Defence Science Journal, Vol 45, No 1, January 1995, pp 5-16

REVIEW PAPER

Spontaneously Igniting Hybrid Fuel-Oxidiser Systems

S.R. Jain

Department of Aerospace Engineering, Indian Institute of Science, Bangalore-560 012

ABSTRACT

After briefly outlining the recent developments in hybrid rockets, the work carried out by the author on self-igniting (hypergolic) solid fuel-liquid oxidiser systems has been reviewed. A major aspect relates to the solid derivatives of hydrazines, which have been conceived as fuels for hybrid rockets. Many of these *N-N* bonded compounds ignite readily, with very short ignition delays, on coming into contact with liquid oxidisers, like HNO_3 and N_2O_4. The ignition characteristics have been examined as a function of the nature of the functional group in the fuel molecule, in an attempt to establish a basis for the hypergolic ignition in terms of chemical reactivity of the fuel-oxidiser combination. Important chemical reactions occurring in the pre-ignition stage have been identified by examining the quenched reaction products. Hybrid systems exhibiting synergistic hypergolicity in the presence of metal powders have been investigated. An estimation of the rocket performance parameters, experimental determination of the heats of combustion in HNO_3, thermal decomposition characteristics, temperature profile by thin film thermometry and product identification by the rapid scan FT-IR, are among the other relevant studies made on these systems. A significant recent development has been the synthesis of new *N-N* bonded viscous binders, capable of retaining the hypergolicity of the fuel powders embedded therein as well as providing the required mechanical strength to the grain. Several of these resins have been characterised. Metallised fuel composites of these resins having high loading of magnesium are found to have short ignition delays and high performance parameters.

1. INTRODUCTION

This presentation pertains to hybrid propellant systems. It is recognised that hybrid rockets combine the technical advantages of both solid and biliquid engines, besides being safe and economical. In the usual mode, a hybrid propellant system comprises a solid fuel and a liquid oxidiser. The two are stored in separate chambers; the chamber having the solid fuel grain also acts as combustion chamber. In the so called 'hypergolic' system, ignition starts the moment the oxidiser is brought in contact with the solid fuel and stops on closing the oxidiser flow. The flow of the oxidiser thus provides on-and-off capability without using any additional igniter. The thrust depends on the rate of flow of the oxidiser. These parameters make the hybrid system simpler to operate than the biliquid systems, and superior to solid rockets in providing controlled thrust.

In rocketry, although maximising performance has always remained the major criterion, many other considerations have assumed greater significance in recent times. These are safety, reliability, environmental impact, cost, transportation, etc. The hybrid system, it so happens, wins on all these aspects. The hybrid system is safe in several ways: (a) the fuel and the oxidiser are stored separately and hence, unlike in solid rockets, there is hardly a chance of accidental explosion, (b) the inert fuel grain having no oxidiser is safe and can be transported easily without requiring any special license, and (c) regression of the fuel grain during combustion being normal to the flow of oxidiser and not to the grain surface, makes the oxidiser-free grain

---

Received 04 October 1994

* Based on a Plenary Lecture delivered at the VII National Seminar on High Energy Materials held at VSSC, Trivandrum, in February 1994

insensitive to cracks, bond line separation and joint openings—factors often responsible for catastrophic failures in solid motors.

Since the thrust control in hybrid systems is achieved simply by one delivery system, it makes them operationally simple and more reliable. Also, the combustion process being a function of the oxidiser flow, permits (a) incorporation of an abort mode and (b) meeting the needs of all launch vehicles—big or small–in future. Besides safety and reliability features, there is substantial cost savings in manufacturing, storage, ground processing, transportation and launch operation since no detailed precautions are required. A hybrid system could be fired, terminated, inspected, evaluated and restarted easily. These aspects also reduce the non-recurring developmental cost. Yet another feature of hybrids is that most often there is no production of HCl or Al_2O_3 as exhaust products, which is a distinct disadvantage of the solid rockets being recognised as serious, of late, from the pollution point of view.

In spite of these distinct advantages, these systems have not been used in major launch programmes, although the Russians are reported to have fired hybrid rockets as early as in 1933. This is mainly because the alternatives were available. The solid rockets served well for small missiles and met the defence needs fairly adequately. The biliquid rockets were available whenever large thrusts were required, especially for space applications. In this scenario the hybrids lost out. It was not considered wise to invest in a new system, which although advantageous, would essentially do the same job.

In the past decade or so the situation however has changed especially after the space shuttle Challenger disaster in January 1986, caused by the failure of one of the solid rocket boosters. Intensive efforts are now on mostly in the US to develop the hybrid systems[1,2]. As regards the cost, a study conducted by Martin-Marietta in 1982 showed that, of the twenty technologies investigated, hybrid propulsion offered the greatest return for the dollar invested. Another study, carried out by Hybrid Propulsion Industry Action Group compared a hybrid rocket booster sized for space shuttle to the existing solid rocket booster. It concluded that in propellant cost alone the hybrid rocket booster could yield a savings of $ 5.7 million per flight. Realising 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 potential advantages in 'safety, reliability and economy'. The main effort in developing the hybrid propulsion system in the US has been made by a private company, namely, American Rocket Company (AMROC). Since 1986, this company has built 94 hybrid rocket motors and conducted 180 test firings up to July 1992.

In early 1991, AMROC proposed[3] an all-hybrid vehicle for maintaining Motorola's 66 Iridium Satellites. AMROC's 4-stage 'Aquila' is capable of boosting a 1,500 lb payload into a 300-mile polar orbital for half the cost of current alternatives. The company has already developed an H-500 motor which is capable of giving 75,000 lb thrust using LO_2/HTPB propellant. The development of a commercial H-1,800 motor capable of giving 250,000 lb thrust is on its way since 1992. It is, thus apparent that the hybrid systems are bound to gain prominence in this or the next decade.

