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Los Angeles, CA 90067-2199 (US)

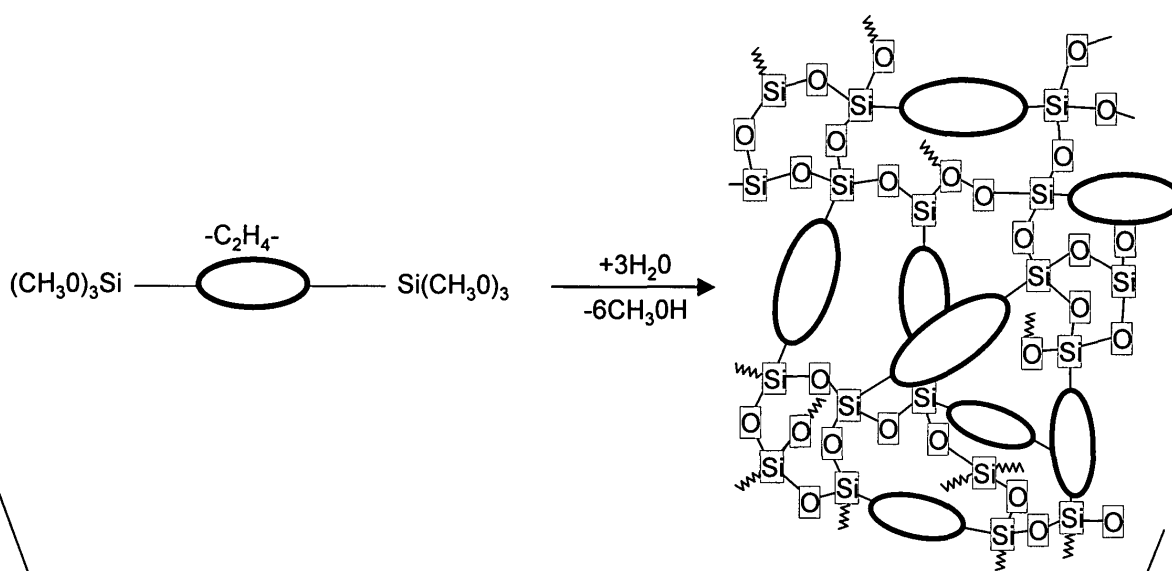
(72) Inventors:

- **Crofoot, Thomas A.**
Riverside, CA 92503 (US)
- **Starkovich, John A.**
Redondo Beach, CA 90278 (US)

(74) Representative: **Mackenzie, Andrew Bryan et al****Marks & Clerk****45 Grosvenor Road****St. Albans, Hertfordshire AL1 3AW (GB)**(54) **Polymer-gelled propellant and method for its production**

(57) A liquid propellant is converted to a gelled propellant by use of a nanogellant material having a three-dimensional polymeric structure that either is formed in the propellant itself, or is formed separately from the propellant and later dispersed in the propellant. In one form of the invention, the nanogellant material is bis-trimethoxysilylethane (BTMSE), which, when mixed with a suit-

able liquid propellant, such as monomethyl hydrazine (MMH), in the presence of water, polymerizes to form a gelled propellant with desirable properties. In the other form of the invention, the nanogellant is polymerized in a solvent separate from the propellant, and is then recovered from the solvent and redispersed in the propellant.

**FIG. 2****EP 1 721 881 A1**

Description**BACKGROUND OF THE INVENTION**

[0001] This invention relates generally to rocket propellants and, more particularly, to gelled propellants. It is well known in the field of rocket propulsion that gelled propellants offer significant advantages over solid and liquid propellants. Solid propellants have inherently high energy but offer no mission flexibility because once ignited they must normally be burned to completion. Liquid propellants are less energetic than solids, as measured by specific impulse, but offer high mission flexibility because the flow of liquid fuels can be controlled as desired. Gels combine the advantages of solids and liquids and have additional advantages that are well known to designers of rocket engines for use both in space and within a planet's atmosphere.

