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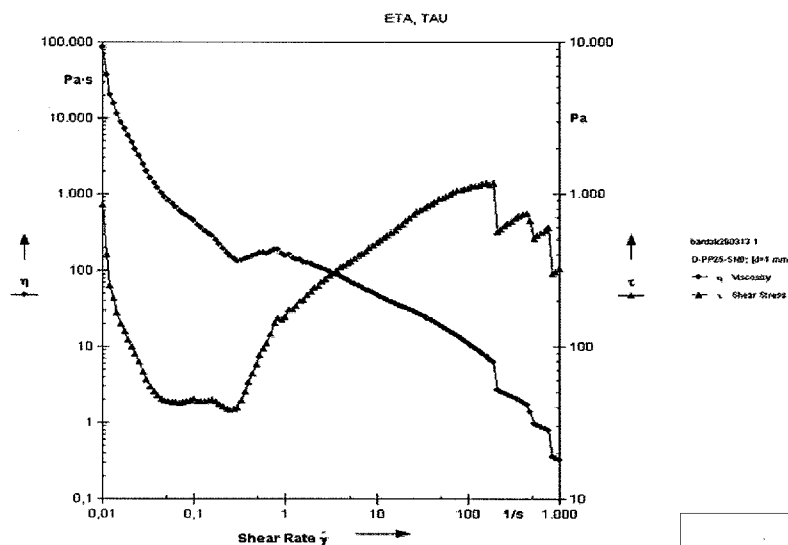


Fig. 3

(57) Abstract: The present invention relates to a formulation applied in order to keep powder ceramics added to non-Newtonian fluids with shock absorption property stable and to improve their shock absorption property and a material thus obtained. The aim of the invention is to ensure long term-use and industrial utilisation of the material obtained by keeping powder particles contained in non-Newtonian mixtures with shock absorption property prepared by using various carbides and boron nitride stable within the fluid.

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## DESCRIPTION

### A NON-NEWTONIAN MATERIAL WITH SHOCK ABSORPTION PROPERTY

#### Technical Field

5           The present invention relates to a formulation applied in order to keep powder ceramics added to non-Newtonian fluids with shock absorption property stable and to improve their shock absorption property and a material thus obtained. The aim of the invention is to ensure long term-use and industrial utilisation of the material obtained by keeping powder particles contained in non-Newtonian mixtures with shock absorption  
10           property prepared by using various carbides and boron nitride stable within the fluid.

#### Prior Art

          Liquids are examined in two separate groups depending on the factors changing their viscosity. These are Newtonian and non-Newtonian liquids. Newtonian liquids are ideal  
15           liquids and their viscosity is only affected by heat change. The viscosity of a non-Newtonian liquid, on the other hand, changes on the basis of the content of the liquid and the flow rate. The behaviour of non-Newtonian fluids is not static and changes between gaining viscosity and losing viscosity. Non-Newtonian liquids with Shear Thickening characteristic exhibit solid-like properties against high forces and liquid-like properties in the absence of force.

20           In the prior art, a non-Newtonian fluid exhibiting Shear Thickening property is utilised for armour production in the US20050266748 A1 numbered patent document. Materials used for this fluid are powder particles of ethylene glycol, polyethylene glycol and silicon dioxide. Oxides, calcium carbonate and natural minerals are deemed worthy as particles.

          Another document according to the prior art is the WO201012393 A2 numbered  
25           patent document which relates to an armour made of composite material. Ultra high density Polyethylene (UHDPE), ceramic plates and a nanotube named HOLLYSITE are used. Said ceramics are used in solid state and one piece.

          Another document related to the prior art is the US2009026029 numbered patent  
30           document wherein the surfaces of the materials (powder or plate) used are modified by silane coating. As a result of this modification, silane surface interacts with the matrix instead of the powder surface. The matrix used is an epoxy which, after a certain period of time, is polymerised by cross linking. The aim herein is, instead of mere physical compression of

powders (granules) as a result of said polymerisation, to further support said compression with chemical bonds by introducing a bridge such as silane.

### **Aim and Brief Description of the Invention**

5           As is well-known, non-Newtonian fluids exhibiting Shear Thickening property behave like solids when pressure is applied on them. The aim of this invention is to provide a non-Newtonian liquid mixture exhibiting Shear Thickening property that comprises shock and force absorption attributes; consists of nano-sized carbide based ceramics or boron nitrite in powder form and a solvent to which said powder adsorbs; is not sustainable prior to the  
10 surface modification of said powder, but exhibits sustainability and stability following surface modification with silanes and consists of a carbide-based powder ceramic whose surface is coated with silane following the surface modification process and a solvent to which said coated powder adsorbs.

