Hypergolic Systems: A Review in Patents

Gilson da Silva¹*, Koshun Iha²

¹Instituto Nacional da Propriedade Industrial – Rio de Janeiro/RJ – Brazil
²Instituto Tecnológico de Aeronáutica – São José dos Campos/SP – Brazil

Abstract: *Hypergolic reactions may be useful in civil and military applications. In the area of rocket propulsion, they constitute a potential field due to the reduced weight and complexity of fuel injection systems, allowing yet controlled use of the propulsors. This manuscript aimed at presenting different hypergolic systems and their particularities, comparing them with chemical propulsion systems, which are most commonly employed in rocket motors, for example.*

Keywords: *Hypergolic, Propellant, Monomethylhydrazine, Hydroxyethylhydrazine, Liquid hydrogen, Liquid oxygen.*

LIST OF SYMBOLS

DETA	Diethylenetriamine
EDA	Ethylenediamine
TNT	2, 4, 6-trinitrotoluene
HMX	Octogen
RDX	Hexogen
DNAZ	2-(N,N-dimethylamino)ethylazide
TMEDA	N,N,N',N'-tetramethyl-ethylene-diamine
TMPDA	N,N,N',N'-tetramethyl-1,3-diaminopropane
TMBDA	N,N,N',N'-tetramethyl-1,4-diaminobutane
AU	Astronomical unit (149,597,870,700 km)
LH	Liquid hydrogen
LOX	Liquid oxygen
MON	Mixed oxides of nitrogen
GLP	Gelled liquid propane
MMH	Monomethylhydrazine
HGF	Hypergolic green fuel
HEH	Hydroxyethylhydrazine
HEHN	Hydroxyethylhydrazinium nitrate
FTIR	Fourier transform infrared spectroscopy
NTO	Nitrogen tetroxide

INTRODUCTION

The term 'hypergolic' includes igniting spontaneously upon contact with the complementary explosive or energetic substance. Then, hypergolicity is the propriety of self-ignition

within milliseconds after fuel and oxidizer contact (Hawkins *et al.*, 2011). This propriety is very important in propellant systems, because it can substitute the multistage rocket with the separate ignition system, resulting in high combustion efficiency and low costs. To exemplify these systems, the hypergolic reactions can be used to improve ignition of nitroarene explosives, applied in unexploded ordnance, like bombs and mines, to neutralize these explosives, in agreement with the research of Koppes *et al.* (2010).

Koppes *et al.* (2010) taught a method to chemically neutralize a nitroarene explosive composition comprising in order to provide a nitroarene hypergol, having α, ω-amine and an accelerant by applying the nitroarene hypergolic to the explosive composition to improve its ignition. The α, ω-amine of the nitroarene hypergolic may include linear polyamines with or without nitrogen or other heteroatom within the structure of the compound, such as diethylenetriamine (DETA), ethylenediamine (EDA), propanediamine, and so on. The accelerant of the nitroarene hypergol may include appropriate hydridoborate salts (M^+BH_4), hydrazine, alkylated derivatives of hydrazine, or combinations.

The nitroarene hypergol provides a decrease in the delay to ignition of 90% or more, in agreement with Koppes *et al.* (2010), and an increase in heat generation. The nitroarene compounds that can be neutralized with the hypergolic system include nitrotoluenes, nitrobenzenes, nitronaphthalenes, nitrophenoxyalkyl nitrates, and their derivatives. The hypergols are added as pure liquids or as mixtures with other liquid or solid hypergols. In an unusual coupling with TNT, the amines with terminal amine groups (primary amines), i.e., α, ω-diaminoalkanes, reacted at both amine functionalities to provide a TNT-amine-TNT bridged product, with amines attaching at the ring carbons of the TNT bearing the methyl

group. DETA does this by leaving the central amine function unreacted. To the extent that this bridging could be maximized on the surface of TNT, there would be an energy release compressed into the smallest time scale, which is a condition favoring the evolution and conservation of heat, and thus a decrease in delayed ignition.

CIVIL APPLICATION OF A HYPERGOLIC SYSTEM

An inflatable restraint system (airbag) using a hypergolic reaction is taught by Blackburn (2006). In agreement with Blackburn (2006), the gas generating system or inflator used in many occupant restraint ones tends to be the heaviest and most complex component of the restraint system. Then, Blackburn (2006) systems can simplify the design and manufacturing of airbag inflators.