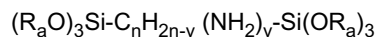
[0002] Although the advantages of gelled propellants are widely appreciated, gelled propellants available prior to this invention have been produced by mixing essentially inert solids with liquids. A commonly used gellant is silicon dioxide. US Patent No. 6,165,293 entitled "Thixotropic IRFNA Gel," discloses a gelled monomethyl hydrazine (MMH) fuel in which cellulose is the principal gellant and aluminum is added to increase energy density, and a gelled oxidizer in which the gellant is silicon dioxide and lithium niobate. US Patent No. 6,063,219 entitled "Higher Density Inhibited Red Fuming Nitric Acid (IRFNA) Oxidizer Gel," discloses an oxidizer gellant is either silicon dioxide, an unspecified metallic oxide, or an unspecified swellable polymer. Polymers that are typically considered as gellants for propellants are cellulose or cellulose derivatives.

[0003] Because the materials previously considered as gellants add little or nothing to the energy content of a gelled fuel, there is still a significant need for a gelled propellant that uses a gellant with a combustion enthalpy that adds energy content to the propellant, as well as serving to form a gel that supports the uniform suspension of other materials added to load the propellant with more dense particles. The present invention satisfies this need.

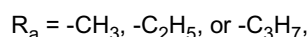
SUMMARY OF THE INVENTION

[0004] The present invention resides in the use of a polymeric gellant that satisfies the physical requirements for a gelled propellant, but also adds energy content to the propellant. Briefly, and in general terms, the invention may be defined as a gelled propellant, comprising a polymeric nanogellant formed from a monomer having molecular properties that promote three-dimensional polymerization; and a propellant to which the polymeric nanogellant is added. The resulting gelled propellant has desirable rheological properties and the polymeric nanogellant adds energy content to the propellant.

[0005] Monomers suitable for use in the invention may be generally characterized by the chemical formula:



where:



$$2 \leq n \leq 6, \text{ and}$$

$$y \leq 2n.$$

[0006] In one embodiment of the invention, the polymeric nanogellant is added directly to the propellant as a monomer and is polymerized *in situ* to form a gel. More specifically, in one disclosed example of the invention the propellant is monomethyl hydrazine (MMH) and the monomeric form of the nanogellant is bis-trimethoxysilylethane (BTMSE), which is mixed with the propellant and water. The propellant catalyzes polymerization of the nanogellant, resulting in the gelled form of the propellant. By way of example, the relative proportions of propellant, monomeric gellant and water are approximately 94%, 5% and 1% by weight, respectively.

[0007] In another embodiment of the invention, the polymeric nanogellant is polymerized before being added to the propellant. The polymeric nanogellant is first polymerized in a solvent different from the propellant, then recovered from the solvent and dried before being added to the propellant as a gellant. In this embodiment of the invention, the monomeric form of the nanogellant may also be bis-trimethoxysilylethane (BTMSE). The propellant may be monomethyl hydrazine (MMH), or some other liquid fuel, such as a cryogenic liquid fuel.

[0008] In terms of a novel method, the invention may be defined as a method for producing a gelled propellant, comprising the steps of placing a propellant in a reaction vessel; mixing a selected monomer with the propellant in the reaction vessel; and polymerizing the monomer in the reaction vessel, and thereby forming a gelled propellant containing

a nanogellant that provides the propellant with desired rheological properties and adds energy content to the propellant.

[0009] More specifically, the selected monomer is characterized by a molecular structure that promotes formation of a three-dimensional polymer. For this embodiment of the invention, the selected monomer is soluble in the propellant and the propellant catalyzes the polymerizing step. In a disclosed example of the method, the selected monomer is bis-trimethoxysilylethane (BTMSE) and the propellant is monomethyl hydrazine (MMH). More specifically, the mixing step mixes the monomer in the amount of approximately 5% by weight of the total mixture, and further adds water in the amount of approximately 1% by weight.

[0010] In accordance with a second embodiment of the method, the invention comprises the steps of placing a selected monomer in a reaction vessel with a selected solvent; polymerizing the selected monomer in the reaction vessel, to produce a nanogellant polymer in solution with the selected solvent; recovering the nanogellant polymer from the solvent by a process that utilizes solvent processing or drying methods that effectively reduce or eliminate liquid surface tension during solvent removal and recovery of dry nanogellant materials. These methods include: use of surfactants, freeze drying or solvent sublimation, and super-critical or near critical point fluid processing; and dispersing the recovered nanogellant polymer in a selected propellant to form a gelled propellant. In this embodiment of the method, the selected monomer may be bis-trimethoxysilylethane (BTMSE) and the propellant may be monomethyl hydrazine (MMH). However, the propellant may also be selected from other liquids, such as other forms of hydrazine and such as cryogenic liquid fuels, including liquid propane or liquid ethane.

