

1

3,395,055

METHOD OF MAKING A HYBRID LIQUID-SOLID PROPELLANT SYSTEM WITH ENCAPSULATED OXIDIZING AGENT AND METALLIC FUEL

William J. Sparks, Westfield, and Lawrence Spenadel, Elizabeth, N.J., assignors to Esso Research and Engineering Company, a corporation of Delaware
No Drawing. Filed Mar. 26, 1959, Ser. No. 802,257
5 Claims. (Cl. 149-21)

The present invention relates to encapsulating liquids and propellant systems wherein the liquid portion is encapsulated in a polymeric substance. The invention is concerned not only with the method for encapsulating the liquid, which is thereafter compounded with solid materials, but also the novel propellant system obtained.

There is considerable interest in the use of solid propellant systems in rockets because they are less difficult to handle and the rocket itself is simpler to design and construct. The type of rocket to which the present invention has particular application is the type of rocket propulsion device commonly designated as a "pure" rocket, that is to say, a thrust producer which does not make use of the surrounding atmosphere. The propellant system in these rockets comprise fuel and oxidizing material which react either spontaneously or upon ignition to produce gases which escape from the combustion chamber through a thrust nozzle to impart thrust to the rocket. Liquid oxidizing agents are generally more effective than their solid counterparts because of their high reactivity. However, considerable difficulty has been encountered in attempting to combine liquid oxidizing agents with solid fuels because of the tendency of the two materials to prematurely react.

An object of the invention is to provide a new rocket propellant system which utilizes a liquid oxidizing agent and a solid fuel. Another object of the invention is to provide a method for encapsulating liquid oxidizers so as to render them stable in the presence of fuel until ignited.

In accordance with the present invention a liquid oxidizing agent is encapsulated with a polymeric substance and the capsule is combined with fuel to produce a hybrid propellant system having good stability and high thrust. In carrying out the invention, drops of oxidizing agent pass through a zone containing polymer in a liquid form and the drops coated with a thin film of said polymer are recovered from the encapsulating zone. The encapsulated drops of oxidizing agent may be washed with a liquid which is either a solvent or nonsolvent for the polymeric substance surrounding the drop. The washing removes any excess polymer and reduces its tackiness. While tackiness is not an undesirable property because it assists in bringing the oxidizing agent into closer contact with the fuel, which sticks to the surface of the polymer, it may be desirable in some instances to have a tack-free capsule. The capsule of oxidizing agent, which may vary in diameter from $\frac{3}{64}$ " to $\frac{1}{4}$ ", is admixed with a solid fuel, preferably a metal selected from Groups II-A, III-A, IV-A and IV-B of the Periodic Chart of Elements, Lange's Handbook of Chemistry, 8th Edition, pages 56-57, or metal hydride in a weight ratio of 1 to 2:1. Suitable fuels include aluminum powder, magnesium powder, boron powder, aluminum hydride, magnesium hydride, titanium hydride and boron hydrides. The two components may be contacted with each other in any suitable manner which may be either batchwise or continuous. It is often advantageous to have between about 0.5 and 50 wt. percent, including the weight of the encapsulating polymer, of a binder present which will maintain the oxidizing agent and fuel in a semi-rigid form which is somewhat flexible and has a tensile strength of at least 50 lbs. p.s.i. The binder, which may be a low molecular weight resin, rubber or

2

asphalt, can be blended with the fuel prior to mixing the fuel with the oxidizing agent. Some examples of suitable binders are isoprene-isobutylene butyl rubber, polyisobutylene, polyethylene and polypropylene. In order to obtain very high specific impulses, it is best to use less than about 10 wt. percent of both binder and polymer. The compounded propellant may be molded into any desired shape prior to placing it in the combustion chamber of the rocket.

