting the bullet-proof fabric by the generation of a fluid cluster of nanoparticles during external impact while absorbing and dispersing the impact energy to improve the ballistic performance This is to improve the wearing comfort by maintaining the same level of flexibility as the fabric, while also reducing the weight.

To this end, the optimum conditions of the shear thickening fluid are suggested, and the rear deformation caused by high-speed fragmentation bullets and pistol bullets is minimized through the gradient design that varies the shear thickening fluid according to the stacking position of the fabric.

## [0024]

1 is a configuration diagram showing a bulletproof material according to an embodiment of the present invention.

#### [0025]

As shown in Figure 1, the bulletproof material 100 according to the embodiment of the present invention, a first laminate (front part) 110 comprising a plurality of fabric layers; a second laminate (central part) 120 including fabric layers impregnated with a shear thickening fluid; and a third laminate (rear part) 130 including fabric layers impregnated with the shear thickening fluid, wherein the amount of impregnation of the shear thickening fluid impregnated in the second laminate 120 (for example, 3 to 15% or 7%) is set lower than the impregnation amount (eg, 15 to 30% or 20%) of the shear thickening fluid impregnated in the third laminate 130.

## [0026]

In addition, the number of layers of the fabric 140 included in the first laminate 110 , the second laminate 120 , and the third laminate 130 may be added or reduced according to the designer's intention or required ballistic performance. can

The fabric component used in the fabric layer may be any one or more of aramid fibers, polyethylene fibers, polypropylene fibers, xylon fibers, nylon fibers, glass fibers, and carbon fibers.

Denier used in the fabric of the aramid fiber (Denier: 1g per 9000)) includes 200 to 1000.

Forms of the fabric include plain weave, main weave, twill weave, nonwoven fabric, and knitted fabric.

The plain weave includes 25 to 30 of the same number of warp and weft yarns per inch, respectively.

The plain weave fabric may have a structure in which the number of yarns per inch varies.

## [0027]

The bulletproof material 100 according to the embodiment of the present invention protects the high-speed Cal.22 (5.56mm) fragmentation bullet, and the bulletproof material 110, 120, 130 to simultaneously satisfy the "NIJ Standard 0101.06 level III-A" standard. It is composed of a laminate that has been placed and laminated.

#### [0028]

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The shear thickening fluid is a suspension in which the viscosity of the solution increases discontinuously and greatly while forming a hydro-cluster of dispersed particles with an increase in shear stress due to the flow characteristics of a non-Newtonian fluid in a concentrated colloidal dispersion solution.

When the fabric is impregnated with the shear thickening fluid, it normally exists in a liquid state and maintains its flexibility, but when the bullet impacts, the liquid phase changes to a solid phase due to a sudden increase in the viscosity of the shear thickening fluid. and dispersion can greatly increase the bulletproof performance.

#### [0029]

The nanoparticles used in the preparation of the shear thickening fluid in the present invention are silica sols of 45 nm, the dispersion medium is polyethylene glycol (molecular weight: # 200), and the volume fraction of the particles constituting the shear thickening fluid is 0.5 to 0.60.

#### [0030]

The shear thickening fluid is a sol-type fluid in which inorganic nanoparticles are dispersed in an organic solvent. The nanoparticles used may include silicon oxide, aluminum oxide, calcium carbonate, natural minerals or a mixture thereof, and the organic solvent is ethylene It may contain one of glycol and polyethylene glycol.

The diameter of the particles of the shear thickening fluid may be 10 ~ 100nm.

#### [0031]

As a fabric (or fiber) according to an embodiment of the present invention, a high-strength filament may be used as Heracron 600 denier polyaramid (Kolon Co., Ltd.).

The fabric (fiber) has a plain weave structure, and the number of warp X weft yarns per inch is 28 X 28 and 34 X 34, and the areal densities are 150 g/m2 and 180 g/m2, respectively.

The tensile strength of the filament of the polyaramid fiber is 26 g/d, the tensile elongation is 3.3%, and the modulus of elasticity is 750 g/d.

## [0032]

2 is a view showing a first laminate (front part) of the bulletproof material according to an embodiment of the present invention.

## [0033]

As shown in FIG. 2 , the fabric layers 110a of the first laminate 100 do not contain the shear thickening fluid, and are cut to 400  $\times$  400 mm.

Here, the number of layers of the fabric layer 110a of the first laminate 100 may be 7 to 45 layers, and the number of layers may be added or reduced according to the designer's intention or required ballistic performance.

## [0034]

Figure 3 is a view showing a second laminate (central portion) of the bulletproof material according to an embodiment of the present invention.

## [0035]

As shown in FIG. 3, before impregnating the fabric layer 120a of the second laminate 120 with the shear thickening fluid, the fabric is cut to 400 x 400 mm and then dried in an oven at 100° C. for 30 minutes.

Dispersion and impregnation of the shear thickening fluid by applying a constant pressure (for example, a pressure of 20 kg/cm2) in a press after applying the dispersion solution diluted in methanol at a certain ratio to the fabric layer 120a make it uniform.

At this time, the shear thickening fluid is impregnated from the edge of the fabric layer (specimen) 120a to the range of 50 to 80 mm, and the amount of the shear thickening fluid impregnated is the shear thickening fluid impregnated in the fabric layers of the third laminate 130. The impregnation is lower than the amount of impregnation of the fluid.

In addition, the central portion 120b of the specimen is maintained in a woven state without being impregnated with the shear thickening fluid.

## [0036]

In addition, the amount of impregnation (add-on%) relative to the weight of the fabric is impregnated with the shear thickening fluid only in the range of 50 to 80 mm from the edge of the fabric layer of one or more layers of the second laminate 120 at 1 to 15 wt%, The central portion 102b may not be impregnated with the shear thickening fluid.

#### [0037]

4 is a view showing a third laminate (rear part) of the bulletproof material according to an embodiment of the present invention.

#### [0038]

As shown in FIG. 4, the fabric layer (specimen) 130a of the third laminate (rear part) 130 has an impregnation amount of the shear thickening fluid higher than that of the specimen 120a, and the central part (130b) does not impregnate the shear thickening fluid.

After the impregnation is completed, apply an appropriate pressure in a hydraulic press so that the solution is uniformly impregnated and dispersed with the shear thickening fluid.

Here, before impregnating the fabric layer 130a of the third laminate 130 with the shear thickening fluid, the fabric may be cut to 400 x 400 mm and then dried in an oven at 100° C. for 30 minutes.

#### [0039]

Thereafter, the fabric layers (specimen) of the second laminate 120 and the third laminate are dried in an oven at 70° C. for 20 minutes.

The dried second laminated material 120 and the third laminated material 130 are arranged in the 110, 120, and 130 stacking order together with the first laminated material 110, and then the edges of the laminated materials 110, 120, and 130 are sewn with a cotton-nylon blended yarn. The bulletproof material 100 is manufactured.