          Carbide ceramics are materials with high hardness. They have several uses in  
15 industry. Carbide-based ceramics are even used in production of drills used for metal processing. Carbide-based materials are used in armour production for all military vehicles and tanks. The aim of this invention is to obtain a material exhibiting unprecedented flexibility and strength by combining the strength provided by Shear Thickening behaviour and certain carbide classes and boron nitrite's high level of hardness. This is already possible  
20 in theory. However, mixtures that can remain stable and homogenous for a long period of time cannot be obtained due to the weak interaction between said materials with liquids. In this invention, formulation and methods are provided required for maintaining stability and homogeneity. The invention enables use of the said liquids in military industry and civil fields by turning non-Newtonian liquid mixtures that may be prepared with powders of said nano-  
25 sized materials into stable mixtures.

          The chemical interaction (secondary atomic bond) of carbide powders with a liquid mixture is very weak. Consequently, carbide powders cannot interact with liquid. In a mixture obtained by using carbide powders, after a certain period of time, carbide powders precipitate. In order to avoid this, surface modification is performed so that nano-sized  
30 powder granules interact better with the liquid and disperse homogeneously in the liquid. Thus, the non-Newtonian liquid's shock absorbing property is preserved. The material is thereby becomes suitable for industry.

## Definitions of Figures Illustrating the Invention

The figures used for a better explanation of the non-Newtonian material with shock absorption property developed with the invention and their corresponding definitions are as follows.

5 Figure-1: Graphic showing Zeta potential measurement of SiC without silane coating

Figure-2: Graphic showing Zeta potential measurement of SiC with silane coating

Figure-3: Rheometer graphic of the material mixture exhibited in example 1:  
Process

10 Figure-4: Rheometer graphic of the material mixture exhibited in example 2:  
Process

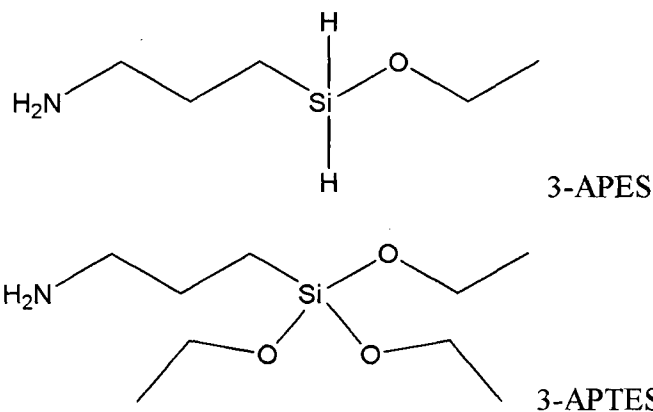
## Detailed Description of the Invention

The carbide groups used in this invention are carbides that form covalent bonds. These are silicon carbide, boron carbide and interstitial carbide compounds. Tungsten carbide may be provided as an example for interstitial carbide compounds.

15 In order for the carbide powders suspend stably in the chemical mixture for a long period of time a chemical group called "Silane" is used. Owing to this chemical group, a strong secondary bond is formed between the carbide molecules and the mixture. The most important characteristic of this material is being a transition material between inorganic and organic substances. The silane group is a material having a silicone molecule in the middle  
20 and comprising 2 tails both of which possess distinct chemical properties.

Hydrophilic solvents forces the particles surrounded by the silane groups to disperse homogenously by forming hydrogen bonds with amino and ethoxy groups of silane. This improves stability. The reason for using methyl alcohol here is to disturb non-Newtonian behaviour caused by the combination of powder and polyethylene glycol and facilitate  
25 mixing. Polyethylene glycol 300, Polyethylene glycol 400, ethylene glycol and bisphenol-A chemicals may be used as solvents. Solvent is between 90% and 5% of the mixture weight with respect to the particle size and specific mass of powder materials.

The Silane groups used in this invention form aggressive oxygen groups by hydrolysing in water environment. These groups form a covalent bond between the  
30 material's surface and surfaces such as ceramic, metal, glass, plastic. 3-aminopropylethoxysilane (3-APES) or 3-aminotriethoxypropylsilane (3-APTES) that are used in the examples



comprise aminopropyl group, a bond that is stable against hydrolysis. Uncontrolled polymerisation of the silane structure is thus prevented. Hydrolysed Alkoxy groups, on the other hand, will form a hydrogen bond with the surface.

