Def Sci J, Vol 38, No. 3, July 1988, pp 273-286

Ignition Delay Studies on Hypergolic Fuel Grains

S.R. Jain, K.N. Murthy and B.C. Thanoo

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

ABSTRACT

The ignition delays of several solid hypergolic fuel compositions, casted using various polymeric binders, or as melts, have been determined with fuming nitric acid as oxidizer. The ignition delays of various hypergolic fuel compositions increase drastically on casting with binders like, carboxyl or hydroxyl terminated polybutadiene. Fuel grains cast using some newly synthesised epoxy resins with other ingredients, such as curing agent, magnesium powder and fuel, have short ignition delays of the order of 200 ms, and also good mechanical strength. Increasing the amount of binder in the composition retards the hypergolicity of the rain. Similar studies have been made on melt-cast systems using low melting hypergolic fuels for casting fuel powders. The ignition delays of the melt-cast grains, are longer than those determined taking the composition in the powder form. The effect of highly hypergolic additives, and metal powders, on the ignition delay of the cast compositions has been determined. Grains having good mechanical strength and short ignition delays have been obtained by optimising the fuel grain composition.

INTRODUCTION

In order that a hybrid propulsion system has repeating on-off capability, the propellants chosen must be hypergolic in nature. Short ignition delays are of definite advantage as they prevent 'hard' starts. Consideration of this aspect alone led us to investigate on variety of solid organic fuels in order to assess their hypergolicity with liquid oxidizers, such as fuming nitric acid, in our earlier studies[1-3]. Some of these fuels when examined in the powder form were found to be highly hypergolic having very short ignition delays. However, these measurements have little meaning from

---

Received 15 June 1987; revised 1 March 1988

the application point of view, since in actual usage, the fuel is taken in a cast 'grain' form. On casting, since the surface area available for chemical reaction with the oxidizer decreases drastically, it is only expected that the ignition delays will increase significantly. In some instances, a fuel which is hypergolic as a powder, may not ignite at all in the cast form. Apparently, there is no systematic study reported in the open literature on the ignition delay of cast hypergolic fuel compositions, apart from a preliminary report from this laboratory[4]. Studies made on grains[5] having a coating of highly reactive material on the surface are of little relevance since the coated system lack multiple start capability.

The casting of hypergolic fuel composition grains having good mechanical strength and at the same time igniting with short ignition delay is an involved task. Although several fuel compositions cast using polymeric binders have been reported[6-9], apparently, no study has been made relating to the effect of casting on the hypergolicity with liquid oxidizers. Furthermore, there is no standard technique described in the open literature to cast hypergolic fuel compositions using polymeric binders.

A recent development in the studies relating to the hypergolicity of organic fuels has been the use of metal powders, particularly, magnesium in large amounts, as ingredient of the fuel compositions[10,11] When examined in the powder form these give short ignition delays and highly consistent ignition with white or red fuming nitric acid (WFNA or RFNA), as oxidizers. It is, therefore interesting to examine the ignition delays of these systems in the cast form.

In the present study, the fuel grains have been prepared by using various polymeric binders, and also by melt-casting technique. Using a polymeric binder the fuel mix is processed in a manner similar to that used in solid composite propellants. Since most of the commercially available polymers when used as binders impart the structural strength at the expense of desirable ignition delay, new epoxy resins have been synthesised and used as binders. Using the melt-cast technique, hypergolic organic fuels, synthesised earlier, which melt at relatively low temperatures without undergoing decomposition, have been cast with suitable additives by melting and subsequent cooling. The effect of casting and composition on the ignition delay and mechanical strength of the fuel grain is reported in this investigation.

2. EXPERIMENTAL

2. Materials

The phenylhydrazones of furfuraldehyde, formaldehyde and *p*-dimethylaminobenzaldehyde (FRPH, FMPH and DBPH), *p*-dimethylaminobenzaldehydedimethylhydrazone (DBDMH), thiocarbohydrazide (TCH), monoacetonethiocarbonohydrazone (ACTCH), monocyclohexanonethiocarbonohydrazone (CHTCH), benzylideneaniline (BA), dimethylaminobenzylideneaniline (DBA) and vanillylideneethylenediamine were synthesised as reported in the earlier studies[1-3,11,12]. *p*-Phenylenediamine (PD) and ethylenediamine were purchased from commercial sources. Magnesium powder was supplied by M/S Sarabhai Chemicals. Trimethylamineborane (TMAB) was purchased from M/S PCR

Incorporated, USA. The hydroxyl- and carboxyl-terminated polybutadienes (HTPB and CTPB respectively), ter-polymer of butadiene, acrylic acid and acrylonitrile (PBAN) prepolymers and tris (2-methyl-azridinyl) phosphineoxide (MAPO), a curing agent for CTPB and PBAN, were supplied by VSSC, Trivandrum.

