Self-igniting Fuel-oxidizer Systems and Hybrid Rockets

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Fuel-oxidizer combinations capable of self-igniting simply on coming into mutual contact have been extensively used in bi-liquid rockets. In hybrid (solid fuel-liquid oxidizer) rockets too the self-igniting (hypergolic) propellant could be suited ideally. The relative non-existence of the hybrid rockets has been partly because of the paucity of suitable hypergolic solid fuels. The development of such fuels is hampered because of the lack of understanding of the chemical reactions occurring between the fuel and the oxidizer leading to ignition. The chemistry of these highly exothermic reactions occurring in sub-millisecond condns in the pre-ignition stage is being studied for the past several years, in an effort to evolve suitable self-igniting systems. A major aspect of this work relates to the solid N-N-bonded derivatives of hydrazines, which have been conceived as self-igniting fuels for the first time. Many of these compounds ignite readily, with short ignition delays on coming into contact with liquid oxidizers, like HNO₃ and N₂O₄. Polymeric resins having N-N bonds and reactive end-groups have been evolved to serve as fuel-binders for self-igniting compositions. This review narrates briefly the main highlights of the work carried out on hypergolic systems. A report on the hybrid rockets and their current status is also included.

Introduction

Combustion of a fuel-oxidizer combination has been the main source of energy world over. By 'combustion' is meant a rapid oxidation reaction producing heat and light. A 'fuel' in the presence of an 'oxidizer', when initiated by an appropriate impetus like, a spark, a heat source or a catalyst gets ignited resulting in the onset of combustion. Once ignited the process is self-sustained by its own heat release and usually lasts till one or both the components (fuel and oxidizer) are exhausted, unless the process is blown-off (extinguished) by other means. The initiation of ignition is essential to overcome the activation energy barrier for the combustion reaction to take place. Fuels like wood, kerosene or gasoline for that matter do not ignite spontaneously though they are constantly in contact with aerial oxygen.

Like many other energy driven devices the propulsion of the chemical rockets is based on the combustion of a fuel-oxidizer combination (propellant). Burning propellant gives off hot gases, which are expelled through a nozzle to produce the thrust that lifts the vehicle off the ground. In the commonly used bi-liquid (liquid fuel-liquid oxidizer) propellant rockets based on kerosene or 'alcohol-liquid oxygen (LOX), e.g., the fuel and oxidizer are stored separately, and pumped into the combustion chamber where they are made to ignite by a separate energy device, namely an igniter. Once ignited, the thrust is controlled by varying the rate of pumping of the fuel and oxidizer into the combustion chamber. Similarly the solid propellant rockets, wherein the powder oxidizer is embedded in a matrix of polymeric fuel, and thus in constant touch with one another, do not ignite, as such. In fact the ideal fuel-oxidizer combination for solid rockets must not react at all chemically for years, during storage. The propellant is made to ignite by a separate hot-spot producing igniter incorporated in the grain-port, whenever required.

There are, however, certain chemicals (fuels) which ignite spontaneously simply on coming into contact with oxidizers, and do not need a separate source for ignition. For example, liquid fuels like anhydrous hydrazine (AH), monomethylhydrazine (MMH) and unsymmetrical dimethylhydrazine (UDMH) ignite on coming into immediate contact with oxidizers such as, nitric acid or dinitrogen tetroxide (N₂O₄), giving off hot gases. Evidently, such fuel-oxidizer combinations could be a natural choice as rocket propellants, since they simplify the engine design by not using an igniter, and provide a
convenient way of achieving repeated on-and-off capability at no extra cost. Indeed the self-igniting, also known as ‘hypergolic’ systems, have been widely used in bi-liquid propellant rockets. Besides the high reliability of chemical ignition has made them the propellant of choice in the well-known missions, like the Apollo manned lunar-landing expedition. Much of the credit for landing on the moon and bringing the astronauts back safely goes to the hypergolic fuel MMH, which was used in the command service and lunar excursion modules in the descent and ascent stage, respectively.

Self-igniting (hypergolic) propellants are of special importance in hybrid rockets. In hybrid systems the propellant usually comprises a solid fuel and liquid oxidizer, which are stored separately and brought together only when fired. When the propellant is hypergolic, all that is needed is spraying of the liquid oxidizer onto the solid fuel to initiate ignition. Since no separate igniter or firing mechanism is needed the system could be conveniently used for on-and-off capability, and modulating thrust simply by operating a single valve controlling the oxidizer-flow. Also the hybrids being inherently safer than the solid rockets, have received increasing attention in the recent past.

However, unlike the hypergolic bi-liquids the evolution of practical self-igniting hybrid propellants is a highly involved task. Most often the solid fuels do not ignite with the usual liquid oxidizers. Even when they do so the ignition precedes a long delay after they come in contact, which leads to the ‘hard’ start of the engine. On the other hand, if a highly reactive oxidizer like liquid fluorine is used, the ignition delay (ID), no doubt will be reduced, but other serious problems like the corrosive nature of the combustion products besides handling and transportation, are encountered. Hypergolic hybrid systems comprising commonly used storable chemicals, having short ignition delays, and producing innocuous combustion products are indeed rare.

The main cause of the self-ignition of hypergolic systems is believed to be the rapid generation of heat by the exothermic chemical reactions ensued in the pre-ignition stage. In hybrid systems, when the liquid oxidizer comes into contact with solid fuel exothermic reactions start at the surface of the fuel. A complex array of chemical reactions occurs before the onset of ignition. The chemistry of these reactions is highly complex because several types of reactions occur, often simultaneously, in very short intervals. The heat evolved decomposes and/or vaporizes the solid fuel and liquid oxidizer, and raises the gaseous products to ignition temperature. The understanding of these reactions, which invariably last sub-milliseconds only, being poor, there is not even a rule of thumb for predicting a priori the hypergolicity of a particular fuel-oxidizer system, leave aside the actual estimation of the ignition delay. Surprisingly, not many systematic studies have been made to understand the chemistry of these reactions.

The present review is an overall summary of the investigations carried out, mainly by the author and his group for over the past two decades. The studies carried out mainly pertain to evolving an understanding of the pre-ignition chemical processes that lead to hypergolic ignition, in an effort to evolve solid fuels, having short ignition delays with storable oxidizers like nitric acid and dinitrogen tetroxide. Earlier reports on the hypergolic systems by Jain covered only some aspects of the subject as the work progressed. A status report on the development of hybrid rockets is also presented.

Earlier Studies

The ignition delay i.e. the elapsed time preceding ignition after the oxidizer comes in contact with the fuel, is a complex function of many physico-chemical processes. However, it primarily depends on the chemical reactivity of the fuel with the oxidizer. The complexity of the pre-ignition reactions and the number of other process parameters involved, has precluded the development of any theoretical model to predict the ID of any particular system. The IDs have to be measured by experimental methods, not only for screening out the promising systems but also for determining their magnitude. While the ID should be as short as possible, it largely depends upon the chemical nature of the fuel-oxidizer system chosen. Several studies pertaining to the measurement of IDs of hybrid systems are available in the literature.

Oxidizers

The choice of suitable liquid oxidizers for self-igniting hybrid propellants is rather limited. Fluorine based oxidizers like, $F_2$, CIF$_3$, and FCIO$_3$ are excluded because of the highly corrosive and toxic nature of their own and the combustion products. Other
suitable oxidizers are: HNO₃, N₂O₄, and H₂O₂. Of these, pure nitric acid, i.e., white fuming nitric acid (WFNA), N₂O₄ and red fuming nitric acid (RFNA), which is a mixture of nitric acid and dinitrogen tetroxide, have been used most often. Highly concentrated H₂O₂ is too risky to handle, and as a result it is largely avoided.