The number of hydrolysed bonds in the structure should be at least 1 and at most 3. When a single bond is hydrolysed as it is the case with the 3-APES structure, polymerisation is prevented. In the 3-APTES structure, on the other hand, the polymerisation rate may be controlled with the amount used. Thus, even if polymerisation occurs, silane will still be able to form a hydrogen bond on at least one branch.

Consequently, hydrolysis of all 4 groups in the chosen tetra-functional silane is an undesired property.

The material is thus coated with silane and is isolated from the external world. The silane's other active tail is in communication with the external world. In this invention, a hydrogen bond is formed between the solvent in the external world and the silane's other active tail. Thus, the strongest secondary atomic bond will be formed and stable suspension of nano-sized carbide powder particles will be enhanced. In addition, zeta potential of particles with polar surfaces is higher than their original zeta potential. This increase strengthens the tendency of particles with the same charge to push each other within the solvent and supports a homogenous distribution in the solvent. The combination of these two chemical mechanisms allows us to use these strong ceramics for armours and in several other areas. Formulation examples are listed below.

#### Formulation 1;

- Ethyl alcohol
- Methyl alcohol
- Silicon carbide

- 3-aminopropylethoxysilane
- Polyethylene glycol 300 (PEG 300)
- Deionised water

## Formulation 2;

- 5
- Ethyl alcohol
  - Methyl alcohol
  - Boron carbide
  - 3-aminopropylethoxysilane
  - Bisphenol A
- 10
- Deionised water

## Formulation 3;

- Ethyl alcohol
  - Methyl alcohol
  - Boron carbide
- 15
- 3-aminopropyltriethoxysilane
  - Polyethylene glycol 300 (PEG 300)
  - Deionised water

## Formulation 4;

- Ethyl alcohol
- 20
- Methyl alcohol
  - Boron Nitride
  - 3-aminopropyltriethoxysilane
  - Bisphenol-A
  - Deionised water

25

## Example 1: Process

- In order to prepare the silane mixture, silane molecules are firstly activated by hydrolysing. In order to achieve this, 1 gram of deionised water is mixed with 98 grams of ethyl alcohol and it is stirred for approximately 10 minutes.
- 5      • Following mixing, 1 gram of 3-aminopropylethoxysilane is added to the deionised water + ethyl alcohol mixture (in this example, silane:powder ratio by weight is 1:250. It can be between 1:2000 to 1:100). The said mixture is stirred to hydrolyse with a magnetic stirrer and a stir bar for approximately 1 hour.
- 10     • The activated silane mixture is stirred with 250 grams of silicon carbide for approximately 3 hours. The particle size of carbide based powder ceramics may vary between 10 nanometers and 250 micrometers. The mixture may be stirred in one time or in several times in amounts that the mechanical stirrer can handle without being stuck. The mixture should be stirred for 3 hours.
- 15     • The powder whose surface is coated with silane is filtered with a gooch crucible and is vacuumed by a vacuum pump. Then, the powder remaining on the surface is left for drying. If drying will be performed at room temperature, then approximately 24 hours will be sufficient, while 2 hours will suffice if it is to be performed at a temperature around 70 degrees.
- 20     • The dried powder is mixed with 99.65 grams of polyethylene glycol.
- Powder particles can be between 10% and 95% of the mixture weight with respect to the particle size and specific mass of powder materials.
- After the process is over it is subjected to rheological measurement and zeta potential measurement.

25

#### Example 2: Process

- 30      • In order to prepare the silane mixture, silane molecules are firstly activated by hydrolysing. In order to achieve this, 1 gram of deionised water is mixed with 98 grams of ethyl alcohol and it is stirred for approximately 10 minutes.
- Following mixing, 1 gram of 3-aminopropylethoxysilane is added to the deionised water + ethyl alcohol mixture (in this example, silane:powder ratio

by weight is 1:250. It can be between 1:2000 to 1:100). The said mixture is stirred to hydrolyse with a magnetic stirrer and a stir bar for approximately 1 hour.