The full advantage of a hybrid system is achieved when the propellant used is hypergolic, i.e., it ignites on immediate contact of the fuel and oxidiser. This way, the on-and-off capability is achieved easily. In this sense, although the LO_2/HTPB system, used by AMROC, has some other distinct advantages, it is not a hypergolic system. Development of a working hypergolic hybrid propellant is still in the infancy stage. It may be said that the absence of a suitable hypergolic fuel-oxidiser system is one of the main reasons for scarcity of the hybrid rockets.

One of the major problems of a hypergolic hybrid system is the onset of ignition. To avoid 'hard start' of the engine, the ignition delay (ID), i.e., the elapsed time preceding ignition after the liquid oxidiser comes in contact with the solid fuel, must be as short as possible. It is generally believed that the main cause of self-ignition of hypergolic systems is rapid generation of heat by the exothermic chemical reactions occurring between the fuel and the oxidiser in the pre-ignition stage. The chemistry of these reactions is highly complex because several types of reactions occur, often simultaneously, in a very short interval of time. The understanding of these reactions being poor, there is not even a rule-of-thumb to predict *a priori* whether a system will ignite or not, leave aside the magnitude of ID. Nevertheless, it is conceivable that short IDs could be achieved by using extremely reactive materials, like fluorine oxidisers and metal hydride fuels. However, the fluorine-based systems are highly toxic and present processing, handling and storage problems. Non-toxic systems having high chemical reactivity are indeed rare, which apparently explains the paucity of suitable hypergolic hybrid systems.

2. STUDIES ON HYPERGOLIC SYSTEMS

In an attempt to gain understanding of the complex chemistry involved in the pre-ignition process and to evolve new hypergolic hybrid systems, a comprehensive programme of research was undertaken in the author's laboratory several years ago. This review paper presents the chronological story of these studies.

As regards the choice of the oxidiser, the problems involved with fluorine oxidisers were well recognised. We based our studies entirely on HNO_3 or N_2O_4, which do not present high risk in handling and storage. The main emphasis of research was thus placed on solid fuels which could ignite on coming into contact with HNO_3 or N_2O_4.

Liquid-liquid hypergolic propellant systems are well-known and have been used extensively. Liquid hydrazines, such as anhydrous hydrazine, monomethyl hydrazine (MMH) and unsymmetrical dimethyl hydrazine (UDMH) ignite instantaneously with white or red fuming nitric acid (WFNA or RFNA). The high reactivity of hydrazines with oxidisers is usually attributed to the presence of *N-N* bond in them. It was, therefore, envisaged that solid organic compounds having one or more *N-N* bonds in the molecule would similarly ignite on coming into contact with HNO_3/N_2O_4.

Solid products of hydrazines with aldehydes and ketones, namely, the hydrazones are well known and can be prepared easily. For example, according to the reaction

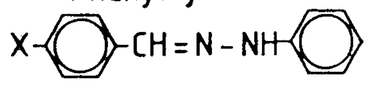
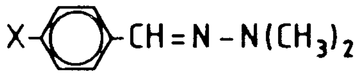
$$RCHO + H_2N\text{-}NR_1R_2 \longrightarrow RCH{=}N\text{-}NR_1R_2 + H_2O.$$

The hydrazones are non-hygroscopic and thermally stable compounds. Till we initiated our study, however, no one had examined their ignition behaviour with HNO_3 or N_2O_4. As expected, several of the hydrazones investigated[4-6] were found to ignite readily with HNO_3. Some of them indeed had very short ignition delays as measured by a drop-tester-type device[6]. A comparison of the IDs of the derivatives of substituted benzaldehydes with phenylhydrazine (phenylhydrazones) and dimethylhydrazine (dimethylhydrazones), given in Table 1, shows that the ID depends upon the substituent group[6]. It may be mentioned here that, although the magnitude of ID depends upon physical parameters (such as particle size, compactness of the fuel, experimental device) and also upon compositional factors (such as concentration of oxidiser, oxidiser/fuel ratio, additives, etc.), more basically it depends upon the chemical reactivity between the fuel and the oxidiser. The variation in IDs, determined under a given set of conditions of the various fuels, having basically the same structures but differing only by a substituent group, should clearly reflect the role of chemical reactivity in determining the ID. The IDs of the two series of hydrazones given in Table 1, amply demonstrate this point. It is also seen that the IDs depend upon the nature (electron donating and electron withdrawing) of the substituent (X) on the aldehyde benzene ring, especially in the case of phenylhydrazones. Shorter IDs with WFNA are obtained when X is an electron donating group, whereas the system becomes non-hypergolic when the substituent is an electron withdrawing group, like NO_2. Incidentally, the presence of NO_2 groups on the N-phenyl ring, as in the case of 2,4-dinitrophenylhydrazones, also results in the non-ignition of the system with *WFNA*[6]. The dimethylhydrazones ignite with relatively short ID, but their IDs do not show a clear cut dependence on the nature of the substituent group. From the data presented in Table 1, it is also apparent that shorter IDs are obtained with WFNA as compared to RFNA.

Effects of various other variables, such as O/F ratio, composition of the oxidiser, compactness of the fuel, etc. on the ID were examined[7]. In a related study, analysis of the products of combustion of some of the typical hydrazones-nitric acid systems using mass spectrometry was also carried out[8].

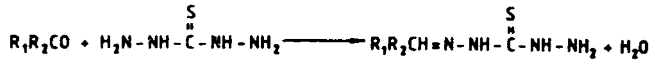
Encouraged by the studies on hydrazones, the search for hypergolic solid fuels was extended to other *N-N* bonded compounds. Compounds containing two *N-N* bonds in a molecule were the next targets. However, the aldehyde derivatives of carbohydrazide were all found to be non-hypergolic with WFNA. It is thus clear that not all compounds having *N-N* bonds are hypergolic. However, by chance, we also examined some of the solid derivatives of thiocarbohydrazide (TCH) and to our surprise, they ignited readily with

Table 1. Ignition delays (ms) of various hydrazones with nitric acid

	Phenylhydrazone 		Dimethylhydrazone 	
X	WFNA	RFNA	WFNA	RFNA
-H	102	1280		
	83	650		
	297	1730	37	103
$-OCH_3$	158	418		
$-N(CH_3)_2$	108	181	164	195
-Cl	420	NI	60	218
$-NO_2$	NI	NI	69	230

NI NO IGNITION

WFNA[9]. A comprehensive study on monothiocarbonohydrazones, which could be easily synthesised by reacting an aldehyde/ketone with thiocarbohydrazide (according to the following reaction) was undertaken.

