April 23, 1963 E. N. HALL 3,086,354

UTILIZATION OF PROMOTERS IN EFFECTING REACTIONS

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Fig. 1

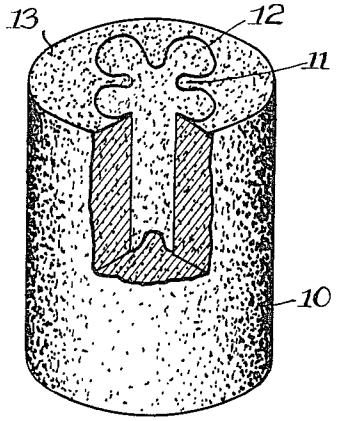


Fig. 2

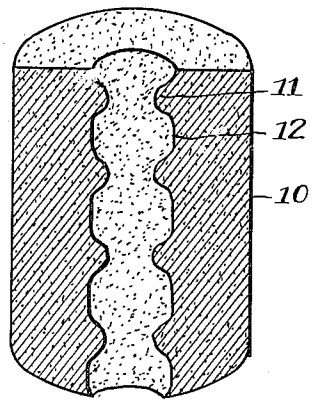


Fig. 3

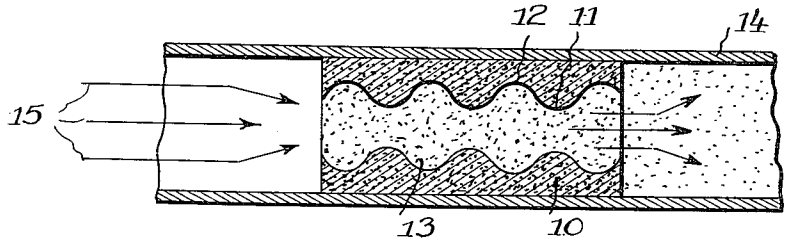
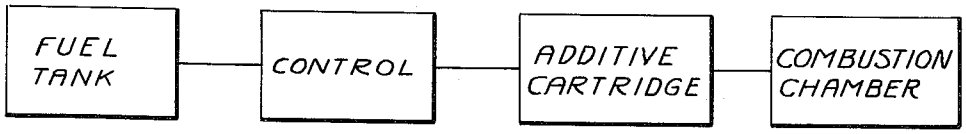


Fig. 4



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UTILIZATION OF PROMOTERS IN EFFECTING REACTIONS

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

This application is a continuation-in-part of my co-pending application Serial No. 460,787, entitled "Method of Utilizing Solid Fuel Additives and Device Therefor" which was filed on October 6, 1954, now abandoned.

This invention relates generally to the improved introduction of a promoter into a reaction region in a carrier which comprises one of the reactants to thereby more effectively carry out the reaction. More particularly, the invention relates to a method and means for releasing highly reactive promoters from an inert material and into a fluid stream comprising a reactant, the mixture being then introduced into a reaction region. The invention is especially important in jet and rocket propulsion fuel systems wherein it is desirable to add one or more substances to the fuel or oxidant component to thereby improve its ignition, combustion or other functional features.

In effecting various reactions, it is often desirable to promote controlled reaction as by stabilizing, triggering, or catalyzing the reaction. As is well known, this can be done by adding various agents, such as catalysts, stabilizers or triggering agents to the reactants in the reaction region. For purposes of this application, such catalysts, stabilizers, triggering agents and agents which promote or more effectively carry out a reaction are referred to as promoters. The promoters are usually highly reactive, are often difficult to handle, and are not readily added to the reactants.

By way of example, various types of propulsion systems, including pulse engines, turbo-engines and ram jet engines, and rockets, and particularly those devices or engines using hydrocarbon fuels, are subject to fuel combustion deficiencies under certain conditions of operation. One very important problem in connection with such propulsion systems concerns the combustion instability which gives rise to "cycling" wherein the flame front in the combustion chamber tends to fluctuate back and forth causing marked reduction in operating efficiency. This combustion instability, under certain conditions, such as rich fuel mixtures or a high angle of attack of a plane or rocket, may cause the flame in the combustion chamber to become extinguished. It will be readily apparent that this is a highly dangerous condition under certain operating conditions.