- The activated silane mixture is stirred with 250 grams of boron carbide for approximately 3 hours. The particle size of carbide based powder ceramics may vary between 10 nanometers and 250 micrometers. The mixture may be stirred in one time or in several times in amounts that the mechanical stirrer can handle without being stuck. The mixture should be stirred for 3 hours.
- The powder whose surface is coated with silane is filtered with a gooch crucible and is vacuumed by a vacuum pump. Then, the powder remaining on the surface is left for drying. If drying will be performed at room temperature, then approximately 24 hours will be sufficient, while 2 hours will suffice if it is to be performed at a temperature around 70 degrees.
- The dried powder is mixed with 204.54 grams of bisphenol A.
- Powder particles can be between 10% and 95% of the mixture weight with respect to the particle size and specific mass of powder materials

After the process is over it is subjected to rheological measurement.

## MEASUREMENT OF ZETA POTENTIAL

Zeta potential is a measurement concerned with particles' charges. The aim is to observe how much the particles are charged with either + or -. In this invention, however, the type of particles' charges is irrelevant, since our aim is to obtain particles with a charge as large as possible. Particles with a Zeta Potential value of 25mV regardless of (+) or (-) type will aggregate after a certain period of time and start clustering. The underlying reason is that pull force between the particles is higher than push force since their surface charge is less than 25 mV. Inasmuch as each particle is charged with the same zeta charge, they will naturally push each other; the objects with the same charge push each other. When the charge is above 25 mV, these particles will move away from each other since they have sufficient push force, aggregation will be removed and "a liquid mixture that does not precipitate" will be obtained. This proves that our material is a product that is long-lasting and will be used in the industry for a long period of time.

In Figure 1, **SiC** has been subjected to the zeta potential test without performing coating and without any coating on. The results have been observed as an average of -24.5 with a deviation of 1.2 as seen in the Zeta column. In general, zeta is on the limit. In fact, it has dropped below 25 mV. In comparison with the coated one, the one with the coating would provide a much more stable mixture due to its high zeta value. The other one, on the other hand, is below the lower limit of the "stable mixture" concept since it is below the 25 mV threshold. This result clearly shows that using this material in its natural condition would not yield a product suitable for long use.

In Figure 2, on the other hand, **SiC** has been coated with silane and subjected to the zeta potential test. It is observed that the Zeta potential values have changed completely following silane coating. Firstly, the change in the average zeta potential value from -24.5 mV to +34 mV indicates that our silane substance covers the surfaces entirely and isolates the particles from the external world. Moreover, the rise of zeta potential value to +34 mV shows that this material will not form a stable particle and will support a homogenous distribution.

Consequently, after being coated with silane, the particles within the water will be distributed homogeneously in the water and will not precipitate; since precipitation will not occur, the material will preserve its non-Newtonian structure and not lose its shock absorption property.

### **RHEOMETER ANALYSIS**

As for the second test, the tests have been performed regarding whether the material exhibits Shear Thickening property or not. The test has been performed with a rheometer and the results can be seen in Figure 3. It is understood from the graphic that it is non-Newtonian (the shear stress curve is not linear) and exhibits shock absorbing property (as shear stress increases at a point, viscosity also increases). The graphic is a shear stress – shear rate graph. When measuring a normal liquid, the graphic is supposed to be linear. However, as seen in Figure 3, the shear rate grows increasingly. The graphic in Figure 3 proves that it requires much higher stress in comparison with the shear stress applied and consequently more energy is needed to mobilise the material compared to normal liquids and this need further increases along with the shear rate. Exhibiting an increase in terms of

viscosity is also considered as a proof for Shear Thickening. It is also observed that the material requires high shear force which indicates how much force the material absorbs.

5 The test has been performed regarding whether the material exhibits Shear Thickening property or not. The test has been performed with a rheometer and the results can be seen in (Fig 4) It is understood from the graphic that it is non-Newtonian (the shear stress curve is not linear) and exhibits shock absorbing property (as shear stress increases at a point, viscosity also increases). The graphic is a shear stress – shear rate graph. When measuring a normal liquid, the graphic is supposed to be linear. However, as seen in Fig 4,  
10 the shear rate grows increasingly between shear rates 1 and 100. The graphic in Fig 4 proves that it requires much higher stress in comparison with the shear stress applied and consequently more energy is needed to mobilise the material compared to normal liquids and this need further increases along with the shear rate. Exhibiting an increase in terms of viscosity is also considered as a proof for Shear Thickening.

