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FLUIDIZED METAL FUEL COMPOSITION

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1 Claim. (Cl. 149—21)

The invention described herein may be manufactured and used by or for the Government of the United States of America for governmental purposes without the payment of any royalties thereon or therefor.

This invention relates to a propulsion fuel for missiles, more particularly, it relates to a fluidized metal fuel to be used in conjunction with a suitable oxidizer.

The operation and utility of the fluidized metal fuel of this invention is illustrated by its application to the propulsion of underwater missiles, in this case, torpedoes. In this application the fluidized metal fuel is introduced into a combustion chamber of the torpedo in the presence of an oxidizer consisting of decomposed 90 percent hydrogen peroxide where the metal is oxidized to provide heat which in turn produces steam from ambient sea water to operate the turbine of the propulsion machinery. If the combustion products are condensible, as is true of the combustion products of the fuels of this invention, a suitable condenser is provided for their condensation. The fuel is not limited to this particular use as it can be used for propelling jet actuated devices in air in which the oxidizer may or may not be carried by the missile. Ambient air can be used as both oxidizer and diluent in operating such propulsion systems as ram jets, turbo props, etc.

The range and speed of most underwater and airborne missiles are limited by the size of propellant tanks available. In underwater missiles such as torpedoes, where space for fuel storage is limited, it is highly important that the fuel used produce a large amount of heat per unit volume for the production of steam from ambient sea water to drive the propulsion machinery. Accordingly, the fuel should possess a high density and also produce a large amount of heat per unit weight. As the fuel must be delivered to the combustion chamber through small pipes and introduced into the combustion chamber in an atomized form it must be highly fluid. For torpedo applications the fuel should produce water condensable combustion products in order that the efficiency of the engine can be maintained at a high level even at the high ambient pressures encountered when operating several hundred feet beneath the surface, and so that a significant wake is not formed along the path of the torpedo on the surface. In addition to the requirements enumerated above the fuel must possess physical stability, that is, it must be capable of being stored for long periods of time before use, without sedimentation, or deterioration in other respects.

Various fuel-oxidizer systems have been used in the past for torpedo propulsion, for example, alcohol-compressed air, kerosene-nitric acid, and others. These systems do not provide enough heat energy per unit weight or volume to be satisfactory. They do not form condensable combustion products and their use presents a number of storage and operational hazards. Other fuels such as water-reactive fuels produce large quantities of hydrogen and therefore are not suitable for depth operation. The systems which burn hydrocarbons produce carbon dioxide as one of their reaction products. While carbon dioxide may be sufficiently soluble in sea water to prevent a surface wake, its solubility is probably too low to permit the use of a condenser for reducing turbine back pressure and thus improving performance at depth.

It is therefore an object of this invention to provide a fuel for the propulsion of underwater and jet actuated aerial missiles which has a high energy output per unit volume and weight.

It is another object of this invention to provide a fuel as stated which possesses a high degree of fluidity and good storage stability.

It is a further object of this invention to provide a fuel for propulsion of underwater missiles which produces condensable combustion products.

It has been found that the above and other objects are accomplished by a fluidized metal comprising a light metal powder such as aluminum or magnesium suspended in a liquid hydrocarbon and held in suspension by a gel structure produced by the addition of a gelling agent. Specifically the fuel comprises from about 50 to about 80 percent of powders of light metals such as aluminum, magnesium and boron, up to about six percent of a gelling agent as "Bentone 34" and the remainder a hydrocarbon solvent such as diethylbenzene.

By fluidized metals as used in this specification and the claim is meant compositions consisting of metal powders dispersed in a fluid, such as a hydrocarbon. Fluidized metals present a means of utilizing the high energy available from the oxidation of such metals as aluminum and magnesium. Fluidizing the metals solves the problems of introducing the metal into the combustion chamber and reacting it rapidly and efficiently. The presence of finely divided metal powders in a liquid hydrocarbon acting more or less as a pilot fuel gives sufficiently high reaction rates and, if fluid enough, causes little difficulty in injection into the reaction chamber.

When the theoretical energy output of the following systems are compared with that of a parent hydrocarbon (diesel oil)-hydrogen peroxide system as a standard these results are obtained: The 86 percent by weight magnesium and diesel oil-hydrogen peroxide, and 86 percent by weight aluminum and diesel oil-hydrogen peroxide systems both indicate a weight advantage of about 47 percent, and a volume advantage ranging from 49 percent for the magnesium system to 69 percent for the aluminum system. In turn, the 75 percent by weight magnesium system is about 27 percent better on a weight basis and 33 percent better on a volume basis, while the 50 percent magnesium system indicates a seven percent and 13 percent advantage on a weight and volume basis, respectively.