Another problem of importance occurs in connection with hydrocarbon fuel-acid oxidant system because of ignition delay and hazardous starting of the engines. This results from difficulty in igniting the system which inherently causes an excessive build-up of the reaction elements prior to ignition of the mixture, thereby creating a substantial safety hazard.

These problems have caused considerable research to bring about their solution and, in this connection, much has been done to improve mechanical design to overcome the combustion instability and ignition problems so as to minimize delay in starting. Another research approach has concerned the evaluation of many types of fuels having differing properties in respect of ignition characteristics, flame speeds, heats of combustion, smoke formation, and the like. In connection with this approach, fuel additives of various types have been proposed and additives in the form of solids or fluids have been incorporated directly with the fuel in the supply tank of the unit.

In some cases, however, the additives may be incompatible with the fuel to such an extent that premixing of the fuel and additive is neither desirable nor possible. In such case, the additive must be added to the fuel while it is being transmitted or after it has reached the combustion chamber, but usually prior to combustion of the fuel. Under certain conditions, the additives may be readily metered into the fuel system at any desired point in the system by injection or other means of introduction. However, when the desired additive is in a solid phase and one which in insoluble or otherwise incompatible with the fuel and is highly reactive, the problem of introducing the desired amount of additive at the proper time and place in the fuel system causes a great deal of difficulty which has not been satisfactorily solved in connection with engines and rockets of the type herein discussed.

One approach to the problem of handling such additives is to form a slurry or suspension thereof in an appropriate solvent so that the slurry may be injected in such form in the desired amounts. This approach has not proven to be entirely satisfactory because the activity of the suspended additive in liquid media often decreases rapidly so that the combustion stabilization or other properties initially possessed by the additive is not maintained.

While various problems have been detailed in the foregoing in respect of the combustion of fuels in various types of engines and rockets, it will be apparent to those familiar in the art that similar problems can occur with diesel engines, gas turbines and gas generators.

Likewise, similar problems occur in respect of other reactions than oixdation or combustion reactions which involve the addition of promoters for more effectively carrying out the reaction. In this connection, many catalytically effected reactions will be apparent to those familiar with the art.

A main object of this invention is the provision of an improved method and means for introducing a promoter into a reaction. It is a more particular object of this invention to provide an improved method and means for introducing a promoter into a carrier which comprises a reactant in a reaction region. A still more particular object of the invention is the provision of a method and means for introducing a highly reactive fuel additive in particulate form and in particular amounts into a stream of fuel prior to ignition and combustion. A further object of this invention is the provision of an additive dispensing cartridge which, when placed in a stream, results in the transfer of the additive from the cartridge to the stream. It is a still further object of this invention to provide a fuel additive dispensing cartridge which is adapted to liberate substantially uniform amounts of additive into fuel flowing through the cartridge. Other objects and advantages of this invention will become apparent by reference to the accompaning drawings and the following specification.

In accordance with this invention a promoter is carried into a reaction region in a carrier. In carrying out the invention, the promoter is surrounded by a material which is inert relative to the promoter but is reactive with the carrier so that when the carrier is passed over the inert material some of the promoter becomes suspended in the carrier and the carrier reacts with the inert material to activate the promoter for reaction. The carrier is a fluid and is preferably a reactant in the reaction region. The carrier is selected so as to react with the inert material by effecting dissolution, sublima-

tion, disintegration, or decomposition of the inert material at a controlled rate to thereby release the promoter from the inert material into the carrier.

The promoter may be dispersed in the inert material or matrix in the form of a solid or in the form of a liquid. In the event that a liquid is employed, the liquid is desirably capsulated and the capsules are dispersed in the solid material. If the promoter is capsulated, it will be understood that the capsule material should be reactive with the carrier and inert to this promoter so that the carrier can release the promoter from the capsules. Of course, if the promoter is in solid form, the solids are finely ground for dispersion throughout the solid material.

The inert material may either be liquid or solid so long as it is inert relative to the promoter and reactive with the carrier to release the promoter from the inert material for reaction in the reaction region.