#### [0040]

In addition, the amount of impregnation (add-on%) relative to the weight of the fabric is impregnated with the shear thickening fluid only in the range of 50 to 80 mm from the edge of the fabric layer of one or more layers of the third laminate 130 at 5 to 30 wt%, and , the central portion 130b may not be impregnated with the shear thickening fluid.

## [0041]

The surface of the fibers of the fabric constituting the lamination material of the central portion 120 and the rear portion 130 impregnated with the shear thickening fluid may not be subjected to water resistant treatment (WRT).

## [0042]

Hereinafter, a result of measuring the bulletproof performance of the manufactured bulletproof material 100 will be described.

## [0043]

In the bulletproof test, two types of shrapnel and .44 magnum pistol bullets were used.

This is because fragmentation bullets are mainly penetrating bullets, and .44 Magnum bullets cause greater rear deformation upon impact rather than penetration, resulting in injury or death. Bulletproof test is required.

The fragmentation bomb used Cal.22 FSP (1.1g), and according to the Mil-STD-662F (V50 Ballistic Test for Armor) standard, after fixing both sides of the specimen with clamps, the probability of penetration and non-penetration of the bullet was 50%. The V50 (BL) value, which is the indicated protection limit, was calculated. The .44 Magnum bullet belongs to NIJ-STD level III-A, and the depth of the back face signature (BFS) due to the impact of the bullet was measured.

To measure this, oil clay (Roma Plastina No1) was used.

The specimen of the bulletproof material 100 of the present invention was placed on the oil clay and fixed with a band having elasticity according to the NIJ standard.

## [0044]

According to the NIJ standard, 4 to 6 shots were fired at the edge and the center of the shot.

After the test was completed, the clay deformed by impact was pushed flat with a steel plate, and then the depth of deformation was measured with a bunny caliper.

The NIJ standard limits the maximum allowable depth to 44mm.

## [0045]

Hereinafter, the bulletproof test results of the bulletproof material according to various embodiments will be described.

## [0046]

A structure in which the entire area of the first laminate (AN) and the third laminate (rear part) 130 composed only of the fabric 110a to which the shear thickening fluid is not applied is treated with 20% of the shear thickening fluid impregnation amount (CS)), and the results of fragmentation and .44 magnum for specimens with different gradients of impregnation amounts of the second laminate (central part) 120 and the third laminate (rear part) 130 are shown in Table 1.

#### [0047]

Example Lamination order areal density (kg/m2) V50 (m/s) back deformation (mm) edge center 1AN X  $385.5555059542AN \times 25+CS (20\%) \times 105.5554848413AN X 15+BS (10\%) X 10+CS (20\%)X105.605504640$ 

## [0048]

For example, Example 1 shows the ballistic test results of a laminate composed of only 38 layers of fabric, and Example 2 shows 25 layers of fabric and 10 layers of fabric including 20% shear thickening fluid. Shows the ballistic test results of a laminate composed only of The bulletproof test result of the laminated material comprised by the layer is shown.

That is, there was no difference in the V50 value of the fragmentation coal when the pure fabric and the shear thickening fluid were treated.

However, the rear deformation by the .44 Magnum bullet showed a big difference.

When only the back side (CS) is impregnated with the shear thickening fluid, the effect of the shear thickening fluid is reduced by about 19% and 22% for the specimen of Example 2 and the specimen of Example 3 compared to the specimen (fabric layer) of Example 1 can

On the other hand, it can be seen that there is also some effect of applying the shear thickening fluid to the back deformation in the central part of the specimen.

#### [0049]

In the following examples (Table 2), the ballistic performance according to the presence or absence of a gradient of the amount of impregnation of the shear thickening fluid according to the difference in the weave at the same areal density was evaluated.

The weave structure used for the specimens (fabric layer) of Examples 4 and 6 was 28 X 28/inch, and the specimens of Examples 5 and 7 had a more dense structure with a structure of 34 X 34/inch. have

In the shear thickening fluid impregnation, only the edges of the laminate, which is a feature of the present invention, were treated, and the central part was not treated.

## [0050]

Example Lamination order areal density (kg/m2) V50 (m/s) back deformation (mm) edge center 4AN X 456.660751475AN x 376.661351496AN X 7+BS(7%)X18+CS((20%)x176.259841407ANX7+ BS (7%) x 16 + CS (20%) x 146.26244341

#### [0051]

For example, Example 4 shows the ballistic test results of a laminate composed of only 45 layers of fabric layer (AN), and Example 5 shows the ballistic test results of a laminate composed of only 37 layers of fabric layer (AN). In Example 6, 7 fabric layers (AN), 18 fabric layers (BS) containing 7% shear thickening fluid, and 17 fabric layers (CS) including 20% shear thickening fluid ) shows the ballistic test results of the laminated material, and the seventh example is a 7-layer textile layer (AN), a 16-layer textile layer (BS) containing 7% of a shear thickening fluid, and a 20% shear thickening fluid Shows the ballistic test results of a laminate composed of 14 layers of fabric (CS) including

That is, in the fragmentation bomb stopping power, the structures used in the sixth to seventh examples showed almost the same protective power.

However, the back deformation caused by the pistol bullet was reduced by 13% and 20%, respectively, in the specimens (fabric layer) of Examples 5 and 6 compared to Example 4 of the pure fabric.

Therefore, when the impregnation amount of the shear thickening fluid is gradient, the weight can be greatly reduced compared to the pure fabric.

That is, the NIJ standard limits the maximum allowable back deformation to 44 mm, so that the specimens of Examples 6 and 7 can reduce the weight by 13% or more compared to the pure fabric.

## [0052]

Therefore, the bulletproof material 100 according to the design of the gradient of the amount of impregnation of the shear thickening fluid according to the embodiment of the present invention can protect the fragmentation bullet of high-speed flight compared to the existing pure textile bulletproof material, and also NIJ Standard It can satisfy the 0101.06 level III-A standard at the same time, and in particular, it can be reduced in weight by applying shear thickening fluid and grading.

## [0053]

In addition, by treating the fabric with a shear thickening fluid, the flexibility of the fabric is maintained as it is, thereby increasing the wearer's activity.

In particular, the present invention can greatly improve the bulletproof performance by treating the shear thickening fluid on the edge of the fabric-type bulletproof material, which has the weakest bulletproof power.

#### [0054]

The anti-tank material according to an embodiment of the present invention can be used as a mine removal suit including personal body armor, an explosion-proof blanket, a field tent, and a protection product for transporting soldiers, a fragmentation protection tent, a vehicle bulletproof material, a protective material for an ammunition transport vehicle, and various bulletproof materials.

#### [0055]

As described above, the bulletproof material and its manufacturing method according to an embodiment of the present invention impregnate a fabric used as a body armor with a shear thickening fluid containing nanoparticles, thereby generating a fluid cluster of nanoparticles upon external impact. It is possible to improve the bulletproof performance by absorbing and dispersing the impact energy by appropriately increasing the frictional force between the fibers constituting the bulletproof fabric.

