US 20040094026A1

(19) United States

(12) Patent Application Publication

(10) Pub. No.: US 2004/0094026 A1

Efim et al.

(43) Pub. Date: May 20, 2004

(54) **METHOD OF MAKING A PROTECTIVE MATERIAL AND ARTICLES MADE THEREFROM**

(75) Inventors: **Litovsky Efim**, Richmond Hill (CA); **Litovsky Tatyana**, Richmond Hill (CA); **Jacob I. Kleiman**, Thornhill (CA)

Correspondence Address:
VIDAS, ARRETT & STEINKRAUS, P.A.
6109 BLUE CIRCLE DRIVE
SUITE 2000
MINNETONKA, MN 55343-9185 (US)

(73) Assignee: **Integrity Testing Laboratory Inc.**, Markham (CA)

(21) Appl. No.: **10/299,987**

(22) Filed: **Nov. 19, 2002**

Publication Classification

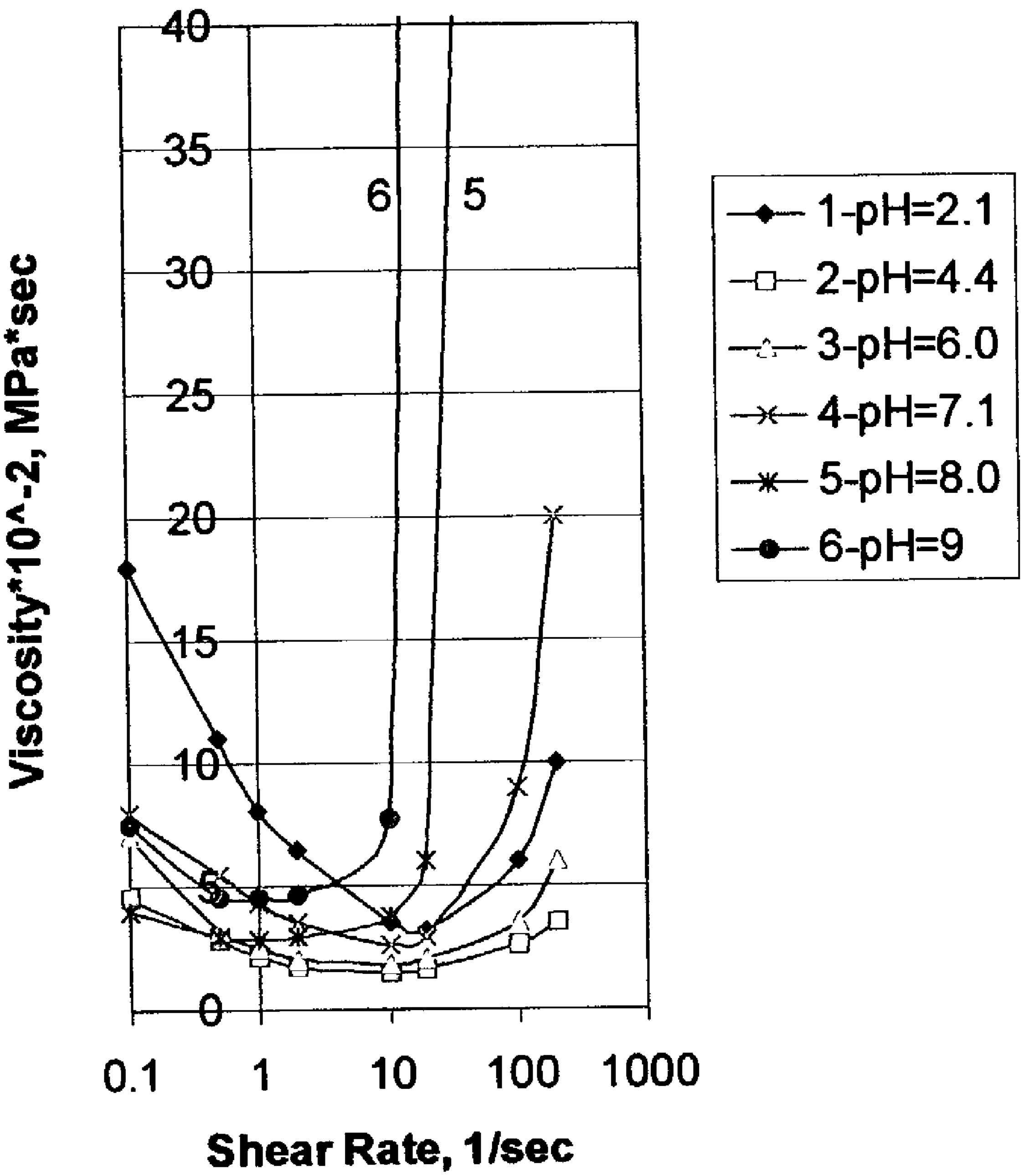
(51) Int. Cl.[7] **F41H 5/02**

(52) U.S. Cl. **89/36.02**

(57) **ABSTRACT**

A method of preparing a protective material is shown. In one aspect the method includes the steps of providing a powder mixture of solid particles having a size in the range of colloidal up to 100 μm. The particles have a ceramic or mineral composition. Then a liquid is provided to form an external phase of a suspension when mixed with the powder, to yield a solids volume concentrating greater then 0.5. The solid powder liquid mixture forms a thixotropic-dilatant liquid material. The rheological curve of the TDLM is adjusted to suit the application, resulting in thixotropic properties at low strain rates and dilatant properties at higher strain rates to yield a material that solidifies upon impact. The rheological curve is adjusted by one or more of additives, material composition and gravity mixing. In another aspect protective articles made from TDLM are provided.