[0011] It will be appreciated from this brief summary that the invention provides a significant advance in the field of propellants for rocket engines and the like. In particular, the invention provides a technique for gelling liquid propellant fuels and oxidizers using a gellant of nanometer proportions, which provides desirable rheological and other physical properties not obtainable using conventional gallants. Other aspects and advantages of the invention will become apparent from the following more detailed description, taken in conjunction with the drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

[0012] FIG. 1 is graph showing the rheological properties of monomethyl hydrazine (MMH) propellant that has been gelled in accordance with the invention, using bis-trimethoxysilylethane (BTMSE) as the gellant.

[0013] FIG. 2 is diagram showing the chemical structure of bis-trimethoxysilylethane (BTMSE) before and after polymerization.

[0014] FIG. 3 is a temperature-pressure phase diagram showing recovery of nanoparticulate gellant by solvent sublimation / freeze dry and critical fluid processing techniques.

[0015] FIG. 4 is a pair of graphs showing the rheological properties of cryogenic fuels, namely liquid propane and liquid ethane, which have been gelled in accordance with the invention using bis-trimethoxysilylethane (BTMSE) as a gellant.

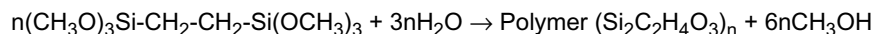
DETAILED DESCRIPTION OF THE INVENTION

[0016] As shown in the drawings by way of illustration, the present invention is concerned with gelled rocket fuels. In the past, gellants for rocket propellants have been formed by mixing practically inert solid particles in suspension with a liquid propellant. Although these mixtures or suspensions have provided the desired physical properties of a gelled propellant, they have not added energy content to the fuel, which therefore does not perform as efficiently as it might.

[0017] In accordance with the present invention, a gelled propellant is produced using a polymeric gellant that also adds energy content to the fuel. There are two basic embodiments of the invention. In one embodiment, the gellant is formed by a process of polymerization that takes place in the liquid fuel itself. This is referred as the *in-situ* method. In the other embodiment, the polymeric gellant is formed separately and later added to the fuel. This is referred to as the *ex-situ* method.

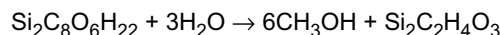
[0018] In the *in-situ* method, the polymer gellant material is produced directly in the liquid propellant by carrying out a polymerization reaction involving a selected monomer species dissolved in the liquid rocket propellant. The liquid propellant is thereby converted to a semi-solid or gel, which consists of a meso-porous nano-fibril structure with entrapped liquid. The gel exhibits a low yield stress compared with regular solids but it is sufficient for stably dispersing micrometer-scale and larger-scale metal and other energetic solids in the liquid propellant. The monomer is converted to the nanofibril structure during the course of the polymerization reaction and typically no further processing is required, except perhaps for the addition and mixing of other energetic materials. With the *in-situ* approach, the liquid rocket propellant may be a monopropellant such as hydrazine, either mono-, di-, tri-, or tetra-methyl hydrazine, or one of the fuel-oxidizer components for a bipropellant system, such as the fuels designated RJ-4, RJ-5, RJ-7, JP-4, JP-5, JP-9, JP-10. These are fuels specified by the US military for various ram-jet (RJ) and other jet engine powered missiles.

[0019] An efficacious gelling agent for mono-methyl hydrazine (MMH) is the *in-situ* polymer derived from the hydrolysis and condensation polymerization reaction of bis-trimethoxysilylethane (BTMSE) as shown in the following equation:



[0020] The *in-situ* grown polymer is able to produce a clear MMH gel at polymer concentrations as low as 5% by weight, and unlike silica gellants has a combustion enthalpy that adds energy content to the propellant. The polymerization reaction is carried out at ambient temperatures and requires a low moisture content for initiation and completion. Typical rheological properties for the MMH gel are presented in FIG. 1.