The device comprises a cartridge formed from a container, two materials stored in the container; however, the second one is separated from the first material. The combination of the materials forms a hypergolic mixture upon contact with each other. Under exposure of the gas generating to an elevated temperature, a portion of the container separating the first and second materials is breached, enabling the materials to combine to form the hypergolic mixture. A propellant charge may be used to generate gas, being the decomposition of the propellant initiated by the hypergolic reaction. The propellant can be a composition such as the ammonium nitrate.

According to Blackburn (2006), the hypergolic reaction can be produced by the contact of a first material in the liquid form, like glycerol or any suitable alcohol such as polyvinyl alcohol, and a second material comprising potassium permanganate. The first material in liquid form is important to increase the surface interaction between the materials.

MILITARY APPLICATION OF A HYPERGOLIC SYSTEM

Hypergolic reactions can be used to defense systems according to Thuman *et al.* (2011). A projectile comprising a reactive charge is used to promote the destruction of an explosive-charged weapon, such as bombs, homemade explosive devices, and air, water or ground craft comprising explosives.

An explosive can be made to detonate by the shock effect, which is generated by a splinter when it hits the explosive at high speed or by a pressure wave from an explosive charge (blasting). Then, the systems proposed by Thuman *et al.* (2011) consist in a projectile configured to penetrate the surface of the

shell upon impact so that a passage is opened into the explosive of the shell, through which passage the reactive charge is transferred to the explosive of the shell under the influence of the kinetic energy of the projectile. The projectile has a reactive charge disposed in at least one gas-and liquid-tight cavity to react and start a hypergolic reaction with the explosive.

The projectile can have the gas- and/or liquid-tight container charged with zinc, zinc stearate, zirconium, magnesium perchlorate, bismuth trioxide, or a liquid, such as pyrrolidine. The gas- and liquid-tight container is constituted by the all-covering metal foil for preventing undesirable reactions with the surrounding atmosphere.

When the reactive charge of the projectile is mixed with the weapon explosive, under effect from the kinetic energy of the projectile penetration, a reaction with the explosive occurs. Gas that is formed in the course of the burning generates an overpressure inside the weapon unit, which leads to splitting and destruction of the weapon unit. A suitable composition, being 99% by weight zinc and 1% by weight zinc stearate, is used, like a termed hypergolic composition, which, upon contact with the explosive weapon, spontaneously reacts.

PROPELLANTS

Useful propellant compositions were taught by Fawls *et al.* (2005), who described the effect of the oxygen in the metal passivation in the compositions of explosives and propellants. During the combustion process, the metal ingredients have an oxide shell formed in the surface that inhibits the oxidation of the metal, thereby reducing the overall available energy and forming a totally oxidized metal.

To improve the efficiency of the compositions, Fawls *et al.* (2005) taught how to increase the metal surface area, by means of the nanosized metallic particles, in combination with a halogenic oxidizer, to enhance the combustion of the metal by means of preventing the chemically-inhibiting coating formation in the metal surface. The fluorochemical species is pyrolytically or chemically degraded in the combustion or explosive zones, releasing halogens in the system. The fluorochemical compounds/atoms form a metallic fluoride in the surface, but they do not inhibit the further oxidation to the final desired product, metallic oxide, increasing the overall energy released.

In general, the conventional metal nanoparticles can be boron, aluminum or carbon in propellants, and the fluor compound can be a fluoroorgano chemical compound or fluoropolymer like microbeads, nanoparticles, powder or

other larger sized fluoroadditive (such as Teflon®, Viton®, or some other halogenated fluoropolymer additive). Additionally, energetic ingredients may be added to the fuel or hybrid grain to improve the energy output of these propellants, such as HMX, RDX, or other energetic ingredients.

Liquid rocket propellant systems produce thrust by means of expulsion of high velocity exhaust gases made by the reaction between a fuel and an oxidizer. Non hypergolic systems are useful, but they need complex ignition systems with igniters and/or catalyst beds, which are expensive, introduce extra weight to the thrust, and increase the risk of failure (Natan *et al.*, 2011).

HYPERGOLIC PROPELLANTS

The conventional hypergolic system is composed of hydrazine as the fuel component, being very toxic. Hawkins *et al.* (2011) taught a bipropellant fuel based upon salts containing the dicyanamide anion, employing nitrogen-containing, heterocyclic-based cations such as the imidazolium cation. While salt molecules contain highly energetic (formation of enthalpy), high nitrogen anions, the dicyanamide-based molecule solely displays fast ignition.

The fuel proposed by Hawkins *et al.* (2011) is stored in a propulsion system fuel tank and the oxidizer in a separate one. The ignition happens just after the contact of the fuel and oxidizer sprayed into a chamber in a rocket. The ionic liquid fuel can provide greater than 40% improvement in density over hydrazine fuels.