Figure 1 Dependence of the viscosity of the dispersions on the shear rate



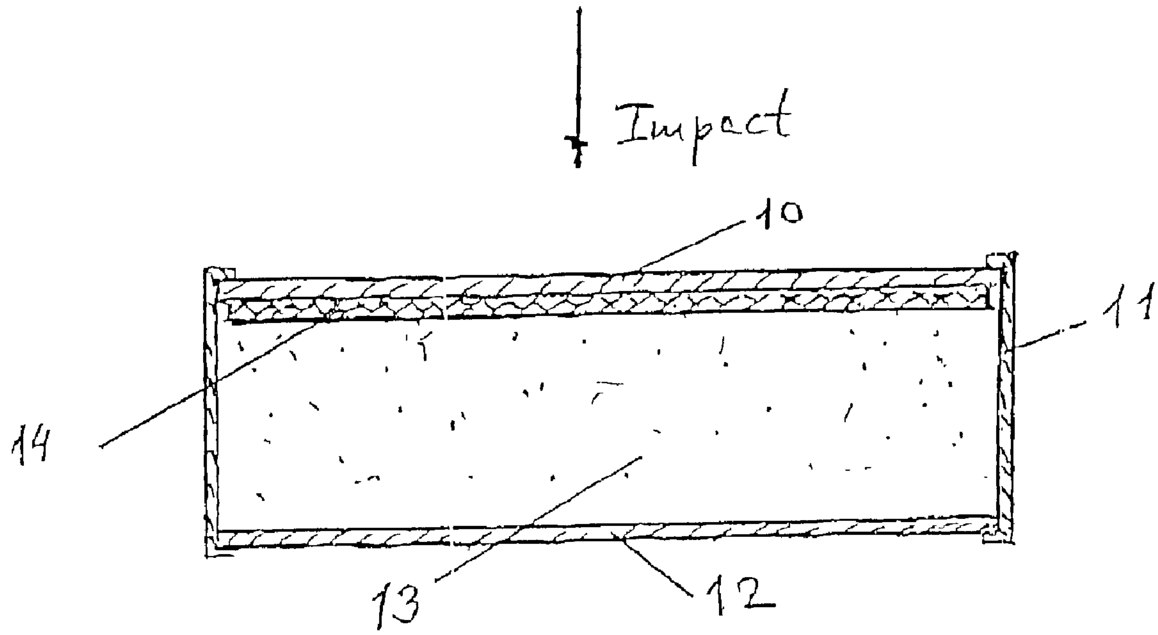


Figure 2

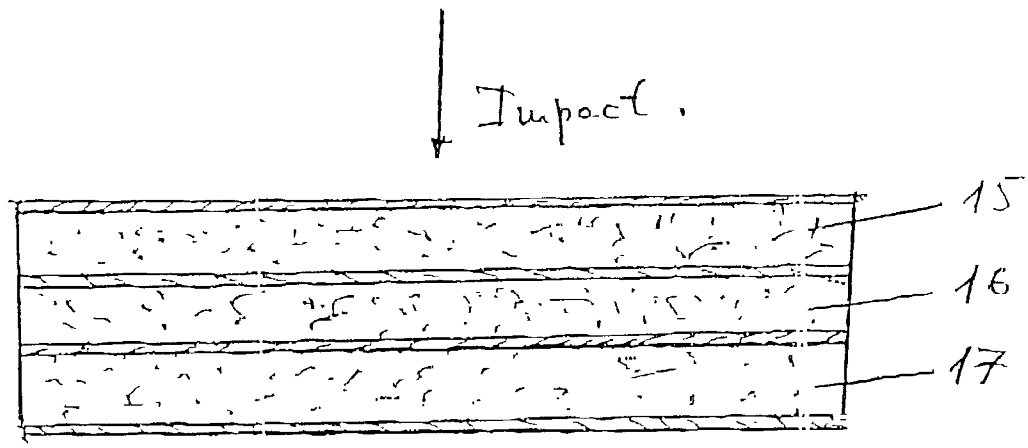


Figure 3

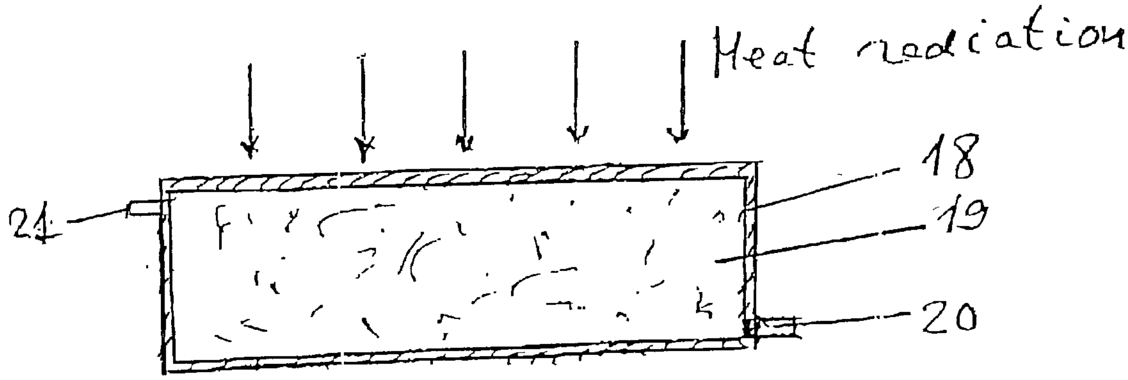


Figure 4

METHOD OF MAKING A PROTECTIVE MATERIAL AND ARTICLES MADE THEREFROM

FIELD OF THE INVENTION

[0001] The invention relates generally to the field of material sciences and more specifically to liquid materials which exhibit non-linear changes in shear strength with changes in shear rate. More particularly this invention relates to materials which when properly formulated may be used for antiballistic protective applications and other mechanical applications and to methods of making, using, and storing such materials.

BACKGROUND OF THE INVENTION

[0002] It is well known that certain liquid materials exhibit a non-linear increase of shear strength with an increase in shear rate. This property is referred to as dilatancy. Typically such materials are concentrated suspensions of a solid material in a liquid. The solid may be an organic material or an inorganic material, and the liquid may be water or an organic liquid. Examples of known solid materials include polyvinyl chloride, polymethyl methacrilate, polystyrene, titanium dioxide, various pigments, kaolin, silica and others.

[0003] Dilatants have been proposed for use in many applications, including personal armour. For example, U.S. Pat. No. 3,649,426 proposes flexible fluid dilatant armour for the insulation and protection of personnel and equipment from intense sound rays, heat, light, and high velocity projectile impacts. The patent teaches mixing a dilatant fluid and powder solid mixture containing over 75% solid particles of for example silica, having a particle size of from colloidal to about 100 mesh size, with a continuous liquid phase and encasing the mixture in a container. However, the patent fails to teach the rheological properties of the mixture.

