

[54] **SOLID HYPERGOLIC PROPELLANT SYSTEMS**

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[56] **References Cited**
UNITED STATES PATENTS

2,981,060	4/1961	Barnes	149/2 UX
3,103,782	9/1963	Olah et al.	60/219
3,141,295	7/1964	Olah	60/219

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3,203,171	8/1965	Burke et al.	149/19 X

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[57] **ABSTRACT**

Hypergolic solid oxidizer and fuel systems are provided whereby ignition and combustion of the separate solid fuel and oxidizer grains can be obtained by contacting of the respective grains. Suitable solid oxidizers include NOBrF₄, LiClO₄ · NOF, MgClO₄ · 2NOF, NO₂ClO₄, NO₂BF₄, (NO₂)₃ (AlClO₄)₆, NO₂AsF₆, NO₂SbF₆, and NO₂PF₆. Suitable solid fuels include LiAlH₄, LiBH₄, Li₂AlH₅, BeH₂, LiH₂ · BeH₂, tetramethylammonium hydrotriborate, triaminoguanidinium diazine, diaminotetrazine, 4-amino-3, 5-dihydrazine-1,2,4-triazole, N₂H₄(BH₃)₂, μ-(hydrazino)decaborane, 3,6-dihydrazine-s-tetrazine, NH₄N₃, (CH₃)₄NB₃H₈ and borane complexes with ammonia such as B₁₀H₁₂ · 2NH₃.

Completely fluorinated polyethylene resin is a suitable binder for the oxidizer system.

8 Claims, No Drawings

SOLID HYPERGOLIC PROPELLANT SYSTEMS

This invention relates to hypersolid combustion systems and, more particularly, to a novel hypersolid oxidizer and fuel composition. The term hypersolid relates to a system in which solid oxidizer bodies and solid fuel bodies are hypergolic with respect to each other. The broad concept of using such systems as heat and light generators as well as thrust generators is described in co-pending application Ser. No. 328,156 filed Nov. 29, 1963 by Iwanciw and MacLaren. The aforementioned application discloses that a hypergolic system can be formed when alkali metal hydrides are employed as fuels and solid interhalogen alkali metal fluorides are employed as oxidizers by forming the fuel and oxidizer materials into separate solid grains. When the grains are controllably brought into contact, a controllable combustion process is produced. A steady state combination process can be maintained by feeding the grains together at a constant predetermined rate. Merely by separating the two grains, the process can be stopped and combustion may be reinitiated by again bringing the grains together. Such systems have great utility as heat generators where the hot combustion gas can be used to turn a turbine or passed over heat exchange coils; as light generators wherein the hypersolid pairs can be substituted for the carbon arc source in search lights for example, and as thrust generators when the hypersolid pairs are combusted within a reaction motor and the combustion gas is exhausted through a suitable nozzle. Subsequent work, both experimental and theoretical, has led to a more complete understanding of the process of hypergolic solid combustion. This process requires that the fuel and oxidizer species react spontaneously when they are brought into intimate physical contact. This reaction is an ignition process that leads to a steady state combustion condition when the fuel and oxidizer elements are advanced at a constant rate. When the advancement of the element ceases or reverses in direction, the combustion process terminates. This type of behavior places very stringent requirements upon the physical and chemical nature of the compounds that may be successfully employed. The ignition phenomena must, of necessity, be a reaction whose energy of activation is extremely low. This energy is to be supplied by merely physically contacting the elements. In some cases, slight contact is sufficient to cause ignition and, in other cases, a higher degree of physical contact is required and is obtained by pressure on the contacting surfaces or by agitation of the contacting surfaces.

In addition, the reaction must supply sufficient energy to result in a gasification of fuel and oxidizer species from their respective surfaces. The transport dynamics require that the solids possess a sufficiently low thermal diffusivity which will not allow dissipation of the energy as sensible heat at a rate which limits the gasification process. In addition, the propellant elements must have sufficient strength and physical integrity to insure that mechanical failure does not occur on contact. Therefore, the chemical nature of the elements and their physical properties must be such that neither the oxidizer nor the fuel species exhibits monopropellant tendencies or are capable of self degradation when raised to temperatures that will exist at the solid surface during steady state combustion. In addition, impact or shock sensitive materials are undesirable from both this standpoint and from the standpoint

of use of the materials as propellant compositions in rocket motors. Further, the materials must have adequate thermal and physical properties such that the formation of a significant melt zone will not occur. A significant melt zone at the interface could cause operational difficulties as a result of the loss of grain integrity. Fuel and oxidizer systems other than those disclosed in the above patent application are described in U.S. Pat. Nos. 3,103,782 and 3,141,295.