The oxidizing agent which is a liquid, such as red fuming nitric acid (RFNA), white fuming nitric acid (WFNA) or concentrated nitric acid, may be sprayed in the form of discrete drops onto the surface of a solution containing from about 10 to 75 wt. percent polymer dissolved therein. If the oxidizing agent does not react with the polymer to form a film around it, it is necessary to add reactive substances to the agent to promote encapsulation. In the case of RFNA this may be a catalyst or promoter for nitration reactions such as HF, BF₃, acetic anhydride, acetone, sulfur and inorganic salts. It has been noted that the drops are most advantageously encapsulated with a film of polymer when the solution contains about 20 to 30 wt. percent of polymer. Since the thickness of the encapsulating substance will vary according to the contact time and the viscosity of the polymer solution, the encapsulating solution should be adjusted accordingly. In order to obtain capsules having walls of 0.5 to 40 mils thick, the drop should be in contact with the encapsulating solution for 10 seconds to 30 minutes. In order to avoid the presence of an excess amount of polymer in the propellant system, it is advantageous to control the encapsulating reaction to produce capsules which are about $\frac{1}{16}$ of an inch in diameter having wall that are 1 to 5 mils thick.

The oxidizing agent is preferably one which reacts with the polymer to form an insoluble film which surrounds the oxidizing agent. However, any oxidizing agent which is compatible with a nitrating substance, e.g. concentrated nitric acid, may be used in admixture with said nitrating substance. In one embodiment, relatively small drops of an oxidizing agent containing a minor amount of nitrating agent, i.e. about 1 to 20 wt. percent, are contacted with a polymer solution at about 80° F. which is not too viscous to permit the drops of oxidizing agent to pass through it. In many instances the nitrating agent is also an excellent oxidizer, e.g. RFNA. Among the oxidizing agents which may be combined with say an inorganic nitrating agent are the nitroparaffins, especially the methane, ethane and propane derivatives, e.g. tetranitromethane, nitromethane, nitroethane and nitropropane. Substituted C₁ to C₃ nitroparaffins, such as bromotrinitromethane, may also be employed. The polymer should contain reactive sites which permit it to combine with the oxidizing agent-nitrating agent mixture and thus form a semi-rigid film around the drop. Suitable polymers include such substances as polybutadiene, styrene-butadiene rubber, polyisobutylene, isobutylene-isoprene rubber (butyl rubber), polyethylene, polypropylene, styrene-isobutylene polymer and fluorohydrocarbon polymers. The polymers generally have a hydrocarbon backbone and preferably have a Staudinger molecular weight of about 10,000 to 150,000. The encapsulating reaction may be carried out from 30 to 125° F. under atmospheric pressure, and for economic reasons it is preferable to employ temperatures of 60 to 90° F. The solvent, which is generally organic, should be inert and capable of dissolving substantial amounts of polymer. As the polymer reacts with the oxidizing agent it forms an insoluble film around each drop and the coated drops are recovered by any suitable manner, such as filtration or decantation. Suitable solvents for the encapsulating reaction include

such things as carbon tetrachloride, hexane, heptane, octane, dichloroethane, etc.

Since it may be desirable in some instances to have a strong polymer film around the oxidizing agent which is capable of withstanding conventional handling, it is advantageous to include curing and accelerating agents in the rubber solution so that the polymer film encapsulating the oxidizing agent may be cured either at room temperature or elevated temperatures. For instance, a small amount of sulfur may be compounded with the polymer before it is dissolved in the solvent and treated with the oxidizing agent. Of course, curing agents should only be used where the polymer is capable of being vulcanized, e.g. a polymer having double bonds or active groups. Additional strength may be imparted to the polymer by compounding it with other well known compounding substances before dissolving it in the inert organic solvent. Any excess polymer may be removed from the capsules by washing them with additional solvent. Known solvents, such as organic alcohols and ethers, may be used to reduce the tackiness of the capsules.

The following examples are given to more fully illustrate the encapsulating process of the present invention.