15

**CLAIMS**

1. A non-Newtonian material exhibiting Shear Thickening property characterised by a stable, sustainable and shock absorbing structure comprising
  - 5           • Silicon carbide, boron carbide, boron nitrate or interstitial carbide compounds in powder form,
  - Polyethylene glycol 300 or Polyethylene glycol 400 or ethylene glycol or bisphenol-A as solvent,
  - Silane comprising aminopropyl group that is a stable bond against hydrolysis and alkoxy groups
  - 10          • Ethyl alcohol,
  - Methyl alcohol and
  - Deionised water.
2. A non-Newtonian material according to Claim 1, characterised in that carbide powders are prevented from precipitating by performing surface modification with  
15 silane.
3. A non-Newtonian material according to Claim 1, characterised in that the size of the said powder (granule) particles in the mixture is between 10 nanometre and 250 micrometre
4. A non-Newtonian material according to Claim 1 wherein Powder, characterized by  
20 being between 10% and 95% of the mixture weight with respect to the particle size and specific mass of powder materials.
5. A non-Newtonian material according to Claim 1 wherein silane is characterised by being 3-aminopropylethoxysilane (3-APES).
6. A non-Newtonian material according to Claim 1 wherein silane group is characterised  
25 by being 3-aminotriethoxypropylsilane (3-APTES).
7. A non-Newtonian material according to Claim 1 wherein silane is characterised by having a ratio between 1:100 to 1:2000 to the powder's weight.
8. A non-Newtonian material according to Claim 1 wherein solvent is characterised by  
30 being between 90% and 5% of the mixture weight with respect to the particle size and specific mass of powder materials.

9. A production process for the non-Newtonian material exhibiting Shear Thickening property according to Claim 1, characterised by comprising the steps;

- 1 gram of deionised water is mixed with 98 grams of ethyl alcohol and stirred for approximately 10 minutes,
- 5       • 1 gram of 3- aminopropylethoxysilane is added to the deionised water + ethyl alcohol mixture.
- The mixture is stirred with a magnetic stirrer and a stir bar for approximately 1 hour to hydrolyse.
- 10       • The activated silane mixture is stirred with 250 grams of silicon carbide for approximately 3 hours.
- The powder whose surface is coated with silane is first filtered by a gooch crucible and then vacuumed by a vacuum pump.
- Drying is performed by keeping for 24 hours at room temperature or 2 hours at a temperature around 70 degrees.
- 15       • The dried powder is mixed with 99.65 grams of Polyethylene glycol.

20

25

Run	Pos.	KCps	Mob.	Zeta	Width	Time
1	50.0	1395.3	2.496	31.8	1.6	20:42:21
2	50.0	1475.2	2.399	30.5	1.6	20:42:53
3	50.0	1515.6	2.506	31.9	1.6	20:43:24
4	50.0	1554.4	3.375	43.0	1.6	20:43:56
5	50.0	1598.2	2.598	33.0	1.6	20:44:27
6	50.0	1470.3	2.672	34.0	1.6	20:44:58
7	50.0	1482.2	3.072	39.1	2.7	20:45:30
8	50.0	1572.7	2.515	32.0	1.6	20:46:01
9	50.0	1513.2	2.516	32.0	1.6	20:46:32
10	50.0	1530.2	2.580	32.8	1.6	20:46:32
Average		1510.7	2.673	34.0	1.7	20:47:04
+/-		58.5	0.307	3.9	0.4	