Presently, both the fuel and oxidizer grains are fabricated by compression molding techniques. Consequently, in addition to the properties described above, the particular oxidizer and fuel species employed must also lend themselves to fabrication by this technique. Considerable difficulty has been encountered in obtaining satisfactory pressing with the oxidizers and fuels described in the aforementioned patent application. In particular, uniform compaction is not always achieved resulting in poor grain integrity and, in some cases, grain fracture occurs on ejection of the pressing from the die. One of the problems at present is to achieve all the desired physical and chemical properties described above in a single grain.

According to this invention, we have discovered a new group of oxidizer and fuel materials which are hypergolic with respect to each other. We have also invented compositions containing both these new materials and the materials previously disclosed that exhibit improved physical characteristics.

It is, accordingly, a primary object of this invention to provide a new class of solid oxidizer and fuel materials that exhibit hypergolic properties.

It is a further object of this invention to provide a source of combustion gases utilizing these new classes of hypergolic solid materials.

It is another object of this invention to improve the physical characteristics of hypersolid oxidizer and fuel grains.

These and other objects of this invention will be readily apparent from the following disclosure.

In view of the characteristics we determined to be necessary for the successful operation of a hypergolic solid system, the following broad parameters are considered to generally define the nature of the fuel and oxidizer species. Since the activation energy of the reaction is produced solely by intimate contact of the materials, oxidizers of a strongly acidic nature should be used in conjunction with basic fuels since acid-base reactions possess relatively low activation energies. Secondly, the products of this initial reaction should be capable of oxidative reaction to produce a high temperature for continuous combustion and the generation of heat, light and hot combustion gases. Since most oxidation-reduction reactions have relatively high activation energies, the approach is to use oxidizer-fuel pairs which undergo an acid-base reaction to supply the activation energy for a redox reaction.

As oxidizer components, we have discovered a large number of materials other than the metallic complex fluorides of the prior art and the aforementioned patent application that function in hypergolic solid systems. These oxidizers are nitrosyl and nitronium compounds and complexes thereof with metallic perchlorates. Preferred compounds consist of nitrosyl tetrafluorobromate (NOBrF_4) and complexes of lithium perchlorate and magnesium perchlorate with nitrosyl fluoride ($\text{LiClO}_4 \cdot \text{NOF}$ and $\text{MgClO}_4 \cdot 2\text{NOF}$). The preferred ni-

tronium compound is nitronium perchlorate (NO_2ClO_4) but other compounds such as nitronium aluminum chlorate [$(\text{NO}_2)_3(\text{AlClO}_4)_3$], nitronium tetrafluoroborate (NO_2BF_4), nitronium hexafluoroarsenate (NO_2AsF_6), nitronium hexafluoroantimonate (NO_2SbF_6), and nitronium hexafluorophosphate (NO_2PF_6) may be used. These materials may be used alone or in combination with a small amount of an ignition aid comprising an alkali metal hexafluorobromate such as CsBrF_6 . These solid oxidizers are hypergolic with solid fuels consisting of metallic hydrides such as LiAlH_4 , LiBH_4 , Li_2AlH_5 , BeH_2 , $\text{LiH}_2 \cdot \text{BeH}_2$, tetramethylammonium hydrotriborate, triaminoguanidinium diazide, diaminotetrazine, 4-amino-3,5-dihydrazino-1,2,4-triazole, $\text{N}_2\text{H}_4(\text{BH}_3)_2$, and μ -(hydrazino)decaborane, 3,6-dihydrazino-s-tetrazine, NH_4N_3 , $(\text{CH}_3)_4\text{NB}_3\text{H}_8$ and borane complexes with ammonia $\text{B}_{10}\text{H}_{12} \cdot 2 \text{NH}_3$.

