THIXOTROPIC GAS PRODUCING GEL

Assignee: The Susquehanna Corporation, Fairfax County, Va.
Filed: Aug. 25, 1969
Appl. No.: 852,904

U.S. Cl. 149/42, 60/217, 149/18, 149/21, 149/22, 149/36, 149/44, 149/75, 149/76, 149/87, 149/89, 149/113, 149/114
Int. Cl. C06b 11/00, C06b 19/04
Field of Search 149/18, 19, 21, 22, 42, 44, 149/76, 112, 113, 114, 115, 75, 87, 89, 60/217

References Cited

UNITED STATES PATENTS
3,023,094 2/1962 Morton et al. 149/18
3,388,554 6/1968 Hodgson 149/18 X
3,396,537 8/1968 Lissant et al. 149/18 X


Primary Examiner—Leland A. Sebastian
Attorney—Martha Ross

ABSTRACT

A combustible gas producing gel having a viscosity up to about 200 poise at a 100 reciprocal second rate of shear and a temperature of minus 65° F. and being thermally stable at temperatures up to about 165° F. comprising the combination of solid consumable particles suspended in a hydrocarbon carrier having eight to 10 carbon atoms and containing an argonoluminum phosphonate gelling agent. The solid consumable particles may be present in a concentration of from about 77 percent to about 95 percent by weight based upon the total weight of gel. the hydrocarbon carrier may be present in a concentration of from about 5 percent to about 23 percent by weight based upon the total weight of the gel; and the weight ratio of the hydrocarbon carrier to the gelling agent is less than about 100. The solid consumable particles may be all oxidizer particles or a combination of oxidizer and fuel particles.

7 Claims, No Drawings
THIXOTROPIC GAS PRODUCING GEL

BACKGROUND OF THE INVENTION

Compositions capable of generating gases containing large amounts of available energy for such purposes as producing thrust, heat or gas pressure may be divided generally into monopropellants which are compositions that are substantially self-sufficient with regard to oxidant requirements and bipropellants wherein a fuel is maintained separately from an oxidizer source until admixture at point of combustion.

In oxygen deficient atmospheres, monopropellants possess considerable advantage over bipropellants and both liquid and solid monopropellants are used extensively. For use, liquid monopropellants require only one set of equipment such as a storage tank, propellant pump, feed lines and valves thereby eliminating elaborate systems which are necessary to ensure proportioned flows of the separate components of fuel and oxidizer in bipropellant systems and their adequate mixing in combustion chambers. Liquid monopropellants may be injected into a combustion chamber in the form of finely divided droplets or sprays to give mass burning rates which may be controlled by varying the rate of injection. Combustion can be stopped by shutting off the flow and resumed at will, and performance is not dependent generally upon the temperature environment of the system. Further, operation is limited only by the capacity of the storage tanks or reservoirs, and combustion chambers need to be large enough only to provide sufficient space for completion of the combustion reaction.

The known liquid monopropellants are characterized by certain disadvantages such as low density, low specific impulse, high toxicity, and excessive sensitivity to heat and shock, all which may cause low performance, detonation and corrosion of various parts of the propellant system such as valves and lines. When liquid monopropellants are used as fuels for rocket motors, unburned droplets of the liquid propellant may leave the combustion chamber and be cooled during expansion in the nozzle before combustion occurs lowering performance of the rocket motor system. Also, the attitude of the system may affect the performance of the system. In certain liquid monopropellant systems, catalyst beds are required for combustion, and vibration of the rocket motor often makes retention and fixing of the catalyst bed in the combustion chamber difficult. Storage and transportation of liquid monopropellants also are difficult because of ever present leak hazards of both fire and toxicity.

Solid monopropellants possess the advantages of high density, low heat and shock sensitivity, good stability, long storage ability, absence of leakage problems, low corrosiveness and toxicity, and propellant filling and injection equipment is not needed since all of the solid propellant generally is contained directly in the combustion chamber. Solid monopropellants do not require purgings of systems after firings; do not need any external combustion catalyst; and are not affected by the attitude of the system. Solid monopropellants, however, do possess a number of their own disadvantages.