Watkins (2004) suggested a hypergolic fuel system comprising hydrogen peroxide, silane, and liquid fuel. In agreement with Watkins, in order that hydrogen peroxide is used as a propellant in rocket engines, a decomposition catalyst is required, which accelerates the decomposition of the hydrogen peroxide, however this technology is expensive. Therefore, a system where the hydrogen peroxide (H_2O_2) and silane (SiH_4) are contacted to improve the decomposition of the peroxide, forming a gas that is contacted with a liquid fuel, igniting the liquid fuel (such as kerosene), was proposed.

To thrust a rocket engine, the hydrogen peroxide is contacted with the silane in the combustion zone, at room temperature, to provide effective ignition. Upon ignition, a liquid fuel is fed to the combustion zone and combusted therein to provide thrust, since exhaust gases exit combustion zone of the rocket chamber through the exhaust outlet port.

A hypergolic fuel propulsion system containing a fuel composition (azide compound) and an oxidizer composition (hydrogen peroxide) is showed by Hallit and Bauerle (2004).

The azide compound in the fuel has at least one tertiary nitrogen and one azide functional group in combination with a catalyst, which has at least one transition metal compound (preferably, cobalt and manganese). An azide functional group is represented by $-N_3$. Upon oxidation after contact with the oxidizer composition, the azide compound loses nitrogen and reacts to produce the energy needed to provide thrust. The catalyst is added to the azide compound to produce a transition metal level in the fuel composition of about 0.2% or greater. The fuel composition and the oxidizer composition are brought into contact in stoichiometric ratios, which lead to the desired ignition. In general, with hypergolic fuels in rocket motor or missile engines, the oxidizer to fuel ratio may vary over a relatively wide range, depending on the performance desired, propellant tank pressures, and other operating parameters.

In such bipropellant mixtures, the fuel and oxidizer are unstable when mixed together, and they are generally stored separately. Bipropellant rocket motor propulsion systems consist of oxidizer and fuel propellant tanks, pressurizing system, plumbing, valves, and engine.

Currently known hypergolic, bipropellant rocket propulsion systems have a number of drawbacks. For example, one system consists of monomethylhydrazine (MMH) and red fuming nitric acid.

Stevenson *et al.* (2011) proposed a fuel mixture to use as hypergolic liquid or gel fuel in bipropellant propulsion systems, with the chemical compounds preferably having similar ignition characteristics as monomethyl hydrazine, and not being toxic or classified as a suspected human carcinogen. Fuel combinations consist of one or more of a family of hypergolic amine azides or hypergolic imidic amide compounds (first compound), mixed with one or more hypergolic tertiary diamine compounds (second compound). The hypergolic amine azides have the general structure $(R_1)(R_2)(R_3)N$, in which R_1, R_2, an R_3 can be an hydrogen and an aliphatic alkene, alkyne, or cycloalkyl group, without hetero-atoms or heterocyclic atoms, but where at least one of the R groups have an azide. Examples of hypergolic amine azides are the 2-(N, N-dimethylamino) ethylazide (DNAZ), 2-(N-cyclo-propylamino)ethylazide, bis(2-azidoethyl)methylamine, and so on.

The tertiary diamines have the general formula $R_4R_5N-R_6-NR_7R_8$, where R_4, R_5, R_7 e R_8 are aliphatic groups and R_6 may be aliphatic, alkene, or alkyne groups. Examples of hypergolic diamines include the N,N,N',N'-tetramethyl-ethylene-diamine (TMEDA), N,N,N',N'-tetramethyl-1,3-diaminopropane (TMPDA), N,N,N',N'-tetramethyl-1,4-diaminobutane (TMBDA), etc.

For optimal motor specific and density specific impulse values, it is generally desirable to incorporate into the fuel the maximum percentage of amine azide compound, which will still allow an acceptably low ignition delay of about 3 milliseconds to about 15 milliseconds. For example, a fuel containing about 33.3% DMAZ and about 66.7% TMEDA has an ignition delay of about 9.0 milliseconds.