Fuels

Unlike the hydrocarbons, used in most combustion driven devices including rockets, hypergolic solid fuels are rather rare. One of the early hypergolic combinations tested in hybrid motors was polyethylene-H₂O₂ (90 per cent)⁴. Polymers like, polystyrene and butyl rubber also ignite with highly concentrated hydrogen peroxide. Bernard⁴ found furfuralamide and furylarylène filled polymers to be hypergolic with nitric acid. Mouet and Barrere⁵ used solid amines like, p-toluidene, p-phenylenediamine and p-anisidine to make hypergolic polymeric composites with HN0₃. Similarly, mixtures of amines and metal or metal hydrides powders embedded polymeric composites have been tried as fuels for hypergolic hybrid systems. Invariably, however, a powder fuel becomes non-hypergolic or its ignition delay becomes intolerably long when used as filler in polymeric composites. Also, fuels like amines and metal hydrides have to be handled and stored carefully to avoid surface oxidation. p-phenylene-diamine, LiAIH₄ etc., e.g., easily undergo aerial oxidation and could become deactivated during storage and lose their hypergolicity altogether.

Pre-ignition Reactions

Ignition delays of several amine-based systems have been measured as a function of certain variables, and based on their trends tentative conclusions have been drawn concerning the nature of the exothermic reactions taking place in the pre-ignition stage. Only in very few cases an attempt to actually identify the pre-ignition products was made using chemical methods. Measurement of ignition delays of powdered α- and p-phenylenediamine and furfuraldehyde with HNO₃ and N₂O₄ by Bernard and coworkers⁶ led them to emphasize the role of surface reactions in hypergolic ignition of liquid-solid (hybrid) systems. The study revealed that the reaction occurs in an adsorbed phase on fuel-surface, and the active agent responsible for promoting the hypergolic reaction with nitric acid is NO₂⁺. Munjal and Parvatiyar⁷ examined the pre-ignition products of aniline formaldehyde-fuming nitric acid system and found these to contain the nitrated products of the parent compound, and trinitrobenzene. These studies indicate the occurrence of nitration reaction in the pre-ignition stage with nitric acid oxidizer. On the other hand, in liquid amine-nitric acid systems, a Lewis-type acid-base reaction with the formation of a salt occurs⁸. Likewise, a pre-ignition product of the bi-liquid, hydrazine-RFNA system has been found to be hydrazinium nitrate⁹.

Hydrazones

It is apparent that till about mid 1970s, approaches to develop solid fuels for hypergolic hybrid rockets were based on hit and trial methods. Not many self-igniting solid-liquid systems were reported in the open literature. A systematic study leading to an understanding of the initial exothermic reactions leading to ignition had not emerged. It was at this stage, that the author initiated a research program to examine the chemical aspects of hypergolic ignition, in an attempt to evolve new solid fuels for self-igniting hybrid systems at the author’s Institute.

Our approach was simple and straightforward. An analogy to the fact that the liquid hydrazines ignite instantaneously on coming in to contact with liquid oxidizers such as, white or red-fuming nitric acid (WFNA or RFNA) and N₂O₄, suggested that solid hydrazines could be considered as suitable fuels for hypergolic hybrid propellants. Indeed, solid hydrazines ignite on coming into contact with RFNA, but they are rather rare and difficult to prepare.

It is generally realized however, that the main cause of enhanced reactivity of hydrazines towards oxidizers is the presence of the nitrogen-nitrogen (N-N) bond in their structures. It was envisaged that solid organic compounds containing one or more N-N bond/s, like the hydrazines, might ignite on coming into contact with liquid oxidizers. Of the simplest solid compounds having N-N bonds are the condensed products of hydrazines with aldehydes and ketones, namely the hydrazones. The hydrazones are non-hygroscopic, high melting solids, which most often decompose exothermally at higher temperatures. A preliminary examination of some randomly selected hydrazones indeed showed that they do ignite on coming into contact with HNO₃ (ref. 11). The ignition behavior of hydrazones, thus became the prime focus of our investigation in
relation to developing new hybrid hypergolic systems. It may be worthwhile to mention that prior to our work no study concerning the self-igniting nature of hydrazones had been reported in the literature.

Our initial work was concerned with the condensed products of phenylhydrazine and UDMH with various aldehydes. Specifically, substituted benzaldehydes having different groups at the para position were chosen so that the products have very similar chemical structures but differ in chemical reactivity. These hydrazones could be synthesized in a single step by the following reaction:

\[ \text{R} - \text{CO} - \text{CHO} + \text{H}_2\text{N} - \text{NR}_2 \text{R}_2 \rightarrow \]

\[ \text{R} - \text{C} = \text{N} - \text{NR}_2 \text{R}_2 + \text{H}_2\text{O} \quad \ldots (1) \]

As envisaged, several of the hydrazones in the powder form were found to ignite readily with both WFNA and RFNA. Some of them had very short IDs indeed as measured by a newly-designed and fabricated drop-tester-type device, having an electronic timer and a photo-sensitive transistor circuit. In general the ignition delays of the derivatives of UDMH were shorter (35 to 165 ms) than those of phenylhydrazine (~100 to 400 ms). These hydrazones ignite with shorter IDs with WFNA as compared to RFNA. It was also noticed that while all the dimethylhydrazones ignited readily with no particular order in ID, a comparison of the IDs measured under identical set conditions of several para-substituted benzaldehydehydrazones indicated that the ignition delay perhaps depends on the nature of the substituent group of benzaldehyde. Indeed, a remarkably consistent variation in the ID was observed with different substituents, and the p-nitrobenzaldehyde derivative did not ignite at all on coming into contact with WFNA. The ID increases with the substituent (R) in the following order:

\[ \text{CH}_3 < \text{H} < \text{N(CH}_3)_2 < \text{OCH}_3 < \text{OH} < \text{Cl} < \text{NO}_2 \]

This order suggests that substitution by an electron donating group causes a decrease in the ID, while an electron-withdrawing group like -NO₂ makes the system non-hypergolic. In this context, it is worth noting here that the velocity of nitrination reaction of benzene with HNO₃ decreases more or less in the same order with these substituent groups on the ring. The observed trend in the ID with the variation in the substituent, thus indicated the role of the nitrination reaction in the pre-ignition stage. Incidentally the presence of -NO₂ group on the N-phenyl ring also results in non-ignition; e.g., the various 2,4-dinitrophenylhydrazones examined during this study were all found to be non-hypergolic with WFNA.

Further evidence for the occurrence of nitrination reaction in the pre-ignition stage was provided by a chemical analysis of the quenched reaction products of benzaldehydehydrazon-nitric acid system. The isolation of p-nitrobenzoic acid and benzoic acid as reaction intermediates confirmed the occurrence of the nitrination and also the oxidation reactions in the pre-ignition stage. These observations established firmly that the hypergolicity is related to the chemical reactivity in these systems.

The importance of this work was duly recognized by the Soviets, who translated and published the author’s paper in Russian in their journal, Rocket Techniques and Cosmonautics, as a select paper of their choice, with permission of the AIAA.

Parameters Affecting ID

It is recognized that the magnitude of ID of powder materials depends upon physical (particle size, compactness etc.) as well as the compositional parameters (oxidizer concentration, fuel/oxidizer ratio, additives, etc.). The effect of these parameters was determined carefully using suitable systems.

Particle Size and Compactness

The ignition delay of some selected compounds namely, furfuraldehyde- and p-dimethylaminobenzaldehyde-phenylhydrazones (FPH and DBPH), with RFNA decreases with decrease in the particle size, to some extent. Fine powders (<125 μm) show two ignition delays corresponding to two flames: the first flame extinguishes soon after appearing but the second flame persists. This strange ignition behavior of fine powders was observed for the first time in our laboratory, which appears to be a general phenomenon. Powder amine fuels, benzidine and p-phenylenediamine also exhibited successive two flames below a certain particle size. Compacting the powder fuel results in increasing the ID. Pellets of two hydrazones, FPH and DBPH, made by
compressing the powders of selected particle size (212-106 μm) at different pressures (0-100 kg/cm²) ignited readily with nitric acid but the ID increased with pressure.

**Oxidizer Concentration**

The effect of NO₂ concentration in nitric acid on the IDs of phenylhydrazones and dimethylhydrazones powders was evaluated under carefully controlled experimental conditions. As anticipated the IDs are greatly influenced by the composition of the acid. The lowest IDs are obtained with pure anhydrous acid rather than RFNA. Increasing the concentration of NO₂ in the acid results in longer IDs. In some cases, a maximum in the ID vs NO₂ concentration plots was observed, with acid having around 12-16 per cent NO₂, giving longest IDs.