Burning magnesium or aluminum in a combustion chamber presents serious technical problems. The melting points of these metals (about 650° C.) are so high that liquid injection is impractical, while in the gross solid state their reaction rates are relatively slow. This problem was solved by suspending the metals as fine powders in a liquid medium. The proper choice of metallic particle size and distribution, liquid fluidizing medium, and additives to adjust physical properties, results in a stable, high-metal-concentration slurry which flows readily through tubing and valves and can be atomized by certain types of injectors. These small metal particles ignite

spontaneously when they are sprayed into a stream of oxygen and steam produced by the catalytic decomposition of 90 percent hydrogen peroxide. Less non-condensable gas is produced by the combustion of these fuels than is the case for other hydrocarbon fuels such as diesel oil because, (1) less hydrocarbon is burned since the bulk of the fuel is metal powder and (2) the metals have a greater heat of oxidation than the hydrocarbon, require more diluent water to maintain the same combustion temperature, and the larger amount of steam reduces the percentage of carbon dioxide, and (3) the oxidation products of magnesium reduce the concentration of carbon dioxide by formation of carbonates.

The production of heat from the fuel and its application for propelling a torpedo is accomplished as follows. The final fuel mixture has the consistency of a soft paste or grease, will not sediment on prolonged storage, and can be sprayed from extremely small diameter orifices under 20 to 100 p.s.i. pressure, depending on the number of holes and the flow rate desired. The fuel spontaneously ignites when sprayed into the decomposition products of 90 percent hydrogen peroxide (a mixture of steam and oxygen at about 1350° F.). The reaction products are magnesium oxide, steam and carbon dioxide. Diluent sea water is added to bring the gas temperature down to, typically 1800° F. After the reaction products and steam pass through the turbine, they are quenched in a direct contact jet condenser which condenses the steam and causes the carbon dioxide to be absorbed by the magnesium oxide to form magnesium carbonate. The effluent from the condenser consists of water, solid magnesium carbonate and excess magnesium oxide. The solids content of about 12 percent was found to have no detrimental effect on the turbine blades. The catalytically decomposed 90 percent hydrogen peroxide is used to atomize, ignite, and oxidize the fuel. The catalyst for decomposition of the hydrogen peroxide consists of 16-mesh silver-plated steel screen treated with potassium permanganate. It was found to decompose hydrogen peroxide with more than 98 percent efficiency. Other methods may be used to decompose the hydrogen peroxide before its introduction into the combustion chamber. Other oxidizing agents may be used for oxidizing the fuel of the invention, 90 percent hydrogen peroxide being used as an example to illustrate the invention. Because it was found that a high velocity decomposed hydrogen peroxide gas stream gave better atomization of fluidized metal fuels than conventional spray systems, 25 percent of the oxidizer gas produced is directed to impinge on the fuel jets; the remainder is introduced into the reaction zone to complete the combustion of the fuel. The fresh water or sea water diluent is introduced into the combustion chamber through a number of jets; some of these jets impinge half the water in a finely atomized spray at the axis of the chamber; the remaining jets direct the water on the chamber walls to keep them cool. The water is vaporized, producing steam at a temperature compatible with the prime mover. While various types of combustion chambers may be used and the introduction of fuel oxidizer and water may be adjusted according to varying conditions, the following illustrates typical conditions under which the fuel of this invention was used. An automatic timer was used to regulate the introduction of all components into the combustion chamber. The hydrogen peroxide was started and allowed to decompose for ten seconds, by which time it was at equilibrium conditions of 94 p.s.i.a. chamber pressure and 1360° F. Then the fuel was introduced, followed about one second later by introduction of the diluent water. Most runs were made with diluent water flows of approximately 0.300 lb./sec., giving a combustion temperature of 1800° F. Runs generally lasted from 40 seconds to more than two minutes. The fuel flow was controlled to deliver 0.052 lb./sec. of 80 percent magnesium fuel, with the 90 percent hydrogen peroxide flow at 0.132 lb./sec. The combustion products were exhausted through a single converging-diverging nozzle. The chamber was operated at pressures of 319 to 349 p.s.i., giving pressure ratios of 22.5 to 24.6. Chamber pressures in all runs were smooth with no severe oscillations. The ease of injection of the fluidized metal fuel is evidenced by the low pressure required to inject the paste fuel. Pressure drops across the injector ranged from 10 to 42 p.s.i. All runs with an 80 percent fluidized magnesium fuel, for example, showed combustion efficiencies above 90 percent with a majority approximately 93 percent. Eighteen runs were made under the above conditions.