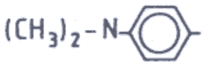
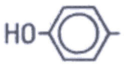
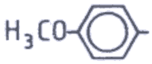
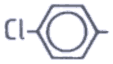
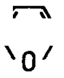


$$R_1R_2CO + H_2N-NH-\overset{S}{\overset{\|}{C}}-NH-NH_2 \longrightarrow R_1R_2CH=N-NH-\overset{S}{\overset{\|}{C}}-NH-NH_2 + H_2O$$

These derivatives are solid non-hygroscopic powders, which exist in two isomeric structural forms–linear and cyclic–depending upon the type of the aldehyde[10]. Determination of the IDs of some of the typical mono- as well as bis-thiocarbonohydrazones[11] with nitric acid given in Table 2, shows that the monoderivatives, in general, give shorter IDs[9,12]. Here again, the effect of phenyl ring substituent group on the ID is quite evident. Substitution by NO_2, an electron-withdrawing group, makes the system non-hypergolic while highly electron-donating groups result in very short IDs, of the order of 15 ms. Thus, the study provides a methodology to develop systems having the desired IDs. The results also show that the ID variation with a substituent group is similar to that observed in the case of phenylhydrazones, although much shorter delays are obtained with thiocarbonohydrazones. These data have been explained in terms of the prominent role of nitration reaction in the pre-ignition stage. An analysis of the pre-ignition products of mono-benzaldehydethiocarbonohydrazone (MBTCH) with WFNA, indeed showed the presence of a nitrated product, namely *p*-nitrobenzoic acid, besides, of course, the oxidised products[12]. It is thus evident that oxidation and nitration reactions indeed occur in the pre-ignition stage.

Besides the ignition-related studies, several other aspects of thiocarbonohydrazone were examined to assess their suitability as solid hypergolic fuels. A detailed study of the thermal decomposition process was carried out using the DTA-TG techniques and product analysis data[13]. A calorimeter was designed, for the first time, to determine accurately the heat of combustion of hypergolic propellants[14]. Actual experimental heats of combustion of the mono-thiocarbonohydrazones in HNO_3 were evaluated using a new calorimeter, which compared reasonably

Table 2. Average ignition delays of thiocarbonohydrazones

		Average ignition delay (ms)			
		Monothio-carbonohydrazone S $RR'C{=}NNHCNHNH_2$		Bis-thio-carbonohydrazone S $RR'C{=}NNHCNHN{=}CRR'$	
R	R'	WFNA	RFNA	WFNA	RFNA
H	H	64	82	87	486
	H	48	Inconsistent ignition	74	140
	CH_3	38	31	70	148
	CH_3	43	48	63	162
	H	53	68	NI	NI
	H	15	92	1360	NI
	H	40	9	NI	NI
	H	48	9	NI	NI
	H	6		NI	
	H	30	69	782	

NI No ignition; data reported earlier[9,12]; some of these compounds have cyclic structures[10]. Particle size of the fuel, 300-210 μm. Fuel/oxidiser ratio, 0.38.

well with those calculated (Table 3). The fact that the heats of formation of most of these compounds being positive, makes them suitable for propellant formulations. The theoretical performance parameters, such as specific impulse (I_{sp}), chamber temperature (T_c), characteristic velocity (C^*) and mean molecular weight of the product species ($\bar{\mu}$), of the proposed hybrid systems were evaluated[15] using a NASA-SP 273 computer program.

A significant development in hybrid systems in recent years has been the discovery of synergistic hypergolic ignition. A variety of fuels become hypergolic with WFNA on mixing with metal powders especially with magnesium[16]. In the absence of magnesium powder, these fuels are either non-hypergolic or have longer IDs (Table 4). The observation is significant considering the fact that the metallised fuels having short IDs are preferred in propellant systems. The highly hypergolic systems, however, show longer IDs on mixing with *Mg*. A detailed study of the metallised hypergolic systems with WFNA has been made[16,17]. It is noticed that minimum

Table 3. Heats of combustion in oxygen (ΔH_c) and in nitric acid (ΔH_{HNO_3}), and formation (ΔH_f) of monothio-carbonohydrazones, kcal/m

Thiocarbonohydrazone	$-\Delta H_c$	ΔH_f	$-\Delta H_{HNO_3}$	
			Obs	Calc
Benzaldehyde $C_6H_5CH{:}NHNC{:}SNHNH_2$	1239.2	+ 6.5	925.4	1179.5
p-Dimethylaminobenzaldehyde $p\text{-}(CH_3)_2NC_6H_4CH{:}NHHC{:}SNHNH_2$	1624.1	+31.0	1208.7	1550.0
2-Furfuraldehyde $C_4H_3OCH{:}NHNC{:}SNHNH_2$	964.0	-11.3	870.3	934.7
Formaldehyde $CH_2NHNC{:}SNHNH$	537.6	+ 8.6	502.7	515.7
Acetone $(CH_3)_2\,\underline{CNHNHC{:}SNHNH}$	*856.4*	*- 0.2*	*792.8*	*817.6*
Cyclohexanone $(CH_2)_5\,\underline{CNHNHC{:}SNHNH}$	1236.7	-39.8	1024.8	1179.2

Table 4. Ignition dealys of various organic compounds and their mixtures with magnesium powder (60:40) using WFNA as oxidiser

