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ENCAPSULATION OF PARTICULATE METAL HYDRIDE IN SOLID PROPELLANTS

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This invention relates to a means for encapsulating ingredients. More particularly, the invention relates to a method for the encapsulation of highly reactive products useful in solid propellant ingredients.

In composite solid propellants, a fuel-binder compound serves as a matrix material. Dispersed within the matrix is a solid particulate oxidizer. The binder matrix is normally a polymeric constituent. For example, polybutadienes are used as binder materials. A typical oxidizer commonly utilized in composite solid propellants is ammonium perchlorate. To increase the performances of the solid propellant, there is usually also disposed throughout the matrix, metal particles which serve as additional fuel. Perhaps the most commonly used metal found in composite solid propellants is aluminum. The addition of the light metal such as aluminum as auxiliary fuels in current solid propellants has increased the delivered specific impulse to about 245 seconds. The specific impulse of solid propellants can be further increased giving high performance through the utilization of light metal hydrides. Some of these hydrides, however, are extremely reactive with the other components normally found in the composite type propellants and will not remain in a quiescent state prior to ignition. Values of specific impulse as high as 280 seconds have been calculated for a system comprised of a hydrocarbon binder and ammonium perchlorate oxidizer utilizing lithium aluminum hydride. With more sophisticated binders such as nitro-poly-urethane or nitramine type binder, the presence of a hydride gives specific impulses up to 300 seconds.

As indicated, the highly energetic hydrides cannot, by themselves, be incorporated directly into the conventional propellant systems. During the mixing and curing, binders and other ingredients with functional groups such as COOH and OH react with the hydrides to yield hydrogen. This not only decreases the hydride concentration but causes voids in the finished propellant. Nitramine binders and other ingredients containing nitro groups which may be utilized in making propellants are reduced by the presence of the hydrides. Additionally, propellants containing a compound such as lithium aluminum hydride is more sensitive to heat, impact and friction.

In order to utilize such reactive components, attempts have been made to encapsulate the material in a less active one. Various techniques have been attempted, all directed to encapsulation of the active particle of material. Among such techniques are a nozzle process, dipping, vapor deposition, and electrolytic plating. More elaborate and classic processes involve sealing the reactive material into minute containers of aluminum or other appropriate material by crimping, plastic sealing, and ultrasonic welding. All of these methods give rise to new problems in the processing of propellants. Among some of the problems is the difficulty of forming a continuous, reliable, impervious film around each active particle. There is also the probable puncturing or rupturing of the capsule during normal solid propellant mixing, in forming applications, as well as during mandrel removal and grain trimming. Further problems result in trying to prevent agglomeration

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after encapsulation and in effecting adequate inspection for complete protection. These processes are further limited as to the capsule material which may be used as set by the encapsulation process, the characteristics of the reactive material, and the ability of the coating to adhere to the remainder of the propellant in the cured state.

One of the processes most similar to the one disclosed herein relates to the coating of the reactive material with a single thermoplastic polymer which is subsequently cured often with a curing agent to form a hard shell about the material. The disadvantage of this type of encapsulation is that the polymer is often soluble in the binder material utilized for a solid propellant, thus decreasing its encapsulation effect. Further, the single polymer procedure often results in a two-phase system during the encapsulation, making control more difficult.

It is thus an object of this invention to provide a solid propellant grain having a high impulse.

A further object of this invention is to provide a method for encapsulating a reactive component.

A still further object of this invention is to provide encapsulated reactive materials for utilization in solid propellants wherein the encapsulating material is not soluble in the solid propellant grain.

The above and other objects of this invention will become apparent from the following detailed description.

The method of this invention involves the copolymerization of two pre-polymers about the reactive particles to form the protective capsule. The process of encapsulation is performed by first dissolving the polymers in a suitable solvent. The reactive ingredient is then suspended in the resultant solution. A non-solvent liquid component is then added slowly to the suspension. During addition of the non-solvent the suspension is heated and continually stirred. The non-solvent effects phase separation. The resultant slurry is heated at the reflux temperature, with continual stirring, for a period of time sufficient to effect the copolymerization of the pre-polymers in a film about the reactive material. The encapsulated solid is then separated from the liquid by decantation and air dried at room temperature. It is particularly desired that the two pre-polymers utilized form an addition type polymerization when cured. Pre-polymers that have a condensation polymerization upon curing can be utilized providing the by-product does not interfere with the encapsulation.