#### [0056]

The bulletproof material and its manufacturing method according to an embodiment of the present invention, by impregnating the fabric used as the body armor with a shear thickening fluid, reduce the weight of the body armor, and maintain the flexibility of the same level as that of the fabric to improve the fit can

#### [0057]

Those of ordinary skill in the art to which the present invention pertains will be able to make various modifications and variations without departing from the essential characteristics of the present invention.

Therefore, the embodiments disclosed in the present invention are not intended to limit the technical spirit of the present invention, but to explain, and the scope of the technical spirit of the present invention is not limited by these embodiments.

The protection scope of the present invention should be construed by the following claims, and all technical ideas within the equivalent range should be construed as being included in the scope of the present invention.

#### [0058]

110: First laminate 120: second laminate 130: third laminate



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#### **CLAIMS KR101189457B1**

1.

A ballistic material comprising fabric layers, comprising: a front part including first fabric layers; a central part including second fabric layers impregnated with a shear thickening fluid; and a third fabric layer impregnated with the shear thickening fluid. wherein the amount of impregnation of the shear thickening fluid impregnated in the second fabric layers is set to be different from the impregnation amount of the shear thickening fluid impregnated in the third fabric layers, and the shear thickening fluid is A bulletproof material having a shear thickening fluid, characterized in that only the edge portions of the second and third fabric layers are impregnated.

2.

delete

3.

The shear thickening fluid according to claim 1, wherein an impregnation amount of the shear thickening fluid impregnated in the second fabric layers is set lower than the impregnation amount of the shear thickening fluid impregnated in the third fabric layers. bulletproof material with.

4.

The shear according to claim 1, wherein the amount of the shear thickening fluid impregnated in the second fabric layers is 7%, and the amount of the shear thickening fluid impregnated in the third fabric layers is 20%. Bulletproof material with thickening fluid.

5

According to claim 1, wherein the first to third fabric layer, Shear thickening characterized in that it comprises any one of aramid fibers, polyethylene fibers, polypropylene fibers, xylon fibers, nylon fibers, glass fibers, carbon fibers Bulletproof material with fluid.

6.

The ballistic material having a shear thickening fluid according to claim 1, wherein the shear thickening fluid includes silica sol, and the dispersion medium of the shear thickening fluid includes polyethylene glycol.

7.

The method of claim 1, wherein the shear thickening fluid is a fluid containing inorganic nanoparticles dispersed in an organic solvent, and the inorganic nanoparticles include silicon oxide, aluminum oxide, calcium carbonate, natural mineral particles, or a mixture thereof., The organic solvent is a ballistic material having a shear thickening fluid, characterized in that it comprises at least one of methanol, ethanol, ethylene glycol and polyethylene glycol.

8.

In the method of manufacturing a bulletproof material including a front part, a central part, and a rear part, each including a plurality of fabric layers by cutting the fabrics and stacking the cut fabrics, the shear thickening fluid is applied to the first fabric layers included in the central part and impregnating the second fabric layers included in the rear part with a shear thickening fluid, wherein the amount of impregnation of the shear thickening fluid impregnated in the first fabric layers is the second fabric It is set differently from the impregnation amount of the shear thickening fluid impregnated in the layers, and the shear thickening fluid is impregnated only at the edge portions of the first and second fabric layers. manufacturing method.

delete

10.

The shear thickening fluid according to claim 8, wherein the amount of impregnation of the shear thickening fluid impregnated in the first fabric layers is set lower than the impregnation amount of the shear thickening fluid impregnated in the second fabric layers. A method for producing a bulletproof material having.

11.

The method according to claim 8, wherein the amount of impregnation of the shear thickening fluid impregnated in the first fabric layers is 3 to 15%, and the impregnation amount of the shear thickening fluid impregnated in the second fabric layers is 15 to 30%. Method for producing a bulletproof material having a shear thickening fluid, characterized in that.

12.

The method according to claim 8, wherein the fabric layers of the front part, the central part, and the rear part include any one of aramid fiber, polyethylene fiber, polypropylene fiber, xylon fiber, nylon fiber, glass fiber, and carbon fiber. A method for producing a bulletproof material having a shear thickening fluid.

13.

The method of claim 8, wherein the shear thickening fluid includes silica sol, and the dispersion medium of the shear thickening fluid includes polyethylene glycol.

14.

The method according to claim 8, wherein the shear thickening fluid is a fluid containing inorganic nanoparticles dispersed in an organic solvent, and the inorganic nanoparticles include silicon oxide, aluminum oxide, calcium carbonate, natural mineral particles, or a mixture thereof. , The organic solvent is a method of manufacturing a bulletproof material having a shear thickening fluid, characterized in that it comprises at least one or more of methanol, ethanol, ethylene glycol and polyethylene glycol.



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#### **DESCRIPTION CN102926211A**

A kind of shear thickening fluid based on molecular colloid and its preparation method and use

[0001]

Technical field:

[0002]

The present invention relates to a shear thickening fluid based on molecular colloid and its preparation method and use.

#### [0003]

Background technique:

#### [0004]

Since the late 1980s, people began to study how to use the shear thickening phenomenon. N.J.Wagner et al. of the University of Delaware studied the shearing effect of nano-silica with different particle sizes dispersed in polyethylene glycol system. Rheologically, shear-thickening fluids have begun to see many new applications, and different kinds of shear-thickening fluid compositions have been invented and applied to sports products and body protection products.

## [0005]

The British D30 company has developed a "shear thickening liquid" foam, which is applied to the gloves of goalkeepers on football fields, ski boots of skiers, ski suits, etc. Provide security.

## [0006]

Aramid fiber (also known as Kevlar) and ultra-high molecular weight polyethylene fiber are used as protective substrates, and their applications started early and have a wide range. These high-performance fibers have the characteristics of low quality, high strength and high energy absorption. Sting and bulletproof requirements, about 20 to 50 layers of fibers are required, so the U.S. Army Research Laboratory and the University of Delaware have collaborated to invent "liquid armor", the main components of which are shear-thickening fluids and aramid fibers, The shear-thickening fluid penetrates into every layer of the Kevlar vest, which greatly reduces the number of fabric layers required for puncture and ballistic resistance.

## [0007]

CN 102191680A discloses a preparation method of a shear thickening fluid based on silicon dioxide (SiO 2) micronanospheres, and the application of the shear thickening fluid prepared by the preparation method in a soft protective composite material.

The preparation method of the shear thickening fluid based on silica micro-nano balls provided by the invention belongs to the technical category of particle colloid shear thickening system.

## [8000]

In the current prior art, the components of the shear-thickening liquid are basically composed of nano-silica dispersed in a polyethylene glycol system. At high shear rates, silica nanoparticles and polyethylene glycol are dispersed. Due to the interaction of hydrogen bonds between alcohols, particle clusters will be formed, resulting in the viscosity of the system having a solid-like behavior at high shear rates, thereby achieving good stab and bulletproof properties.