[0021] The preparation of gelled monomethyl hydrazine (MMH) using 1,2 Bis(trimethoxysilyl)ethane is based on the equation above, which has been rewritten in different form as follows:



The three-dimensional polymerization of this reaction is depicted in FIG. 2. It should be noted that the high effective pH of MMH catalyzes the reaction. In addition, the polymerization requires water and produces methanol (CH_3OH). It will be observed from the diagrammatic representation of the polymer structure that each of the silicon atoms in the structure provides tetrafunctional branch points from which four linear chains emanate. One of the four possible chains provides a link to a C_2H_4 group and the other three provide links to oxygen atoms. The tetrafunctional property of the structure allows it to grow efficiently in three dimensions and provide the desired mechanical gelling properties. Prior to gelling the MMH, the initial concentration of water in the MMH is determined, preferably using a gas chromatographic method. An amount of water to add to the MMH is then calculated to make the final mix 1.0% percent by weight water. The gelling of the MMH is then carried out in a manner to exclude exposure to atmospheric moisture, carbon dioxide and oxygen. These gases can be absorbed by the MMH and detract from its value as an eventual fuel.

[0022] Working in an inert atmosphere (void of moisture, carbon dioxide and oxygen) the weight percentages of the ingredients listed in Table 1 (below) are combined. The mixture is stirred and allowed to react for 24 hours at ambient temperature. The mixture must be stored in a container that is compatible with the ingredients and prevents exposure to atmospheric moisture, carbon dioxide and oxygen.

Table 1: Ingredients of Gelled MMW

Monomethyl Hydrazine	94% wt/wt
1,2 Bis(trimethoxysilyl)ethane	5.0% wt/wt
Water (total)	1.0% wt/wt

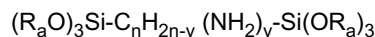
[0023] In the *ex-situ* method, the polymerization reaction is carried out in a different solvent from the liquid propellant itself and the nanometer particulate reaction product is subsequently recovered from this reaction medium or some exchange solvent in a manner that preserves its high specific surface area and morphological structure. The recovered dried nanoparticulate material may then be re-dispersed in the desired rocket propellant to produce a gelled propellant. Nanoparticulate recovery in the *ex-situ* method uses either a drying process or a solvent elimination process in which the liquid surface tension forces are minimized or near completely eliminated. This is accomplished by taking advantage of the solvent's phase diagram and operating in a cyclic manner around either the reaction medium's or exchange solvent's triple or critical points. In FIG. 3, the paths ABCD and AB'C' are possible temperature-pressure cycles around a triple point (TP) and a critical point (CP), respectively, in the solvent's phase diagram. These product recovery methods are commonly referred to as freeze drying and critical point drying. Alternatively, surfactants or solvents with inherently very low surface tensions under ordinary ambient conditions may be used, provided these materials are selected to be effective and compatible with the monomer and polymer products.

[0024] In the gellant synthesis procedure, a dilute solution of BTMSE in ethanol is prepared, a small quantity of water is added and the reaction mixture warmed to approximately 60° C and allowed to react at this temperature for approximately 12 hours. A soft alcohol gel is formed. To recover the nanogellant via freeze drying, the alcogel is exchanged with water and then frozen and sublimated at -10° C. Recovery of nanogellant via critical fluid processing requires exchanging alcohol with liquid carbon dioxide (critical temperature 33° C) or some other fluid with a conveniently low critical temperature in a pressure vessel. Upon exchange of alcohol, the temperature of the CO_2 -exchanged gel is raised to 40° C and the elevated pressure allowed to vent slowly. Other exchange fluids with conveniently low critical temperatures may also be used in place of CO_2 .

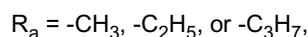
[0025] FIG. 4 shows the rheological properties of ethane and propane fuels after gelling with BTMSE gellant in accordance with the *ex-situ* method described above.

[0026] It will be understood that the foregoing examples of the invention have focused for purposes of illustration on the use of BTMSE as a suitable monomer. Many other monomers also fall within the scope of the invention, including,

for example, bistrimethoxysilylmethane, bis-trimethoxysilylpropane, and so forth, and also including various amine compounds (derivatives of ammonia in which one or more hydrogen atoms are replaced by alkyl groups). Monomers suitable for use in the invention may be generally characterized by the chemical formula:



where:



$$2 \leq n \leq 6,$$

and

$$y \leq 2n.$$

Similarly, although the invention is described by way of example as gelling monomethyl hydrazine (MMH) propellant, it will be understood that other propellants, such as hydrazine, di-methyl hydrazine, tri-methyl hydrazine and tetra-methyl hydrazine, are also candidates for gelling in accordance with the invention. As also mentioned above, cryogenic propellants such as liquid methane, liquid ethane, liquid butane and liquid hydrogen may also be used.