The concentration of water in nitric acid has a drastic effect on IDs. The IDs of some typical p-substituted benzaldehydephenylhydrazones become longer with an increase in the water content. At about 12 per cent water concentration, no ignition takes place. It is therefore desired that the water content be kept as low as possible, for short IDs. The addition of fuming sulphuric acid in small amounts further increases the IDs of phenylhydrazones, but has virtually no effect on the dimethylhydrazones.

These results point further to the nitration of the phenyl ring in the pre-ignition stage and supplement the chemical evidence viz. isolation of benzoic acid and p-nitrobenzoic acid from the pre-ignition reaction products of benzaldehydephenylhydrazone-HNO₃ system, obtained earlier. Based on these evidences, a scheme of reactions occurring in the pre-ignition stage (as shown below) was proposed.

**Oxidation**

\[
\begin{align*}
2 \text{HNO}_3 & \rightarrow \text{NO}_2 + \text{NO} + \text{H}_2\text{O} + \text{O}_2 \\
\text{C}_6\text{H}_5-\text{CH} = \text{N}-\text{NH}-\text{C}_6\text{H}_5 & \rightarrow \text{C}_6\text{H}_4-\text{CH} = \text{N} = \text{N}^- - \text{C}_6\text{H}_5 + \text{OH}^- \\
\text{C}_6\text{H}_5-\text{CHO} & \rightarrow \text{C}_6\text{H}_6\text{COOH} \\
\text{N} = \text{N}^- - \text{C}_6\text{H}_5 + \text{OH}^- & \rightarrow \text{N}_2 + \text{C}_6\text{H}_5\text{OH}
\end{align*}
\]

**Nitration**

\[
\begin{align*}
2 \text{HNO}_3 & \rightarrow \text{NO}_2^+ + \text{NO}_3^- + \text{H}_2\text{O}
\end{align*}
\]

\[
\begin{align*}
\text{C}_6\text{H}_5-\text{CH} = \text{N}-\text{NH}-\text{C}_6\text{H}_5 & \rightarrow \text{NO}_2, \text{C}_6\text{H}_5-\text{CH} = \text{N} = \text{N}^- - \text{C}_6\text{H}_5, \text{NO}_2 \\
\text{O} & \rightarrow \text{NO}_2, \text{C}_6\text{H}_5-\text{CHO} + \text{N}_2 + \text{HO}-\text{C}_6\text{H}_4\text{NO}_2 \\
\text{NO}_2, \text{C}_6\text{H}_5-\text{CHO} & \rightarrow \text{NO}_2, \text{C}_6\text{H}_5-\text{COOH} \\
\text{HO}-\text{C}_6\text{H}_4, \text{NO}_2 \text{or } \text{C}_6\text{H}_5\text{OH} & \rightarrow \text{HO}-\text{C}_6\text{H}_4(\text{NO}_2)_3 \\
\Delta & \rightarrow \text{CO}_2, \text{N}_2, \text{H}_2\text{O}, \text{etc.}
\end{align*}
\]

**Oxidizer/Fuel Ratio**

The effect of relative amounts of fuel and oxidizer on the ID of hydrazones with nitric acid has been studied in detail. Several of these hydrazones give minimum IDs at the mixture ratio close to the stoichiometric ratio, although the variation is not large. This is expected since the heat liberated by a fuel-oxidizer reaction should be maximum at stoichiometric ratio.

**Combustion Related Studies**

Studies relating to the combustion behavior of hydrazones with nitric acid include, experimental determination of the heats of combustion both with nitric acid and oxygen (calorific value), volume of the gases generated and identification of the gaseous products. Apparently, both the heats of combustion (with HNO₃) and volume of gases generated depend on the substituent in the phenyl ring of the hydrazones. The electron releasing groups enhance these parameters in the case of phenylhydrazones, whereas no such effect was observed in the case of dimethylhydrazones. The heats of formation of the hydrazones determined from the calorific values are high, even positive in some cases, which is a desirable feature for their use in propellants. The major products of combustion with nitric acid were found to be, N₂, CO, NO, H₂O, N₂O, and CO₂ along with trace amounts of O₃, as determined by mass spectra of the gaseous product samples collected at room temperature.

**Monothiocarbohydrazones**

Our discovery of the hypergolic nature of phenyl- and dimethylhydrazones with nitric acid led
us to examine other compounds having N-N bonds in their structures. Realizing that the hypergolicity could be related to the number of N-N bonds, compounds having two N-N bonds in a molecule became the next targets. Derivatives of carbohydrazide (which has two N-N bonds), with several aldehydes were examined. Interestingly, they were all found to be non-hypergolic with WFNA. It is thus apparent that not all compounds having N-N bonds are hypergolic. Coincidentally, however, we also examined the solid derivatives of thiocarbohydrazide (TCH) and to our surprise, they all ignited readily with nitric acid\textsuperscript{16}. Like the hydrazones, the monothiocarbohydrazones are non-hygroscopic solids which could be prepared easily by the following reaction:

\[
\begin{align*}
\text{H}_2\text{N}-\text{NH-C(=S)}-\text{NH}-\text{NH}_2 + \text{R}_1\text{R}_2\text{C}=\text{O} & \rightarrow \\
\text{H}_2\text{N}-\text{NH-C(=S)}-\text{NH}=\text{CR}_1\text{R}_2 + \text{H}_2\text{O}
\end{align*}
\]  

A detailed examination of the \textsuperscript{1}H NMR spectra shows that these derivatives exist in two isomeric structural forms: linear (as shown above) and cyclic, depending upon the type of aldehyde or ketone used\textsuperscript{17}. A total of eighteen mono-derivatives of thiocarbohydrazide (TCH) were synthesized. Considering the high purity of these compounds the Sadlier Research Laboratories Inc. requested for the samples, to include their NMR and IR spectra in their Standard Spectra supplements, which were subsequently published\textsuperscript{18}.

\textbf{Ignition Related Studies}

The monothiocarbohydrazones are extremely reactive towards anhydrous nitric acid and ignite with very short ignition delays (15 to 50 ms), much shorter than those of the hydrazones. Here again the IDs of over a dozen of the various p-substituted benzaldehydethiocarbohydrazones were found to vary more or less in the same order with the substituent as those of the hydrazones. Substitution by an electron releasing - group, like the -N(CH\textsubscript{3})\textsubscript{2} tend to decrease the ID, whereas the electron-withdrawing -NO\textsubscript{2} group makes the system non-hypergolic. There was no significant effect of either the particle size or the O/F ratio on the IDs. In most cases, however, the IDs were found to increase with the NO\textsubscript{2} content of the acid\textsuperscript{16}.

In order to get an insight of the chemical reactions occurring in the pre-ignition stage, a blended mixture of benzaldehydethiocarbohydrazone diluted with glass powder (to prevent ignition) was reacted with nitric acid and subjected to chemical analysis. Benzoic acid, p-nitrobenzoic acid, benzaldehyde, sulphur trioxide, nitrogen dioxide and nitrogen were isolated as pre-ignition reaction intermediates. A scheme of reactions involving neutralization, nitration and oxidation occurring in the pre-ignition stage was proposed based on the formation of these products\textsuperscript{16}. It is likely that the neutralization (acid-base) reaction which is known to be one of the fastest reactions, plays a predominant role and occurs in the preliminary stages in these systems. However, unlike in the amine or hydrazine-nitric acid systems\textsuperscript{8,10} no 'salt' product could be isolated in the present case. It is likely that the heat evolved in the neutralization process decomposes immediately the salt formed evolving more heat, and adds to the overall exothermicity.

\textbf{Calorimetric Values}

There was no suitable device available to evaluate accurately the experimental heats of combustion of hypergolic system, till we commenced our studies. The method used earlier was crude and gave lower than the expected values. A new calorimetric bomb device was developed during the course of our investigations. The usual bomb calorimeter was modified to release the liquid oxidizer on to the fuel (solid or liquid) in the closed calorimeter bomb by remote control. The technique involved snapping a fuse wire connecting the two electrodes of the bomb, which, in turn, tilted a container inside the bomb having liquid oxidizer to pour on to the fuel, by switching on electric current from outside. It was an ingenious device designed and fabricated for the first time in our laboratory\textsuperscript{80}. The heats of combustion of several hypergolic systems, including the monothiocarbohydrazones, with nitric acid oxidizer, were determined. The values obtained by this method matched very closely to the theoretical heats of combustion.