However, the existing technology still has the following problems: due to the low content of organic groups on the surface of silica, the affinity between it and high-performance fiber fabrics is poor; in the process of configuring the nano-shear thickening

fluid, Only the nano-particles with larger particle size and the high-concentration nano-particle system show shear thickening properties at lower shear rates; the preparation process required for the preparation of nano-SiO 2 particles with larger particle size is more complicated. In addition, the phenomenon of agglomeration of nano-silicon dioxide during the preparation process is serious. Based on these problems in the preparation process, there is still a large room for improvement.

#### [0009]

Invention content:

## [0010]

The purpose of the present invention is to provide a shear thickening fluid based on molecular colloid and its preparation method and use, the shear thickening fluid is formed by inorganic nanoparticles, boric acid, hydroxy silicone oil and plasticizer. Molecular colloid system and organic solvent It is used to impregnate high-performance fiber fabrics to improve the stab resistance of composite materials, and to make the preparation process simple, the preparation cycle is short, the operation controllability is strong, the stability of product performance is improved, and energy consumption is reduced, which is conducive to the realization of mass production.

#### [0011]

The present invention is a shear thickening fluid based on molecular colloid, which is composed of a molecular colloid system formed by inorganic nanoparticles, boric acid, hydroxy silicone oil and plasticizer and an organic solvent. In the shear thickening fluid, the mass concentration of the molecular colloid is  $40 \sim 70\%$ , preferably  $45 \sim 65\%$ , it is characterized in that: the basic composition and mass fraction of molecular colloid are:

## [0012]

Inorganic nanoparticles 0.5-1.5 parts, boric acid 0.5-1.5 parts, hydroxy silicone oil 9.5-10.5 parts, plasticizer 0.05-0.5 parts.

#### [0013]

Preferably: 0.8-1.2 parts of inorganic nanoparticles, 0.8-1.2 parts of boric acid, 9.8-10.2 parts of hydroxy silicone oil, and 0.08-0.48 parts of plasticizer.

#### [0014]

More preferably: 1 part of inorganic nanoparticles, 1 part of boric acid, 10 parts of hydroxy silicone oil, and 0.1 part of plasticizer.

## [0015]

The present invention also provides a kind of preparation method of the shear thickening fluid based on molecular colloid, concrete steps and method are as follows:

## [0016]

(1) The inorganic nanoparticles and boric acid are uniformly dispersed in the hydroxy silicone oil, and fully stirred to obtain a uniform suspension and dispersion system of the inorganic nanoparticles, boric acid and the hydroxy silicone oil;

## [0017]

(2)

The dispersion system of step (1) is reacted at 265-350°C for 2.5-3.5h, preferably 280-320°C for 2.8-3.2h.

After cooling, grinding, adding a plasticizer to obtain a polyborodimethylsiloxane (PBDMS) molecular colloid;

#### [0018]

(3) The molecular colloid of step (2) is dissolved in a volatile hydroxyl-containing polar organic solvent to obtain a shear thickening fluid based on the molecular colloid.

## [0019]

In the above-mentioned preparation method, it is preferable to first mix the inorganic nanoparticles with the hydroxysilicone oil, stir well to disperse uniformly, and then add boric acid and stir to obtain a dispersion system of uniformly dispersed inorganic nanoparticles, boric acid and hydroxysilicone oil.

Agitation can be achieved by using any of a high speed mixer, a low speed mixer or a medium speed mixer, preferably a high speed mixer.

The rotating speed of the high-speed agitator is 800 ~ 1200rpm/min, preferably 900 ~ 1100rpm/min.

The high-speed stirring method is more conducive to uniformly dispersing the inorganic nanoparticles and boric acid in the hydroxysilicone oil.

#### [0020]

The inorganic nanoparticles are selected from any one of the following substances or their mixtures: nano-silica, nano-montmorillonite, nano-calcium carbonate, nano-titanium dioxide or nano-mica powder.

The inorganic nanoparticle mixture can be a mixture of nano mica powder and nano titanium dioxide, a mixture of nano calcium carbonate and nano montmorillonite, a mixture of nano silica and nano mica powder, a mixture of nano titanium dioxide and nano montmorillonite, nano The mixture of mica powder, nano titanium dioxide and nano calcium carbonate, nano montmorillonite, nano silica and nano calcium carbonate mixture, nano montmorillonite, nano silica, nano mica powder, nano titanium dioxide and nano calcium carbonate mixture.

The inorganic nanoparticles can achieve better synergistic effect when used in combination.

The particle size of the inorganic nanoparticles is 1 to 100 nm, preferably 1 to 50 nm.

Due to the size effect, surface and interface effect, and volume effect of nanoparticles, they exhibit a series of excellent physical and chemical characteristics in applications.

However, nanoparticles have large surface energy, are easy to agglomerate, and have poor compatibility with polymers.

In order to prevent the nanoparticles from agglomerating, so as to be better dispersed in the hydroxy silicone oil, the present invention preferably adopts the nanoparticles after surface treatment with a silane coupling agent, and the method of surface modification treatment is the prior art well known to those skilled in the art.

For example, a coupling agent can be used to coat the nanoparticles by in-situ polymerization of organic monomers.

#### [0021]

The hydroxy silicone oil is preferably a hydroxy silicone oil with a degree of polymerization of 1 to 10, more preferably a hydroxy silicone oil with a degree of polymerization of 2 to 8.

For the selection of hydroxy silicone oil, hydroxy silicone oil with different degrees of polymerization can be selected according to the desired properties of the synthesis product.

#### [0022]

The plasticizer is one or a mixture of at least two of oleic acid, tributyl citrate or epoxidized soybean oil.

## [0023]

Described organic solvent is preferably volatile polar organic solvent containing hydroxyl; more preferably isopropanol or ethanol.

## [0024]

The inorganic nanoparticles, boric acid and hydroxyl silicone oil dispersion system were reacted at  $265\sim350\,^{\circ}$ C for  $2.5\sim3.5$ h, foamy substances were observed in the later stage of the reaction, and the mixed liquid no longer flowed.

When the reaction is completed, the material generated by the reaction is cooled, and after grinding, a plasticizer is added for plasticization, and the PBDMS molecular colloid with excellent damping performance can be obtained.

## [0025]

The shear thickening fluid can be obtained by dissolving the PBDMS molecular colloid in a volatile hydroxyl-containing polar organic solvent.

Through the rheological property test of the shear-thickening fluid, it can be observed that the shear-thickening fluid exhibits shear-thickening phenomenon under critical shear stress.

## [0026]

Hydroxy silicone oil is a colorless, transparent, odorless, non-toxic oily liquid with high flash point, low freezing point, good thermal stability, and hydroxyl end capping can provide active reactivity.

## [0027]

The present invention also provides the use of a molecular colloid-based shear thickening fluid for impregnating high-performance fiber fabrics to prepare soft protective materials, and the molecular colloid-based shear thickening fluid of the present invention is used to impregnate high-performance fiber fabrics, After the impregnation is complete, drying is carried out to a constant weight to obtain the soft protective material.

The high-performance fibers refer to fibers with a tensile strength greater than 2.5 GPa and an elastic modulus greater than 55 GPa: preferably aramid fibers or ultra-high molecular weight polyethylene fibers.