DiSalvo (2012) described problems to prepare a low-storage temperature bipropellant for missions far from the sun greater than 3 AU, because the portion of the power budged consumed by heaters to prevent propellant freezing increases significantly. Then, fuels and oxidizers having low freezing points such as liquid hydrogen (LH) and liquid oxygen (LOX) are not suitable for using on planetary probes, because they require cryogenic storage vessels capable of containing them within several AU of the sun. In agreement with such author, propane is a potential low-temperature propellant, because it is readily liquefied by compression and cooling, melts at -189.9 ºC, and boils at -42.2 ºC. However, mixed oxides of nitrogen (MON) have freezing points not low enough to be ideal on deep space missions. Then, DiSalvo (2012) taught a method for preparing a bipropellant system comprising gelled liquid propane (GLP) fuel, which is well-suited for outer planet missions with additives, such as powders of boron, carbon, lithium and/or aluminum added to the fuel to improve its performance and enhance hypergolicity. The gelling agent can be silicon dioxide, clay, carbon, organic or inorganic polymers.

The oxidizer for the low-temperature propellant combination is MON-30 ($70\%N_2O_4+30\%NO$), produced by an exothermic reaction (6000 kcal/kg) between nitric oxide and dinitrogen tetroxide/nitrogen dioxide. The reaction should be done in vacuum system with the tank into the ice water bath to maintain the temperature of the reactants at 0 ºC. The MON-30 can be gelled at around -25 ºC with 3% of fumed silica by weight, using a plate churn mixer and its freezing point is of -81 ºC.

Propane can be gelled using a plate churn mixer placed inside an insulated polyethylene drum filled with a water-ethylene glycol mixture cooled at -55 ºC. A total of 20g of fumed silica is introduced into the mixing vessel, which is attached to a vacuum pump and cooled in dry ice. 500 grams of liquid propane is introduced into the mixing vessel. For the churning phase, the system is submerged in a 70/30-ethylene glycol/water bath and cooled to -55 ºC. The gelled propane has a freezing point of -189.9 ºC.

GREEN PROPELLANTS

Natan *et al.* (2011) showed a composition comprising a gelled fuel in which catalyst or reactive particles are suspended. The particles can ignite hypergolically with an oxidizer. The fuel and the oxidizer can be chosen from a wide spectrum of materials that are environmentally friendly (green propellants), without the need of carrying a complex ignition system. The catalyst or reactive particles can react spontaneously with an oxidizer or can be as catalysts to promote the ignition reaction. The rheological properties of the gelled fuel, e.g., the yield stress and the high viscosity while at rest, assure that no particle sedimentation takes place even at high acceleration levels of the vehicle. The hypergolic composition taught by them comprises at least one fuel in the form of a gel, at least one particulate ignition agent suspended in the fuel, and one oxidizer.

The ignition agent is selected from the group consisting of hydrazine, its derivatives and a metal hydride (selected from the group consisting of sodium borohydride, lithium borohydride and potassium borohydride), it can comprise a hypergolic catalyst too, like an alkyl-substituted amine and metal salt (selected from the group consisting of an alkyl-substituted diamine and triamine and metal salt of an aliphatic carboxylic acid – such as acetate, propionate, and butyrate).

The fuel is chosen from the group consisting of hydrocarbons, alcohols, amines, amides, metal-organic liquid compounds, alkaloids, and liquid hydrogen, with a gelling agent (nano-silica fumed powder, aluminum stearate and gelling polymers), and an oxidizer (hydrogen peroxide, liquid oxygen, nitrous oxide, nitrous acid, nitric acid, perchloric acid, cerium compounds, chlorites, bromites, fluorites, chlorates, bromates, fluorates and hyperchlorites).

The method for preparing a hypergolic composition for rocket propellant comprises adding a gelling agent to the liquid fuel and suspending a particulate ignition agent in this fuel, upon contact with an oxidizer, the ignition agent initiates the reaction between the fuel and the oxidizer.

MMH is a widely employed fuel in hypergolic and bipropellant systems. It has desirable propellant properties, but it is highly toxic, carcinogenic, and corrosive.

A rocket fuel composition comprising one or more tertiary amine azides is taught by Sengupta (2008). The fuel is hypergolic when combined with a strong oxidizer, such as red fuming nitric acid, hydrogen peroxide, nitrogen tetroxide, or hydroxyl ammonium nitrate.

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In agreement with Smith *et al.* (2010), hypergolic green fuel (HGF) can be produced from 2-hydroxyethylhydrazine (HEH) by means of its nitration, resulting in hydroxyethylhydrazinium nitrate-acetone.