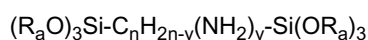
[0027] It will be appreciated from the foregoing that the present invention represents a significant advance in the field of gelled rocket propellants. In particular, the invention provides a gellant that can be produced either *in situ* to form a gel in certain categories of fuels, such as monomethyl hydrazine, or the gellant can be produced *ex situ* and added to various fuels. Regardless of which technique is used to produce the gelled fuel, it has desirable rheological properties that render it more useful than liquid fuels. It will also be appreciated that, although specific embodiments of the invention have been described in detail for purposes of illustration, various modifications may be made without departing from the spirit and scope of the invention. Accordingly, the invention should not be limited except as by the appended claims.

Claims

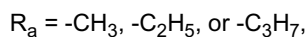
1. A gelled propellant, comprising:

a polymeric nanogellant formed from a monomer having molecular properties that promote three-dimensional polymerization; and
a propellant to which the polymeric nanogellant is added;
wherein the gelled propellant has desirable rheological properties and the polymeric nanogellant adds energy content to the propellant.

2. A gelled propellant as defined in claim 1, wherein the monomer is **characterized by** the chemical formula



where:



$$2 \leq n \leq 6,$$

and

$$y \leq 2n.$$

3. A gelled propellant as defined in claim 2, wherein the polymeric nanogellant is added directly to the propellant as a monomer and is polymerized *in situ* to form a gel.

4. A gelled propellant as defined in claim 3, wherein:

the propellant is monomethyl hydrazine (MMH);
 the monomeric form of the nanogellant is bis-trimethoxysilylethane (BTMSE), which is mixed with the propellant and water; and
 the propellant catalyzes polymerization of the nanogellant, resulting in the gelled form of the propellant.

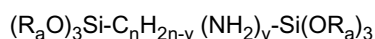
- 5 5. A gelled propellant as defined in claim 4, wherein the proportions of propellant, monomeric gellant and water are approximately 94:5:1 by weight, respectively.
- 10 6. A gelled propellant as defined in claim 2, wherein the polymeric nanogellant is polymerized before being added to the propellant.
7. A gelled propellant as defined in claim 6, wherein the polymenc nanogellant is polymerized in a solvent different from the propellant, then recovered from the solvent and dried before being added to the propellant as a gellant.
- 15 8. A gelled propellant as defined in claim 7, wherein the monomeric form of the nanogellant is bis-trimethoxysilylethane (BTMSE).
9. A gelled propellant as defined in claim 8, wherein the propellant is form of hydrazine.
- 20 10. A gelled propellant as defined in claim 8, wherein the propellant is a cryogenic liquid fuel.
11. A method for producing a gelled propellant, comprising:

placing a propellant in a reaction vessel;
 25 mixing a selected monomer with the propellant in the reaction vessel; and
 polymerizing the monomer in the reaction vessel, and thereby forming a gelled propellant containing a nanogellant that provides the propellant with desired rheological properties and adds energy content to the propellant.

- 30 12. A method as defined in claim 11, wherein:

the selected monomer is **characterized by** a molecular structure that promotes formation of a three-dimensional polymer;
 the selected monomer is soluble in the propellant; and
 the propellant catalyzes the polymerizing step.

- 35 13. A method as defined in claim 12, wherein the monomer is **characterized by** the chemical formula



40 where:

$R_a = -CH_3, -C_2H_5, \text{ or } -C_3H_7,$

$2 \leq n \leq 6, \text{ and}$

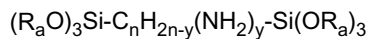
45 $y \leq 2n.$

14. A method as defined in claim 13, wherein the selected monomer is bis-trimethoxysilylethane (BTMSE).
- 50 15. A method as defined in claim 13, wherein the propellant is monomethyl hydrazine (MMH).
16. A method as defined in claim 13, wherein the mixing step mixes the monomer in the amount of approximately 5% by weight of the total mixture, and further adds water in the amount of approximately 1% by weight.
- 55 17. A method for producing a gelled propellant, comprising:

placing a selected monomer in a reaction vessel with a selected solvent;
 polymerizing the selected monomer in the reaction vessel, to produce a nanogellant polymer in solution with

the selected solvent;
 recovering the nanogellant polymer from the solvent by a process selected from freeze drying and critical point drying; and
 dispersing the recovered nanogellant polymer in a selected propellant to form a gelled propellant.