The promoter, as before indicated, may serve to effect more improved reactions in various ways but, in the case of various engines and rockets, the promoters are highly reactive chemical materials having very low ignition energy requirements, such as various known pyroforic and auto igniting substances. These substances include alkali metals, chelates of many metals, organic metallic compounds. phosphorous, and others.

These promoters, in accordance with this invention, are dispersed in an inert, solid substance in the form of a device so that the entire device is inert and storable until used. As previously indicated, the inert solid substance is inert relative to the promoter but, at the same time, should be selected so that the carrier releases the promoter therefrom at a desired rate for reaction. It will be apparent that the selection of the solid material will be a function of the type of carrier which is employed for the promoter. For example, if the carrier is an acid, the promoter may be dispersed in a metallic substance. On the other hand, if the carrier is a hydrocarbon, the solid material may be a solid hydrocarbon, such as wax which will dissolve at a controlled rate in said carrier. In this connection, the carrier will usually comprise a relatively short chain hydrocarbon, as compared to the hydrocarbon from which the inert material is formed.

In summary, in accordance with this invention, the inert material in which the promoter is disposed may either be solid or liquid but it must be reactive with the carrier to release the promoter to the carrier. If a solid inert material is utilized, the promoter disposed therein may either be in the solid form or in a liquid form. The solid form of promoter may be either capsulated or merely dispersed. When a liquid promoter is used, it should be capsulated for dispersion in the inert material.

If a liquid inert material is employed, the solid promoter may also be capsulated or merely dispersed in the liquid inert material. Of course, if a liquid promoter is utilized in a liquid material, the promoter will be capsulated.

By way of a particular example of this invention, a fuel additive (promoter) substances including alkali metals such as sodium and the like may be readily transferred to the fuel stream (carrier) of an engine in the required concentrations without encountering the difficulties previously mentioned. This is made possible by forming an "additive stick" or cartridge device utilizing the additive as a dispersed phase in an apertured matrix (inert material) formed from a bodying agent having predetermined solubility characteristics in the fuel. By positioning the additive-containing cartridge within the fuel system upstream of the combustion zone, the flow of the fuel through the apertured core disintegrates or reacts with the aperture-forming surface of the matrix at a rate sufficient to release the prerequisite amount of additive for pickup and utilization by the fuel.

It is thus seen that the incorporation of a fuel additive into the fuel in accordance with the method of this invention is independent of metering or injection devices feeding the additive from an external source. By contrast, an excess of the additive is inserted directly into the fuel stream and the availability of the additive to the fuel is regulated by the eroding or solubilizing action of the fuel itself on the solid core. Where extremely small amounts of the additive are sufficient to produce the desired ignition or combustion modification, the solubility of the bodying agent constituting the solid matrix of the cartridge need be only minimal. Where relatively higher concentrations of the additive are required, the solubility of the matrix material may be varied accordingly. Similarly, the concentration of the additive in the solid core can be varied to provide for the release of proportionately differing amounts of additive as required. Since the amount of releasable additive is also dependent upon the total surface of the cartridge exposed to the solubilizing or eroding action of the fuel in contact therewith, the geometry of the cartridge surfaces exposed to the fuel flow becomes of importance in minimizing changes in total area.

It is known that alkali metals such as sodium, potassium, etc. and alloys thereof exert a beneficial effect particularly when used in conjunction with hydrocarbon fuels and acid oxidants. For example, the autoigniting effect, i.e. the ignition reaction acceleration produced by the addition of sodium and other substances into hydrocarbon fuels designated as JP–3 and JP–4 which are subsequently oxidized with red or white fuming nitric acid oxidants has been clearly established. Other fuel additive substances capable of forming a dispersed phase in solid matrices can be used in accordance with the present invention and illustrative substances in addition to sodium and potassium include lithium, calcium, and alloys of sodium and potassium and the like. Alkali metal salts of organic acids such as abietic, olaic, stearic, etc. may also be used and metal complexes with compounds such as anthracene, naphthalene, and the like wherein the metal is loosely held in the molecule can also be utilized. The particle size of the additive material should be maintained at a minium in order to maintain the maximum inherent reactivity thereof and also to provide for improved distribution upon its release into the fuel stream. Preferably, the average particle size should be below 50 microns and agglomeration between the particles during processing of the mixture to form the dispersed phase in the solid matrix should be avoided as much as possible. As before indicated, the additive may be in liquid form and capsulated for dispersion in the matrix.