At the beginning, the precursor HEH is pumped into a reactor under nitrogen atmosphere, set at 0.5 ºC, and deionized water is slowly added to the reactor under agitation. At 1 ºC and under agitation, nitric acid (HNO_3) is slowly added, in order to prevent the temperature increasing above 10 ºC. The pH of the mixture is about 8 to 9 at the beginning and the nitric acid should be slowly added until pH is in the range of 4.8 to 5.0. The produced hydroxyethylhydrazinium nitrate (HEHN) is light yellow and should be transferred into a rotary evaporator, where the water is removed and neutralized until reaches 10% of water.

The remaining water is removed by means of sparging the HEHN with nitrogen, then from the rotary evaporator and put into a storage vessel under nitrogen. To produce a hypergolic green fuel, HEHN produced must be mixed with the solvent acetone.

Smith *et al.* (2010) showed a one-step synthesis process to prepare a HGF propellant from HEH. In agreement with them, the process included: providing a solution of acetone in 2-hydroxyethylhydrazine, wherein the solution is about 15 to 50% by volume acetone in HEH; and adding nitric acid containing less than 5% water to the acetone-HEH solution to form the HGF propellant, wherein the molar ratio of nitric acid to HEH is less than about 0.05:1 to 1.4:1. The process efficiency of Smith *et al.* (2010) can be evaluated by means of a comparison between the sample and the reference Fourier transform infrared (FT-IR) spectrum.

INJECTORS

Bipropellant injection elements are useful in a typical liquid propellant rocket engine to facilitate the injection, distribution, mixing, and combustion of the elements in a combustion chamber. The injector may be composed by a system assembly, spark, to ignite the propellants by creating a standing flame or torch, whose composition is different from the propellant one. The size and mass are undesirable characteristics to this kind of system assembly, when used in small rocket engines (Fisher, 2009).

There are also known spark ignition systems for providing ignition sparks within a reaction zone in the combustion chamber. However, such systems present difficulties in fabricating system components and pose problems with component degradation during use. For instance, special injection orifices and manifolds are required to direct fuel and oxidizer and to create an easily ignited mixture of propellants at the exposed electrodes. Direct spark ignition systems through an injector faceplate can also add weight, increase design complexity, and typically operate at off-optimum mixture ratios (usually at fuel-rich rations) to preclude thermal damage to the electrodes, but which lower overall combustion performance.

Brown *et al.* (2010) taught a fuel manifold for the injector of a hypergolic rocket engine. According to them, hypergolic rocket engines that use the MON-25/MMH ((25% mixed oxides of nitrogen and 75% nitrogen tetroxide)/ (Monomethylhydrazine)) propellant combination may be relatively sensitive to pulsing frequencies imparted form the propellant system. Thus, compact vehicles that provide relatively small packaging envelopes may only further complicate this sensitivity.

The rocket engine proposed by Brown *et al.* (2010) includes a fuel manifold defined within an injector body, it comprises a main fuel chamber that is generally frustroconical in shape and defined about an axis. An oxidizer manifold is formed within the injector body, generally along the axis such that the main fuel chamber is defined around at least a section of oxidizer manifold.

The rocket engine includes yet a combustion chamber having an acoustic resonance frequency and a fuel manifold having a resonance frequency, which is at least an order of magnitude lower than the acoustic resonance frequency. An engine generally includes a thrust chamber assembly powered by a propellant system having a fuel and an oxidizer system. The fuel and oxidizer systems provide a fuel and an oxidizer into the thrust chamber assembly. The propellant combination self-ignites within the thrust chamber assembly to provide reliable performance and thrust.

MON-25 is highly reactive with MMH and has a tendency to drive unstable combustion processes. It should be understood that other oxidizers, such as nitrogen tetroxide (NTO) and other fuels, may alternatively or additionally be utilized.

The combustion chamber is retained adjacent to an injector body through a chamber retention ring. A valve system selectively communicates the propellant combination into the injector body. The oxidizer manifold may be at least partially defined along the thrust axis and the fuel manifold may be at least partially defined there around in an annular relationship. The fuel manifold may be utilized for any bipropellant rocket engine that operates at several thrust levels from, for example, relatively small thrust attitude control thrusters, medium thrust divert engines, or large axial engine rocket engines.

FINAL CONSIDERATIONS

The useful common propulsion systems need a complex ignition system, which are expensive and introduce extra weight to the thrust. Solid rocket systems do not allow a controlled actuation of the propulsion and show increased risk of the failure in the ignition step. The liquid propulsion brings security (LH/LOX) and/or healthy (MMH) problems. Then, a hypergolic propellant system seems to be the most secure and controlled system to be developed. On the other hand, considering the interaction between liquid compounds for hypergolic reaction, it is important to give special attention to the configuration of the nozzles in order to promote greater contact area between the hypergolic system components.

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