Typical characterization data of some of the mono-thiocarbohydrazones are given in Table 1.

\textbf{Performance Parameters}

The theoretical calculation of the rocket performance parameters such as, specific impulse (\(I_\text{sp}\)), chamber temperature (\(T_c\)), characteristic velocity (\(C^*\)) and mean molecular weight of the gaseous products (M) requires the heats of formation data of the propellant ingredients, as an input parameter. The
heats of formation of the thiocarbohydrazones being unknown, these were calculated by the experimental heats of combustion determined using a calorimeter in oxygen, for the first time. The observed high heats of formation of these materials indicated further their usefulness as potential fuels.

The calculation of the performance parameters performed by making use of the NASA-SP273 computer program was carried out under both the frozen flow and equilibrium flow conditions at various Of/F ratios and exit pressures. These parameters were derived at $P_e = 30$ atm and exit pressure, $P_e = 0.5$ atm, i.e. expansion ratio, $P_e / P_e = 60$. It is seen that the thiocarbohydrazones-HNO$_3$ systems have $I_{sp}$ in the range 240-250 s. It may be mentioned that these $I_{sp}$ values compare well with other hybrid systems, like R005-RFNA (250 s) or a non-hypergolic hybrid, rubber-RFNA (260 s), reported at expansion ratio, 68 to 1 atm. However, an exact comparison of the $I_{sp}$ and other data could not be made because of the different chamber and exit pressure conditions assumed.

**Thermal Decomposition**

Thermal analysis of monothiocarbohydrazones by DTA/TG techniques show that they all decompose exothermally soon after melting. The cause of exothermal decomposition is attributed to the presence of N-N bonds. The products of decomposition of benzaldehyde-thiocarboxyhydrazole were analyzed on a gas chromatograph, and by other methods of chemical analysis. Some of the products identified were, $N_3$, $NH_3$, $H_2S$, benzonitrile, thiobenzaldehyde, $2,4,6$-triphenyl-$s$-triazine and complex condensation products containing $C=N$ linkages. A probable mechanism of decomposition was proposed based on the formation of these products, assuming homolytic cleavage of the N-N bond as a primary step.

**Bis-Thiocarbohydrazones and Thiosemicarbazones**

The exceptional hypergolicity of the mono-derivatives of thiocarbohydrazide with nitric acid led us to investigate the bis-thiocarbohydrazones. Like the mono-, the bis-derivatives of thiocarbohydrazide with aldehydes and ketones could be easily prepared by changing the reactant ratio and altering the reaction conditions suitably. Over a dozen bis-thiocarbohydrazones were synthesized and characterized by their chemical analyses, melting points, IR and $^1$H NMR spectra. Thiosemicarbazones were prepared by reacting thiosemicarbazide and the appropriate carbonyl compound, and characterized by their melting points.

**Ignition Delays**

In the studies carried out so far the effect of change in the substituent in potentially hypergolic systems (hydrazones and mono-thiocarbohydrazones) on the ignition delay was determined to understand the role of chemical reactions occurring in the pre-ignition stage. It is interesting, however, to compare the minimum IDs of series of closely related compounds, to get a deeper understanding of the role of the basic chemical structures.

The three series of compounds selected for study are represented by the following chemical structures:
The average minimum ignition delays of these series of compounds (a total of 28 derivatives) were determined with nitric acid under identical experimental conditions. It was observed that the derivatives of aliphatic carbonyl compounds of all the three series are hypergolic both with WFNA. In general the IDs of the bis-derivatives are somewhat longer than the mono-analogs. Here again, longer IDs are obtained with RFNA as compared to WFNA. The bis-derivatives of aromatic aldehydes are almost all non-hypergolic in contrast to the mono-analogs. The IDs of the thiosemicarbazones are longer than the corresponding mono-thiocarbohydrazones. This difference has been attributed to the one less number of basic nitrogen, and N-N bond in thiosemicarbazones. However, it is interesting to note that the trend observed in the IDs as a result of the substitution of different groups in the phenyl ring of the benzaldehyde derivatives is the same as in the case of the mono-thiocarbohydrazones as well as phenylhydrazones.

**Metallized Systems**

An interesting development in hybrid propellants has been the effect of mixing certain metal powders with organic fuels resulting in enhancing the hypergolicity. The addition of metals to the propellant composition is preferred as they generally enhance the performance parameters because of high heats of combustion. However, when metal like aluminum is added it was found that the IDs become intolerably long. Surprisingly, some metal powders (e.g. Mg, Cu, Zn and Fe) on mixing with certain solid fuels ignite immediately on coming into contact with nitric acid. Almost all hydrazones and thiocarbohydrazones are ignited readily, most with reduced ignition delays, on mixing particularly with magnesium powder, both with WFNA and RFNA. Also, many non-hypergolic solid hydrazones became hypergolic on mixing with metals, although the metal powder by itself does not ignite with nitric acid. This strange effect of powder metals in hypergic ignition was envisaged to have high potential for developing new hybrid fuel systems. Furthermore the chemistry of these so-called ‘synergistic reactions’ leading to ignition, being completely unknown, it was considered worthwhile to investigate this phenomenon in detail.

**Synergistic Hypergolic Ignition**

In order to appreciate the scope of the effect, a wide variety of solid organic compounds such as Schiff bases, azines, hydrazones, thiocarbohydrazones, thiosemicarbazones, hydroxy compounds and aromatic hydrocarbons (a total of 37 compounds) were examined. All of these excepting the hydrocarbons, ignited readily with WFNA on mixing with Mg powder although as such many were non-hypergolic or exhibit longer IDs. A variation of the Mg content in a typical case shows that the minimum IDs obtained are around 40 per cent. The minimum IDs of the mixtures having fuel/Mg weight ratio, 60:40, were determined to compare their relative hypergolicity. Interestingly, although the monothiocarbohydrazones ignite with WFNA with very short IDs (~ 40 ms), their mixtures exhibit longer IDs (~140 ms). It thus appears that the IDs decrease generally further on mixing with Mg powder. However, highly hypergolic fuels having IDs - say, shorter than 100 ms, the IDs of their mixtures are increased instead.

In a parallel study the effect of various metals on ID was examined to determine if the effect of Mg was specific in some way. However, many other metals like, Zn, Cu, and Fe also exhibit the synergistic hypergolic effect similar to Mg on mixing with fuels. In fact, the shortest IDs are observed with Zn powder and not with Mg, though Zn has other undesirable properties like low heat of combustion and high molecular weight.

Although the complete mechanism of synergistic hypergolic ignition still remains unresolved the effect has been attributed primarily to the increased exothermicity of the system due to the mutual contributions of the heat evolving chemical reactions between the organic fuel, metal and nitric acid. The main exothermic reactions between an organic fuel and WFNA have been identified as neutralization, nitration, and oxidation. These reactions may lead to the formation of unstable intermediates that decompose exothermally, thereby contributing to the overall exothermicity of the system. The primary product of the reaction between metal, e.g. Mg with WFNA is magnesium nitrate. The heat evolved during its formation may help in accelerating the rates of other reactions occurring between the organic fuel and WFNA. Magnesium nitrate may act as a dehydrating agent, removing water from the system, which may facilitate the nitration reaction between the organic fuel and WFNA. Also, the oxygen formed by the decomposition of magnesium nitrate may oxidize the
organic fuel, and thereby contribute to the overall exothermicity. Heats of Combustion with WFNA

Heats of combustion of several self-igniting Mg-organic fuel-WFNA systems were determined using the modified bomb calorimetric device described earlier. The measured heats of combustion of fuel mixtures having 40-50 per cent Mg at different O/F ratio show a maximum around the stoichiometric ratio, as expected. Also, the heats of combustion of the metallized systems are higher than the organic fuels alone, with WFNA.