The solid grain must be sufficiently strong and free from mechanical flaws so that cracking or shattering does not take place under pressure or vibrational stresses; and many solid monopropellants tend to be excessively brittle at low ambient temperatures which reduces fracture resistance. If solid propellants are fractured, burning surfaces may be increased causing uncontrolled burning in the combustion chamber resulting in pressures exceeding the design pressures of the combustion chamber walls and complete failure of the propellant system.

Although burning solid monopropellants may be quenched, if necessary, reignition generally is not feasible and unburned portions may be a total loss. Intermittent operation of a motor system containing solid monopropellants, therefore, is generally impractical, and the ambient temperature of a solid propellant is an important parameter in determining burning rate which cannot be compensated for during use by variation of the area of the burning surface in that solid monopropellant must be predesigned with respect to burning surface area for each particular application.

Further, when using solid monopropellants, a combustion chamber must be of sufficient size to accommodate all of the propellant and is generally larger than that required for combustion of a liquid propellant. This requires the walls of the entire combustion chamber to be sufficiently strong to withstand high combustion gas pressures and to be completely insulated, secondly, to withstand the high combustion gas temperatures, both of which may cause a serious weight problem in non-stationary applications.

It is obvious, therefore, that a monopropellant which has the advantages of both a liquid monopropellant and a solid monopropellant, while having substantially none of the disadvantages of either, is a worthwhile advance in the art. Motor systems could be started and stopped as desired, and the attitude of the system would not affect its operation. Catalyst beds could be eliminated. Leakage problems would be nonexistent. Temperature sensitivity could be eliminated, and small combustion chambers could be used. Further, low heat and shock sensitivity with attending good stability for long periods would permit ease in handling and storage. Therefore, a thixotropic monopropellant gas producing gel having a low viscosity at low temperatures and being thermally stable at high temperatures is a worthwhile advance in the art.

SUMMARY OF THE INVENTION

In accordance with this invention, there is provided a thixotropic combustible gas producing monopropellant gel having a low viscosity up to about 200 poise at a 100 reciprocal second rate of shear and a temperature of minus 65° F. and which is thermally stable at temperatures up to about 165° F. The monopropellant gel comprises solid consumable particles suspended in a hydrocarbon carrier having eight to 10 carbon atoms and containing gelling agent. The solid consumable particles are present in an organoauminum phosphonate a concentration of from about 77 percent to about 95 percent by weight based upon the total weight of the hydrocarbon carrier is present in a concentration of from about 5% to about 23% by weight based upon the total weight of the gel; and the weight ratio of the hydrocarbon carrier to the gelling agent is less than about 100. The solid consumable particles may be oxidizer particles or a mixture of oxidizer and fuel particles and may be present in a particle size range of from about 5 microns to about 300 microns in one or more modal distributions.

The advantages of the thixotropic combustible gas producing monopropellant gel of this invention are myriad. The monopropellant gel may be injected or sprayed into small combustion chambers in the manner of liquid monopropellants and large high-strength combustion chambers and elaborate systems of duplicate pumps and lines are not necessary. Also, storage, handling, thermal stability and shock resistance problems common to usual liquid monopropellants are not present in the monopropellant gel of this invention. Moreover, these advantages are all present in the monopropellant gel of this invention over a wide temperature range of from about minus 65° F. to about 165° F. Other advantages will be readily apparent to those skilled in the art from the more detailed description of the invention.

DESCRIPTION OF PREFERRED EMBODIMENTS

The monopropellant gel of this invention comprises solid consumable particles suspended in a hydrocarbon carrier having eight to 10 carbon atoms and containing an organoauminum phosphonate gelling agent. Solid consumable particles may be present in a concentration of from about 77% to about 95% by weight based upon the total weight of the gel and may comprise oxidizer particles or a mixture of oxidizer and fuel particles. The oxidizer particles may be any of well-known oxidizers such as ammonium perchlorate, hydrazyl ammonium perchlorate, hexanitromethane, hydrazine perchlorate,
hydrazine diperchlorate, hydrazine nitroform and mixtures thereof. When only oxidizer particles are present in the gel, it is preferred that ammonium perchlorate particles be used.

When fuel particles are used in combination with oxidizer particles in accordance with this invention, any of the well-known particulate fuels may be used such as beryllium, beryllium hydride, aluminum, aluminum hydride, boron, boron hydride, zirconium and mixtures thereof. When fuel particles are used in combination with oxidizer particles in accordance with this invention, it is preferred that aluminum or boron particles, or a mixture thereof, be used in the gel.