[0004] U.S. Pat. No. 5,854,143 teaches a material for use in antiballistic clothing comprising a single layer or multilayer package or laminate including at least one layer of a flat structure containing an organic dilatancy agent. This patent teaches that an organic agent can be used to improve the antiballistic effect. This patent further states that the stopping power of the material proposed in U.S. Pat. No. 3,649,426 is too low, thereby requiring excessively thick layers. Again however, this patent fails to teach the rheological properties of the dilatant material comprising the package.

[0005] To date neither prior art approach of U.S. Pat. Nos. 3,649,426 or 5,854,143 has achieved any significant commercial success.

[0006] It is also well known that certain materials have a property opposite to dilatancy, in which the liquid material becomes less viscous with a higher rate of shear. This property is known as thixotropy, and materials having this property include asphalt, emulsions, ceramic suspensions and many food products.

SUMMARY OF THE INVENTION

[0007] What is needed is a protective material for personnel protection which is both comfortable and lightweight and yet exhibits superior stopping power to projectile impacts. What is further required is a material which is relatively viscous in its undisturbed shape, which becomes less viscous under slight to moderate shear and which exhibits a non-linear increase of shear strength when subjected to high shear rates. Such a material therefore exhibits thixotropic properties for low shear rates and dilatant properties for high shear rates and may be referred to as a thixotropic-dilatant liquid material ("TDLM").

[0008] What is further needed is a method of formulating such a material to achieve such preferred properties and a method of storing an article made from such a material to retain such preferred properties.

[0009] Therefore, according to the present invention there is provided a method of preparing a protective material comprising the steps of:

[0010] providing a powder mixture of solid particles having a particle size in the range of colloidal size up to 100 μm, said solid particles being of ceramic and/or mineral composition;

[0011] providing a liquid to form an external phase in the form of a suspension when mixed with said powder with a solids volume concentration of greater than 0.5;

[0012] mixing said powder and said liquid together to form a thixotropic-dilatant liquid material having a Theological curve;

[0013] adjusting the Theological curve; and

[0014] producing a material having dependence of viscosity on strain rate which is thixotropic or constant at lower strain rates and dilatant at higher strain rates wherein said TDLM solidifies on impact.

BRIEF DESCRIPTION OF THE DRAWINGS

[0015] Reference will now be made, by way of example only, to preferred embodiments of the present invention in which:

[0016] **FIG. 1** is a graph showing the rheological curve for the present invention at various pH values;

[0017] **FIG. 2** is multilayered protective structure;

[0018] **FIG. 3** is a diagram of a protective structure -according to one aspect of the invention; and

[0019] **FIG. 4** is a sealed protective structure.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0020] The present invention is directed to the formulation of a thixotropic-dilatant liquid material (TDLM) which has use in protective armour as well as in various mechanical applications. The first step in the method is to provide a powder mixture of solid particles having a particle size range from colloidal size up to about 100 μm. While ceramic solids are preferred various forms of ceramic and/or mineral compositions can be used. Some examples include fused silica, silica, quartz, alumina, vermiculate, mica, crystalline substances and amorphous materials. Other materials may also be suitable as will be understood by those skilled in the art. Essentially what is required in the TDLM is that the material exhibit the property of non-linear increase in shear strength in response to an increase in shear rate when placed in a liquid suspension.

[0021] The preferred method of obtaining the powder is to wet grind the solid particles. An important aspect of the invention is the particle size distribution. What is preferred is to carefully control the wet grinding conditions, such as rate and duration, until the volume content of solids in the suspension is over 50%, preferably reaches over 75% and most preferably is over 80%. Another desired property of the powder according to the present invention is that it has, in suspension, a specific surface area of greater than 0.5 m^2 per gram that corresponds to a content of colloidal fraction >0.5%. Other methods to control the colloidal particle content are also available, for instance, centrifugal separation.

[0022] The next step is either to use the prepared suspension directly, or if a different external liquid is preferred, to dry the suspension to yield a powder with the required particle size distribution and which, when mixed in the correct proportions with the liquid, provides the specific surface properties as aforesaid.

