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COMBUSTIBLE SOLID DISPERSIONS

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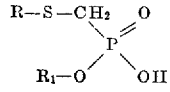
This invention relates to dispersions of combustible lids such as metals and the like. More particularly, is concerned with dispersions of certain metals having ixotropic properties.

It is known that finely-divided metals such as magne- ım may be suspended in jet fuel and can be used for ıproving combustion and imparting higher volumetric ergy levels in the after burners of jet engines. Because the density of the finely-divided metals other than ɛali metals and their higher melting points, it is difficult obtain a suspension of the metal wherein the distribu- ın of the metal can be retained over extended periods time. When employing these dispersions for purposes ɔre particularly given hereinafter, it is desirable that ɛ metal or equivalents be uniformly distributed in hy- ocarbon oil for easy handling and that they be essen- lly non-settling. While it is desirable to maintain ıximum dispersion of the combustible solids in the hy- ocarbon medium, it is also desirable for many mecha- ıms that the compositions be thixotropic so that they ıy be pumped and sprayed at will.

It is an object of the present invention to improve dis- rsions of metals and the like. It is a particular object the invention to provide dispersions which are in the ːm of mobile slurries or gels having thixotropic prop- ies. Another object is to provide novel metal dis- rsions having thixotropic properties which are stable settling, having uniform properties over a wide tem- rature range and do not settle at higher temperatures. ll further objects include the provision of novel sus- ısions of metals ideally suited as fuels or additives for ɛls for ram jet and turbo jet engines, and bipropellants missiles, rockets, flame throwers, and the like. Other jects will become apparent from the discussion herein- er.

Now, in accordance with this invention, novel thixo- pic dispersions having the desirable properties of high ısity fuels comprise suspensions of combustible solids a hydrocarbon base, the thixotropic properties being ɔvided by the presence of 0.25–5% by weight of a tal salt of a C_{1-8} alkyl monoester of a C_{4-18} alkyl- rcaptomethylphosphonic acid, the metal being at least ɛ of the group consisting of groups III, IV and VIII the periodic system and having an atomic number ween 13 and 28. More particularly, the invention ɔvides compositions having a major proportion of ɔdered metals, said metal being selected from lithium l groups II, III and IV of the periodic table and having mic numbers between 3 and 40, their hydrides, borides l mixtures thereof, the powdered metal being sus- ıded in a normally liquid hydrocarbon and thickened form a thixotropic composition by means of the above ined metallic phosphonate salts. Special objectives are ained by the additional presence of wetting or dis- sing agents and oxidizing agents such as ammonium ːate or ammonium perchlorate.

The metallic salts used as the thickening agent to provide thixotropic properties may be a basic or neutral metallic salt of phosphonate having the general configuration



wherein R has from 4 to 18 carbon atoms and R_1 is an alkyl radical having from 1 to 8 carbon atoms. The metals to be utilized in the salt formation are derived from groups III, IV and VIII of the periodic table and have atomic numbers from 13 to 28, the most favored metals being aluminum, iron, titanium, cobalt and nickel. Suitable species for the present purpose include the following:

Fe salt of monobutyl decylthiomethylphosphonate
Al salt of monobutyl decylthiomethylphosphonate
Ti salt of monohexyl dodecylthiomethyl phosphonate
Co salt of monoethyl octadecylthiomethyl phosphonate
Ni salt of monooctyl octylthiomethyl phosphonate

The powdered metals are selected from metals including lithium and groups II, III and IV of the periodic table and include particularly beryllium, boron, magnesium, aluminum, and titanium. It is preferred that the particles of the powders be less than 200 microns in diameter and preferably between 0.1 and 1.0 micron on average. Mixtures of the metals may be used and mixtures of particle sizes may be employed for the purpose of providing more stable suspensions and suspensions having special properties. In the event that metals tend to react with the phosphonate salts and cause breaking or weakening of the thixotropic gel, the particles of the metal may be provided with superficial coating to isolate the metal such as resins, plastics or metal oxides. Alumina and perfluoro carbons are examples of materials for this purpose.

Certain accelerators may be employed in conjunction with the powdered or flaked metals. Of these, high molecular weight fatty acid soaps of groups III and IV metals are preferred. Optimum results are obtained if the fatty acid has from 14 to 18 carbon atoms per molecule. Soaps of aluminum, magnesium, titanium, zirconium and tin are most efficient, particularly if they are the stearates, palmitates, oleates, or ricinoleates thereof. The term "fatty acid" is meant in this case, to include saturated fatty acids, unsaturated fatty acids and hydroxy fatty acids. Typical species for this purpose are the following:

Al stearate
Mg palmitate
Tin oleate
Zirconium ricinoleates

It is preferred that from about 0.1 to 5% by weight of the soap, based on the weight of the combustible solid, be employed for this purpose.