Performance Parameters of Synergistically Igniting Systems

The unexpected hypergolicity of metallized systems led to exploration of other relevant parameters pertaining to their performance. Several new synergistically igniting Mg-organic fuel-nitric acid systems were chosen for evaluating their theoretical rocket performance parameters \( \text{I}_{\text{sp}}, T_{c}, C^{*} \) and M in order to assess their viability. These parameters were calculated varying O/F ratios, metal loading and equivalence ratios at chamber pressure, \( P_{c} = 30 \text{ atm} \) and expansion ratio, \( P_{c} / P_{e} = 60 \), assuming equilibrium flow conditions. Interestingly the maximum \( \text{I}_{\text{sp}} \) for various fuels is obtained at 40 per cent Mg content. These systems were found to give superior performance parameters \( \text{I}_{\text{sp}} \sim 255 \text{ s} \) than the unmetallized systems.

A comparison of the relevant parameters, such as ignition delay, heat of combustion and specific impulse of some typical metallized systems is given in Table 2.

Hypergolic Ignition with \( \text{N}_{2}\text{O}_{4} \)

Hypergolic ignition studies carried out thus far were confined to nitric acid oxidizer. With dinitrogen tetroxide (\( \text{N}_{2}\text{O}_{4} \)) most of the solid organic fuels are either non-hypergolic or ignite with very long IDs. Consequently, there was no serious study on hypergolic systems with liquid \( \text{N}_{2}\text{O}_{4} \) as an oxidizer. However, a preliminary examination showed that some of the fuels ignite readily on mixing with metal powders. In other words, \( \text{N}_{2}\text{O}_{4} \) could participate in synergistic hypergolic ignition.

Schiff-base-Mg-\( \text{N}_{2}\text{O}_{4} \) Systems

The idea of using \( \text{N}_{2}\text{O}_{4} \), a low boiling liquid oxidizer in synergistically igniting hybrid propellant systems was first conceived and examined in our laboratory. Fuel compositions comprising mixtures of Mg powder with a variety of Schiff-bases (the

<table>
<thead>
<tr>
<th>Fuel composition (per cent weight)</th>
<th>Ignition delay* (ms)</th>
<th>( \Delta H_{\text{r}} ) (HN03) (kcal/g reactants)</th>
<th>Specific impulse* (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-Dimethylaminobenzylideneaniline (PDBA)</td>
<td>No ignition</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PDBA (30) + Mg (70)</td>
<td>158</td>
<td></td>
<td>246</td>
</tr>
<tr>
<td>PDBA (30) + Zn (70)</td>
<td>70</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PDBA (30) + Cu (70)</td>
<td>162</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PDBA (30) + Fe (70)</td>
<td>787</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PDBA (30) + Al (70)</td>
<td>No ignition</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PDBA (60) + Mg (40)</td>
<td>118</td>
<td></td>
<td>258.1</td>
</tr>
<tr>
<td>Acetonethiocarbohydrazone (50) + Mg (50)</td>
<td>156</td>
<td>1.67</td>
<td>248.5</td>
</tr>
<tr>
<td>Benzylideneaniline (40) + Mg (60)</td>
<td>167</td>
<td>1.0</td>
<td>256.4</td>
</tr>
<tr>
<td>Furfuraldehydephenylhydrazone (50) + Mg (50)</td>
<td>138</td>
<td>1.19</td>
<td>250.2</td>
</tr>
<tr>
<td>Benzaldehydethiocarbohydrazone (50) + Mg (50)</td>
<td>171</td>
<td>1.38</td>
<td>246.5</td>
</tr>
</tbody>
</table>

*Oxidizer : WFNA
condensed products of anilines with aromatic aldehydes) were found to ignite with short IDs with liquid N\textsubscript{2}O\textsubscript{4} (ref. 26). The ignition delays were measured using a modified device. Considering the low volatility of N\textsubscript{2}O\textsubscript{4} the apparatus was redesigned not only to cool the liquid and hold at lower pressure, but also to release the oxidizer with minimum personal error. It was observed that the minimum IDs are obtained at about 1:1 ratio (by weight) of the Schiff-base to Mg, both with N\textsubscript{2}O\textsubscript{4} and WFNA. A comparison of the IDs determined under identical conditions of a total of 16 Schiff-bases-Mg mixtures show that the ID values with WFNA are considerably shorter than with N\textsubscript{2}O\textsubscript{4}.

The ignition delay was found to vary with the nature of the substitution in both the benzene rings. In fact, a linear relationship emerges when the IDs are plotted against the Hammett substitution constant (\(\rho\)) (ref. 26). This constant being a measure of the reactivity of the phenyl substituted compounds the linear relationship establishes unequivocally the dependence of ID on chemical reactivity. Furthermore the pre-ignition products of the reaction of N\textsubscript{2}O\textsubscript{4} with Mg and benzylidineaniline have been analyzed to be magnesium nitrate, benzzenediazonium salt and benzaldehyde. Based on these products, a probable reaction mechanism occurring in the pre-ignition stage has been proposed\textsuperscript{26}.

**Anilines-Mg-N\textsubscript{2}O\textsubscript{4} Systems**

Like the Schiff bases, solid anilines were also found to ignite when mixed with magnesium powder, with dinitrogen tetroxide.\textsuperscript{27} Of the six anilines examined, p-toluidine and p-anisidine, and their mixtures with Mg ignite readily. Others do not ignite without mixing with Mg either with N\textsubscript{2}O\textsubscript{4} or RFNA. Interestingly, p-toluidine does not ignite either with WFNA or RFNA but ignites with very short ignition delay with N\textsubscript{2}O\textsubscript{4}. This particular system was chosen for a detailed examination of their pre-ignition products, to get an insight of the exothermic reactions occurring prior to ignition.

The quenched products of p-toluidine-N\textsubscript{2}O\textsubscript{4} system were found to contain p-toluidinium nitrate, 1,3-bis(p-tolyl)-triazene-1-oxide, \(p,p'\)-dimethylazo-benzene and possibly a mixture of p-cresoles. A probable pre-ignition reaction pathway involving nitrosamine ion and the formation of nitrosamine intermediate was proposed, which to certain extent explains the synergistic ignition of amines and magnesium powder mixture with N\textsubscript{2}O\textsubscript{4} (ref. 27).

**Temperature Profiles**

A possible way of studying the pre-ignition process is to measure and record the temperature profile prior to the onset of ignition. The usual thermocouple methods being not suitable because of their slow response, a thin metal film thermometric technique was devised and set up in our laboratory for the first time. It records the temperature as sensed by the thin platinum film and also the ignition delay of a self-igniting system in a single run\textsuperscript{28}. The device essentially consists of a probe cup with a micron-thin platinum ribbon deposited on the inside surface near the bottom, which acts as a quickly responding temperature sensor, and a set of sensitive photo diodes for sensing the flame. Both the ignition delay and the temperature profiles are recorded and displayed simultaneously on the two channels of a dual trace storage digital oscilloscope, which is interfaced to a microcomputer.

This device was test checked, using both the liquid-liquid and solid-liquid systems. The recorded temperature profiles of aniline-furfuryl alcohol-WFNA system shows synergic effect. Whereas, pure aniline is non-hypergolic, it ignites readily on mixing with furfuryl alcohol with WFNA in as short a time as 0.1 ms only\textsuperscript{29}.

The basic chemical reactions occurring between organic fuels and pure nitric acid are not clearly understood because of their exceedingly high rate and exothermicity. Most often, charred end products are formed in sub-second periods. It was envisaged that a study of the temperature profiles of closely related (structurally similar) simple fuel-oxidizer systems might be helpful in understanding the nature of these reactions. A comparison of the temperature profiles of the reactions between mono-substituted benzenes and anhydrous nitric acid, showed that the extent of exothermicity and the rate of heat evolution depend on the substituent. The initial reaction was identified to be nitration, which is accompanied by other exothermic reactions, especially in systems leading to ignition. The profiles of the self-igniting systems, amine-HNO\textsubscript{3} and amine- N\textsubscript{2}O\textsubscript{4}, suggest that, apart from their individual exothermicities the specific nature of the fuel-oxidizer reactions also plays an important role in the onset of ignition\textsuperscript{29,30}.

The temperature profiles of several hybrid systems were recorded in an effort to establish a relationship between, temperature at ignition point, slope of the temperature-time (rate of heat build-up)
and ignition delay. However, although an approximate correlation emerged, a definite relation could not be established. Of course the IDs of hybrid systems recorded by this technique matched closely with that determined earlier by the drop-tester method.