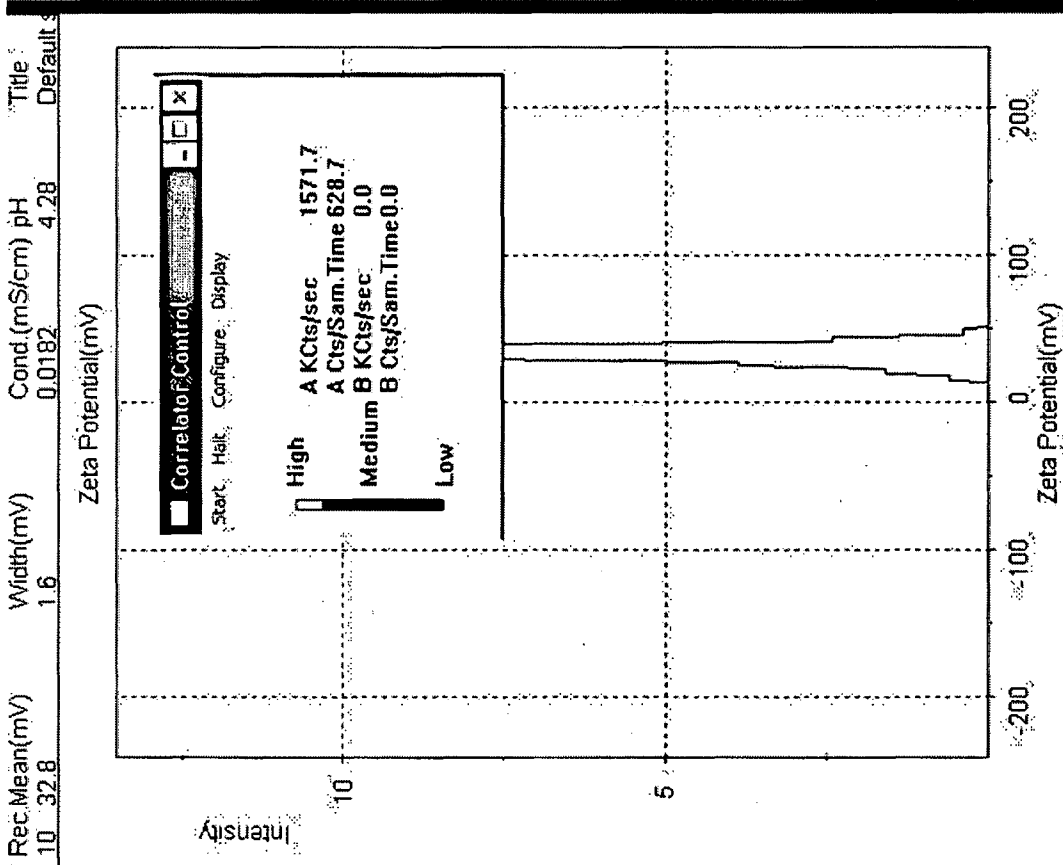


Fig. 1