Example 1

Granular nitronium perchlorate was added to granules of $(\text{CH}_3)_4\text{NB}_3\text{H}_8$. A hypergolic combustion occurred upon application of slight pressure of the materials producing a maximum temperature estimated at 3,788°K with a maximum theoretical specific impulse of 295 seconds.

Example 2

The procedure of Example 1 was repeated, substituting LiAlH_4 for $(\text{CH}_3)_4\text{NB}_3\text{H}_8$; hypergolic combustion occurred upon application of pressure to the materials producing a maximum temperature estimated at 4,250°K and theoretical specific impulse of 300 seconds.

Example 3

The procedure of Example 2 was repeated substituting $\text{B}_{10}\text{H}_{12}(\text{NH}_3)_2$ for LiAlH_4 . Hypergolic combustion was obtained upon vigorous stirring of the granules to provide intimate contact. A maximum temperature of 4,110°K was estimated with a theoretical specific impulse of 287 seconds.

The procedure of Example 3 was repeated using $\text{B}_{10}\text{H}_{12} \cdot 2\text{NH}_3$, tetramethylammonium hydrotriborate, amino dihydrazino triazole, dihydrazino tetrazine and solid mixture comprising 25% Li, 25% LiH, 37.5 percent polyethylene and 12.5 percent polypropylene-glycol. All the systems exhibited hypergolic combustion upon vigorous stirring of the granules.

Example 4

Granules of NOBrF_4 were added to granules of $(\text{CH}_3)_4\text{NB}_3\text{H}_8$ and hypergolic combustion occurred upon contact of the materials.

Example 5

Cast granules of a 50-50 mixture of triaminoguanidinium diazide and polyethylene were used as fuel in the procedure of Example 4 and hypergolic combustion occurred on contact.

Example 6

Granules of NOBrF_4 were added to granules of $\text{B}_{10}\text{H}_{12}(\text{NH}_3)_2$ and hypergolic combustion occurred on contact of the materials. This procedure was repeated using LiAlH_4 as a fuel and hypergolic combustion occurred upon application of slight pressure to the material.

The above examples are illustrative of hypergolic combustion of representative nitronium and nitrosyl compounds with a wide variety of fuel materials. The

above procedure can be repeated with combinations of the hereinbefore defined fuels and oxidizers of this invention and hypergolic combustion can be produced.

Up to this point, the invention has been described with respect to the simplest form of hypergolic system in which granules of the fuel and oxidizer are physically mixed. Such systems are useful in the batch-wise production of heat and light and in continuous systems wherein the generation of heat and light is regulated by controlling the mixing rate of the materials. In such systems the physical properties of the granules are not too important since the entire granule is consumed in a relatively short time. However, when the fuel and oxidizer are formed into separate grains and the combustion process controlled by regulating the rate at which the grains are fed together, as hereinbefore described, the physical properties of the materials assume greater importance.

Propellant candidates have been found which have ideal hypergolic properties, but fall short with respect to the thermal or physical properties when compressed into grains. Cesium hexafluorobromate (CsBrF_6) is a good example to illustrate this point. Its ignition characteristics are ideal, but it has a tendency to melt under steady state combustion conditions. Nitronium perchlorate, on the other hand, has adequate physical and thermal properties, but has exhibited difficulties in promoting easy ignition with many candidate fuels when compressed into a grain. The use of a binder to improve the physical characteristics of the fuel and oxidizer grains was considered. Considerable difficulty was encountered in using a binder, particularly with respect to the oxidizer, the more reactive of the components. Since most binders for fuel compositions also comprise substances that will burn once combustion has started, the choice of a fuel binder is not as critical. The oxidizer binder, however, must be compatible with the oxidizer and not cause the oxidizer grain to have monopropellant characteristics. Further, if a binder is used with the oxidizer grain, the material used and the amounts used must not impede the hypergolicity of the system. Prior to our discovery, no single chemical species has exhibited the desired chemical and physical properties as well as the necessary hypergolicity.

We have found that by incorporating a completely halogenated polyethylene resin (i.e., Teflon) into the oxidizer grain in amounts up to approximately 12 percent, a grain having hypergolic properties with respect to the aforementioned fuels can be produced which has the desired physical properties. The following examples are illustrative of this aspect of the invention.