18. A method as defined in claim 17, wherein the monomer is **characterized by** the chemical formula



where:

$R_a = -CH_3, -C_2H_5, \text{ or } -C_3H_7,$

$2 \leq n \leq 6,$ and

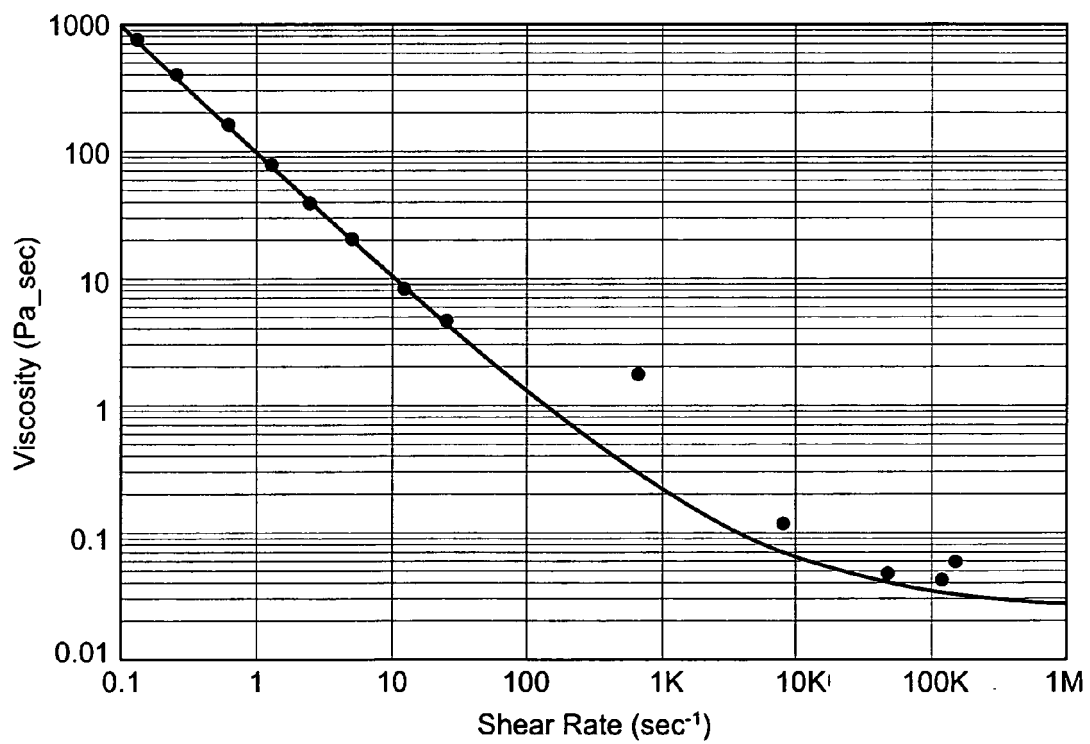
$y \leq 2n.$

19. A method as defined in claim 18, wherein the selected monomer is bis-trimethoxysilylethane (BTMSE).

20. A method as defined in claim 18, wherein the propellant is a form of hydrazine.

21. A method as defined in claim 18, wherein the propellant is a cryogenic liquid fuel.

22. A method as defined in claim 21, wherein the propellant is selected from the group consisting of liquid propane, liquid ethane and liquid methane.