A particular example of the method of this invention would be the dissolution of a polyamide resin and a diepoxide in an aromatic solvent such as benzene. The compound to be encapsulated could be magnesium hydride which would then be suspended in the solution. A non-solvent such as hexamethyl disiloxane is then added slowly to the suspension which is heated and stirred during the addition. The polyamide and epoxide separate from the solution as a single phase and distributes itself as a film around the solid magnesium hydride particles. The stirring is continued and the mixture is heated at a reflux temperature for a period up to four hours until a cure of the resinous film is effected. The encapsulated solid is then separated from the liquid through decantation and finally air dried at room temperature.

As indicated, the binder material or matrix normally used in solid propellants is a polymeric substance such as polybutadiene or polybutadiene acrylic acid, PBAA. The particular advantage of the coating of this invention resides in the cross-linking of the prepolymers about the individual encapsulated particles. The solubility of the

encapsulating material in the binder is substantially reduced and is usually negligible as compared to a coating of particles from a single uncured polymer such as a thermoplastic polymer.

In general, amino-acid condensation polymers, synthetic linear condensation polymers including the polyamides and polyesters, linear addition polymers such as hydrocarbon and vinyl-type polymers may be employed in conjunction with a cross-linking agent to prepare the products of this invention.

The condensation-type polymers are cellulose, cellulose, cellulose acetate, cellulose acetate-butyrate, ethylcellulose, and the cellulose ethers such as methyl, carboxymethyl, hydroxyethyl, cyanoethyl and benzyl cellulose.

Examples of the amino-acid condensation polymers are regenerated proteins such as casein and vegetable globulins. Synthetic linear condensation polymers which may be employed in the practice of this invention include the polyamides such as nylon, and polyurethane resins, polyesters such as the alkyl and fiber-forming types, polyester and polyesteramide rubbers.

Applicable linear addition polymers include natural and vulcanized rubbers such as gutta-percha, balata, and chicle, cyclized or isomerized rubber, rubber hydrochloride, polybutadiene rubbers including GR-S and nitrile rubber, polychloroprene and its copolymers, polysulphide rubbers and copolymers similar to the following polymers but containing functional groups for cross-linking: polyisobutylene and the butyl rubbers, the various polyethylenes including chlorosulphonated polyethylene rubber, polytetrafluoroethylene, polystyrene, polyvinylcarbazole and polyacenaphthylene, indene and coumarone-indene resins polyvinyl acetate, polyvinyl alcohol, polyvinyl pyrrolidone, polyvinyl formal, polyvinyl acetal, and polyvinyl butyral, polyvinyl chloride, vinyl chloride-vinyl acetate copolymers, polyacrylonitrile, vinyl chloride-acrylonitrile copolymers, polyvinylidene chloride and its copolymers, polymethyl methacrylate and related polyacrylates, ketone aldehyde polymers and polyacrylate rubbers. The functional groups attached to above polymers could include, for example, amino, epoxy, carboxy, hydroxy, sulfo and the like. Additionally, the above linear polymers without functional groups can be used when reacted with copolymers containing such functional groups.

Cross-linking polymers applicable to the present invention include cross-linking type polyester resins, various epoxy resins, polyamides, polymerized drying oils, aniline formaldehyde resins, sulphonamide-formaldehyde resin, urea-formaldehyde resins, melamine-formaldehyde resins, the various phenol-formaldehyde condensation resins and particularly combinations of some of these.

Furthermore, organic polymers containing elements other than carbon, hydrogen, oxygen, and nitrogen may be employed. For example, silicon-containing polymeric materials are advantageously adapted to the practice of this invention. The silicon-containing polymers fall into two general classes; that is, those having direct silicon-carbon bonds (the silanes) and those having silicon-bonded to carbon through oxygen (the siloxanes). The silicon-containing materials often have a halogen in the molecule.

The above pre-polymers are merely illustrative of those that may be cross-linked to encapsulate particles in accordance with this invention. As indicated, virtually any cross-linkable pre-polymer that is nonreactive with the material to be encapsulated can be successfully utilized. The selection of such pre-polymers and the possibility of cross-linking is entirely within the skill of the art.