**Rapid-scan FTIR and Thermal Profiles**

A simultaneous rapid-scan FTIR/thermal profiling technique was made use of for the first time after carrying out necessary modification in the cell and fuel injection technique, to examine the exothermic reactions of some self-igniting fuel-HN\textsubscript{3} systems. The thermal profiles show a sudden rise in temperature when the liquid oxidizer was dropped on to the solid fuels. Simultaneous monitoring of the gas products of the reaction between \textit{p}-phenylenediamine and nitric acid revealed the formation of CO\textsubscript{2}, NO\textsubscript{2}, NO and HONO, within two seconds. Immediate evolution of NO\textsubscript{2} was observed in some typical synergistically igniting systems comprising amines, Mg and HNO\textsubscript{3}. Thiacarbohydrazide and its acetone and benzaldehyde mono-derivatives on reacting with \textit{p}-phenylenediamine and nitric acid revealed the formation of CO\textsubscript{2}, NO\textsubscript{2} and possibly OCS. These results were explained in terms of the oxidation and nitration reactions occurring in these systems. 

**Hypergolic Fuel Grains**

The relevance of ignition studies on fuels in the powder form was to evolve a basic understanding of the role of exothermic chemical processes and reactions occurring in the pre-ignition stage in hypergolic ignition. In this context several new hypergolic hybrid systems were also discovered. Studies pertaining to ignition delays of various systems reflect their relative hypergolicity quite accurately. However, these measurements have little meaning from the application point of view, since the fuel is used as a continuous mass cast in a particular shape (called 'grain') in actual usage. On casting, since the surface area available for chemical reaction with the oxidizer decreases drastically, it is only expected that the IDs will increase significantly. In some cases, a fuel which is hypergolic as a powder, may not ignite at all in the cast form. Strangely, there was no systematic study of IDs reported on cast fuels in the open literature till we commenced our work.

Consolidating hypergolic fuel grains having good mechanical strength and at the same time igniting with tolerable IDs is an involved task. We adopted two methods to give shape to the powder fuel: (a) Melt-cast technique and (b) Casting with polymeric binders. The former method was adopted in cases where the melting and decomposition temperatures of fuel are well separated. Such fuels with suitable additives could be cast by melting in a suitable mould and subsequent cooling to room temperature. The second method was akin to casting of solid composite propellants, with fuel powder as filler and a functionally terminated polymer as binder.

**Melt-cast Self-igniting Grains**

Several highly hypergolic powder fuels including the hydrazones and thiocarbonohydrazones, and their mixtures with other self-igniting fuels, like monocyclohexanethiocarbohydrazone (CHTCH), were melt-cast in test tubes or teflon moulds were examined as cut-pellets. Invariably the IDs of the melt-cast pellets were longer than those determined, taking the composition in the powder form, with WFNA or RFNA. Similarly the IDs of the melt casts of synergistically igniting compositions having magnesium were found to be longer. However, minimum IDs of the order of 150 to 250 ms could be obtained after optimizing the ratio in many cases. Several of these melt-fuel composites had fairly good compression strength too.

**Polymer-cast Self-igniting Grains**

Highly hypergolic fuel powders when cast using conventional binders like, carboxyl- or hydroxyl terminated polybutadiene (CTPB or HTPB) which are widely used in solid propellants, either become non-hypergolic or ignite with intolerably long delay. For example, a derivative of thiacarbohydrazone, CHTCH, which ignites within 15 ms in the powder form with WFNA, the ID of its CTPB cast having 85 per cent powder loading increases to 2.74 s. It is thus obvious that the usual polybutadiene binders used in solid propellants are unsuitable for consolidating the hybrid fuels. Fuel grains cast using some newly synthesized epoxy resins with ingredients comprising hypergolic fuels and curing agents, and magnesium powder, however, gave promising results, having minimum IDs about 200 to 400 ms. Some of these casts also had fairly good mechanical properties. Increasing the amount of binder though improved the mechanical strength but retarded the hypergolicity of the grain. Here again the usual bis-phenol epoxy resin was found to be unsuitable as it made the fuel grain non-hypergolic. The epoxydes based on amine and
azine moieties only were found to yield grains having reasonably short IDs with nitric acid\textsuperscript{19,24}.

**N-N-bonded Resins as Binders**

From our ongoing study of the self-ignition behavior of powder hydrazones and thiocarbohydrazones with nitric acid, it was envisaged that the polymeric resins having N-N bonds in their structures could have desirable ignition properties. A literature search revealed\textsuperscript{35} however, that polymers based on N-N bonds are relatively few, and none suitable as binder because of the lack of suitable end groups capable of curing easily without formation of volatile by-products. A comprehensive program of synthesizing viscous resins having N-N bonds in their structures and suitable end groups, to cast hypergolic propellant grains was therefore undertaken in our laboratory. Our initial attempts to prepare viscous N-N-bonded polymers were unsuccessful\textsuperscript{35}. Most often the polymers obtained were solid products which were unsuitable for casting powder compositions.

**Resins based on bis-Carbohydrazones and bis-Thiocarbohydrazones**

Eventually, however, the epoxidation of bis-carbohydrazones and bis-thiocarbohydrazones yielded resins having adequate viscosity for high solid loading. The resins could be cured easily with amines like, diaminodiphenyl methane (DDM). This was indeed a turning point in our research. Subsequently, we synthesized and characterized a series of epoxy resins by various, chemical, spectroscopic and thermoanalytical techniques\textsuperscript{36-38}. The di-epoxy resins had about two end groups per molecule. The tetra-epoxides could also be prepared when the parent compound had additional hydroxyl groups, like in the case of bis-vanillin-thiocarbohydrazone. Apparently, the epoxidation takes place both on the -NH and -OH protons in these systems. The structure of a typical di-epoxy resin based on bis-aldehyde-thiocarbohydrazone could be represented as follows:

\[
\text{CH}_2 \text{CH} \text{CH}_2 \text{N} \text{C} (=\text{S}) \text{N} \text{CH}_2 \text{CH} \text{CH}_2
\]

\[
\begin{array}{c}
\text{H} \\
\text{H} \\
\text{CR} \\
\text{CR}
\end{array}
\]

Several such resins with various substituent (R) groups were synthesized by epoxidizing the parent bis-thio- or bis-carbohydrazones. The resins were found to be thermally stable at room temperature and undergo decomposition exothermally at high temperatures, as shown in DTA studies.

Interestingly, some of the cured resins were found to be igniting as such, on coming into contact with WFNA, although with long IDs. Solid fuel composites processed with these resins as binders had adequate mechanical strength, and ignite smoothly with short IDs with WFNA. The effect of variables such as, fuel composition, O/F ratio, types of curatives, effect of solid loading, amount of metal powder in the composition, etc. on the ignition delay, was determined\textsuperscript{19,26}. Composites having high loading of magnesium powder exhibit synergistic ignition with nitric acid, and ignite with short IDs. In general the epoxy compositions of bis-carbohydrazones have shorter IDs than those based on bis-thiocarbohydrazone resins. This is surprising, considering the fact that the bis-hydrazones are nonhypergolic as powders, while the bis-thiocarbohydrazones are highly hypergolic with WFNA\textsuperscript{19,24}. The cast grain composites are stable in air with no evidence of oxidation on storage. These studies clearly show that the N-N bonded binders have several desirable characteristics for processing hypergolic fuel grains for hybrid propellant systems.

**Dicarboxyl Bis(hydrazones) and their Epoxides**

Yet another class of N-N bonded compounds were synthesized with a view to prepare new epoxy resins having varying amount of chain flexibility to provide improved mechanical properties to the grain. These were based on N, N'-aliphatic dicarboxyl bis(hydrazones), the aldehyde/ketone derivatives of dihydrazides of various aliphatic dicarboxylic acids. It was anticipated that the linear hydrocarbon spacer groups, -(CH\textsubscript{2})\textsubscript{n} present in the parent hydrazone would impart flexibility to the resin backbone. These bis(hydrazones) could be prepared easily by converting the dicarboxylic acids like, malonic, adipic or sebacic acid to their methyl esters, reacting them with hydrazine hydrate and subsequently condensing with an aldehyde or ketone\textsuperscript{41}. The structure of a typical dicarboxyl bis(hydrazone) can be represented as follows:

\[
\text{R}_1 \text{R}_2 \text{C}=\text{N}-\text{NH-C(=O)-(CH}_2)_\text{n-C(=O)}-\text{NH-N}=\text{CR}_1 \text{R}_2
\]

Over a dozen bis(hydrazones) were prepared with different substituents (R\textsubscript{1} and R\textsubscript{2}) and methylene spacer groups (n = 1, 4 and 8). These compounds are
non-hygroscopic, stable in air and decompose after melting at high temperatures.