[0028]

The present invention utilizes the property of the shear thickening fluid based on molecular colloid to change the viscosity of the system under high shear rate, and is compounded with high-performance fiber fabric such as aramid fiber to prepare soft protective material.

#### [0029]

The impregnation of high-performance fiber fabrics can be carried out by manual impregnation, calender impregnation or spray impregnation, and calender impregnation can be impregnated by a paddle.

#### [0030]

In order to prevent adhesion between fibers and improve the stab-proof performance of the protective material, the aramid fibers are completely impregnated with any one of polyvinyl chloride film, polypropylene film, polyethylene film or aluminum foil to be coated before proceeding. Drying, the drying temperature is  $70 \sim 90$  °C, preferably  $75 \sim 85$  °C.

#### [0031]

The soft protective composite material prepared by the method of the present invention has good protective performance, and has the characteristics of lightness and comfort.

#### [0032]

Compared with the prior art, the present invention has the following beneficial effects:

#### [0033]

(1) The method for preparing a shear-thickening fluid based on molecular colloid provided by the present invention can effectively prevent the agglomeration between nanoparticles, the nanoparticles are uniformly dispersed in the polymer matrix, and are mutually bonded with the polymer in the form of chemical bonds. It can effectively prevent the nanoparticles from falling off the surface of the fiber fabric, so that the shear thickening fluid and the fiber fabric have a better composite effect.

#### [0034]

(2)

The traditional high-performance fiber fabric and rubber composite process adopts a "sandwich" sandwich structure. The high-performance fiber fabric is located between two layers of rubber, and the interface compatibility between the fiber fabric and the rubber is not good. Only after chemical modification can the affinity between it and the rubber interface be improved, and then the fiber and the rubber can be compounded during the vulcanization process of the rubber.

Compared with the traditional process for preparing rubber fiber composite materials, the method for preparing a soft body protection composite material by using a shear thickening fluid based on molecular colloid provided by the present invention has simple process and lower cost.

## [0035]

(3)

Compared with the commonly used particle colloid system, the soft protective composite material prepared by using the molecular colloid-based shear thickening fluid of the present invention has good protective performance, and also has the characteristics of lightness, comfort and flexibility.

It is suitable for soldiers' protective clothing and police's protective equipment, and can also be widely used in sports protective equipment.

## [0036]

Description of drawings:

#### [0037]

Figure 1: The rheological property curve of the molecular colloid-based shear-thickening fluid obtained in Example 1.

It can be observed in the rheological curve that at higher shear rates, the system exhibits shear thickening and occurs at lower critical shear stress, which is due to the introduction of boron atom B into the organosiloxane In the main chain of , the boron atom is the bridge between the electron-deficient structure and the oxygen atom to form a reversible electron pair. At a higher shear rate, the system forms a bridge network structure, so the viscosity of the system increases;

## [0038]

Figure 2: The DSC curve of the PBDMS molecular colloid in Example 1, where SD rubber represents the boronated polydimethylsiloxane filled with nano-silica, and the boronated polydimethylsiloxane (PBDMS) can be observed through the curve. The glass transition temperature of ) is higher than that of polydimethylsiloxane (PDMS), due to the formation of reversible electron pairs between boron and oxygen, which reduces the activity of molecular chain movement, thereby increasing its glass transition temperature;

#### [0039]

Figure 3: The DSC curve of the PBDMS molecular colloid in Example 2, where OD rubber represents the boronated polydimethylsiloxane filled with nano-montmorillonite, and it can be observed from the curve that the boronated polydimethylsiloxane (PBDMS The glass transition temperature of ) is higher than that of polydimethylsiloxane (PDMS), due to the formation of reversible electron pairs between boron and oxygen, which reduces the activity of molecular chain movement, thereby increasing its glass transition temperature;

## [0040]

Fig. 4: the scanning electron microscope photo of the soft body protection composite material in the embodiment 1, it can be observed that there is a good composite effect between the shear thickening fluid and the aramid fiber;

#### [0041]

Fig. 5: the scanning electron microscope photo of the soft body protection composite material in the embodiment 2, it can be observed that there is a good composite effect between the shear thickening fluid and the aramid fiber, and the molecular colloid is uniformly distributed on the surface of the aramid fiber;

#### **[0042]**

Figure 6: Infrared spectrum of the PBDMS molecular colloid in Example 2, 891 cm-1 and 684 cm-1 correspond to the characteristic peaks of B-O-Si, indicating that boron atoms are introduced into the main chain structure of -Si-O-.

#### [0043]

Detailed ways:

#### [0044]

The present invention will be further described below in conjunction with comparative examples and embodiments.

## [0045]

Example 1

## [0046]

Preparation of PBDMS (filled with nano-silica) molecular colloid:

## [0047]

(1)

Weigh the nano-silicon dioxide, boric acid and hydroxy silicone oil with a mass ratio of 1:1:10 respectively, wherein the quality of the hydroxy silicone oil (Zhonghao Chenguang Chemical Research Institute, the brand name is GY-209-3, the degree of polymerization is 3-5) It is 350g, and the mass of boric acid and nano-silica (Degussa Silica Co., Ltd., brand name is VN 3) is 35g respectively.

First, the nano-silicon dioxide was added to the hydroxy silicone oil, and stirred at a high speed (the rotation speed was 1000 rpm/min), and after the nanoparticles were evenly distributed in the hydroxy silicone oil, the boric acid particles were added, and the beaker was fully stirred for a stirring time of 0.5h;

#### [0048]

(2) The above suspension dispersion system was poured into an aluminum pan, and then the aluminum pan was placed on a heating plate with a constant temperature of 300 ° C. The reaction time was 3h. It can be observed that foamy substances were formed in the aluminum pan in the later stage, and the mixing the liquid no longer flows;

## [0049]

(3) After the reaction is completed, the material in the aluminum plate is cooled to room temperature, and after being placed in a mortar and fully ground for 15min, oleic acid of 1/10 of the quality of boric acid is added for plasticization to obtain a PBDMS molecular colloid with good damping performance.

## [0050]

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Preparation of shear thickening fluid based on molecular colloid: The PBDMS molecular colloid synthesized by the above reaction was dissolved in isopropanol, and the molecular colloid shear thickening fluid system with a mass fraction of 45% was configured.

The single-layer aramid fiber fabric of 20cm×20cmwas impregnated with the molecular colloid shear thickening fluid, and the single-layer dipping time was 2min. Layer fibers, and then put them into a blast drying oven at 80 °C until the isopropanol solvent is completely evaporated, and take it out when the weight is constant.

#### [0051]

#### Example 2

#### [0052]

Preparation of PBDMS (filled with nano-montmorillonite) molecular colloid:

#### [0053]

(1)

Weigh the nano-montmorillonite, boric acid and hydroxy silicone oil with a mass ratio of 1:1:10 respectively, wherein the quality of the hydroxy silicone oil (Zhonghao Chenguang Chemical Research Institute, the grade is GY-209-3, the degree of polymerization is 3-5) is 350g, and the mass of boric acid and nano-montmorillonite (Zhejiang Fenghong New Material Co., Ltd., brand DK 1) is 35g respectively.