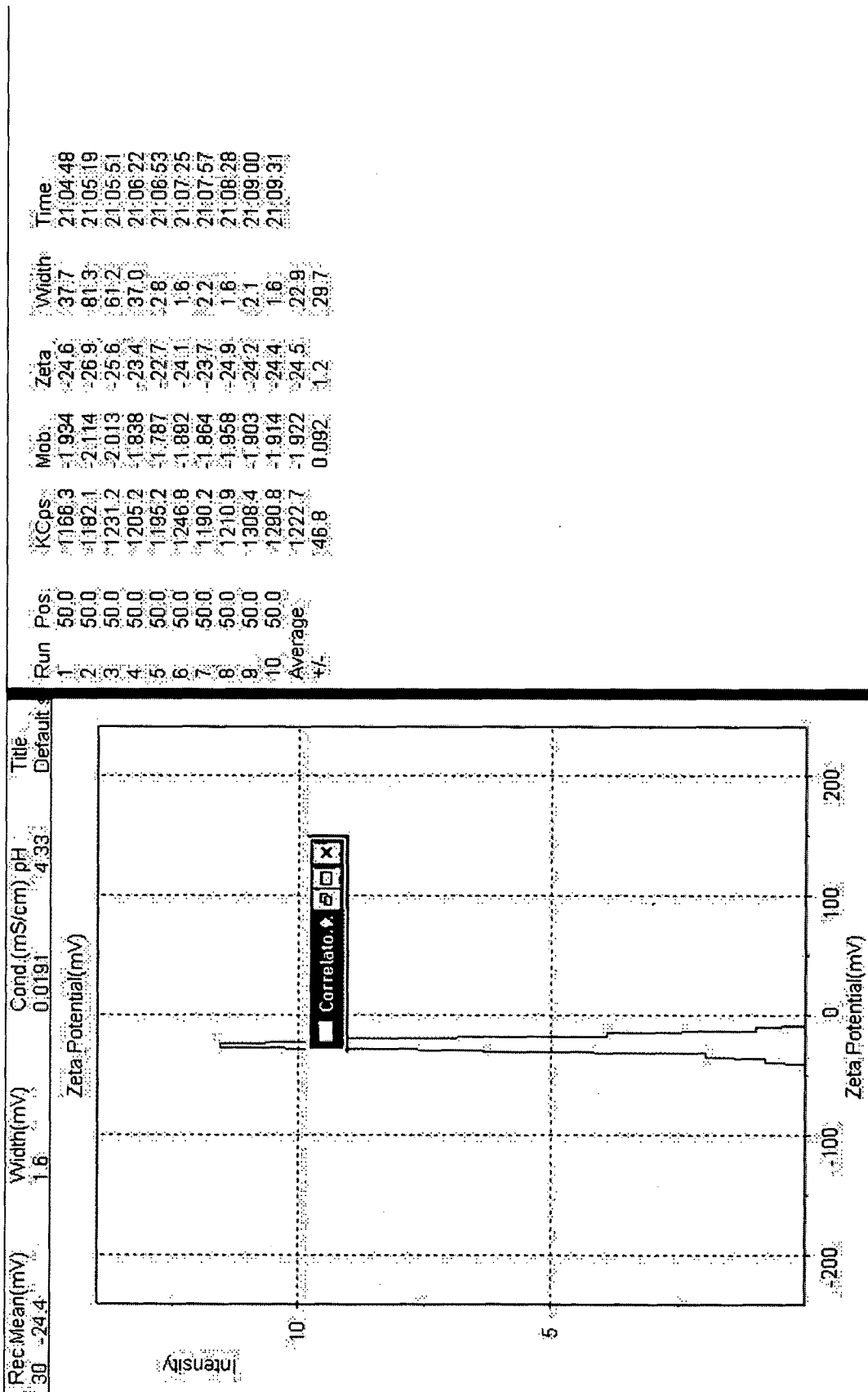


Fig. 2

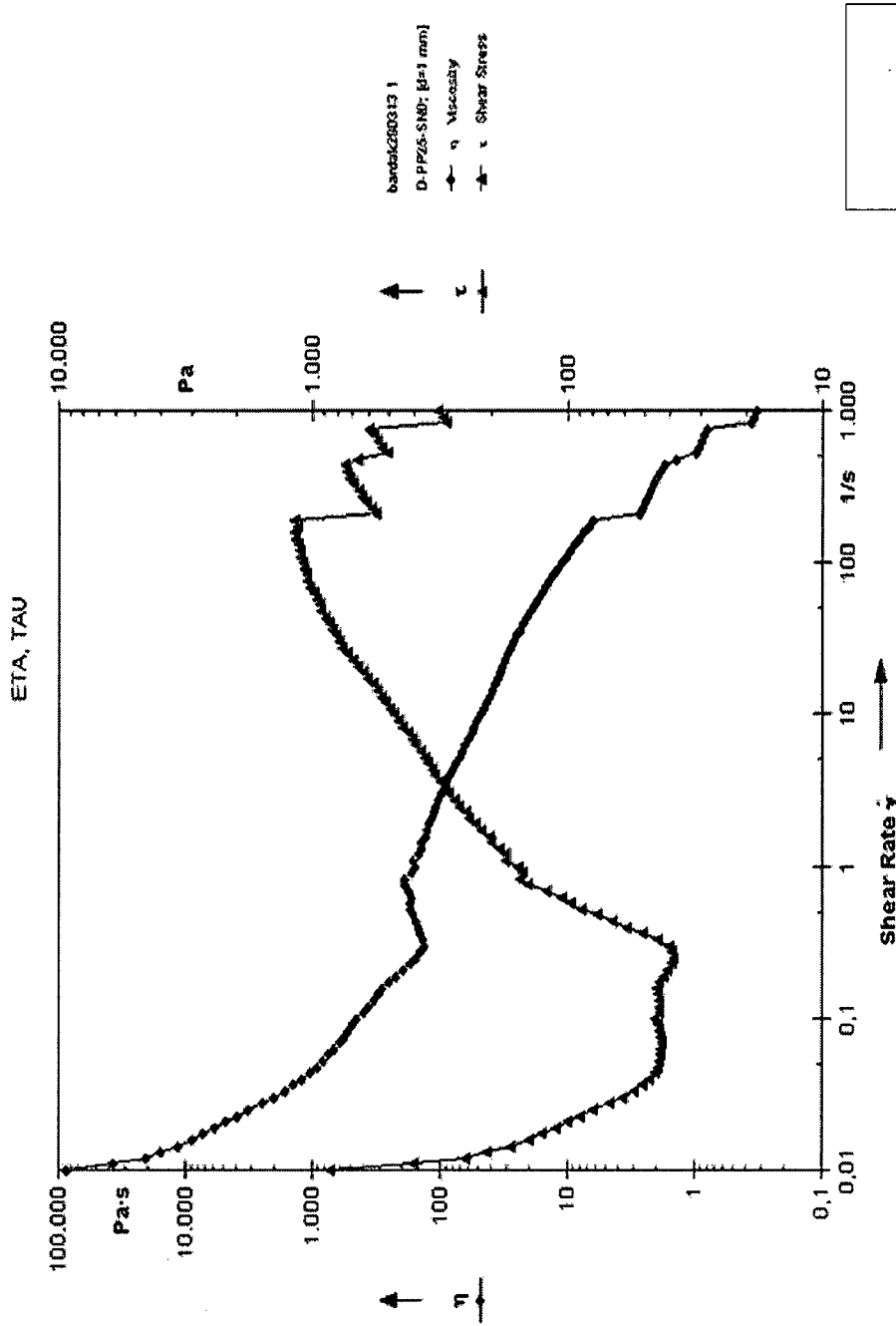