Compound	Melting/Decomposition point (°C)	Ignition delay(ms)	
		Compd	Compd : Mg 60 : 40
N-Benzylideneaniline (BA)	52	NI	132
N-*P*-Dimethylaminobenzylideneaniline (PDBA)	98/336	NI	118
2-Furfuralphenylhydrazone (FRPH)	97/258	40	119
mono-Acetonethiocarbonohydrazone (MATCH)	195/214	42	130
bis-Benzaldehydethiocarbonohydrazone (BTCH)	195/220	NI	1179
bis-Furfuralthiocarbonohydrazone (FTCH)	189/220	782	154
bis-Butanonethiocarbonohydrazone (BuTCH)	91/146	63	150
Thiocarbonohydrazide (TCH)	172/177	Inconsistent ignition	204
p-Hydroxy, m-Methoxybenzaldehyde (Vanillin)	78	NI	237
β-Naphthol	124	NI	299
Catechol	105	308	110
Glucose	146	NI	1049

NI: No ignition, for Sl Nos. 8-12, fuel:*Mg* = 30:70

IDs are normally observed at 40 to 50 per cent *Mg* content (Fig. 1). A calculation of the performance parameters of the metallised systems shows that the maximum values of specific impulse are also obtained around the same loading of *Mg*[17] (Fig. 2). This is an important result from the propellant formulation point

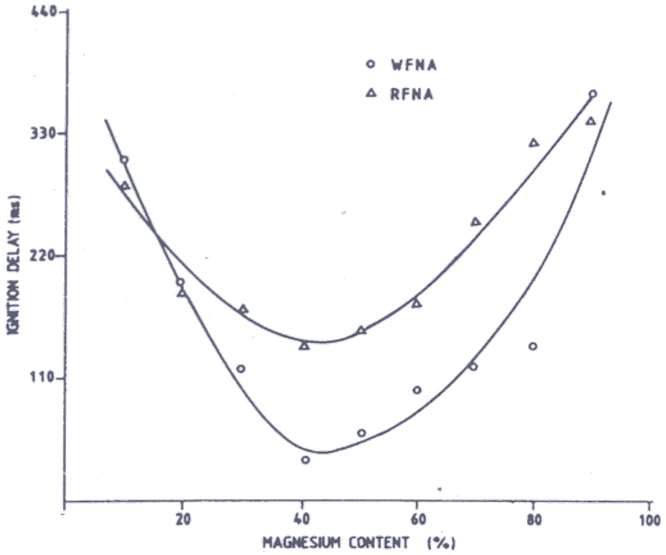


Figure 1. Effect of fuel composition on the ignition delay of PDBA-Mg mixture with WFNA and RFNA.

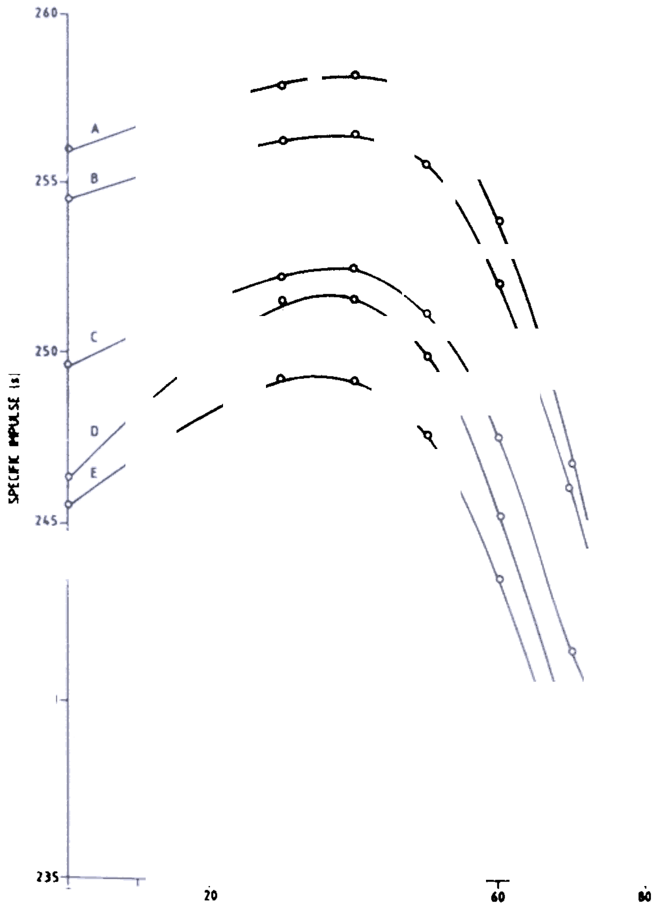


Figure 2. Variation of specific impulse with magnesium loading in various HNO_3-Mg-Fuel systems (A, PDBA; B, BA; C, FRPH; D, MATCH and E, MBTCH) under equilibrium flow conditions, $P_c = 30$ atm, $P_c/P_e = 60$.

of view. Further, the data presented in Fig. 2 are indicative of high values of I_{sp} which could be achieved by these systems.

Studies on synergistic hypergolic ignition were also performed using N_2O_4 as oxidiser. Several new systems showing synergistic hypergolic ignition with N_2O_4 have been evolved[18,19]. A variety of Schiff bases were found to ignite with N_2O_4 on mixing with Mg[18]. Here again minimum IDs were obtained when the magnesium content was between 40 and 50 per cent by weight. An examination of the mixtures of Mg with aromatic Schiff bases having different substituent groups shows that their IDs vary with the nature of the substitution in both the benzene rings. A linear relationship emerges when the IDs are plotted against the Hammett substitution constants (σ) (Fig. 3). The relationship once again indicates a strong dependence of IDs on the chemical reactivity in hypergolic systems. Similarly, mixtures of aromatic amines with Mg were found[19] to exhibit synergistic ignition with N_2O_4. A detailed analysis of the quenched products of *p*-toluidine-N_2O_4 reaction was made to elucidate reaction pathways in the pre-ignition stage.