The nano-montmorillonite was added to the hydroxysilicone oil, and stirred at a high speed (the rotation speed was 1000rpm/min), after the nanoparticles were evenly distributed in the hydroxysilicone oil, then the boric acid particles were added, and the beaker was fully stirred for a stirring time of 0.5h;

## [0054]

(2) The above suspension system was poured into an aluminum pan, and then the aluminum pan was placed on a heating plate with a constant temperature of 300 ° C. The reaction time was 3 hours. It can be observed that foamy substances were formed in the aluminum pan in the later stage, and the mixed liquid in the aluminum pan was no longer flow;

#### [0055]

(3) After the reaction is completed, the material in the aluminum plate is cooled to room temperature, and it is placed in a mortar and fully ground for 15min, and the oleic acid plasticizing of 1/7 of the boric acid quality is added to obtain a PBDMS molecular colloid with good damping performance.

## [0056]

Preparation of shear thickening fluid based on molecular colloid: The PBDMS molecular colloid synthesized by the above reaction was dissolved in isopropanol solvent, and the shear thickening fluid system with mass fraction of 45% and 50% was respectively configured.

Impregnate a 20cmx20cmsingle-layer aramid fiber fabric with the above two molecular colloid shear thickening fluid systems, and use artificial impregnation. The single-layer dipping time is 2min. After the single-layer aramid fiber fabric is completely impregnated, it is wrapped with PVC film. The single-layer fiber is then put into a blast drying oven at 80°C until the isopropyl alcohol solvent is completely evaporated, and the soft-body protective composite material is taken out when the weight is constant.

## [0057]

## Example 3

## [0058]

Preparation of PBDMS (filled with nano-titanium dioxide) molecular colloid:

## [0059]

(1)

Weigh nano-titanium dioxide, boric acid and hydroxy silicone oil with a mass ratio of 0.5:0.5:9.5 respectively, wherein the quality of the hydroxy silicone oil (Zhonghao Chenguang Chemical Research Institute, trade name GY-209-3, degree of polymerization 3-5) is 285g, the mass of boric acid and nano titanium dioxide (Henan Billions Chemical Co., Ltd., brand BLR-688) is 15g respectively.

Add the nano titanium dioxide into the hydroxy silicone oil, stir at a high speed (the rotation speed is 800rpm/min), after the nanoparticles are evenly distributed in the hydroxy silicone oil, then add the boric acid particles, and place it in a beaker and stir

well, and the stirring time is 0.5h;

#### [0060]

(2) The above suspension system was poured into an aluminum pan, and then the aluminum pan was placed on a heating plate with a constant temperature of 350°C, and the reaction time was 2.5h. the liquid no longer flows;

#### [0061]

(3) After the reaction is completed, the material in the aluminum plate is cooled to room temperature, and it is placed in a mortar and fully ground for 15min, and then oleic acid with 1/5 of the mass of boric acid is added to plasticize to obtain a PBDMS molecular colloid with good damping performance.

#### **[0062]**

Preparation of shear-thickening fluid composites based on molecular colloids: The PBDMS molecular colloids synthesized by the above reaction were dissolved in ethanol solvent, and the shear-thickening fluid systems with mass fractions of 45% and 50% were respectively configured.

The 20cmx20cmsingle-layer aramid fiber fabric was impregnated with the above two molecular colloid shear thickening fluid systems, impregnated by spraying, and the single-layer dipping time was 1min. After the single-layer aramid fiber fabric was completely impregnated, it was wrapped with polyethylene film. A single layer of fiber was covered, and then placed in a blast drying oven at 70°C until the ethanol solvent was completely evaporated, and the soft protective composite material was taken out when the weight was constant.

#### [0063]

#### Example 4

#### [0064]

Preparation of PBDMS (filled as nano-calcium carbonate) molecular colloid:

## [0065]

(1)

Weigh nano-calcium carbonate (Zhongqi Industry (Guangdong) Co., Ltd., trade name CAN-602), boric acid and hydroxysilicone oil with a mass ratio of 1.5:1.5:10.5, among which hydroxysilicone oil (Zhonghao Chenguang Chemical Research Institute, trade mark It is GY-209-3, the mass of polymerization degree 3 ~ 5) is 210g, and the mass of boric acid and nano calcium carbonate is 30g respectively.

Add the nano calcium carbonate into the hydroxy silicone oil, stir at a high speed (the rotation speed is 1200rpm/min), and after the nanoparticles are uniformly dispersed in the hydroxy silicone oil, then add the boric acid particles, place them in a beaker and stir well, and the stirring time is 0.5h;

## [0066]

(2) The above suspension system was poured into an aluminum pan, and then the aluminum pan was placed on a heating plate with a constant temperature of 265 ° C. The reaction time was 3.5h. It can be observed that foamy substances were formed in the aluminum pan in the later stage, and the mixing in the aluminum pan was the liquid no longer flows;

## [0067]

(3) After the reaction is completed, the material in the aluminum plate is cooled to room temperature, and it is placed in a mortar and fully ground for 15min, and then oleic acid with 1/2 of the mass of boric acid is added to plasticize to obtain a PBDMS molecular colloid with good damping performance.

## [0068]

Preparation of shear-thickening fluid composites based on molecular colloids: The PBDMS molecular colloids synthesized by the above reaction were dissolved in isopropanol solvent, and the shear-thickening fluid systems with mass fractions of 45% and 65% were respectively configured.

Impregnate a 20cm x 20cm single-layer aramid fiber fabric with the above two molecular colloid shear thickening fluid systems, respectively, and impregnate by calendering. The single-layer dipping time is 2min. After the single-layer aramid fiber fabric is completely impregnated, a polyethylene film is used. The single-layer fiber is coated, and then placed in a blast drying oven at 90° C. until the isopropyl alcohol solvent is completely evaporated, and the prepared soft-body protective composite material is taken out when the weight is constant.

## [0069]

Application example 1

[0070]

The 45% molecular colloid shear thickening fluid system prepared in the above-mentioned Examples 1 and 2, 3, and 4 was respectively impregnated with a single-layer aramid fiber of 20cm×20cm,and the impregnation method was sprayed, and the impregnated fiber cloth was impregnated with a single layer. The impregnation time of the single-layer fiber cloth is 1min. After the single-layer aramid fiber is completely impregnated, the single-layer fiber is wrapped with polyethylene film, and then placed in a blast drying oven at 80 ° C until the isopropyl alcohol solvent is completely volatilized and soft. Take out the protective composite when it has a constant weight.

Its stab-proof performance test standard is the Public Safety Industry Standard of the People's Republic of China: GA 68-2008.

The test results are shown in Table 1 below. From the data in the table, it can be observed that the aramid fibers impregnated with the molecular colloidal shear thickening fluid system show good protective performance. The number of layers of aramid fiber cloth required is only 2/3 of the number of layers of untreated aramid fiber cloth, which can effectively reduce the cost of the composite material and improve the protective performance of the composite material.