Initially, the cross-linkable pre-polymers and the material to be encapsulated are dispersed in a solvent solution previously referred to. Next, what is referred to as a nonsolvent liquid is added causing the pre-polymers to precipitate about the solid material. Thus, the invention broadly embraces the utilization of a first liquid media

in which the solid material and soluble pre-polymers are unreactive therewith. Secondly, the invention requires the addition of a second fluid media in which the pre-polymers and solid material are insoluble. The first and second fluid media, however, should be miscible with one another in order for the desired precipitation to occur. It should be obvious that nonreactivity of the two solutions with the pre-polymers or the material to be encapsulated is necessary. The nature of the materials must be such that the pre-polymers adhere to the surface of the suspended solid in the form of a thin continuous film. The selection of the solvent/nonsolvent pair is entirely within the skill of the art. Any materials that fulfill the above requirements are satisfactory for the performance of this invention. It is believed to be unnecessary to indicate the particular liquids which are solvent or nonsolvent as the case may be for the particular pre-polymers. However, following is a list which includes some but not all possible compounds that can form the solvent and nonsolvent liquid media required. Examples of mediums which are employed in the carrying out of the process of this invention include aliphatic and olefinic hydrocarbons having from about 5 to about 16 carbon atoms. Examples of these are pentane, hexane, heptane, octane, dodecane and hexadecane as well as 2-octane, 1-dodecene, 1-hexadecene, etc. Examples of cyclic hydrocarbons are cyclohexane, methylcyclohexane, etc. Examples of aromatic and alkyl-aromatic compounds which are employed as dispersion mediums include compounds having from 6 to about 16 carbon atoms such as benzene, toluene, xylene, 2,4-diphenylbenzene, phenyldecane, decalin, 1-hexyldecalin, etc. Halogen derivatives of the above hydrocarbons are also employed as dispersion mediums. Examples of these include ethylenedichloride, trichloroethylene, methylenedichloride, chlorobenzene, bromobenzene, iodobenzene. Compounds of the Freon series such as dichlorodifluoromethane, dichlorotetrafluoroethane, etc., may also be employed.

Other possible mediums are alcohols having from 1 to about 12 carbon atoms and from 1 to about 3 hydroxyl groups. Examples of these are methyl alcohol, ethyl alcohol, benzyl alcohol, glycerine, dodecyl alcohol, etc. Amines may also be used which have from about 2 to 12 carbon atoms and from 1 to about 3 nitrogen atoms. These include such compounds as ethylenediamine, diethylenetriamine, dodecylamine, pyridine, quinoline, etc. Ethers, ketones, aldehydes and esters having from about 2 to about 16 carbon atoms are also used. Examples of these are ethyl ether, acetone, propionaldehyde, ethyl acetate, butyl dodecanoate, butyl Cellosolve, etc. The requirement in all of these cases is that the dispersion medium not be reactive to any of the polymeric or solid components employed. Additionally, siloxanes, silanes, nitriles, and mixtures of all the above compounds can be utilized. The properties of the various above liquid media with respect to miscibility and solvent power are well known within the skill of the art.

The solid particles to be encapsulated could be virtually any material in particulate form. One of the primary purposes of the invention is to encapsulate highly reactive material with inert coatings so that the materials may be utilized in applications such as solid propellant formulations. The size of the particles to be encapsulated can vary from 10 to 450 microns. It is found, however, that best encapsulation results when the particles are from 50 to 350 microns in size. It is felt that it would be needless to recite all possible solid materials that could be encapsulated as the list would be virtually without limit. However, some of the more reactive materials that are highly desirable to encapsulate would include, for example, lithium aluminum hydride, magnesium hydride, beryllium hydride, nitronium perchlorate, and the like. Following are specific examples of the method of the invention:

The amounts or ratios of the individual components

are obviously not critical. The ratio of pre-polymers to each other can be determined by normal stoichiometry. The amount of nonsolvent added depends upon that utilized. One can easily determine when a sufficient amount of nonsolvent is added, since precipitation would stop occurring. The amount of pre-polymers needed to coat a given quantity of reactive material must be determined experimentally for each reactive material and pre-polymers. By weighing the reactive material before coating and weighing the coated product, one can determine the percent of coating. The higher the percent of polymer, the thicker is the coating.