The solid consumable particles used in accordance with this invention may be of substantially any shape; however, it is preferred that the solid consumable particles have an average particle size of from about 5 microns to about 300 microns. It is preferred also that the particles be spherical or substantially spherical. The solid particles may be present in the gel in one or more modal distributions and when the solid particles are present in a bimodal distribution, it is preferred that the larger particles comprise from about 60% to about 80% of the total weight of particles.

The hydrocarbon carrier of this invention is present in the gel in a concentration of from about 5% to about 23% by weight based upon the total weight of the gel. The hydrocarbon liquid must be a saturated hydrocarbon to prevent attack by the oxidizer component. A preferred saturated hydrocarbon liquid is one containing eight to 10 carbon atoms such as trimethylhexane and neocene. Of these 2,2,5-trimethylhexane is preferred.

The organoaluminum phosphonate gelling agent used in accordance with this invention is compatible with the hydrocarbon carrier and not susceptible to degradation or attack by the oxidizer component. The gelling agent should be present in the gel in a concentration sufficient to provide a weight ratio of hydrocarbon carrier to gelling agent of less than about 100. When the hydrocarbon carrier used in accordance with this invention is trimethylhexane, it is preferred that the gelling agent be aluminum tri(monobutyl-2-thiododecyl) phosphonate. In certain gel formulations, the addition of a wetting agent to the hydrocarbon carrier may be necessary or desired for good gel physical properties to permit better wetting of the solid particles with the hydrocarbon carrier. When a wetting agent is used, it is preferred that sufficient wetting agent is used to provide a substantially monomolecular layer of wetting agent to be formed on the surface of the solid combustible particles. Also, it is necessary that the wetting agent not be extremely resistant to attack or degradation by the oxidizer component and compatible with other gel components. Wetting agents which are suitable for use in accordance with this invention are materials such as sorbitan sesquioleate, hydrogenated coconut oils, synthetic coconut oils and like materials. When ammonium perchlorate is used as oxidizer, and trimethylhexane is used as hydrocarbon carrier, it is preferred that sorbitan sesquioleate be used as the wetting agent.

### EXAMPLE I

Performance values, specific impulse (vacuum), were obtained at various expansion ratios for a range of concentrations of solid consumable particles and hydrocarbon carrier. To obtain these values, specific impulse (vacuum) was obtained for expansion ratios of from 10 to 80 at a combustion chamber pressure of 100 p.s.i. and external pressures of from 0.1-5.0 p.s.i. Ammonium perchlorate (AP) was used as the solid consumable particles, trimethylhexane (TMH) was used as the hydrocarbon carrier and the weight ratio of ammonium perchlorate to trimethylhexane was varied from 75:25 to 95:5.

The results of this determination are shown in Table I.

<table>
<thead>
<tr>
<th>Expansion Ratio</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>40</th>
<th>50</th>
<th>60</th>
<th>80</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight Ratio, AP/TMH</td>
<td>229</td>
<td>249</td>
<td>269</td>
<td>289</td>
<td>309</td>
<td>329</td>
<td>349</td>
</tr>
</tbody>
</table>

As can be seen from the above Table I, maximum performance values were obtained at weight ratios of AP/TMH in excess of 75:25 and less than 95:5 at all expansion ratios.

### EXAMPLE II

Performance values were obtained in the manner of Example I with all variables being the same except that a combustion chamber pressure of 200 p.s.i. and an external pressure of 0.1-10 p.s.i. were used. Results of this determination are shown in Table II below.

<table>
<thead>
<tr>
<th>Expansion Ratio</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>40</th>
<th>50</th>
<th>60</th>
<th>80</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight Ratio, AP/TMH</td>
<td>229</td>
<td>249</td>
<td>269</td>
<td>289</td>
<td>309</td>
<td>329</td>
<td>349</td>
</tr>
</tbody>
</table>

As can be seen readily from Table II, maximum performance values were obtained at weight ratios in excess of 75:25 and less than 95:5 for all expansion ratios.