#### [0071]

#### Table 1.

Comparison of puncture resistance of untreated aramid and impregnated with the shear thickening fluid system of the present invention (45%)

## [0072]

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wi="700"/>

#### [0073]

Table 1 is the stab resistance comparison between the molecular colloid shear thickening fluid-impregnated aramid fiber fabric prepared in Examples 1, 2, 3, and 4 of the present invention and the untreated aramid fiber fabric, wherein the molecular colloid The concentration of shear thickening fluid is 45%, the thickness of the single-layer fiber cloth is 0.25mm, the number of test fiber layers is 40, and the size is 20cm×20cm.

The stab resistance test standard adopts the public safety industry standard of the People's Republic of China: GA 68-2008.



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#### **CLAIMS CN102926211A**

1.

A shear thickening fluid based on molecular colloid, which is composed of a molecular colloid system formed by inorganic nanoparticles, boric acid, hydroxy silicone oil and plasticizer, and an organic solvent. In the shear thickening fluid, the mass fraction of molecular colloid is 40~ 70%, the basic composition and mass fraction of molecular colloid are: 0.5-1.5 parts of inorganic nanoparticles, 0.5-1.5 parts of boric acid, 9.5-10.5 parts of hydroxyl silicone oil, and 0.05-0.5 parts of plasticizer; the organic solvent is volatile hydroxyl-containing polar organic solvents.

2.

The shear thickening fluid based on molecular colloid according to claim 1, characterized in that: the mass fraction of the molecular colloid is 45-65%, and the basic composition and mass fraction of the molecular colloid are: 0.8-1.2 parts of inorganic nanoparticles, boric acid 0.8~1.2 parts, hydroxyl silicone oil 9.8~10.2 parts, plasticizer 0.08~0.48 parts.

3.

The shear-thickening fluid based on molecular colloid according to claim 1, wherein the inorganic nanoparticles are surfacemodified with a silane coupling agent, and are selected from any one of the following substances or their mixtures: nano-dioxide Silicon, nanometer montmorillonite, nanometer calcium carbonate, nanometer titanium dioxide or nanometer mica powder.

4.

A kind of preparation method of the shear thickening fluid based on molecular colloid described in claim 1 or 2 or 3, concrete steps and method are as follows:

(1)

The inorganic nanoparticles and boric acid are uniformly dispersed in the hydroxysilicone oil in proportion to obtain a uniform suspension dispersion system of the inorganic nanoparticles, boric acid and the hydroxysilicone oil after full stirring;

(2)

The dispersion system of step (1) is reacted at 265-350° C. for 2.5-3.5 hours, cooled, and after grinding, a plasticizer is added to obtain a boronated polydimethylsiloxane molecular colloid;

(3)

The molecular colloid of step (2) is dissolved in a volatile hydroxyl-containing polar organic solvent to obtain a shear thickening fluid based on the molecular colloid.

5.

The preparation method according to claim 4, characterized in that: the reaction temperature of step (2) is 280~320°C, and the reaction time is 2.8~3.2h.

according to the preparation method of claim 4, it is characterized in that: plasticizer is one or the mixture of at least two in oleic acid, tributyl citrate or epoxidized soybean oil.

7.

The preparation method according to claim 4, wherein the hydroxyl silicone oil is a hydroxyl silicone oil with a degree of polymerization of 1 to 10.

The preparation method according to claim 4, is characterized in that: the volatile polar organic solvent containing hydroxyl is Virahol or ethanol.

9.

The preparation method according to claim 4, characterized in that: in step (1), firstly, inorganic nanoparticles are mixed with hydroxy silicone oil, fully stirred, and uniformly dispersed, and then boric acid is added and fully stirred to obtain uniformly dispersed inorganic nanoparticles, boric acid and Hydroxy silicone oil dispersion system.

10.

A use of the molecular colloid-based shear thickening fluid according to claim 1 or 2 or 3 for impregnating high-performance fiber fabrics to prepare soft body protective materials.



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#### **DESCRIPTION CN104002522A**

Stab and impact resistant material

[0001]

technical field

[0002]

The invention relates to a safety protection material, in particular to a stab-proof and impact-resistant material.

#### [0003]

Background technique

#### [0004]

Shear-thickening fluid is a kind of non-Newtonian fluid. It is slightly viscous at low speed. At high speed, the apparent viscosity changes greatly and becomes a solid-like substance, and this process is reversible.

This characteristic of it makes it harden rapidly when struck at a speed higher than a certain speed, and returns to its original state after the impact is removed.

The use of shear-thickening fluid composites with fiber materials has good puncture resistance and impact resistance. Shear-thickening fluid composites have been widely used in the field of protective materials.

## [0005]

The most commonly used method for the production of the existing shear-thickening fluid composite material is to immerse the fabric in a diluent of the shear-thickening fluid and alcohol, and after the diluent fully enters the fabric, take it out to remove the alcohol, and then the shear-thickening fluid is obtained. Fluid composites.

## [0006]

After a single layer of fabric is impregnated, the anti-stab and impact resistance performance is greatly improved, but the protection requirements cannot be met, and multiple layers must be used.

Simple multi-layer superimposed composite materials will appear delamination during use, reducing the protective performance and service life of the material. If the multi-layer material is directly stitched, it will be difficult to process due to the characteristics of the material being difficult to penetrate.

In addition, although the pure shear-thickening fluid composite material can harden after being impacted, increase the forcebearing area, and reduce the impact strength, it lacks an energy buffer absorption layer and has limited impact protection performance.

Therefore, there is an urgent need for a shear-thickening fluid composite material with stable performance, no delamination and good protective effect during use.

## [0007]

## SUMMARY OF THE INVENTION

## [8000]

The purpose of the present invention is to solve the above problems and provide a stab-resistant and impact-resistant material with stable performance, no delamination and good protective effect during use.

[0009]

In order to achieve the above purpose, the present invention adopts the following technical scheme: a stab-resistant and impact-resistant material, comprising at least two layers of bladder shell structural units and at least one layer of impact kinetic energy absorbing layers, and each impact kinetic energy absorbing layer is respectively sandwiched between two layers of bladder shells. The structural units are bonded and connected with the two-layer capsule shell structural unit; the capsule shell structural unit is composed of multiple layers of shear-thickening fluid composite materials laminated together to form an inner layer, which is made of impermeable high-density flexible coated textiles As an outer layer, it is formed by stitching and stitching; the impact kinetic energy absorption layer is a flexible material layer.

#### [0010]

The shear-thickening fluid composite is formed by impregnating the fabric with a shear-thickening fluid.

#### [0011]

The fabric is selected from one or more of woven fabrics, knitted fabrics, and non-woven fabrics

#### [0012]

The shear thickening fluid is prepared by mechanically stirring hard nano-spherical particles with a particle size of 10 nm-1 m and polyethylene glycol with a molecular weight of 200-400 and putting them into an ultrasonic instrument to remove air bubbles, wherein the nano-spherical particles are The mass percentage is 20-85%.