The bodying agents suitable for use as dispersing media for the fuel additive consists of various substances including rubber, wax, plastic or resin compositions which desirably have the following properties and characteristics: (1) impermeability to air and moisture, (2) reactive with the carrier to release the additive and compatible with the promoter such that the effectiveness of the active ingredient is unimpaired, (3) conducive to shaping into any desired configuration as by casting, molding, etc. and (4) adequate mechanical strength to provide structural integrity under actual conditions of engine operation and storage over the ranges of temperature, acceleration, shock condition and other factors to which the device made therefrom is subjected throughout its life.

Examples of specific materials useful as bodying agents include paraffin waxes, microcrystalline waxes, beeswax, etc. and polymeric compositions such as polybutane rubber, chlorinated rubber, vinyl plastics, coumarone resins and the like. Compounding procedures well known in the art for modifying the properties of the polymeric substances may be utilized in adapting the aforesaid materials for use as herein disclosed.

The invention may be illustrated by reference to the drawings in which FIGURE 1 is a perspective view, part-

ly in section, of a preferred embodiment of the fuel additive device of this invention. FIGURE 2 is a similar view of a modified form of the device. FIGURE 3 is a sectional view illustrating the use of one embodiment of the device within a portion of the fuel system and FIGURE 4 is a diagrammatic drawing of a fuel system incorporating the present invention.

With reference to FIGURES 1 and 2, the bodying agent, prefeerably consisting of a high melting paraffin wax (M.P. above 120° F.), is formed into any desired shape illustrated by the cylindrical solid core designated as matrix **10** provided with an internal aperture throughout its length to permit fuel flow therethrough. The aperture-forming surface is preferably designed to provide for minimum change of total surface as the same becomes gradually eroded by fuel flow and this can be conveniently achieved by a symmetrical arrangement of webs **11** and ports **12** arranged transversely or longitudinally forming the undulated surfaces shown in FIGURES 1 and 2 respectively. The fuel additive component **13** consisting of finely divided particles is shown as a dispersed phase in matrix **10** including the aperture-forming surfaces defined by webs **11** and ports **12** and, in its entirety, the unit is referred to as a reaction promoter dispensing cartridge.

The utilization of the fuel additive dispensing cartridge within the fuel system is illustrated in FIGURE 3 wherein the cartridge is shown inserted in the fuel line **14**. The flow of fuel **15** through the aperture formed by webs **11** and ports **12** during operation of the engine results in a pickup of the additive **13**, the quantity being dependent upon the solubility of the solid core, rate of fuel flow, total surface exposed to fuel flow, and the concentration of additive in the matrix. The positioning of the cartridge within the fuel system as indicated diagrammatically in FIGURE 4 is between the fuel tank and combustion zone and preferably as shortly upstream of the combustion zone as possible prior to mixing of the fuel with the oxidant to minimize deterioration of the additive once it is released from its source.

The amount of additive in the cartridge can be varied broadly as needed for a given application. For example, in the case of the autoigniteability manifested by sodium in the hydrocarbon-fuming nitric acid systems previously mentioned, less than 0.1 percent by weight of sodium in the fuel is sufficient to produce the stated effect. The pre-requisite amount can be made available to the fuel from the cartridge by variation or adjustment of either or all of variables previously mentioned including (1) solubility of the matrix under the fuel flow conditions involved at the temperature of engine operation, (2) surface area available for dissolution and simultaneous release of the additive substances and (3) the concentration of the additive in the matrix. Hence it is seen that the solubility of the substrate material comprising the matrix need not be varied in each and every case where different amounts of the active ingredient are required by the fuel. Ordinarily, upwards of 50 percent by weight of particulate additive substance such as sodium can be mechanically dispersed in wax, rubber, resin or plastic matrix materials utilizing well known techniques including the use of emulsifiers to prevent agglomeration of the particles during the processing of the mixtures.