The three component essential composition of the invention therefore comprises the powdered combustible solid as described above, the hydrocarbon carrier and the phosphonate salt thixotropic gelling agent. Such compositions are particularly useful in the operation of ram jets which fly at altitudes where air provides sufficient oxygen for oxidation of the combustible particulate solid. Under other conditions it is possible to burn such com-

positions in conjunction with an oxidizing agent which may be injected separately or combined with the basic composition described above. For example, bipropellant systems comprise co-injection of the basic three component system described above with separate injection of an oxidizing agent such as liquid hydrogen peroxide, oxygen, and nitrogen tetroxide. Monopropellant systems are classified as those in which the oxidizing agent forms a component part of the fuel charge. In this case it is preferred that the oxidizing agent be added in the form of finely divided solid oxidizers, particularly ammonium or group I metal nitrates or perchlorates, e.g. ammonium perchlorate, amomnium nitrate, etc. Encapsulated components of any of the compositions discussed throughout this specification may be employed as well.

The preparation of the subject metallic salts of the phosphonates is described in copending patent application Serial No. 7,781, filed February 10, 1960.

In many cases it is desirable to provide thixotropic compositions containing the maximum amount of particulate combustible solids possible. In this case it is often desirable to include dispersing agents, otherwise referred to as wetting agents, for the purpose of facilitating mobility and pumpability and maintaining the solid in thixotropic state while at the same time maximum solids content is achieved. A number of classes of dispersing agents are useful for this purpose such as the following:

DISPERSING AGENTS

(1) Hydrocarbon-soluble hydrolyzed copolymers, formed by copolymerizing C_{12-30} straight-chain alpha olefins with 0.5–5 mols (per mole of olefin) of a vinyl ester, e.g. vinyl formate, vinyl acetate, vinyl butyrate or vinyl benzoate, mol wt. 4000–15,000.

(2) Copolymers of (*a*) a mono-vinyl-substituted pyridine, (*d*) lauryl and stearyl methacrylate in a mol ratio between 1:4 and 4:1 and (*c*) a C_{1-4} alkyl acrylate, mol wt. 5×10^4 to 2.5×10^6.

(3) Copolymers of (*a*) a vinyl pyridine, (*b*) C_{16-20} alkyl esters of acrylic or methacrylic acid, mol ratio 1:2 to 1:10, mol wt. 5×10^4 to 2.5×10^6.

(4) Sorbitan, glycol sorbitan, and polyoxyethylene sorbitan esters of C_{14-18} fatty acids.

(5) Polyoxyethylene esters of C_{12-18} fatty acids.

(6) High mol wt. fatty acids, esters or C_{6-16} fatty alcohols. Specific examples include:

Glycol sorbitan laurate
Polyoxyethylene sorbitan distearate
Polyoxyethylene stearate
Hexadecyl alcohol

Copolymers of 2-methyl-5 vinylpyridine, stearyl methacrylate and lauryl methacrylate in 1:5:2.5 mol ratio, 800,000 av. mol wt.

Copolymer of 1 mol hexadecene and 2.5 mols vinyl acetate, av. mol wt. 9,000.

Summarizing the above alternative compositions, the basic thixotripic composition is a three component one containing substantial amounts (90–25% by weight) of combustible solids, suspending proportions preferably 10–70% of a normally liquid hydrocarbon and 0.25–5% by weight of the metallic phosphonates providing thixotropic properties to the thickened compositions. If oxidizing agents are a fourth component of the above composition they are normally present in stoichiometric amounts relative to the combustible solids and hydrocarbon content and normally would be present in amounts between about 50 and about 80 parts by weight. Effective dispersing amounts of dispersion agents will vary from one composition to another, depending upon the specific dispersing agent and the specific solids to be dispersed thereby. This is usually between about 0.1% and about 5.0% by weight. The presence of water in an amount between about 0.1 and 0.5% is often effective in dispersing particulate metals in these compositions. Fuel catalysts such as the soaps are normally present in an amount between about 0.1 and 5% based upon the combustible solid.

The normally liquid hydrocarbon in which the combustible solids are to be suspended may be one or a mixture of hydrocarbons ranging from the gasolines through lubricating oils. For use in ram jets and the like it is preferred that fuels normally employed for jet propulsion be utilized. These are normally special hydrocarbon cuts in the kerosene boiling range but may include gas oils or higher boiling gasolines as well. Still higher volumetric thermal value is obtained by utilizing as the suspending fluid highly saturated naphthenic materials such as decalins and alkylated decalins wherein the alkyl radicals have from 1 to 4 carbon atoms each. These may be modified by the presence of polycyclic hydrocarbons, preferably saturated, such as dimethanodecalins.