Example 1

12.5 grams each of Versamid 140 which is a polyamide resin manufactured by General Mills, Inc., and Epon 828, which is a condensation product of epichlorohydrin and bisphenol-A, manufactured by Shell Chemical Company, was added to a 3-liter resin or reaction flask. 350 grams of -200 mesh spherical magnesium hydride was dispersed in the solution of the pre-polymers in 700 milliliters of toluene as a solvent to the system was added to the flask. The order of addition of the previous reactants was not critical. The flask was then heated and the suspension was stirred while adding 1100 milliliters of hexamethyl disiloxane slowly. The disiloxane acted as a nonsolvent for the pre-polymers and magnesium hydride, while being miscible with toluene. Upon completion of the addition of the disiloxane, heating at reflux temperature (about 95° C.) was continued for four hours. Stirring, however, was continued until the mixture in the flask reached room temperature. At the completion of the four-hour time, the pre-polymers had encapsulated and cross-linked about the magnesium hydride particles. The encapsulated particles settled to the bottom of the flask while the remaining liquid was decanted therefrom. The product was then air-dried at room temperature. The above process was repeated utilizing the product obtained as the solid material dispersed in the pre-polymer solution. This was done to ensure further and more complete encapsulation. Inspection of the product indicated individual encapsulation of particles with minimal coalescence. Aggregates that were formed were relatively uniform in size and quite small.

Example 2

2 grams each of Versamid 140 which is a polyamide resin manufactured by General Mills, Inc., and Epon 828 which is a condensation product of epichlorohydrin and bisphenol-A, manufactured by Shell Chemical Company, dissolved in 100 milliliters of toluene was added to a 500 milliliter resin or reaction flask. 25 grams of macro-crystalline lithium aluminum hydride was dispersed in the solution of the pre-polymers. The order of addition of the previous reactants was not critical. 150 milliliters of hexamethyl disiloxane was added slowly to the flask while stirring and heating. The disiloxane acted as a nonsolvent for the pre-polymers and lithium aluminum hydride, while being miscible with the toluene. Upon completion of the addition of the disiloxane, heating was continued for four hours at reflux temperature (95° C.). Stirring, however, was continued until the mixture in the flask reached room temperature. At the completion of the four-hour time, the pre-polymers had encapsulated and cross-linked about the lithium aluminum hydride particles. The encapsulated particles settled to the bottom of the flask while the remaining liquid was decanted therefrom. The product was dried in a vacuum at 110° F. to keep air away from the product because of possible reaction with any exposed solid. The above process was repeated utilizing the product obtained as the solid material dispersed in the pre-polymer solution. This was done to ensure further and more complete encapsulation. Inspection of the product indicated individual encapsulation of particles with minimal coalescence. Aggregates that

were formed were relatively uniform in size and quite small.

The encapsulated reactive material of the invention as previously disclosed can be incorporated in virtually any type of solid propellant formulations. For example, when the encapsulated material is an oxidizer it may be incorporated in a conventional binder material having a metallic fuel or the like disposed therein. Alternatively, when the encapsulated material is a reactive fuel, it can be incorporated in a binder having an oxidizer dispersed throughout. The polymeric binder material for the propellant may be any of the previously recited polymeric materials that can be utilized for encapsulation of the reactive materials. Additionally, various condensation type polymers may also be utilized for binder material such as the carbohydrate condensation type polymers, the amino acid condensation type polymers, including cellulose, cellulose nitrate, cellulose acetate, casein, and the like. The most prevalently used binder materials found in solid propellants are the rubber type polymers, such as the polybutadienes, carboxy terminated polybutadienes, and the polybutadiene acrylic acid polymers. The oxidizer materials and fuels are numerous and any within the art can be utilized within the scope of the invention. Examples of such oxidizer and fuel materials are found in Patent No. 3,022,149, issued Feb. 20, 1962, to F. B. Cramer. Thus, for example, an encapsulated reactive oxidizer might be a nitronium perchlorate. The encapsulated material would then be dispersed in a binder such as carboxy terminated polybutadiene having a metal solid particulate fuel, such as aluminum dispersed throughout. Alternatively, a reactive fuel material such as lithium aluminum hydride might be encapsulated and dispersed in a carboxy terminated linear polybutadiene binder material having a solid particulate oxidizer such as ammonium perchlorate dispersed therein. Additionally, conventional burning rate modifiers, burning rate depressants, and other burning type and burning catalysts can be disposed in the solid propellant formulations of the invention. The encapsulated oxidizer or encapsulated fuel may be incorporated in the propellant formulation and amount up to 75 percent by weight of the total composition. It is well within the skill of the art to determine the correct percentage of material to be utilized depending upon the desired ballistic characteristics and the density of the material. The minimum amounts of either the oxidizer or fuel which is encapsulated is dependent upon the desired ballistics. Additionally, bi-propellant type formulations can be made to utilize the concepts of this invention wherein the propellant has a fuel rich section and an oxidizer rich section. In such instances, the fuel and oxidizer may be present in amounts up to 85 percent by way of the total composition.