[0023] The next step is to select an appropriate liquid to mix with the dried powder, if the powder has been dried. Then the liquid and powder must be mixed, with the liquid being the external phase and so a step of gravitational mixing to form a suspension is preferred. The gravitational mixing is most preferably in the form of a slow rotational mixing of the suspension which helps to establish the rheological properties of the mixture. Such mixing according to the present invention is to increase the stability of the suspension to resist sedimentation, to permit gas to escape, and thus to generally increase the density of the material.

[0024] One form of gravitational mixing that has yielded satisfactory results is the use of a slowly rotating container in which the liquid suspension is contained. Most preferably such mixing is gentle enough that turbulence, which would otherwise introduce extra gas and voids into the mixture is avoided. Speeds of between 1 and 60 revolutions per minute are preferred with about 20 to 40 revolutions per minute being the most preferred. One of the aspects of the present invention is that the duration of the gravitational mixing has an effect on the rheological properties of the material. For example, mixing for a period of at least 12 hours is desired to achieve a relatively stable and dense material. However, by mixing the suspension as described for over 24 hours, changes to the rheological curve can be made, as described in more detail below in the examples. Thus, the present invention contemplates that one method to adjust the rheological curve is to control the duration of the gravitational mixing step.

[0025] A further aspect of the present invention is to use additives to adjust the Theological curve. These additives can include acids, acid salts, alkaline, or industrial surfactant materials. Thus, one aspect of the invention is to adjust the Theological properties of the TDLM by changing the pH of the material. In addition the liquid selected can be from the range of organic liquids that have low freezing temperatures, such as alcohol and glycerine and the like. In this aspect the present invention provides for low temperature applications for the materials.

EXAMPLE 1

Control of Rheological Curve of TDLM

[0026] One aspect of the present invention is to control the rheological curve of TDLM by selecting a preferred pH which will yield a Theological curve having desired attributes. Thus one realization of the present invention is that the rheological properties can be varied with pH to adjust the negative slope of the curve of change in shear strength for change in shear rate (thixotropy) as well as the positive slope of the same curve at higher shear rates (dilatancy). As well, it is also possible to adjust the position of the inflection point. These discoveries are demonstrated by a test performed on a quartz glass suspension with water in the external liquid.

[0027] A basic suspension of quartz glass (SiO2=99.8%) in water was prepared by wet grinding in a ceramic mill with alumina balls. The solid particle sizes making up the suspension varied from 0.01 μm to 60 μm. A BET specific surface was measured at 2 m^2/g. After grinding the suspension was gravitationally mixed (without balls) for 36 hours to stabilize the rheological properties. The rheological properties were measured by a rotary viscosimeter in a range of angular velocities from 0.7 to 700 1/sec at 20° C., and the pH was varied to generate different rheological curves as set out in **FIG. 1**. **FIG. 1** shows generally the relationship of viscosity to shear rate (in, for example, revolutions per minute of a mixing container). It will be understood by those skilled in the art that the shear rate is related, in a complex way to the strain rate arising in the material. Thus, at high shear rates, shear thickening is desired to prevent a projectile, for example, from passing through the material.

[0028] In addition, the mixtures were tested by applying a load to the mixture. After load removal, relaxation of the solidified material occurred, the suspension regained its fluidity, and shear stress dropped to zero within 1-2 sec or less. Sometimes solidified agglomerates (blocks) could be observed in the material after testing, which then slowly dispersed over time.

EXAMPLE 2

Pistol Shooting Test

[0029] A bullet was fired from a pistol (velocity about 500 m/sec) towards an open surface of a suspension, prepared in accordance with example 1 having a pH of 10. The suspension was carried in a small cup about 5 cm in diameter and 3 cm wall thickness. The stopping distance for the bullet was about 1.5 cm.

EXAMPLE 3

Automatic Rifle Shooting Test

[0030] Another test was carried out with a Kalashnikov automatic rifle from a distance of 10 m. A plastic container was used to contain the suspension, with an open surface, having an amount of suspension of 120 cm^3. The suspension consisted of a TDLM as prepared in example 1 having a pH of 10. After shooting the bullet into the volume, the whole volume was solidified, and the resulting solid was cracked and broken. It was concluded that for such a powerful weapon composite materials, such as a high strength solid thin first layer may be required together with the TDLM.