The pre-ignition process of the hypergolic systems was also examined by monitoring the transient temperature profiles by using a new thin-film thermometric technique[16,20,21]. The technique designed and carried out indigenously measures both the IDs and temperature profiles simultaneously. A typical profile is shown in Fig. 4. More recently, a powerful spectroscopic technique, namely, rapid scan FT-IR/thermal profiling technique was used for the first time, after modifying the FT-IR cell, to examine the exothermic reactions of the hypergolic systems[22]. Besides giving temperature profiles (Fig. 5) it simultaneously monitors the gas products of the igniting system at every 250 ms interval. The gas products of reaction occurring between the *p*-phenylenediamine and HNO_3 reveal the formation of CO_2, NO_2, NO and $HONO$ (Fig. 6). No change in gas composition was observed after about 2 s interval. Synergistically igniting systems comprising substituted anilines, Mg and HNO_3 show immediate evolution of NO_2. Thiocarbonohydrazones-HNO_3 systems produce CO_2, N_2O, SO_2, NO_2 and possibly OCS[22].

3. NEW *N-N* BONDED BINDERS

The work cited so far emphasises clearly the role of

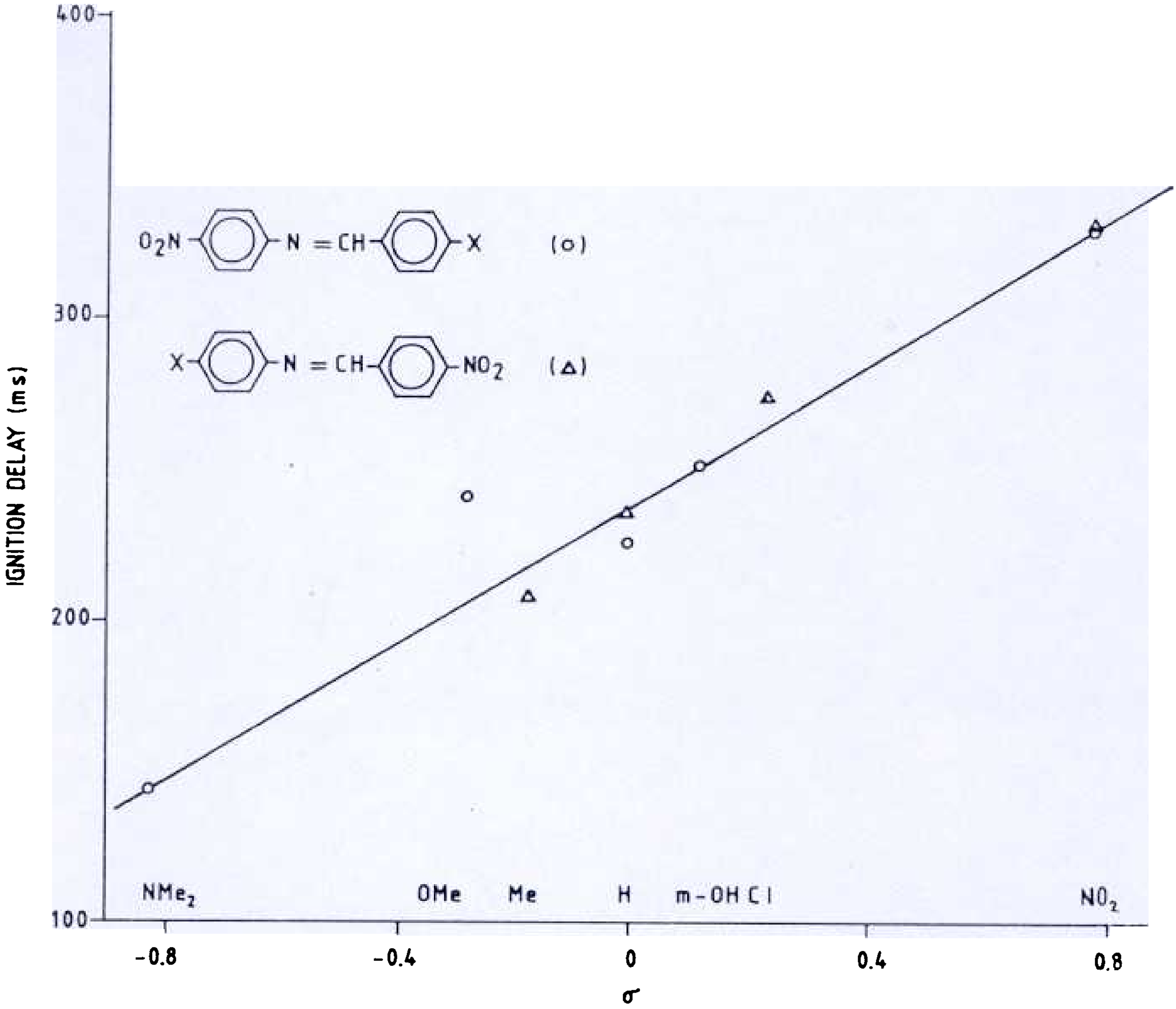
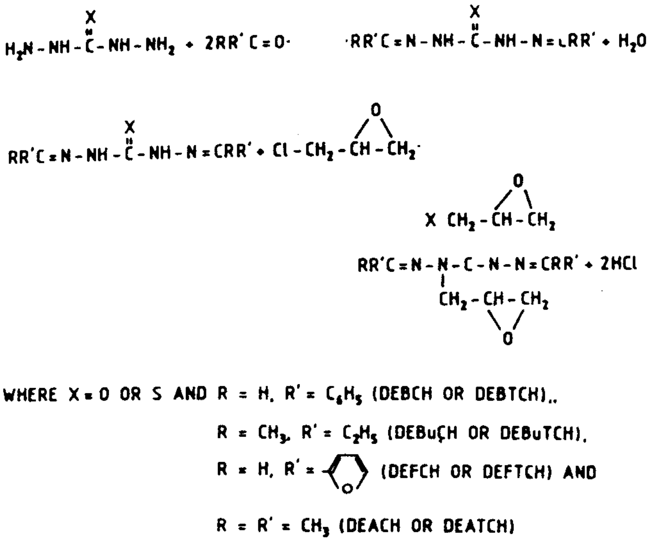


Figure 3. Variation of ID with Hammett substituent (σ) for Schiff bases: *Mg* (1:1)-HNO_3 systems.