After forming the encapsulated products of the invention in accord with the previous description and examples, the material is then incorporated in a normal manner in solid propellant formulations. For example, a binder material is first poured into a propellant mixer to thoroughly blend the binder ingredients. Then, the encapsulated materials are added and thoroughly dispersed in the binder. Finally, either the oxidizer or fuel which is not encapsulated is added to the mixer and blended. Alternatively, the non-encapsulated material may be added prior to the encapsulated material, there being no criticality as to the order of addition. After all the ingredients have been thoroughly mixed in the mixer they are then poured into a mold and cured at the necessary temperature to form a solid cohesive mass which can then be used as the propellant grain.

Example 3

Five-pound mixes of propellant containing magnesium hydride made in accord with the above previous examples were formulated. The binder material utilized was either polybutadiene acrylic acid or copolymer butadiene and methylvinyl-pyridine. Ammonium perchlorate was

used as an oxidizer. In the one batch aluminum fuel was additionally present to show that it also may be present in addition to the coated hydride.

Following is a table indicating the constituency of three of the five-pound mixes made:

PROPELLANT BATCHES CONTAINING COATED MgH_2

Batch No.	Composition, Wt. Percent				
	PBAA Binder	Butadiene Methylvinyl-Pyridine	Coated MgH_2	Ammonium Perchlorate	Aluminum
5-lb. mix 1	-----	24.70	12.50	62.80	-----
5-lb. mix 2	15.00	-----	4.00	65.00	16.00
5-lb. mix 3	26.90	-----	10.45	62.65	-----

All of the mixes above indicated good coating of the hydride and thus little or no reaction. The fact that good resultant propellant was present was further confirmed by tensile strength data which showed the normal elongation to be expected from a propellant containing the same binder material with a comparable solids loading. Propellant containing uncoated hydride would have become brittle after curing and would not have produced good or equivalent elongation.

Although the invention has been described and illustrated in detail, it is to be clearly understood that the same is by way of illustration and example only and is not to be taken by way of limitation, the spirit and scope of this invention being limited only by the terms of the appended claims.

I claim:

1. A method of coating a reactive material useful as a propellant ingredient comprising:

dissolving two polymers capable of copolymerization in a solvent therefor,

suspending a solid particulate ingredient in the polymer solution,

adding a nonsolvent material to the solution effecting phase separation,

heating to a reflux temperature for a sufficient period of time to cure said polymers in a film about individual particles of said material,

continually stirring while heating,

separating the encapsulated material from the remaining liquid.

2. The method of claim 1 wherein said polymers are a polyamide resin and a diepoxide.

3. The method of claim 2 wherein said nonsolvent is hexamethyl disiloxane.

4. The method of claim 2 wherein said solvent is an aromatic hydrocarbon.

5. The method of claim 1 wherein said reactive material is a metal hydride,

said pre-polymers are a polyamide resin and the condensation product of epichlorohydrin and bisphenol-A,

and said nonsolvent is hexamethyl disiloxane.

6. A solid propellant grain comprising:

a binder,

an oxidizer,

and an encapsulated reactive fuel prepared by dissolving two pre-polymers capable of copolymerization in a solvent therefor,

suspending the reactive material in the resultant polymer solution,

adding a non-solvent material to the solution effecting phase separation,

heating for a sufficient period of time to cure said polymers in a film about said reactive material.

7. The solid propellant of claim 6 wherein said reactive fuel is a metal hydride.

8. A solid propellant grain comprising:

a binder,

a fuel,

and an encapsulated reactive oxidizer prepared by dissolving two pre-polymers capable of copolymerization in a solvent therefor,

suspending the reactive material in the resultant polymer solution,

adding a nonsolvent material to the solution effecting phase separation,

heating for a sufficient period of time to cure said polymers in a film about said reactive material.

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