### EXAMPLE III

Performance determinations in the manner of Examples I and II were made at weight ratios of solid consumable particles to hydrocarbon carrier of 85:15 and 88:12 wherein a portion of the solid consumable particles were replaced with fuel particles. The combustion pressure was 100 p.s.i., the external pressure was 0.1-5.0 p.s.i. and specific impulse (vacuum) was determined for expansion ratios of ten to 80 for weight ratios of 75 AP, 10 aluminum (AL), 15 trimethylhexane (55% solid consumable particles to 15% hydrocarbon carrier) and 70 AP, 15 AI and 15 TMH (85% solid consumable particles to 15% hydrocarbon carrier) and 66 AP, 22 AI, 12 TMH (88% solid consumable particles to 12% hydrocarbon carrier). The results of these determinations are shown in Table III below.

<table>
<thead>
<tr>
<th>Expansion Ratio</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>40</th>
<th>50</th>
<th>60</th>
<th>80</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight Ratio, AP/TMH</td>
<td>229</td>
<td>249</td>
<td>269</td>
<td>289</td>
<td>309</td>
<td>329</td>
<td>349</td>
</tr>
</tbody>
</table>

As can be seen from the above Table III, good performance values were obtained at all expansion ratios for both the 85% and 88% solid consumable particle ratios.

### EXAMPLE IV

Two thixotropic gas producing gel compositions were prepared each having a total consumable particle content of 85% by weight. In each composition the consumable solid particles were substantially spherical and were 52.5% ammonium perchlorate having an average particle size of 200 microns, 17.5% ammonium perchlorate having an average particle size
of 20 microns, 11.25% aluminum having an average particle size of 30 microns, and 3.75% aluminum having an average particle size of 6 microns. These consumable particles were mixed with a hydrocarbon carrier, 2,2,5-trimethylhexane (TMH) at a concentration of 14.8% by weight for Composition A and 14.61% by weight for Composition B. A wetting agent, sorbitan sesquioleate, was added in the same concentration to both Composition A and Composition B. A gelling agent, aluminum tri(monomethyl-2-thiadecyl) phosphonate, was added to both Composition A and Composition B in a concentration sufficient to provide a weight ratio of hydrocarbon carrier to gelling agent of 99 in Composition A and 43 in Composition B. Table IV below shows the component concentration for Compositions A and B.

### Table IV

<table>
<thead>
<tr>
<th>Thixotropic Gas Producing Gels</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Gel Composition</strong></td>
<td><strong>Wt. %</strong></td>
</tr>
<tr>
<td>A</td>
<td>70.00</td>
</tr>
<tr>
<td>B</td>
<td>70.00</td>
</tr>
<tr>
<td>Oxidizer (AP)</td>
<td>15.00</td>
</tr>
<tr>
<td>Fuel (AD)</td>
<td>15.00</td>
</tr>
<tr>
<td>Hydrocarbon Carrier (TMH)</td>
<td>14.00</td>
</tr>
<tr>
<td>Wetting Agent</td>
<td>0.05</td>
</tr>
<tr>
<td>H/C Gelling agent wt. ratio</td>
<td>99</td>
</tr>
</tbody>
</table>

Both Composition A and Composition B were thermally soaked in an identical manner at 165°F for 10 days to determine their high temperature stability. Results of this testing showed that Composition A had separated over 2.1% of the total weight whereas Composition B had a total separation of 0.1% of its total weight demonstrating the unacceptable thermal stability of Composition A and the good thermal stability of Composition B.

**Example V**

A thixotropic gas producing gel identical with Composition B above was prepared having the formulation shown in Table V below.

### Table V

<table>
<thead>
<tr>
<th>Thixotropic Gas Producing Gel</th>
<th>Wt. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>AP (200 microns)</td>
<td>52.50</td>
</tr>
<tr>
<td>AP (20 microns)</td>
<td>17.50</td>
</tr>
<tr>
<td>(AD) 30 microns</td>
<td>11.25</td>
</tr>
<tr>
<td>(AD) 15 microns</td>
<td>3.75</td>
</tr>
<tr>
<td>TMH</td>
<td>14.61</td>
</tr>
<tr>
<td>Wetting Agent</td>
<td>0.65</td>
</tr>
<tr>
<td>Gelling Agent</td>
<td>0.34</td>
</tr>
<tr>
<td></td>
<td>100.00</td>
</tr>
</tbody>
</table>

The viscosity of the material was evaluated by means of an extrusion rheometer using only one tube which had a length of 12.752 inches and a diameter of 0.0605 inch giving a length/diameter ratio of 211. A plot of shear rate v. apparent viscosity was prepared and the viscosity of the material at -65°F was found to be less than 100 poise at a 100 reciprocal rate of shear. The slope of the curve obtained in the plot was 0.74 indicating that the material was pseudo-plastic in character and almost Newtonian.