EXAMPLE 4

Impact Test

[0031] A measurement of the mechanical properties of the suspension of example 1 at high strain rates was carried out in an impact test system. The suspension was placed into cylindrical tank. A rigid rod with a metallic ball or cylindrical tip mounted on its end was mounted to the tank in such a way that it could freely move inside suspension in a vertical direction. The diameter of the probing ball or cylindrical tip was varied from 5 to 50 mm. An impact force was applied to the upper end of the rigid rod by an impactor. The impactor was in the form of a half-sphere with radius of 12.7 mm, and a total falling mass was 1.33 kg. The velocities of the impactor were measured by photocell, and the acceleration of the impactor was measured by precision accelerometer. The output signals from the photocell and accelerometer were monitored by oscilloscope and transferred to computer for data processing.

[0032] In the impact test the impactor's acceleration versus time was determined during dynamic loading. The instant velocity and displacement of the impactor were computed by subsequent integration of the acceleration over time. The system thus measured the drag forces, acting on the probing ball moving in the suspension.

[0033] An anomalous energy dissipation in the suspension was demonstrated. Essentially the fluid suspension behaves as a rigid solid during the loading. After unloading, a fast dissipation of energy occurs, which is the characteristic feature of an extremely viscous liquid. Such behaviour characterizes a material with high potential for use as an armour material.

[0034] A second type of impact test was made. In this case a rod 5 mm in diameter and weighing 2.3 kg was dropped from a height of 4 m onto an open surface of the material. The surface of the TDLM (the same in example 1) solidified instantly and the rod did not penetrate into the liquid. After impact the solidified surface was absolutely smooth and unfigured.

EXAMPLE 5

Organic Liquid Based Suspensions

[0035] In this example a highly dilatant suspension based on glyceraol was formulated. At the first stage it was prepared according to example 1 by milling in water. Then, the mixture was subjected to the gravity mixing process for in excess of 24 hours to form a stable suspension. Then water based suspension was dried again during gravity mixing to prevent sedimentation of suspension during evaporation. The organic component in this example glycerin, was then added during gravity mixing until the mixture met the required concentration.

EXAMPLE 6

Impact Test

[0036] The same impact tests as in example 4 were carried out for the suspension of example 5, namely, C_V=85% fused silica, 10% glycerol and 4% water, admixture of sodium silicate up to pH=9. The liquid also solidified instantly and the rod did penetrate past the surface of the material but only just barely. After impact an impression was visible of about 1-3 mm deep for about 2-3 sec.

[0037] As a result of conducting the tests as described above, a table was developed which identifies the recommended solids volume concentration C_V, pH and time of gravitational mixing for different applications. Below, Table 1 presents the information in accordance with the present invention.

TABLE 1

Application	C_V	pH	GM, hour
Armour (first layer)	>0.75	2–7	>24
Armour (second layer)	>0.75	4–13	>24
Armour Composite (with super solid surface layer)	>0.70	7–10	>12
Velocity regulators	>0.70	1–7	>6
Brakes, viscoelastic dampers, packing materials	>0.75	7–13	>6
Amusement devices	>0.55	1–14	>0

[0038] From the above-noted table it is noted that adding water-soluble polymers such as methylcellulose provides an increase of viscosity in the thixotropic part of the rheological curve. On the other hand, a decrease in the viscosity of the thixotropic part of the rheological curve can be provided by extending the gravitational mixing process for longer periods, such as 24 hours for instance.

[0039] Other additives can be used to control the separation of the solids from the liquid, such as alkaline additives, or other materials containing colloidal silica fractions of 1-2 nm, for example, sodium silicate solution. Such additives control the sedimentation stability of the material. In addition, as will be noted from **FIG. 1** and Table 1, improved workability of a TDLM can be obtained by providing a pH in the range of 2 to 3. In this case improved workability means that the material flows fast making it easy to fill different types of containers. Thus, according to the present invention, the material can be provided with one pH on fabrication, to facilitate being placed inside containers, and then the pH adjusted to improve the rheological characteristics once in the container, such as to optimize the thixotropic dilatancy curve for personnel armour protection from projectile impacts.