Example 7

Finely divided nitronium perchlorate, cesium hexafluorobromate and Teflon were thoroughly mixed in proportions, by weight, of 64 percent nitronium perchlorate; 27 percent cesium hexafluorobromate; and 9 percent Teflon, the mixture was compacted under 10,000 psi pressure at 70°F temperature. The resultant grain in the form of a cylinder 1 inch in diameter was ejected from the die and examined for physical defects. No grain fractures were observed. A composite fuel grain comprising 80 weight percent $\text{B}_{10}\text{H}_{12} \cdot 2\text{NH}_3$ and 20 weight percent polyethylene was also compacted in a die to form 1 inch cylindrical grain. This grain was also ejected from the die

and examined for physical defects. No grain fractures were observed. The Teflon employed in manufacturing the oxidizer grain was Allied Chemical Company's HALON TEF TYPE G-80 and polyethylene was Allied Chemical Company's ultrahigh molecular weight polyethylene TYPE AC 1220. The fuel and oxidizer grains were mounted in a hypergolic combustion device which permits the grains to be fed together at a constant controllable rate. The grains were physically contacted and ignition occurred. The grains were then fed at constant rates varying from 0.02 inch per second to 0.37 inch per second and stable combustion was maintained throughout the range of feed rates. The combustion process was terminated both by withdrawing grains from each other and by decreasing the feed rate to below 0.02 inch per second. In the latter case, the combustion process continued until the separation of the grains was so great that the heat transfer and mass transfer processes could no longer sustain combustion. Reignition was obtained by bringing the grains once more into contact. Upon completion of a test cycle, the grains were examined for physical defects and were found to be intact and capable of subsequent reignition.

Example 8

An oxidizer grain was formed from 78 percent nitronium perchlorate, balance cesium hexafluorobromate compressed into a 1 inch grain. The fuel grain was the same as in Example 1. The two grains were mounted in the hypergolic combustion apparatus and ignited as in Example 1. A feed rate of 0.03 inch per second was used on a test burning time of 7.2 seconds. A post-firing inspection of the oxidizer grain revealed longitudinal cracking in several places in the vicinity of the contacting surface. The surface was also jagged and several fragments of the oxidizer were found in the bottom of the combustion apparatus. Apparently the oxidizer grain's integrity was compromised as a result of thermal expansion and contraction experienced during the ignition combustion and termination of the combustion. In the above examples, CsBrF₆ is incorporated as an ignition aid, but is not essential. Ignition will occur without CsBrF₆ if sufficient pressure or agitation of the grain is utilized.

A series of tests were run to determine the operating characteristics of other systems wherein Teflon is employed as a binder for the oxidizer grain. The result of a portion of these experiments is tabulated in Table 1. As can be seen from Table 1, the oxidizer-Teflon composition is compatible with several hypergolic fuel systems. The maximum per cent of Teflon that may be employed without impairing the hypergolicity varies with the systems, but appears to be a maximum of about 12 percent. Above this amount of Teflon, no system exhibits hypergolicity. Of course, it is not desirable to utilize the maximum amount of Teflon since the inclusion of this material with the oxidizer tends to reduce the specific impulse of the system. The best results were obtained in using weights of Teflon from about 9 percent to about 11.3 percent. Below 9 percent, the binding effect and the improvement of the physical characteristics drop off rapidly and below approximately 5 percent

Teflon, there is no notable improvement in the thermal characteristics

TABLE 1

Test No.	(wt %) Oxidizer Comp	Fuel Comp	Results
1	79.8% NO ₂ ClO ₄	B ₁₀ H ₁₂ ·2NH ₃	Ignition with slight agitation
2	11.3% Teflon 8.9% CsBrF ₆ 72.7% NO ₂ ClO ₄	B ₁₀ H ₁₂ ·2NH ₃	Ignition with slight agitation
3	9.1% Teflon 18.2% CsBrF ₆ 64.0% NO ₂ ClO ₄	B ₁₀ H ₁₂ ·2NH ₃	Ignition on slight pressure
4	9.0% Teflon 27.0% CsBrF ₆ 79.8% NO ₂ ClO ₄	Tetramethylammonium hydrotriborate	Ignition on vigorous agitation
5	11.3% Teflon 8.9% CsBrF ₆ 64.0% NO ₂ ClO ₄	Tetramethylammonium hydrotriborate	Ignition on vigorous agitation
6	9.0% Teflon 27.0% BrF ₃ 64.0% NO ₂ ClO ₄	Amino Dihydrazino Triazol	Ignition on vigorous agitation
7	9.0% Teflon 27.0% CsBrF ₆ 79.0% NO ₂ ClO ₄	Dihydrazino Tetrazine	Ignition on vigorous agitation
8	11.3% Teflon 8.9% CsBrF ₆ 64.0% NO ₂ ClO ₄	Dihydrazino Tetrazine	Ignition on vigorous agitation
	9.0% Teflon 27.0% CsBrF ₆		