**Example VI**

A portion of the gas producing gel of Example V above was thermally soaked for 10 days at 165°F and compared with a sample of the same material stored at room temperature for 10 days. The results of the comparison showed that there was a 17% decrease in viscosity at high shear rates and no significant change at lower shear rates due to thermal soaking for 10 days at 165°F.

**Example VII**

The gas producing gel of Example V above was subjected to a sea level motor test in a laboratory test engine and it was found that high combustion efficiencies were obtained with smooth ignition when the gel was sprayed into the combustion chambers. A thrust value of 472 pounds/second at sea level, a gel flow rate of 0.86 pounds/second, a combustion chamber pressure of 653 p.s.i. absolute were measured during the motor test.

**Example VIII**

A sample of the gel of Example V above was subjected to impact testing under a liquid test method conforming to ICIRP Liquid Propellant Test Methods Test No. 4. Results of this test showed that the gel had an impact (liquid test) — E₀ equal to 21 kg. cm. which demonstrated the gel was relatively insensitive to this type of impact initiation even in the heavy confinement of a liquid tester when compared to impact sensitivity of n-propanil nitrate of 8.4 kg.cm. when performed by the same test.

**Example IX**

A sample of the gel of Example V was subjected to friction testing to determine the sensitivity to initiation by friction on a sliding friction machine. The machine contained a pneumatically pressurized arm which applied a set force to a sliding plate containing a sample of the gel. A pendulum dropped from various angles impacted the plate containing the sample causing it to slide horizontally beneath an application arm for a distance of one inch. The comparative friction sensitivity is determined by the zero initiation level or the lowest arm pressure which will result in initiation of the sample. The initiation can be an ignition, spark, explosion or decomposition. In testing, the pendulum is swung from 45° to impact the plate to reduce the arm pressure from 2,000 p.s.i. down to the highest value to which ten consecutive tests fail to ignite the sample. The results of this test showed that the gel of Example V above had a friction test pressure of 600 lb. ft. which is relatively insensitive to initiation by friction when compared to safety match compositions which have a test pressure of 20 lb. ft.

**Example X**

Shock testing, in accordance with Specification TO11A-1-47A dated Jan. 22, 1968, was used to determine the shock sensitivity of a sample of the thixotropic gel of Example V above in accordance with the standard card gap test for solids. Under these rigorous test conditions, negative tests were obtained at zero gap indicating the gel of Example V was insensitive to shock.

**Example XI**

A standard autoignition test was performed on a sample of the thixotropic gel of Example V and the result showed that a temperature greater than 315°C was needed to autoignite the gel. I claim:

1. In a combustible gas-producing, monopropellant gel comprising liquid hydrocarbon, solid oxidizer or mixture of solid oxidizer and solid fuel, and gelling agent, the improvement wherein:
   a. the monopropellant gel has a viscosity up to about 200 poise at a 100 reciprocal rate of shear and a temperature of minus 65°F and is thermally stable at a temperature up to about 165°F,
   b. the liquid hydrocarbon is a saturated hydrocarbon containing from eight to 10 carbon atoms; and
   c. the gelling agent is an organoaluminum phosphonate.
2. The monopropellant gel of claim 1 wherein the gelling agent is aluminum tri(monobutyl-2-thiododecytl) phosphonate.
3. The monopropellant gel of claim 1 which contains in addition sorbitan sesquioleate wetting agent.
4. The monopropellant gel of claim 1 wherein the liquid hydrocarbon is trimethyl hexane.

5. The monopropellant gel of claim 2 wherein the liquid hydrocarbon is trimethyl hexane.
6. The monopropellant gel of claim 3 wherein the liquid hydrocarbon is trimethyl hexane.
7. The monopropellant gel of claim 3 wherein the oxidizer is ammonium perchlorate and the solid fuel is aluminum.