#### [0013]

The hard nano-spherical particles are silica particles or calcium carbonate particles.

#### [0014]

The material of the fabric is selected from one or both of aramid and ultra-high molecular weight polyethylene.

## [0015]

The material of the suture is selected from one or more of high-strength polyester, aramid, ultra-high molecular weight polyethylene, and high-performance nylon.

## [0016]

The flexible material is selected from wool textiles, foamed polyurethane or polyvinyl butyral.

## [0017]

The adhesive used for bonding and connecting is selected from one of polyurethane adhesives, rubber adhesives, epoxy resin adhesives, phenolic resin adhesives, and organic silica gel adhesives.

## [0018]

It is composed of three-layer capsule shell structural units and two layers of wool felt bonded with epoxy resin adhesive, and the shear-thickening fluid composite material is four layers.

#### [0019]

In the present invention, the inner layer of the shell structure unit adopts shear thickening fluid composite material, and an impact kinetic energy absorption layer is sandwiched between the two shell structure units, which is bonded by an adhesive, which is soft and light, and has good puncture resistance and impact resistance. , which not only realizes the protective performance of the material, but also effectively prevents the occurrence of delamination during the use of the material, and can make thicker protective materials without increasing the difficulty of processing.

It can be made into different thicknesses to meet different protection requirements, and can be used as materials for human safety protection equipment.

## [0020]

Description of drawings

## [0021]

Fig. 1 is the sectional structure schematic diagram of the stab-resistant and impact-resistant material of the present invention;

#### [0022]

FIG. 2 is a schematic cross-sectional structure diagram of a layer of capsule shell structural unit in the invention.

#### [0023]

Detailed ways

#### [0024]

1 and 2, the stab-resistant and impact-resistant material of the present invention includes at least two layers of bladder structural units and at least one layer of impact kinetic energy absorbing layer 4, and each impact kinetic energy absorbing layer is sandwiched between the two layers of bladder structural units respectively. And it is bonded and connected with the two-layer capsule shell structural unit; the capsule shell structural unit is composed of multiple layers of shear thickening fluid composite materials laminated together to form the inner layer 2, and the anti-penetration high-density flexible coating textile is used as the outer layer 1, It is sewed and connected by sutures 3; the above-mentioned impact kinetic energy absorption layer is a flexible material layer.

#### [0025]

The shear-thickening fluid composite in the present invention is formed by impregnating the fabric with a shear-thickening fluid.

#### [0026]

The fabric in the present invention is selected from one or more of woven fabrics, knitted fabrics and non-woven fabrics.

## [0027]

The shear thickening fluid in the present invention is prepared by mechanically stirring hard nano-spherical particles with a particle size of 10 nm-1 mand polyethylene glycol with a molecular weight of 200-400 and putting them into an ultrasonic instrument to remove air bubbles, wherein the nanometer The mass percentage of spherical particles is 20-85%.

#### [0028]

The hard nano-spherical particles in the present invention are silica particles or calcium carbonate particles.

## [0029]

The material of the fabric in the present invention is selected from one or both of aramid and ultra-high molecular weight polyethylene.

## [0030]

The material of the suture in the present invention is selected from one or more of high-strength polyester, aramid, ultra-high molecular weight polyethylene, and high-performance nylon.

#### [0031]

The flexible material in the present invention is selected from wool textiles, foamed polyurethane or polyvinyl butyral.

## [0032]

The adhesive used for bonding in the present invention is selected from the one in polyurethane adhesive, rubber adhesive, epoxy resin adhesive, phenolic resin adhesive, and organic silica gel adhesive.

## [0033]

The preferred embodiment of the present invention is formed by bonding three layers of capsule shell structural units and two layers of wool felt with epoxy resin adhesive, wherein the shear thickening fluid composite material is four layers.

The outer layer is made of permeation resistant high density coated UHMWPE plain weave fabric.

The fabric in the shear-thickening fluid composite material is an aramid fabric, and the shear-thickening fluid is a spherical nano-silica particle with a particle size of 600 nm and a polyethylene glycol with a molecular weight of 200, which are mechanically stirred and put into an ultrasonic instrument. It is prepared by removing air bubbles, and the mass fraction of nano-silica is 70%.

The shear-thickening fluid composite material is prepared by diluting the shear-thickening fluid with alcohol, the volume ratio is 2:1, and the aramid fabric is fully immersed in the diluent, then taken out and dried to remove the alcohol.

The material of the suture is ultra-high molecular weight polyethylene.

The impact kinetic energy absorption layer is made of wool felt.



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#### **CLAIMS CN104002522A**

1.

A stab-resistant and impact-resistant material is characterized in that it comprises at least two layers of bag shell structural units and at least one layer of impact kinetic energy absorbing layers, and each impact kinetic energy absorbing layer is respectively sandwiched between the two layers of bag shell structural units and is connected with the two layers of bag shell structural units. The layered capsule shell structural units are bonded and connected; the capsule shell structural units are composed of multiple layers of shear-thickening fluid composite materials laminated together to form an inner layer, and an anti-penetration high-density flexible coated textile is used as an outer layer, which is sutured and connected by sutures The impact kinetic energy absorption layer is a flexible material layer.

2.

A stab-resistant and impact-resistant material according to claim 1, wherein the shear-thickening fluid composite material is formed by impregnating the fabric with the shear-thickening fluid.

3.

The stab-resistant and impact-resistant material according to claim 2, wherein the fabric is selected from one or more of woven fabrics, knitted fabrics, and non-woven fabrics.

4.

The stab-resistant and impact-resistant material according to claim 2, wherein the shear thickening fluid is passed through hard nano-spherical particles with a particle size of 10 nm-1 mand polyethylene glycol with a molecular weight of 200-400. After mechanical stirring, it is put into an ultrasonic instrument to remove air bubbles, wherein the mass percentage of the nanospherical particles is 20-85%.

5.

A kind of anti-stab and impact-resistant material according to claim 2, is characterized in that: described hard nano-spherical particle is silicon dioxide particle or calcium carbonate particle.

6.

The stab-resistant and impact-resistant material according to claim 2, wherein the material of the fabric is selected from one or both of aramid and ultra-high molecular weight polyethylene.

7.

The stab-resistant and impact-resistant material according to claim 1, wherein the material of the suture is selected from one or more of high-strength polyester, aramid, ultra-high molecular weight polyethylene, and high-performance nylon.

8.

A stab-resistant and impact-resistant material according to claim 1, wherein the flexible material is selected from wool textiles, foamed polyurethane or polyvinyl butyral.

The stab-resistant and impact-resistant material according to claim 1, wherein the adhesive used for bonding and connecting is selected from the group consisting of polyurethane adhesives, rubber adhesives, epoxy resin adhesives, and phenolic resin adhesives. One of the adhesives and silicone adhesives.

The stab-resistant and impact-resistant material according to claim 1, characterized in that: it is formed by bonding three layers of bladder shell structural units and two layers of wool felt with epoxy resin adhesive, wherein the shear thickening fluid is compounded The material is four layers.