N-N bonded compounds in hypergolic systems. To gain basic understanding of hypergolic ignition the studies on solid fuel powders have some significance. For actual use in hybrid systems, however, the powder fuels have to be cast in grain form using polymeric binders. The fuel grains after casting should have good mechanical strength without compromising their hypergolicity. Casting of even highly hypergolic powders using conventional binders like HTPB or CTPB results in an ID that is intolerably long[23]. It was envisaged that new binders having *N-N* bonds in the backbone and appropriate end groups may be better suited from the hypergolic point of view. Literature survey, however, showed that no *N-N* bonded polymeric binders were reported[24] or used till now. Our initial attempt to synthesise viscous *N-N* bonded polymers also proved unsuccessful[25]. Eventually, the epoxidation of thiocarbonohydrazones, the highly hypergolic materials discussed earlier, yielded viscous resins, which could be cured easily using amine cross linkers. This was indeed a breakthrough. Subsequently, we synthesised and characterised[26-28] a series of resins using the bis-thiocarbono-and also the bis-carbonohydrazones as base materials. All of these had convenient viscosities and were capable of undertaking high solid loadings. The diepoxy resins were prepared according to the following reactions



$H_2N-NH-\overset{X}{\overset{\|}{C}}-NH-NH_2 + 2RR'C=O \rightarrow RR'C=N-NH-\overset{X}{\overset{\|}{C}}-NH-N=CRR' + H_2O$

WHERE X = O OR S AND R = H, R' = C_6H_5 (DEBCH OR DEBTCH),

R = CH_3, R' = C_2H_5 (DEBuCH OR DEBuTCH),

R = H, R' = (DEFCH OR DEFTCH) AND

R = R' = CH_3 (DEACH OR DEATCH)

The tetraepoxy resins, e.g., vanillin carbono or thiocarbonohydrazone (TEVCH or TEVTCH), were synthesised in a similar way. Using these resins, fuel composites were made having high loading of hypergolic fuels. An examination of their IDs shows that these resins are better suited than the conventional HTPB or CTPB. The fuel grains have adequate mechanical strength and ignite smoothly with WFNA (Table 5)[29]. The effects of variables, such as fuel composition, O/F ratio, types of curatives, etc on the ID were determined. To our surprise, it was observed that the resin composites having high loading of *Mg* powder exhibit synergistic ignition on coming into contact with WFNA[29]. Even the composites prepared using bis-carbonohydrazones, which are non-hypergolic with WFNA, show synergistic ignition. In these cases too, the minimum ID is observed with 40 per cent *Mg* loading in each case (Fig. 7). The diepoxide of furfuralcarbonohydrazone-*Mg* composite gave the shortest ID of the order of 300 ms, which is further reduced to about 150 ms on using catalysed WFNA[30].

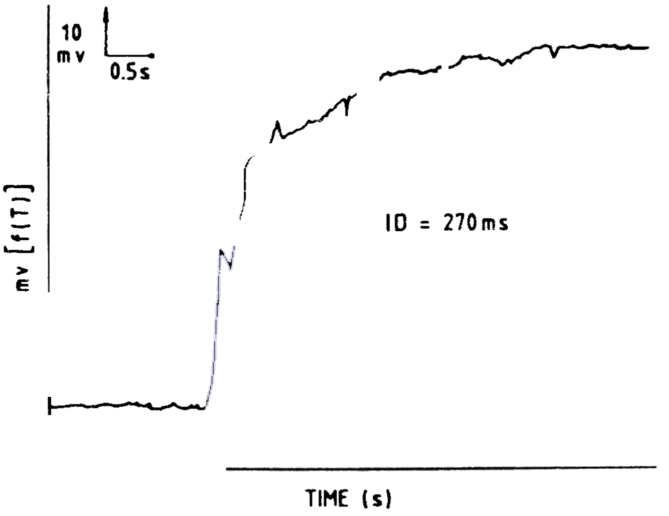


Figure 4. Temperature profile of the system, DEFCH (60) – *Mg* (40)– WFNA; amount of fuel, 40 mg; O/F = 3.5.

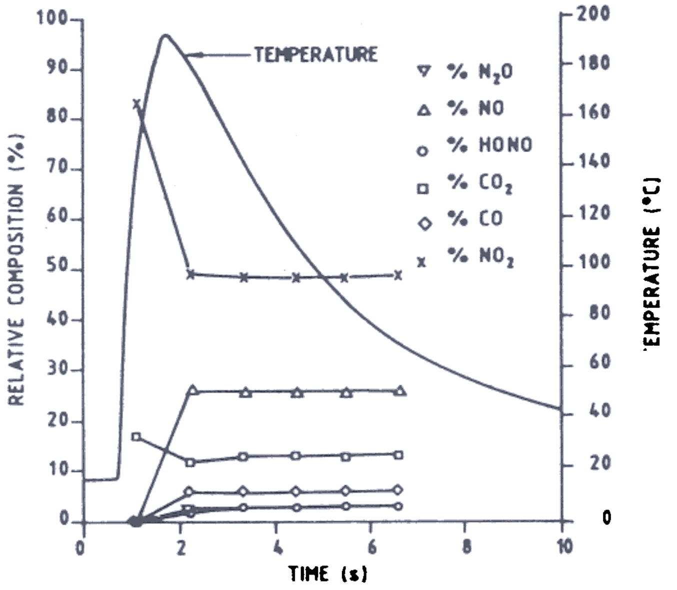


Figure 5. Temperature and gas product profiles of the reaction between p-phenylenediamine (PDA) and HNO_3.