Example 1

A 25 wt. percent solution of styrene-isobutylene copolymer containing 60 wt. percent styrene and having a Staudinger molecular weight of 40,000 was prepared by shaking the polymer in carbon tetrachloride at room temperature overnight. The polymer solution was placed in a vessel which was 2 ft. high and 1 in. wide and drops of red fuming nitric acid were introduced at the top of the vessel and permitted to fall through the polymer solution to the bottom of the vessel where they were recovered in a bucket. It was noted that a film formed around each drop as it passed from the top of the polymer solution to the bottom of the vessel. The polymer coated drops were removed from the vessel by raising the bucket and decanting the carbon tetrachloride from the capsules. The recovered capsules were then washed with additional carbon tetrachloride and then with petroleum ether. The dried capsules were less tacky than those recovered from the encapsulation zone prior to washing. One of the capsules was melted on a hot plate and it was noted that it produced red fumes which indicated the presence of active red fuming nitric acid. The remaining capsules were admixed with aluminum powder in a 1:1 weight ratio and it was noted that no reaction took place at room temperature.

Example 2

Example 1 is repeated except that a liquid mixture consisting of 5 wt. percent RFNA and 95 wt. percent tetranitromethane is used in place of RFNA.

Example 3

Example 1 was repeated except that a polystyrene (100,000 M.W.) solution was used in place of the styrene-isobutylene copolymer.

Example 4

Example 1 was repeated except that styrene-butadiene copolymer (SBR) having a Staudinger molecular weight of 92,000 was used in place of the styrene-isobutylene copolymer.

Resort may be had to various modifications and variations of the present invention without departing from the spirit of the discovery or the scope of the appended claims.

What is claimed is:

1. A solid-liquid rocket propellant system which comprises a mixture of nitric acid as liquid oxidizing agent in a plurality of nitrated polymeric hydrocarbon capsules $\frac{1}{8}$ " to $\frac{1}{4}$ " in diameter and a solid metal-containing fuel selected from the group consisting of aluminum powder, boron powder, magnesium powder and hydrides of said metals, the weight ratio of liquid oxidizing agent in the capsules to the solid fuel mixed with the capsules being about 1:1 to 1:2.

2. A solid-liquid rocket propellant system as set forth in claim 1, in which liquid oxidizing agent in said capsules contains 1 to 20 wt. percent of nitric acid and 80 to 99 wt. percent of C_1 to C_3 nitroparaffin.

3. A solid-liquid rocket propellant system as set forth in claim 1, in which the nitric acid in said capsules is red fuming nitric acid and the nitrated polymeric hydrocarbon is nitrated styrene-isobutylene copolymer.

4. A solid-liquid rocket propellant system which comprises small semi-rigid capsules of a nitrated hydrocarbon rubber containing encapsulated nitric acid as liquid oxidizing agent, said capsules being about $\frac{1}{8}$ " to about $\frac{1}{4}$ " in diameter and being mixed in a weight ratio of about 1:1 to 1:2 of a solid fuel selected from the group consisting of aluminum powder, boron powder, magnesium powder and hydrides of aluminum, boron and magnesium.

5. The method of preparing a solid-liquid propellant system which comprises contacting discrete drops of a liquid containing nitric acid with a solution of a rubbery polymeric hydrocarbon in an encapsulating zone, reacting the discrete drops of liquid with the polymer hydrocarbon in solution to form a nitrated film of the polymer surrounding the drop of liquid containing the nitric acid, controlling the size of said drops, contact time and viscosity of the polymer solution to obtain capsules having a diameter of $\frac{1}{8}$ " to $\frac{1}{4}$ ", withdrawing the resulting capsules from the encapsulating zone, mixing the capsules containing nitric acid as liquid oxidizing agent with a powdered metal fuel selected from the class consisting of aluminum, boron, magnesium and hydrides thereof in a weight ratio of from 1 part of encapsulated liquid oxidizing agent to 1-2 parts of the powdered fuel.

References Cited

UNITED STATES PATENTS

2,541,165	2/1951	Kulp	18—48
2,702,924	3/1955	Plourde	18—48
2,712,497	7/1955	Fox et al.	52—0.5
2,783,138	2/1957	Parsons	52—0.5
2,802,332	8/1957	Orsino	60—35.6
2,960,935	11/1960	Colpitts	102—70
3,143,446	8/1964	Berman	149—2

OTHER REFERENCES

Zaehring, "Solid Propellant Rockets Second Stage," American Rocket Co., Box 1112, Wyandotte, Mich. (1958) pp. 229 to 231.

BENJAMIN R. PADGETT, *Primary Examiner*.