After a suitable vehicle has been selected as the matrix material, the initial phase of fabricating the solid core may be carried out by various procedures involving the use of different types of mixing apparatus such as a colloid mill, ultrasonic mixer, Waring Blendor, and the like, whereby micron size disintegration of the particulate additive can be satisfactorily achieved in the molten matrix medium. In general, the matrix material and the additive are melted together and processed in an inert atmosphere to form the dispersion. If desired, the additive may be previously disintegrated in a suitable solvent such as toluene, in the case of sodium, and the dispersion is then added to the molten matrix material with high speed agitation while maintaining the system under an inert gas. Emulsifying agents consisting of metal salts of fatty acids may be used in concentrations of from .05 to .5 percent by weight to minimize agglomeration or otherwise improve its dispersion.

The molten dispersion maintained in an inert atmosphere is then poured into a suitably shaped mold adapted to provide the desired internal and external configuration of the cartridge. Either casting or molding procedures can be used and preferably a combination of both methods are utilized wherein the molten mass is cast and then compressed in a hydraulic press at between 2000–8000 p.s.i. The dispersion may be formed in long strips if desired and cut to the desired length as required.

While in the foregoing, the invention has been particularly described in respect of introducing an additive into a fuel from a solid matrix, it will be readily apparent that other promoters, such as a nickel catalyst, may be introduced into other carriers, such as liquid edible oil, by dispersion of the catalyst in other inert materials, such as hard edible fats, to introduce the promoter into the liquid material for a reaction, such as hydrogenation.

It is not believed necessary to detail each of the possible combinations for purposes of this invention but one understanding the teachings of the invention will be readily able to employ the invention for promoting a substantial number of reactions.

I claim:

1. In a propulsion system, an operating method which comprises the steps of dispersing a combustion-modifying additive in a material which is chemically inert to said additive, but which is reactable with combustible fluid to release said additive, contacting combustible fluid with said inert material to thereby release at least a portion of said additive from said inert material and disperse said additive in said combustible fluid, and thereafter passing said additive bearing combustible fluid to a combustion zone for combustion of said fluid.

2. In a propulsion system, an operating method which comprises the steps of dispersing a fuel combustion-modifying additive in a material which is chemically inert to said additive but which is soluble in fluid fuel, contacting fluid fuel with said material so as to dissolve at least a portion of said material and uniformly disperse said additive in said fuel, passing said additive-bearing fuel to a combustion zone and therein spark igniting said fuel.

3. In a propulsion system, an operating method which comprises the steps of uniformly dispersing a fuel-modifying additive in a solid material which is chemically inert to said additive but which reacts with fluid fuel to uniformly disperse said additive in said fuel, passing fluid fuel from a fuel supply to a combustion zone and en route reacting said fuel with said solid material, whereby said additive is uniformly dispersed in said fuel, and thereafter spark igniting said additive-bearing fluid fuel in said combustion zone.

4. In a propulsion system, an operating method which comprises the steps of dispersing a fuel combustion-modifying additive in a solid hydrocarbon material which is chemically inert to said additive but which is soluble in liquid hydrocarbon fuel, passing liquid hydrocarbon fuel from a fuel supply to a combustion zone and en route contacting said fuel with said solid hydrocarbon material, whereby at least a portion of said solid hydrocarbon material is dissolved, thereby uniformly dispersing said additive in said fuel, and thereafter spark-igniting the additive-bearing fuel in said combustion zone.

5. The method of claim 4 wherein the fuel combustion-modifying additive comprises alkali metal.

6. The method of claim 4 wherein the fuel combustion-modifying additive comprises an alloy of potassium and sodium.

7. In a propulsion system, an operating method which comprises the steps of inserting an ignition-improving, solid fuel additive-containing apertured cartridge in the

path of fluid hydrocarbon fuel flow at a location upstream of a combustion zone within a spark ignition-actuated combustion system, said cartridge including the ignition-improving solid fuel additive dispersed in a solid matrix soluble in hydrocarbon fuel, flowing fluid hydrocarbon fuel through said apertured cartridge to progressively disintegrate said matrix, thereby releasing said additive into said fuel, and thereafter spark-igniting the additive-bearing fuel in a combustion zone.

8. The method of claim 2 wherein the solid fuel additive comprises alkali metal.

9. The method of claim 2 wherein the solid fuel additive comprises an alloy of potassium and sodium.

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