Fig. 3

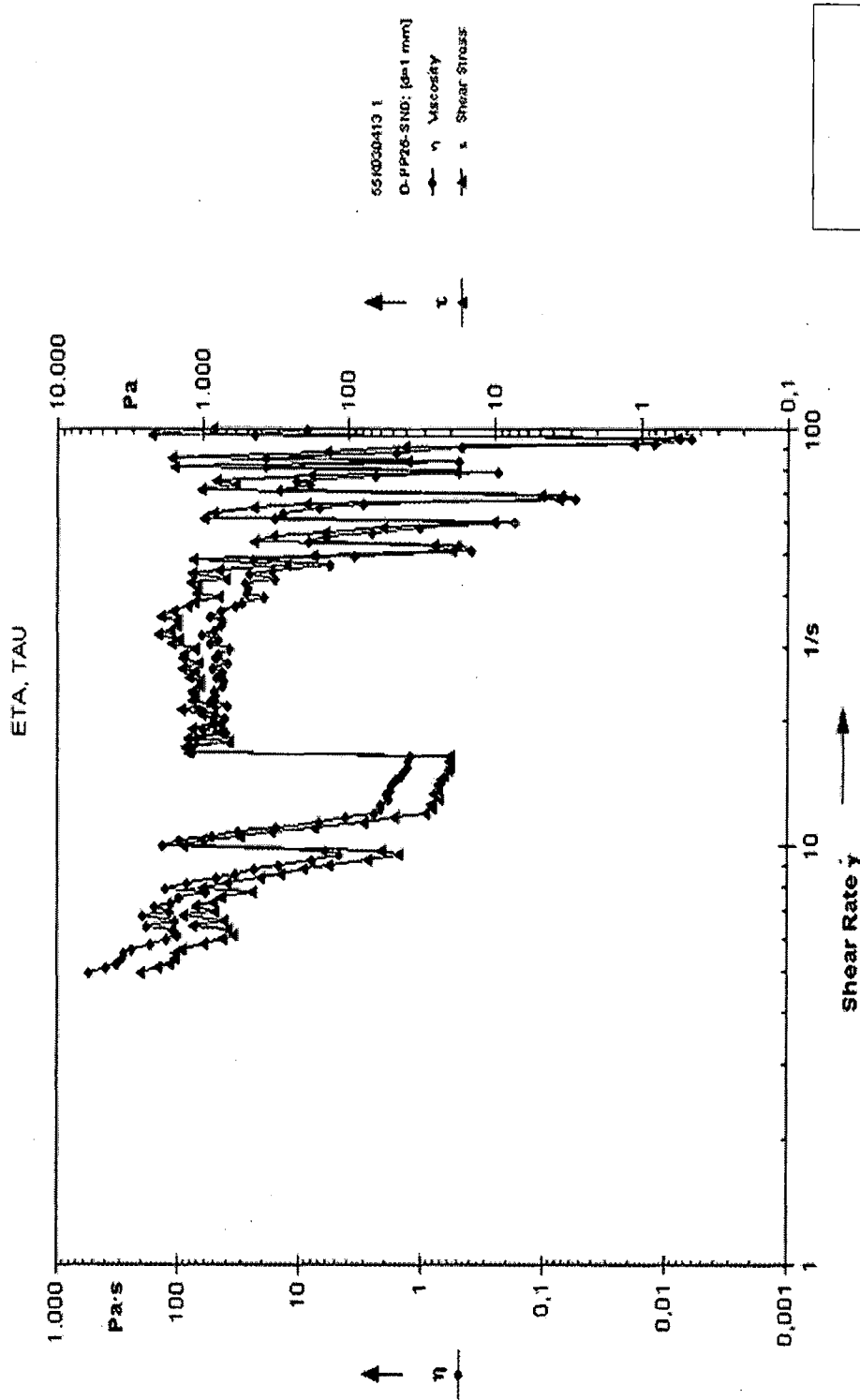


Fig. 4