Interestingly, many of these compounds ignite spontaneously on coming into contact with nitric acid, often with very short ignition delays. The ID increases with increase in the number of methylene spacer groups. Simultaneous DTA/TG study show that typically the bis(hydrazones) that decompose exothermically usually ignite with WFNA; also, those decomposing soon after melting have short IDs. The hydrazones which do not ignite on coming into contact with WFNA, show synergistic ignition on mixing with magnesium powder.

The epoxidation of the bis(hydrazones) resulted in the expected formation of their di-epoxides having convenient viscosity. Several bis(hydrazones) based resins were synthesized and characterized by various techniques. When used as binders for powder compositions these resins are capable of taking high solid loading. In fact, these could be conveniently used as energetic binders for solid propellants based on ammonium perchlorate. The propellant grains processed with these resins not only have good mechanical strength but also significantly high burning rates, and specific impulse. Detailed studies on these and other N-N-bonded resins have been made considering their potential use as binders for propellant compositions; these resins act as good binders for powder fuel composition for hybrid systems too.

Hydroxyl Terminated N-N-bonded Resins

Hydroxyl terminated pre-polymers are preferred binders as they could be converted to polyurethanes on reacting with isocyanates and cured easily with triols. Hydroxyl terminated polybutadiene (HTPB), e.g., has been the work horse binder for solid propellant compositions. Solid propellant grains based on HTPB not only have superior mechanical properties but also give higher specific impulse. Since the use of HTPB binder for hypergolic powder composition results in non-ignition of the fuel grain, it was decided to synthesize new resins having N-N bonds in the structure but terminated with hydroxyl groups. However, synthesis of a viscous resin having terminal -OH groups turned out to be an involved task. Ultimately, we were successful in synthesizing resins that contained a carbonyl or thiocarbonyl moiety; N-N bonds; ethereal linkage; and terminal hydroxyl groups.

The resins were synthesized by condensing bisvanillincarbono- and bisvanillinithiocarbono-hydrazone, respectively, with 1,4-dibromobutane. The resins were characterized by various chemical and spectroscopic techniques, and other properties relevant to their use as propellant binders, such as calorific values, thermal analysis, viscosity and ignition behavior. They have convenient viscosity, indicating their suitability as binders for processing high solid loading, and could be cured easily with toluene diisocyanate and glycerol. These resins ignite immediately on coming in contact with pure nitric acid indicating their hypergolic nature. It thus seems that these resins could be highly suited as binders for hypergolic hybrid systems.

Typical characterization data of some of the N-N-bonded resins are given in Table 3.

Findings in-Brief

The hypergolic ignition is an area, which was largely unexplored. The earlier reports aimed primarily at developing workable hypergolic hybrid

<table>
<thead>
<tr>
<th>Resin*</th>
<th>Calorific value (kcal/g)</th>
<th>Viscosity at 35 °C (Poise)</th>
<th>Glass transition/ Decomposition temp (°C)</th>
<th>Density (g/cc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DEFCH</td>
<td>7.185</td>
<td>404.7</td>
<td>300 dec</td>
<td>1.37</td>
</tr>
<tr>
<td>DEMFH</td>
<td>5.32</td>
<td>350</td>
<td>55/215</td>
<td>1.27</td>
</tr>
<tr>
<td>DESFH</td>
<td>6.45</td>
<td>100</td>
<td>-5/220</td>
<td>1.22</td>
</tr>
<tr>
<td>DEABuH</td>
<td>6.64</td>
<td>157</td>
<td>30/205</td>
<td>1.15</td>
</tr>
<tr>
<td>DESBuH</td>
<td>7.13</td>
<td>75</td>
<td>-13/205</td>
<td>1.12</td>
</tr>
<tr>
<td>DVCBE</td>
<td>6.29</td>
<td>150</td>
<td>220 dec</td>
<td>1.18</td>
</tr>
</tbody>
</table>

*DEFCH, diepoxide of bis-furfuraldehydatehydroxydrazone; DEMFH, diepoxide of malonyl bis-furfuraldehydehydrazone; DESFH, diepoxide of sebacoyl bis-furfuraldehyde hydradrazone; DEABuH, diepoxide of adipoyl bis-butanonehydradrazone; DESBuH, diepoxide of sebacoyl bis-butanonehydradrazone; DVCBE, di(bis-vanillincarboxydradrazine-4-oxy) butane 1,4 diyl diether. *Cured resins
Progress in Hybrid Rockets

Why Hybrids?

It is recognized that hybrid rockets combine the technical advantages of both solid and bi-liquid engines. Several distinct advantages associated with hybrid rockets have deservedly made them center of attraction for several years. Some of these are:

(a) Safety – Since the fuel and oxidizer are stored in different chambers the hybrids provide safety during storage, fabrication, transportation and operation without any possibility of accidental explosion.

(b) Control – The hybrids offer stop-start-and-restart capability like the bi-liquid hypogolic systems, and yet are simple to operate more or less like the solid motors which have no thrust variation control.

(c)Insensitive Combustion – In hybrids the regression of the fuel grain during combustion being normal to the flow of the oxidizer and not to the grain surface, makes the oxidizer-free grain insensitive to cracks, bond line separation and joint openings – factors often responsible for catastrophic failures in solid motors.

(d) High Isp – The theoretical vacuum specific impulse of hybrids is considerably higher than the solid rockets, and the density impulse is higher than the bi-liquid rockets.

(e) Aging – Unlike the solid propellants, the hybrids have no serious aging problems since the fuel and the oxidizer are not in physical contact prior to use.

(f) Cost – The cost of fabrication, handling, transporting, and even that of the propellant used is much lower than either the solid or liquid rockets.

Among the major disadvantages of the hybrids may be mentioned:

(a) Slow Regression Rate – The regression rates of the existing solid fuels are relatively low — about \(1/10\) of solid propellants.

(b) Lower Combustion Efficiency – Hybrid rockets typically have 93 to 95 per cent efficiencies, slightly lower than the other types.

(c) Lower Density Impulse – In comparison to solid propellant rockets the hybrids have lower density impulse, thereby resulting in larger volume.

However the problems associated with the hybrids are not inherent and could be overcome by addressing them appropriately.

Hybrid rockets are well suited for missions like putting satellites into low earth orbit, and raising the orbit of a satellite from near earth to geo-stationary orbit — a process that needs thrust control as well as high-energy propellants. They could be well used for sounding rockets, maneuvering spacecraft during ascend and descent flights on other planets, as payload carriers to the International Space Station, and even in missiles where thrust control is required.

In spite of many advantages and wide applicability, however, the hybrids are hardly in use in any major mission. This is largely because the technology of both the bi-liquid and solid rockets is well established. The two types work well and singly or jointly they cover the mission requirements of all types. It is considered wasteful to spend money on perfecting another technology for the same purpose.
There appears to be reluctance in supporting a new system by the monopoly manufacturers of solid or liquid propellant rockets although the hybrids may prove beneficial in the long run.

Another major reason could be the non-availability of suitable self-igniting solid fuels that have short ignition delays in the cast form, with liquid oxidizer like HNO₃. Since no serious efforts were made to understand the pre-ignition process, it is not surprising that there is a paucity of non-hazardous efficient hypergolic hybrid systems. As a result, all recent hybrid systems use non-hypergolic propellants. The studies have virtually converged to HTPB-LOX system only. Needless to say that additional ignition device or injection of a pyrophoric material is needed to initiate ignition of such a system. Obviously, the system becomes complicated and a major advantage of the hybrids i.e. the 'simplicity' is lost. It is in this context that our studies become relevant.