In compounding the fuel the "Bentone 34" is disbursed in the diethylbenzene by means of a high-shear stirrer to insure maximum gelation. The metal powders are mixed together dry and then added to the gel. The final mixture has the consistency of soft grease or paste, will not sediment on prolonged storage, and posseses sufficient fluidity to be sprayed through small diameter orifices and to pass through small diameter tubing under pressure.

The preferred metals for use in the fuels are aluminum, magnesium, boron and their alloys and mixtures thereof. The metal may be used in a percentage range from about 50 to about 85 weight percent. When magnesium, for example, is present in an amount from 50 to 80 percent by weight it will constitute approximately 30 to 60 percent by volume of the fuel, this indicating the high fuel content per unit volume of the fluidized metal fuel. The metal powder should be of spherical shape to provide high metal concentration and greater fluidity in the fuel.

The following examples which typify the invention are submitted for illustrative purposes only and are not to be taken as limiting of the invention.

Table I

	Composition A, wt. percent	Composition B, wt. percent	Composition C, wt. percent
Magnesium	75.0	75.0	80.0
Diethylbenzene	24.0	23.5	18.0
"Bentone-34"	1.0	1.0	2.0
Cellosolve (additive to improve gelation)		0.5	

In the following described tests, physical stability was measured by the extent of liquid separation, and fluidity was measured by the rate of extrusion through a 0.040 inch orifice at 100 p.s.i. pressure. It was found that commercial magnesium powders of ordinary size distribution could not be used alone to obtain optimum fluidized magnesium fuels. Several grades of spherical magnesium powder were tested alone in 75.0 percent fuels of Compositions A and B. The powders of 74 microns, maximum, and 24–35 microns, average, size formed the best fuels.

The principle of bimodal grist distribution was applied to fluidized magnesium fuels with considerable success. A bimodal grist distribution is defined as one made up of two uniform-particle-size fractions with essentially no intermediate particle-size material. A small size magnesium powder of 1.5 microns diameter was blended with another powder of 74 microns, maximum, 24–35 microns, average, size, in an 80:20 weight ratio of large to small powder, and used in 75.0 percent magnesium fuels of Compositions A and B. These bimodal fuels were stable, had satisfactory fluidity, and were successfully burned in a number of combustion tests. In other tests a small powder of 74 microns, maximum, and 24–35 microns, average, size, was blended with a large powder of 210 microns, maximum, and 139 microns, average, size. When these two powders were used separately in the 75 percent fuels of Compositions A and B, the resulting fuels were stable but did not have acceptable fluidity. When, however, they were used in a bimodal blend in the 80.0

percent fuel of Composition C, the resulting fuel had greatly increased and satisfactory fluidity. This result demonstrates the remarkable effect of bimodal grist distribution in obtaining higher magnesium concentration and greater fluidity in the fuel. It was found that the operable range of particle sizes falls within the diameter ratio of small to large particle sizes of 1 to 5–1 to 20. The bimodal blending ratio of large to small powders was varied in a large number of tests in the 80.0 percent fuel to find the optimum ratio for maximum fuel fluidity. A large powder varying from 105 to 210 microns in size and 148 microns average size was blended with a small powder of the poorest quality obtainable commercially. An acceptable fuel fluidity resulted over the range of 45:55 to 55:45 weight-blending ratio of large to small powder. Consequently a 50:50 ratio of the 105–210 micron large powder to small powder was selected for use in the optimum fuel formulation.

In environmental tests, 80 percent fluidized-magnesium fuel showed good fluidity at low temperature (12° F.). After seventeen alternating storage periods of 16 hours at 12° F. and eight hours at 160° F. (total time, 208 hours at 12° F. and 174 hours at 160° F.) this fuel still had good stability and fluidity.

Hydrocarbons were the only liquids considered for use as a carrier for the fuel because of the great reactivity of magnesium in powdered form. Diethylbenzene was selected as a liquid medium because of its relatively consistent purity, low volatility, and low viscosity. Other hydrocarbon fuels which may be used are JP–4 kerosene, toluene, etc. The liquid carrier should be capable of forming a thixotropic gel with the gelling agent used and be inert to the metal powders under long storage conditions. Amounts varying from about 15 percent by weight to about 45 percent by weight may be used. The preferable or optimum fuel consists of 80 percent magnesium powder by weight, 18 percent of diethylbenzene by weight and 2.0 percent of "Bentone–34" by weight.

The gelling agent used to form a thixotropic gel with the hydrocarbon carrier is preferably "Bentone–34." "Bentone–34" is dimethyldioctadecyl ammonium bentonite. The compound is formed by reacting bentonite which is chiefly montmorillonite with the appropriate ammonium salt. The chemical composition of montmorillonite is ideally $Al_2O_3.4SiO_2.2H_2O$ with isomorphous replacement of aluminum by other cations. The base-exchange reaction between an ammonium salt and montmorillonite results in the formation of an electrovalent linkage between the organic ammonium cations and the mineral. "Bentone–34" may be used in an amount from about one percent by weight to about six percent by weight. Other gelling agents may be used, the requirement being that the gelling agent produce a thixotropic gel in the liquid carrier medium employed and not cause a chemical reaction to occur under storage conditions.