and physical properties of the grains. The tabulated results relate to experiments using nitronium perchlorate as the primary oxidizer; however, the use of Teflon as a binder in grains of the aforementioned oxidizers will also produce a grain having improved physical properties.

This invention has been disclosed with respect to various specific examples; however, these examples are illustrative rather than limiting. The invention includes various obvious modifications and substitutions and is limited solely by the following claim.

We claim:

1. In a process for producing hypergolic combustion which comprises providing a solid oxidizer grain and a solid fuel grain, said oxidizer and fuel being members of an acid-base pair capable of generating sufficient energy from an acid-base reaction to activate an oxidation-reduction reaction between said oxidizer and fuel, and placing said oxidizer grain and fuel grain in intimate contact for sufficient time to initiate said oxidation-reduction reaction, the improvement wherein said oxidizer grain comprises a material selected from the group consisting of NOBrF₄, LiClO₄·NOF, MgClO₄·2NOF, NO₂ClO₄, (NO₂)₃(AlClO₄)₆, NO₂AsF₆, NO₂SbF₆ and NO₂PF₆.

2. The process of claim 1 wherein said oxidizer grain contains an ignition aid comprising an alkali metal hexafluorobromate.

3. The process of claim 1 wherein said oxidizer grain contains from 5 to 12 percent by weight of a totally fluorinated polyethylene resin.

4. A hypergolic solid oxidizer grain consisting essentially of 64% NO₂ClO₄, 27% CsBrF₆ and 9 percent totally fluorinated polyethylene.

5. The process of claim 1 wherein said fuel grain comprises a material selected from the group consisting of metal hydrides, tetramethylammonium hydrotriborate, diaminotetrazine, 4-amino-3,5-dihydrazino-1,2,4 triazole, $N_2H_4(BH_3)_2$, μ -(Hydrazino) decaborane, 3,6-dihydrazino-s-tetrazine, NH_4N_3 , triaminoguanidinium diazide, $(CH_3)_4NB_3H_8$ and $B_{10}H_{12} \cdot 2NH_3$.

6. The process of claim 5 wherein the fuel grain contains up to 50 percent by weight of polyethylene as a binder.

7. In a method for producing thrust from a reaction motor which comprises providing a solid oxidizer grain and a solid fuel grain within said reaction motor, said oxidizer and said fuel being members of an acid base pair capable of generating sufficient energy from an acid base reaction to active an oxidation-reduction reaction between said oxidizer and fuel; placing said oxidizer and fuel grains in intimate contact within said re-

action motor for sufficient time to initiate said oxidation-reduction reaction whereby gaseous combustion products are produced within said reaction motor and exhausting said gaseous combustion products from said reaction motor whereby a propulsive thrust is produced; the improvement wherein said oxidizer grain comprises a material selected from the group consisting of $NOBrF_4$, $LiClO_4 \cdot NOF$, $MgClO_4 \cdot 2NOF$, NO_2ClO_4 , $(NO_2)_3(AlClO_4)_6$, NO_2AsF_6 , NO_2SbF_6 and NO_2PF_6 .

8. The method of claim 7 wherein said fuel grain comprises a material selected from the group consisting of metal hydride, tetramethylammonium hydrotriborate, diaminotetrazine, 4-amino-3,5-dihydrazino-1,2,4-triazole, $N_2H_4(BH_3)_2$, μ -(hydrazino)decaborane, 3,6-dihydrazino-s-tetrazine, NH_4N_3 , triaminoguanidinium diazide, $(CH_3)_4NB_3H_8$ and $B_{10}H_{12} \cdot 2NH_3$.

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