The following examples illustrate compositions according to the present invention.

Example I

A kettle equipped with a high speed stirrer is used in the preparation of the following composition. Amorphous boron having an average particle size of about 1 micron diameter was dispersed by means of high speed stirring in 30 parts by weight of jet fuel meeting JP–4 jet fuel specifications, 70 parts by weight of amorphous boron being so dispersed. The fuel was modified by the addition of 1½% by weight of the basic iron salt of monobutyl decylmercaptomethylphosphonate.

Example II

A similar composition was prepared by dispersing powdered aluminum bearing a superficial coating of alumina in JP–4 jet hydrocarbon fuel, the thixotropic gelling agent being the aluminum salt of monobutyl decylmercaptomethylphosphonate.

Example III

Magnesium powder having an average particle size of about 20 microns diameter is dispersed in a gas oil, the thixotropic agent being the iron salt of monoethyl dodecylmercaptomethylphosphonate. The composition contained 1% by weight of the phosphonate, 40% by weight of magnesium, the balance being gas oil.

Example IV

High energy fuel compositions are provided by the combination of 70% zirconium decaboride, 1% of the aluminum salt of mono-octyl octylmercaptomethylphosphonate suspended in 29% by weight of a mixture of decalins.

Example V

A mono-propellant composition is provided by the suspension of 30% decaborane and 40% ammonium perchlorate in 28% of kerosene hydrocarbons, the dispersion being aided by the presence of 1% by weight of a copolymer of 2-methyl-5-vinylpyridine, stearyl methacrylate and lauryl methacrylate in 1:5:2.5 mol ratio having an average molecular weight of about 800,000. The thixotropic gelling agent for this composition is 1% by weight of the titanium salt of monohexyl octadecylmercaptomethylphosphonate.

We claim as our invention:

1. A thixotropic composition consisting essentially of a major proportion of finely divided aluminum dispersed in a normally liquid hydrocarbon and as a suspending agent for the aluminum 0.25–2.5% by weight of the basic iron salt of monobutyl decylmercaptomethylphosphonate.

2. A thixotropic composition comprising from 25 to 90 percent by weight of a finely divided combustible solid of the group consisting of lithium and metals of groups II, III and IV of the periodic table having atomic numbers between 4 and 50, their hydrides, borides and mix-

ures thereof, suspended in from about 10 to about 70 percent by weight of a normally liquid hydrocarbon and, as a thickening agent for said solids from about 0.25 to 5 percent of weight of an aluminum salt of a C_{1-8} alkyl monoester of a C_{10-18} alkylmercaptomethylphosphonic acid.

3. A composition according to claim 2 wherein the particles of aluminum bear a superficial coating of alumina.

4. A thixotropic composition comprising from 25 to 90% by weight of a finely divided combustible solid of the group consisting of lithium and metals of groups II, III and IV of the periodic table having atomic numbers between 4 and 50, their hydrides, borides and mixtures thereof, suspended in a normally liquid hydrocarbon and, as a thickening agent for said solid, an iron salt of a C_{1-8} alkyl monoester of a C_{4-18} alkylmercaptomethylphosphonic acid.

5. A composition according to claim 4 wherein the particles of finely divided combustible solid bear a superficial coating of a polyvalent metal oxide.

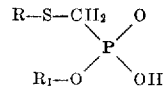
6. A composition according to claim 4 containing in addition 0.1–5% by weight, based on the combustible solid, of a higher fatty acid soap of a group II—IV metal.

7. A composition according to claim 4 containing in addition a minor dispersion improving amount, based on the combustible solid, of a dispersion agent.

8. A composition consisting essentially of the following components in the stated proportions:

	Percent by weight
Finely divided boron	25–75
Kerosene	25–70
Iron salt of mono-butyl decylmercaptomethylphosphonate	0.5–2.5
Water	0.1–0.5

9. A thixotropic composition comprising from 25 to 90% by weight of a finely divided combustible solid selected from the group consisting of lithium, and metals of groups II, III and IV of the periodic table having atomic numbers between 4 and 50, their hydrides, borides and mixtures thereof, suspended in a normally liquid hydrocarbon and, as a thickening agent for said solid, a metal salt of a phosphonate having the general configuration



wherein R is an alkyl hydrocarbon having from 4 to 18 carbon atoms and R_1 is an alkyl radical having from 1 to 8 carbon atoms, said metal being at least one of the members selected from the group consisting of groups III, IV, and VIII of the periodic system and having an atomic number between 13 and 28.

10. A composition according to claim 4 wherein the iron salt is a basic salt.

11. A composition according to claim 4 containing a solid oxidizing agent selected from the group consisting of ammonium and group I metal nitrates and perchlorates.

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