A Brief History and Present Status

The concept of hybrid rockets is hardly new. The Russians are reported to have conceived the idea as early as 1937. In the US too the initial attempt to design a workable hybrid device comprising wood and LOX, was made by California Rocket Society (CRS) in the late 1930s. The CRS was also responsible for the first test flight of a hybrid rocket having rubber/LOX propellant, that reached a height of 9 km in 1951.

The first use of self-igniting propellants in hybrids was made in France and Sweden and USA almost simultaneously in the mid to late 1960s. The French hybrid engine (LEX-02) meant for launching sounding rockets was based on an amine fuel, m-toluidenediamine (96 per cent) in nylon (4 per cent) having a coating of phosphorus tri-N-methylimidide (to initiate quick ignition) and RFNA oxidizer. Swedish workers developed their sounding rockets (HR-4 and SR-1) based on a self-igniting fuel named Tegaform, which comprised an amine having additives like lithium aluminum hydride (to reduce the ignition delay) with RFNA oxidizer. In the US much emphasis was placed on using fluorine based oxidizers for hypergolic systems. Mixtures of fluorine and liquid oxygen (FLOX), OF₂, CIF, etc., were tried. Also, the mixtures of oxides of nitrogen (NO and liquid N₂O₄) were developed as oxidizers. A propellant having mixed oxides of nitrogen (MON), as oxidizer, and magnesium powder embedded in polymethymethacrylate (PMMA) as fuel, was used in Sandpiper target drone by United Technology–Chemical Systems Division (UT-CSD) in 1967. Throttleable engines based on FLOX and Li/LiH in HTPB were demonstrated by UT-CSD in the late 1960s. Aero Jet General conducted test firings of hybrid motors having polymeric fuels with metal additives using OF₂ oxidizer. The Reaction Motors of Thiokol tried polyurethane-based fuels with oxidizers like, FLOX, RFNA and N₂O₄. Lockheed Propulsion Company (LPC) developed a tactical hybrid missile for the US Army that had a rubber-based fuel loaded with boron and CIF₃ oxidizer in 1969.

Hypergolic hybrids based on p-touidine/aminophenol (30/70) fuel and WFNA oxidizer, were investigated in Germany in 1974 for their use in sounding rockets. The DFVLR in Germany also developed space engines based on polyethylene, Li & LiH / FLOX propellant. Around this time, a feasibility of hybrid systems was made at the author’s Institute. Several hybrid motors having organic fuels (undisclosed) hypergolic with RFNA were tested by conducting static-bed firing.

There was virtually no activity in hybrids in the period between 1975 to 1985. It appeared as if the hybrids had lost out to the bi-liquid and solid propellant rockets. A study conducted by Martin-Marietta in 1982, however, revealed that of the twenty technologies investigated, hybrid propulsion offered the greatest return cost-wise. Interest in the hybrids rejuvenated after the space shuttle Challenger disaster in 1986, caused by failure of one of the solid boosters. Another study carried out by the Hybrid Industry Propulsion Action Group compared a hybrid rocket booster sized for space shuttle to the existing solid booster and concluded that in propellant cost alone the hybrid booster could yield a savings of $5.7 million/flight. Realizing the potential of the hybrid systems, NASA in 1989, awarded four contracts for the evaluation of hybrid rockets. All four studies concluded that hybrid merited further development based on the potential advantages in ‘safety, reliability and economy’.

By 1985 the emphasis on propellants shifted from hypergolic to non-hypergolic systems. American Rocket Company (AMROC), USA, a commercial space company that has been engaged in hybrid rocket development based its studies on a non-hypergolic HTPB-LOX system. During 1986 to 1992 the company built 94 hybrid rocket booster engines
having polybutadiene/LOX propellant. Ignition was initiated by injecting triethylaluminum, a pyrophoric liquid. In early 1991, AMROC proposed an all-hybrid vehicle for maintaining Motorola's Iridium satellites. The 4-stage 'Aquila' rocket built by this company was capable of boosting a 1500 lb payload into a 300-mile polar orbit for half the cost of then alternatives. AMROC also developed H-500 and H-1800 hybrid motors capable of giving 75,000 and 250,000 lb thrust, respectively, using HTPB/LOX propellant. A new 'wagon wheel' configuration was used to cast the fuel. It is evident that a fair amount of expertise in hybrids was developed by this company, but due to lack of commercial support it stopped operating by the mid 1990s.

A Joint Government/Industry Independent Research and Development Program (JIRAD) was established in the US during 1991-94 to develop hybrid rocket technology. The participants were Thiokol, UT-CSD, AMROC, Martin Marietta and NASA-Marshall. The main purpose of this group was to acquire data that will eventually allow application of hybrids to boost propulsion for space launches. Many test firings of hybrid motors were conducted using the Thiokol, and UT-CSD's (UTF-29901) solid fuels with LOX or gaseous oxygen (GOX) oxidizers, under the JIRAD program.

A Hybrid Technology Option Project (HyTOP) was initiated in 1994 to bring large-scale hybrid motors to flight status with funding from Defense Advanced Research Projects Agency (DAPRA). The project members included AMROC, Lockheed Martin, UT-CSD and USAF's Phillips Lab, and industry participants. The AMROC's H-250k motor (F = 1.1 MN) that used polybutadiene based solid fuel/LOX propellant, was fired successfully in 1993 and again in 1994. AMROC however, failed to raise its share of HyTOP funding and its leadership was replaced by Lockheed-Martin.

The Hybrid Propulsion Demonstration Program (HPDP) was established in 1995. This was a restructured HyTOP, comprising NASA-NSFC, APRA and Industrial Consortium of Lockheed-Martin, UT-CSD, Thiokol, Boeing-North Am/Rocketdyne, AlliedSignal and Environmental Aeroscience Corp. (EAC). It aimed at a flight test of 1.1 MN booster in 1999. A single-stage Hyperion rocket built by the EAC for the sounding-rocket flight demonstration phase of the program was test-fired to an altitude of 33.5 km in 1997 (ref. 55). The Hyperion uses a low energy HTPB/ nitrous oxide propellant that has an I_sp of about 225 s only. The 1.1 MN thrust turbo-pump fed HTPB/LOX hybrid motor (13.7 m long and 1.78 m diam) was tested at NASA-Stennis in 1999. Apparently, they used non-pyrotechnic ignition — possibly electric operated torch igniter.

Hybrids based on hydrogen peroxide (HP)/polyethylene (PE) have been proposed, and compared with those having HTPB/LOX propellant. According to this study, HP is comparable in both safety and handling risks to LOX, and suitable for auxiliary monopropellant usage. Since monopropellants, like H_2O_2 and N_2H_4 ignite simply on passing through a catalyst bed, these have been considered for using in auxiliary ignition devices with non-hypergolic hybrids. In this dual mode operation the hot exhaust gases of the monopropellant motor ignite the hybrid motor based on say, HTPB/LOX. Thus not only the repeating on-and-off ignition capability of the hybrid is achieved easily but the monopropellant motor can also be operated independently when only small thrust variation is required. Dual mode hybrids have been studied in Israel in 1996 (ref. 57).

An interesting hybrid combination based on hydroxyl ammonium nitrate (HAN) as oxidizer and HTPB as fuel has been proposed. HAN is highly miscible with water and is safe to handle. It is reported to give slightly higher I_sp with metallized HTPB compared to HP or nitrous oxide. A new type of staged combustion hybrid rocket has been proposed recently which is believed to be safe, environmentally tender and inexpensive. Its combustion mode resembles the end burning grain of the solid rocket since the fuel bed burns from the bottom end. However, an auxiliary igniter device is needed to achieve on-off capability in these systems.

Conclusions

It is apparent that a reliable hybrid rocket system is yet to be evolved, in spite of all its conceptual advantages. One of the main advantages of the hybrids has been their simplicity of operation. This major plus-point is marginalized once the propellant chosen is non-hypergolic. The installation of an additional ignition device for achieving start-restart capability adds to the complexity of the system, and makes it less competitive to the bi-liquid as well as solid systems. However, an understanding of the self-ignition process is slowly emerging.
Studies made by our group on N-N-bonded materials point to the possibility of developing solid fuel grains, which ignite smoothly on coming into immediate contact with simple, non-cryogenic liquid oxidizers, suitable for hybrid propellant rockets.

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