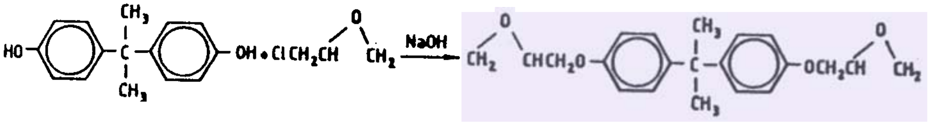
The anhydrous white fuming nitric acid was prepared in the laboratory by distilling from a 3 : 1 mixture of fuming nitric acid and concentrated sulphuric acid, under reduced pressure. On analysis the acid was found to contain, HNO_3 99.8 per cent with traces of NO_2. The red fuming nitric acid having 10 per cent NO_2 was prepared by mixing calculated amount of WFNA and liquid NO_2.

Vanillineazine was prepared by condensing vanillin (*p*-hydroxy, *m*-methoxy-benzaldehyde) and hydrazine. A mixture of powdered hydrazine sulfate (25 g, 0.18 mol), ammonia solution 28 per cent (25 ml) and water (200 ml) was stirred in a flask till a clear solution was obtained. To this, a solution of vanillin (66.12g, 0.435 mol) in ethanol (150 ml) was added slowly and the mixture stirred for two hours. A solid product was obtained which was filtered and recrystallized from aqueous ethanol. It was characterized by its melting point, (mp, reported[13] 177-178°; obtained, 178°C).

2.2 Synthesis of Epoxy Resins

2.2.1 Diglycidylether of Bisphenol A (Resin 1)

This resin was prepared by condensation of bisphenol *A* with an excess of epichlorohydrin in the presence of an alkali[14].



A mixture of bisphenol *A* (34.2 g, 0.15 mol) and an excess of epichlorohydrin (185 g, 2.0 mol) was taken in a two-necked r.b. flask, connected to a Dean-Stark apparatus and heated to 100-120°C. Sodium hydroxide solution (40 per cent, 30 ml) was added slowly to the reaction mixture. During the reaction, water and unreacted epichlorohydrin were continuously distilled. After complete addition of alkali, the excess epichlorohydrin was removed by heating the mixture to 150°C at atmospheric pressure and then at reduced pressure. The salt formed during the reaction was separated from the crude product by the addition of toluene, followed by filtration. The toluene was subsequently removed by distillation at reduced pressure. The resin obtained was yellow, and viscous in nature. It was characterized by its infra-red and proton magnetic resonance (PMR) spectra which matched very well with those reported in the literature[15].

2.2.2 Diglycidylether of Vanillinazine (Resin 2)

This resin was prepared by following exactly, the procedure as described above, excepting that in this case Vanillin azine was used instead of bisphenol *A*. The epoxidation was carried out with the azine to epichlorohydrin mole ratio, 1 : 20. The resin obtained was an amber-yellow fluid which becomes a viscous liquid above 40°C but remains as a solid below 25°C.

2.2.3 Diglycidylether of Vanillylidene Ethylenediamine (Resin 3)

The resin was prepared following the same procedure adopted earlier by reacting the imine (0.1 mol) with an excess of epichlorohydrin (2 mols) in presence of the alkali. The resin thus obtained, was wine red, viscous mass at ambient temperature but a flowable viscous liquid at elevated temperatures.

2.3 Processing

In order to cast fuel grains, the various powder components were mixed with the requisite amount of the resin. A well-mixed fuel powder composition was prepared and added in portions, to the resin taken in a beaker. After addition of the fuel composition, the curing agents were added and mixed well. The epoxy resins 2 and 3 being waxy materials, the mixing operation was done at an elevated temperature (around 50°C). The mix was then packed into a Teflon mould having inner dimensions 1.5 × 1.5 × 10 cm, and cured at 80°C for 20 hours. The cured fuel grain was taken out and cut in the form of approximately 2 mm thick pellets. The pellets were used directly for the ignition delay, and compression strength measurements. The typical sample weight of a pellet was about 300-400 mg. The fuel powders used for ignition delay studies were prepared by crushing the cast pellets.

For melt-casting, a weighed amount of the solid fuel powder was taken in a beaker and heated till the fuel melted. The required additives were added to the melt and stirred to ensure uniform mixing. The resulting mixture was then cast in soft glass test tubes or Teflon mould. It was allowed to set at room temperature for 24 hours.

2.4 Ignition Delays

The ignition delays were measured at room temperature, using apparatus described earlier[2,3]. Those reported in this investigation are averages of at least five readings for the respective system. The deviations observed are of the order of 10 to 12 per cent. The ignition delays, unless stated, were determined using WFNA (0.5 to 0.6 ml).