**FIG. 1**

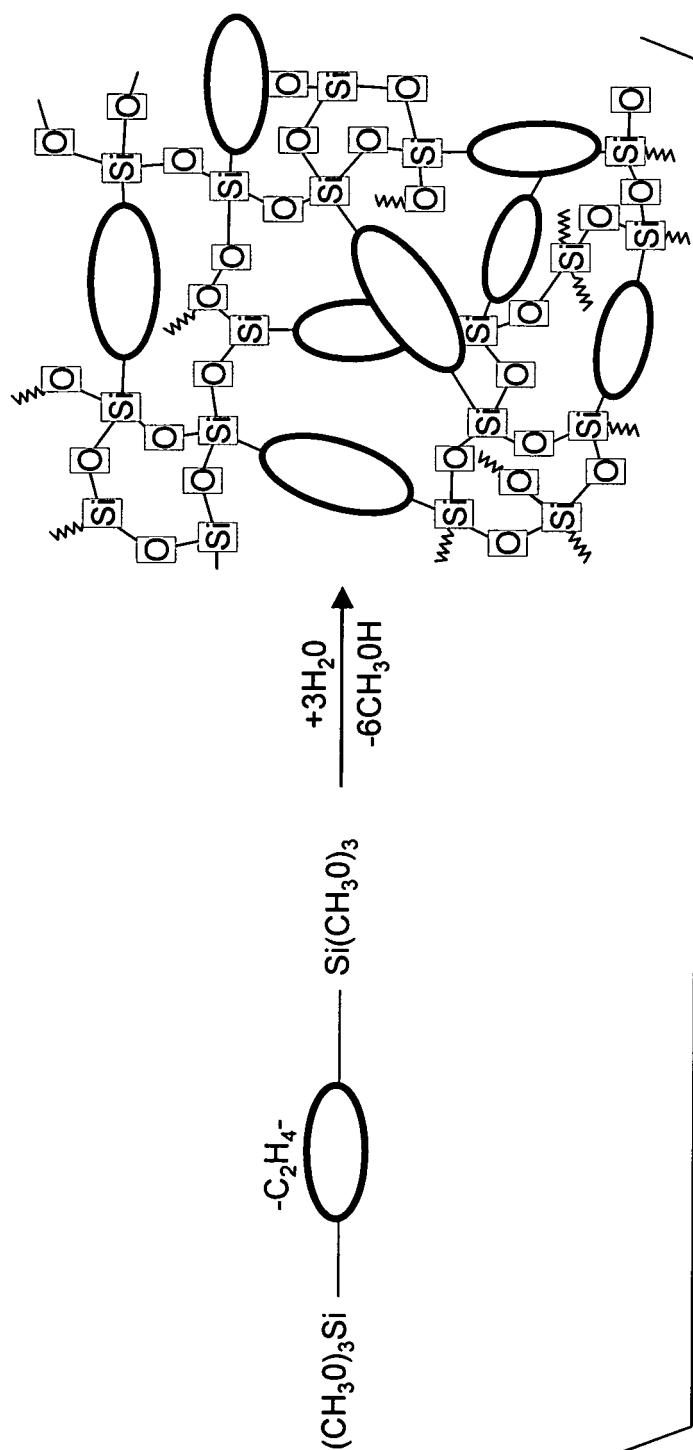
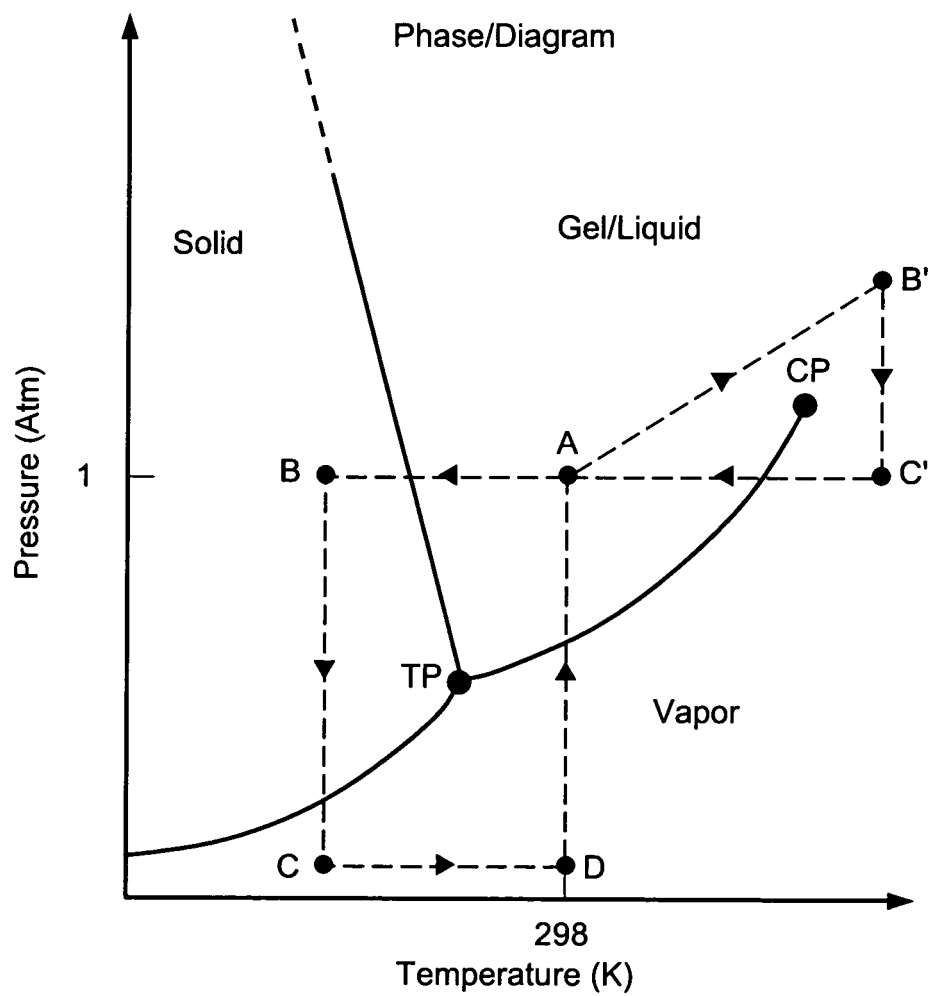