It was necessary to choose a gelling agent which provided proper physical stability and fluidity. Physical stability in this case is the ability of the metal particles to remain homogeneously dispersed in the liquid carrier medium for long periods of time. A liquid with high viscosity or high density or both would increase fuel stability but use of such a liquid proved impracticable. The best available solution to the problem was the use of a gelling agent to provide structural support for the dispersed particles and a paste-like consistency required for stability of fuels with a magnesium concentration, for example, of 75 percent or higher. Such a paste-like fuel must have sufficient fluidity to be pressure extruded through fuel lines and valves and injected into a combustion chamber. Thixotropy is a required quality for the paste-like fuel of this invention. A thixotropic fuel has a stabilizing gel structure when it is not under shear. When shear is applied the gel structure is broken, and fuel fluidity is increased. "Bentone–34," a hydrophobic bentonite, was the most suitable gelling agent found. Aluminum soaps and a variety of non-soap thickeners were unsatisfactory because of insufficient gelling power, low fuel fluidity, or lack of thixotropy. The additional examples in the following table serve to further illustrate the operation of the invention. In the examples JP–4 kerosene was used as a carrier liquid in all of the tests. A magnesium powder size of 24 microns was used in all of the examples except Examples 7, 8 and 9. In these examples the aluminum powder of the bimodal magnesium-aluminum fuel had a particle sizes of four microns. In Examples 5 and 6 particle sizes of 15 microns were used. The remaining component of the compositions was JP–4 kerosene.

Table II

Example No.	Mg, wt. percent	Al, wt. percent	C. Eff., [a] percent	Total N.C.[b] gas, lb. moles/lb. Exp.[c]	JHP [d]
1	50		94		475
2	50		91.2		516
3	75		87.1		408
4	75		87.3	79.0×10^{-4}	
5	75		95.8	28.8×10^{-4}	
6	75		87.2	25.0×10^{-4}	
7	50	25	95.0		
8	50	25	98.9		
9	50	25	97.4	22.1×10^{-4}	
10	75		96.4		
11	75		95.7		
12	75		96.0		

[a] Combustion efficiency—experimental value divided by the theoretical value.
[b] Noncondensable.
[c] Expendables.
[d] Jet horse power; horse power experimental value obtained from a relationship

$$\text{J.H.P.}=\frac{F^2g}{1,100\,W_t}$$

where F is thrust pounds experimentally measured, g is the gravitational constant 32.2 FPS/sec., and W_t is the total flow rate lb./sec.; experimentally measured as the sum of the flow rates of fuel, oxidizer and diluent water.

It is noted that in all cases where combustion efficiency was measured it was satisfactorily high. Further, the amount of non-condensable gas remaining after the combustion reaction was well within acceptable limits. It should be noted that in Examples 5, 6 and 9 it was less than 30×10^{-4} lb.-mole/lb. expendable. Where it is not shown in the examples no attempt was made to measure it. The jet horse power produced by the fluidized fuels is significantly high. In tests 10, 11 and 12 the turbine operated by the gas generator was connected to a dynamometer and the kinetic energy from the gas generator nozzles was converted into mechanical energy which was then absorbed by a Clayton 500-H.P. water-brake dynamometer. In all cases the energy produced was highly satisfactory. The fluidized metal fuel of this invention gives 33 percent more range per volume than diesel oil when both are used with 90 percent hydrogen peroxide decomposition products to power a torpedo under the same operating conditions. When a condenser is used with the fluidized metal fuel system, the range is more than doubled for operation below a depth of 500 feet. It is seen from the above description and results that a fluidized metal fuel has been provided for propulsion of underwater missiles which possesses sufficient fluidity, is highly stable, produces a large amount of heat per unit volume and weight, and produces condensable combustion products.

Obviously, many modifications and variations of the present invention are possible in the light of the above teachings. It is therefore to be understood that within the scope of the appended claim the invention may be practiced otherwise than as specifically described.

What is claimed is:

A fuel for torpedoes consisting essentially of 80 percent magnesium, 18 percent diethylbenzene, and 2 percent dimethyldioctadecyl ammonium bentonite, said magnesium having a bimodal grist distribution of a 50:50 weight ratio of large powder particles ranging in size from 105

to 210 microns and small powder particles ranging in size from 24 to 74 microns.

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