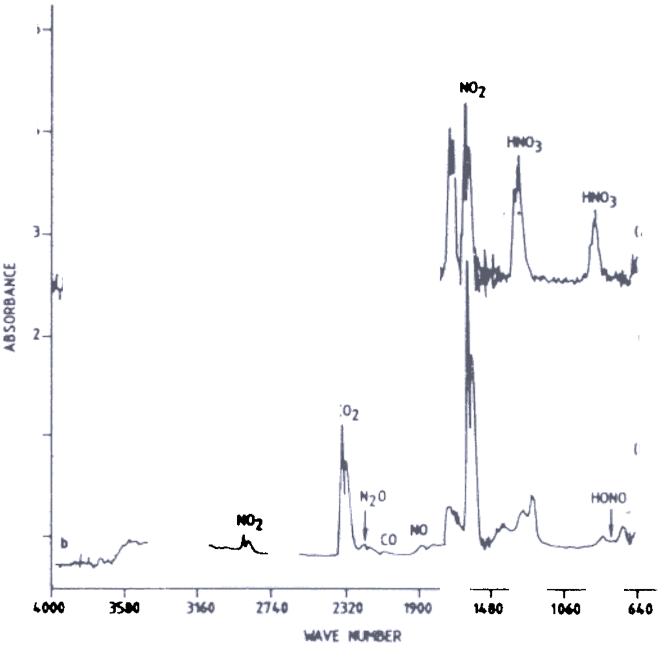


Figure 6. Rapid scan FT-IR spectra of the gas products of PDA–HNO_3 system at: (A), t = 1s and (B), t = 2s intervals.

Table 5. **Ignition delay and mechanical strength of fuel grains**

System		Compressive strength (kg/cm^2)	Ignition delay (s)
Resin (30 %)	Additive (70 %)		
DEFTCH	TCH	>15	1.712
DEACH	TCH	>15	2.815
DEFTCH	FA	>15	0.527
DEFCH	FA	>15	1.251
TEVTCH	FA	>15	0.577
TEVCH	FA	>15	1.044
HTPB	TCH	>15	8.180

Oxidiser: WFNA (0.5 ml); amount of fuel: 200 mg

These IDs being close to the tolerable limits, it is evident that the new fuel composites prepared using the *N-N* bonded epoxides are promising binders. An experimental evaluation of the heats of combustion of the binders and binder-*Mg* (60:40) composites in O_2 and HNO_3 respectively, has been carried out. The rocket performance parameters of the composites have been determined (Table 6) employing equilibrium flow conditions. The data show that use of *N-N* bonded binders not only helps in achieving tolerable IDs but also fairly high performance characteristics.

4. CONCLUSION

In conclusion, it may be pointed out that the work reported here gives only a glimpse of the fascinating area of self-igniting fuel-oxidiser systems. An understanding of the self-ignition process is slowly emerging. No claim is made that the very systems discussed in this review could be used straight away in actual applications. The present research has been carried out using only off-the-shelf chemicals, specifically to derive information on the parameters responsible for hypergolic ignition. The promising application of the *N-N* bonded fuels is, however, evident. The newly synthesised *N-N* bonded epoxides appear attractive and may play an important role in developing hypergolic fuel grains for hybrid rockets.

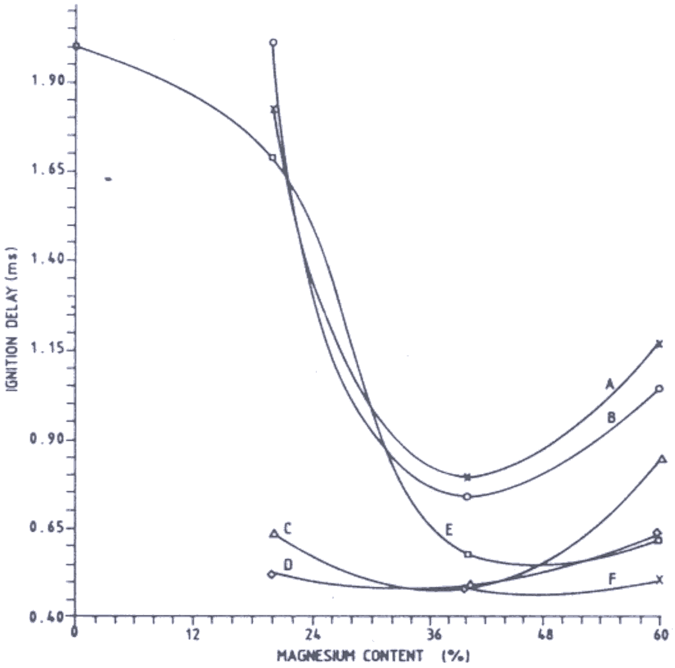


Figure 7. **Effect of magnesium content on the ID of the resin composites (A) DEBuTCH; (B) DEBuCH; (C) DEATCH; (D) DEACH; (E) DEFTCH and (F) DEFCH.**

Table 6. **Performance parameters of the various binders(60 per cent) – Mg (40 per cent)/WFNA systems: P_c = 30 atm and P_c/P_e = 60**

Resin	Parameters					
	O/F	I_{sp}(s)	I_{vac}(s)	T_c,K	$\bar{\mu}$ C^*	(m/s)
DEFCH	1.60	244.5	269.1	3337	32.90	1442
DEBCH	1.62	250.1	274.5	3317	31.40	1480
TEVCH	1.50	249.5	273.5	3251	31.00	1474
DEBuCH	2.00	251.1	276.4	3371	31.00	1505
DEFTCH	1.60	247.2	271.6	3312	32.40	1459
DEBTCH	1.75	249.7	274.5	3355	31.96	1430
TEVTCH	1.60	249.2	273.5	3286	31.50	1473
DEBuTCH	1.80	252.4	276.5	3361	30.69	1507

ACKNOWLEDGEMENTS

The author records his deep appreciation for the research contributions made by his graduate students, PMM Krishna, G Rajendran, KN Murthy and PM Thangamathesvaran, and research associates, Dr JJ Vittal, BC Thanoo and Ms Tanu Mimani. The partial financial assistance received from the Aeronautical Research & Development Board and ISRO-IISc Space Technology Cell during the course of these investigations is also gratefully acknowledged.