[0040] The present invention therefore comprehends using TDLM as an armour material in various embodiments and configurations. The liquid ceramic materials can be modified for use in protection of various engines, compartments and other crucial and strategic places in trucks, tanks, armoured personnel carriers, etc. from high temperature-sudden impact conditions (explosion, fire hazard). Various ways of designing such protection enclosures (portable flexible bags, screens etc.) are comprehended by this invention.

[0041] In one embodiment of the present invention, as shown in **FIG. 2**, there is provided a protective material which comprises an exposed face **10**, a rear face **12**, and side walls **11** which encapsulate or encase a layer of TDLM **13**. A hard strong thin plate **14** such as a dense ceramic plate, Kevlar plate or even metal plate, which is not rigidly fixed to the rigid container, but is simply floating in the TDLM material is also shown. The side walls **11** of the container can be also prepared from rigid and strong materials and the front and rear walls **10, 12** can be of flexible materials. Such a thin plate material **14** will tend to distribute the impact force across the layer **14** and therefore will enhance the armour properties of the layer. Thus, the present invention contemplates the presence of a separate element **14** within the TDLM **13** which acts to distribute impact shear through the material **13**, to spread the impact force to reduce impact shear from being passed through the layer to the item being protected.

[**0042**] In the embodiment of **FIG. 3**, the armour material has a multilayer structure where each layer **15**, **16**, **17** of the structure preferably has different rheological curves. For example, an outer layer **15**, which would first receive the impact energy **16**, would preferably have a critical shear stress that starts at very high rates and a high dilatancy. Subsequent layers **16**, **17** can have lower critical shear stresses. It is believed that such a layered structure would operate to distribute the projectile impact from the local area of the impact more broadly across the first layer and subsequently more broadly across each of the layers below the first layer.

[**0043**] In a further embodiment, as shown in **FIG. 4**, the present invention contemplates that each layer of a multilayer protective material be hermetically sealed or enclosed to prevent any liquid evaporation over time. As noted above, changes in the solids volume concentration arising by reduction in the liquid affects the rheological properties of the TDLM. Therefore, to prevent any such rheological changes occurring, the present invention comprehends hermetically sealing the TDLM **19** into the armour container **18**. Of course, a consequence of a large impact is the generation of heat. Due to the presence of the external liquid phase, generation of heat can cause significant pressure peaks within the hermetically sealed container. Therefore, the present invention further contemplates a pressure release valve or valves **20**, **21** to permit the controlled release of pressure in the event of a sudden pressure build up due to projectile impact or heat radiation.

[**0044**] A further aspect of the present invention relates to the use of rigid lateral or side walls to increase the armour protection. Use of rigid lateral side walls will help absorb energy, laterally transferred by the TDLM material and will likely improve armour characteristics.

[**0045**] In the alternative, the present invention also contemplates flexible side walls for free deformation of the material without damage upon ballistic impact.

[**0046**] In a further embodiment, the present invention contemplates the exterior wall of the armour material having a coating with a coefficient of heat emission less than or equal to 0.3 to reflect heat radiation. Nickel metal would be appropriate for such an external coating. In addition, the layers may contain materials to improve protection against ionizing radiation, such as various types of metal and carbon.

[**0047**] In a further aspect of the present invention, long term storage of the armour and protective materials can be achieved using slow rotation or other type of movement for continual gravitational mixing or stirring. Such long term mixing or stirring will prevent settling of the suspension in the liquid and the subsequent change or loss of desirable Theological properties.

[**0048**] In summary therefore, it can be understood that the present invention contemplates that for a number of armour purposes, control of the rheological curve is very important for specific applications. Control of the properties of the TDLM suspensions can be achieved by small chemical additives and/or by gravitational mechanical treatment. Other aspects affect or control the Theological properties to increase storage time, increase flexibility and alter the critical shear rate or solidification point. Thus, the present invention teaches that the rheological curve of TDLM can be engineered for this purpose of optimizing the material for the application of armour and mechanical properties.