FIG. 2

**FIG. 3**

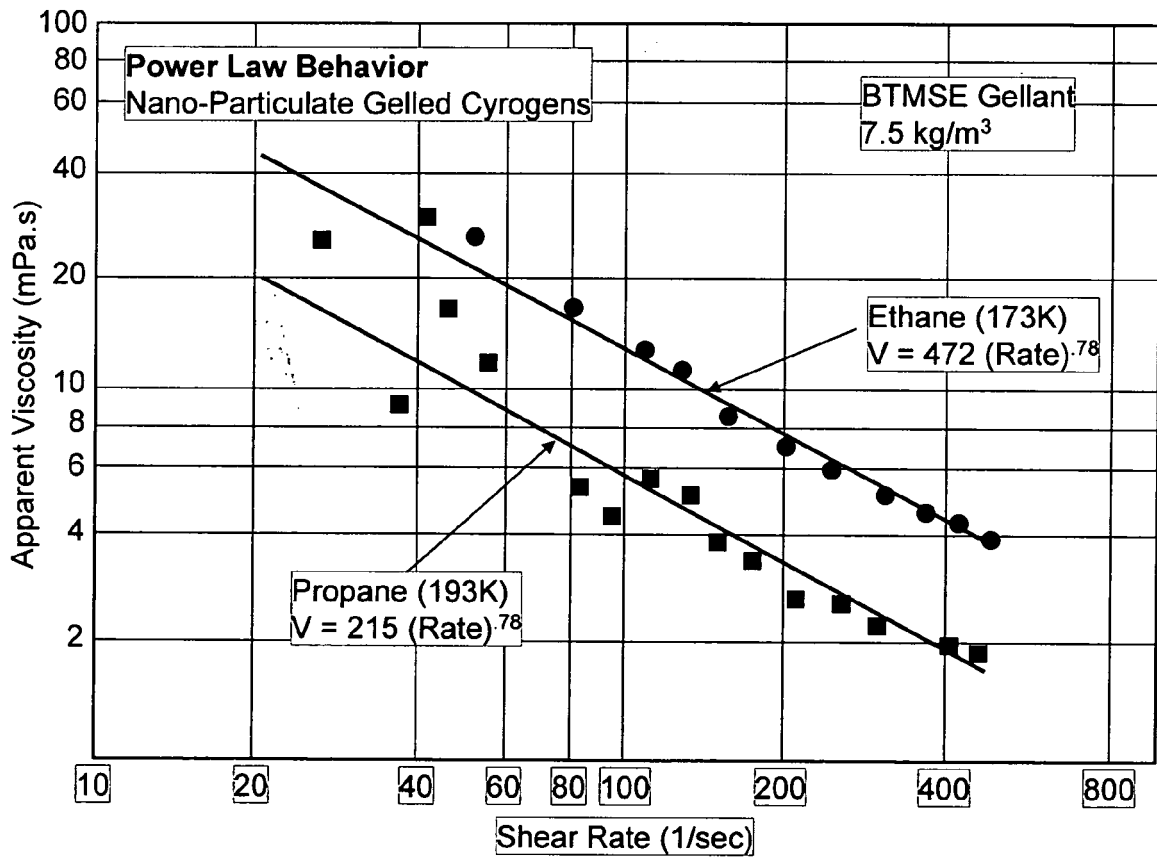


FIG. 4



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EUROPEAN SEARCH REPORT

Application Number
EP 06 25 2111

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Place of search The Hague		Date of completion of the search 1 September 2006	Examiner Schut, Robert
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document	

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EUROPEAN SEARCH REPORT

Application Number
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CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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

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This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
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01-09-2006

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