REFERENCES

1. Cook, J.R.; Goldberg, B.; Estey, P.N. & Wiley, D.R. Hybrid rockets: Combining the best of liquids and solids. *Aerospace America.*, July 1992, 30-33.
2. Esly, P. Hybrid rockets. *Aerospace America.*, December 1992, 62.
3. *Avn Wk & Space Technol.*, January 28, 1991, **134**, 13.
4. Jain, S.R. Ignition and thermal behaviour of solid hydrazones. *Combust. Flame*, 1977, **28**, 101-03.
5. Jain, S.R.; Krishna, P.M.M.; Sai, K.G. & Pai Verneker, V.R. Ignition delay studies on hybrid propellants. *J. Spacecr. Rockets*, 1977, **14**, 573-74.
6. Jain, S.R.; Krishna, P.M.M. & Pai Verneker, V.R. Hypergolic ignition of various hydrazones with nitric acid. *J. Spacecr. Rockets*, 1979, **16**, 69-73.
7. Jain, S.R.; Krishna, P.M.M. & Pai Verneker, V.R. Effect of various variables on ignition delays of hydrazone/nitric acid systems. *Prop. Explos.*, 1980, **5**, 135-38.
8. Jain, S.R.; Krishna, P.M.M. & Pai Verneker, V.R. Studies on the combustion of solid hydrazones with nitric acid. *Prop. Explos.*, 1980, **5**, 119-22.
9. Rajendran, G. & Jain, S.R. Novel solid hypergolic fuels for hybrid propellants. *Fuel*, 1984, **63**, 709-12.
10. Rajendran, G. & Jain, S.R. Structural assignment of monothiocarbonohydrazones by H NMR spectroscopy. *Org. Magn. Reson.*, 1984, **22**, 6-10.
11. Rajendran, G. & Jain, S.R. Synthesis and characterization of bis-thiocarbonohydrazones. *Indian J. Chem.*, 1985, **24B**, 680-82.

12 Jain, S.R. & Rajendran, G. Chemical aspects of hypergolic pre-ignition reactions of some hybrid hypergols. *Combust. Flame,.* 1987, **67**, 207-15.

13. Rajendran, G. & Jain, S.R. Thermal analysis of monothiocarbonohydrazones. *Thermochim. Acta.* 1984, **82**, 311-23.

14 Jain, S.R. & Rajendran, G. A calorimetric bomb for determining heats of combustion of hypergolic propellants. *J. Spacecr. Rockets*, 1986, **23**, 120-22.

15. Jain, S.R. & Rajendran, G. Performance parameters of some new hybrid hypergols. *J. Propuls. Pwr*, 1985, **1**, 500-02.

16 Jain, S.R.; Rao, R. & Murthy, K.N. Studies on the hypergolic ignition of hybrid systems. *Combust. Flame*, 1988, **71**, 233-43.

17 Jain, S.R. & Murthy, K.N. Studies on some novel hypergolic hybrid systems, *Preprint No. IAF-87-271*, International Astronautical Federation Congress, Brighton, U.K., 1987.

18. Jain, S.R.; Mimani, T. & Vittal, J.J. Chemical aspects of the synergistic hypergolic ignition in hybrid systems with N_2O_4 as the oxidiser. *Combust. Sci. & Technol.*, 1989, **64**, 29-41.

19 Jain, S.R.; Vittal, J.J. & Mimani, T. Some mechanistic aspects of hypergolic ignition: Reaction of dinitrogen tetroxide with solid amines and their mixtures with magnesium. *Def. Sci. J.*, 1992, **42**, 5-12.

20. Jain, S.R. & Murthy, K.N. Temperature profile and ignition delay studies on hypergolic systems. *Combust. Flame*, 1990, **81**, 403-05.

21 Jain, S.R. & Mimani, T. Temperature profiles of reactive biliquid systems prior to ignition. *J. Thermal Anal.*, 1990, **36**, 2393-406.

22 Patil, D.G.; Jain, S.R. & Brill, T.B. Thermal decomposition of energetic materials : Products of some self-igniting fuel-HNO_3 systems. *Prop. Explos. Pyrotech.*, 1992, **17**, 260-64.

23 Jain, S.R.; Murthy, K.N. & Thanoo, B.C. Ignition delay studies on hypergolic fuel grains. *Def. Sci. J.*, 1988, **38**, 273-86.

24 Jain, S.R.; Sridhara, K. & Thangamathesvaran, P.M. *N-N* bonded polymers. *Prog. Polym. Sci.*, 1993, **18**, 997-1039.

25. Jain, S.R. Development of solid fuels for hybrid rockets. ARDB Project Report, 1986.

26. Thangamathesvaran, P.M. & Jain, S.R. Synthesis and characterization of thiocarbonohydrazone-based epoxy resins. *J. Polym. Sci: Part A: Polymer Chemistry,* 1991, **29,** 261-67.

27. Thangamathesvaran, P.M. & Jain, S.R. Synthesis, characterization and binding properties of epoxy resins based on carbonohydrazones and thiocarbonohydrazones. *In* Frontiers of Polymer Research, edited by P.N. Prasad & J.K: Nigam. Plenum Press, New York, 1991. pp. 589-94.

28. Thangamathesvaran, P.M. & Jain, S.R. Curing studies on the epoxides of carbono and thiocarbonohydrazones. *J. Appl. Polym. Sci.,* 1994, **53,** 1339-50.

29. Thangamathesvaran, P.M. & Jain, S.R. New *N-N* bonded epoxides as binders for hypergolic fuel grains. *J. Aeronaut. Soc. India,* 1993, **45,** 194-201.

30. Jain, S.R. Combustible fuel binders for hybrid systems. Space Technology Cell Project Report, 1994.