[**0049**] The present invention is therefore directed to preparing TDLM suspensions for armour and other applications all in accordance with the foregoing.

[**0050**] It will be appreciated by those skilled in the art that while mention has been made of various preferred alternatives, the present invention is not limited to the forms and embodiment discussed above. Rather, the scope of the invention is to be determined by the scope of the attached claims.

We claim:

1. A method of preparing a protective material comprising the steps of:

providing a powder mixture of solid particles having a particle size in the range of colloidal size up to 100 μm, said solid particles being of ceramic and/or mineral composition;

providing a liquid to form an external phase of a suspension when mixed with said powder with a solids volume concentration of greater than 0.5;

mixing said powder and said liquid together to form a thixotropic-dilatant liquid material TDLM;

adjusting the rheological curve of said material; and

producing a TDLM having a dependence of viscosity on strain rate which is thixotropic or constant at lower strain rates and dilatant at higher strain rates wherein said TDLM solidifies on impact.

2. A method as claimed in claim 1 wherein said solid particles in the powder mixture are selected from the group of fused silica, silica, quartz, alumina, vermiculate, mica or other crystalline and/or amorphous materials.

3. A method as claimed in claim 1 further including adding admixtures of alkaline and/or acid substances, or industrial surfactants.

4. A method as claimed in claim 1 wherein said step of providing said powder further comprises wet grinding said solid particles in a suspension.

5. A method as claimed in claim 1 wherein said step of wet grinding the solid particles results in a particle size distribution in the range from colloidal to 100 μm with a solid particles volume concentration of C_V>0.80 and colloidal fractions content of C_V>0.005, all having a specific surface of >0.5 m^2/g (larger than 0.5 m^2/g).

6. A method as claimed in claim 4 further including the step of drying said suspension.

7. A method as claimed in claim 1 wherein said step of mixing said liquid and said powder comprises gravitational mixing.

8. A method as claimed in claim 1 further including adding organic fluids to permit applications of said TDLM to be used at temperatures below 0° C.

9. A method as claimed in claim 7 wherein said step of gravitational mixing/treatment comprises slowly rotating a volume of said material in a rotating volume with rotational velocity of 1-60 revolutions/min for at least 12 hours.

10. A method as claimed in claim 1 wherein said step of adjusting the rheological curve further comprises adjusting the solids volume concentration of said material by adjusting the proportions of said powder or said liquid in said material.

11. A method as claimed in claim 1 wherein said step of adjusting the Theological curve further comprises extending a period of gravitational mixing/treatment by at least 24 hours.

12. An armour material comprising:

at least two layers including an outer layer and an inner layer;

the outer layer consisting of a thixotropic-dilatant liquid material having a first rheological curve;

the inner layer consisting of a thixotropic-dilatant liquid material having a second Theological curve;

wherein the first rheological curve has a critical shear stress at a higher shear rate than the second curve.

13. An armour material comprising:

a layer of thixotropic-dilatant liquid material; and

a projectile resistant material that is not rigidly fixed, in contact with said layer, to disperse and redistribute shear forces caused by a projectile across an area within said layer.

14. An armour material as claimed in claims **12** or **13** further including at least one containment structure for containing said layers of thixotropic-dilatant liquid material therein.

15. An armour material as claimed in claims **12** or **13** wherein the layers containing TDLM are hermetically enclosed to prevent liquid evaporation and changes of rheological properties.

16. An armour material as claimed in claim 14 further including a valve on said containment structure for controlled pressure release of gasses arising in the containment structure.

17. An armour material as claimed in claim 12 comprising cells with rigid walls containing the said TDLM structures wherein side walls of cells are made of hard and strong materials and are rigidly fixed to increase armour protection.

18. An armour material as claimed in claim 12 wherein the front wall has a coating with a coefficient of heat emission <0.3 (e.g. Ni, etc.) to reflect heat radiation.

19. An armour material as claimed in claim 12 wherein some layers are made of metal and carbon containing materials to improve protection from ioning radiation.

20. A method for long term storage of the protective materials as claimed in claims **12** or **13** comprising slowly rotating or otherwise gravitational stirring said material while said materials are being tested.

* * * * *