2.5 Compression Strength

The compression strength of the fuel pellets was measured using a Thermonic tablet hardness tester. In some cases, for pellets having strength above 15 kg/cm^2, a Universal Testing machine was used.

3. RESULTS AND DISCUSSION

The ignition delays of the fuel compositions without metal additives using conventional binders, CTPB and PBAN are presented in Table 1. These binders by

Table 1 Ignition delay data

Sl.No.	Composition				Average ignition delay
	Fuel (%)	Binder (%)	Plasticizer (%)	Additive (%)	(sec)
1.	CHTCH (85)	CTPB (13)	DBS (2)		2.74
2.	CHTCH (75)	CTPB (22.8)	DBS (2.2)		6.64
3.	CHTCH (80)	CTPB (16)	DBS (4)		2.95
4.	CHTCH (75)	CTPB (16)	DBS (4)	TMAB (5)	2.87
	CHTCH (90)	PBAN (8)	DBS (2)		10.51

DBS, dibutylsebacate

themselves are non-hypergolic with both oxidizers WFNA and RFNA. From the data, it is obvious that when CTPB is used as a binder, the ignition delay of the fuel, CHTCH cast, having solid loading as much as 85 per cent is of the order of 2-3 sec, an over hundred times increase in ignition delay, observed when the fuel is taken in the powdered form without using the binder. It increases further if the fuel loading is decreased. The effect of using an additive, such as trimethylamineborane (a highly hypergolic compound, having ignition delay of about 8 m sec with WFNA), in the composition, also has only a marginal effect on the ignition delay. The use of PBAN as a binder instead, again has a deleterious effect on the ignition delay.

The ignition delay and compression strength data of various fuel compositions having magnesium powder, using HTPB, as binder are given in Table 2. Here again, HTPB as such or its mixture with magnesium powder are nonhypergolic with WFNA or RFNA. Although DBA is nonhypergolic, its mixtures with magnesium powder are highly hypergolic[11]. The ignition delays of these compositions cast using HTPB binder with different curators, as expected, are much longer for the pellets than their powders. Whereas these vary from 675 to 5000 m sec for the pellets, the variation is much less, from 400 to 600 m sec, for the powders, of various compositions, emphasising the role of the binder processing and curing. The mechanical strength of the cast compositions are good except of those cured with toluenediisocynate (TDI) having small amounts of water. Usually, the TDI-H_2O cured systems result in a foamy mass. The addition of cross-linkers such as thiocarbohydrazide (TCH) or monoacetonethiocarbonohydrazone (ACTCH) enhances the mechanical strength of the casts. It is worthwhile to point out that these additives, not only act as cross linkers but by themselves, are highly hypergolic with WFNA. The NH_2 group of these cross linkers may react with the isocynate ($-NCO$) group much faster, leading to the formation of urea linkage, which is rigid enough to enhance the mechanical strength of the system. Of the two, the systems having TCH as cross-linker, have considerably lower values of ignition delay. However, in general the HTPB-TDI binder system appears to be unsuitable from ignition delay point of view.

Table 2. Ignition delay and mechanical strength data of HTPB cured systems

Sl. No.	Binder composition (%)					Mg Powder (%)	DBA (%)	Average ignition delay* (m. sec)		Compression strength (kg/cm^2)
	HTPB	TDI	H_2O	TCH	ACTCH			Pellet	Powder	
	17	3				40	40	2000		
	25	5				40	30	764	741	
	15	14				50	20	5000		b
	37	25				17.5	17.5	3200		c
	12	12		6		50	20	700	386	
	12	12		6		40	30	884	444	
	12	12		6	–	30	40	675	405	
	12	12			6	50	20	NI	594	
	12	12			6	40	30	1416	545	>15
	12	12			6	30	40	3746	547	>15

NI, no ignition; a, flexible; b, foamy; c, elastomeric

Table 3. Ignition delay and mechanical strength data of cured systems using epoxy resins[1]

Sl. No.	Binder (%)				Mg powder (%)	Fuel (%)		Average ignition delay (m. sec)		Compression strength (kg/cm^2)
	Resin 1	TCH	ACTCH	PD		FRPH	DBA	Pellet		
1.	45	15			40			NI	2300	>15
2.	30	30			40			NI	820	>15
3.	25	15			40		20	NI	400	>15
4.	15	35	–		50	–		NI	200	>15
5.	25		15		40	20		NI	443	>15
6	15		20		40	25		NI	232	>15
7	37.7			12.3	50			NI	NI	>15
8.	42.5			7.5	50			NI	NI	>15
9.	20.5			6.5	36.5		36.5	3430	476	>15
10.	30			30	50			704	310	7.0

The epoxide resin 1, by itself is not hypergolic with WFNA or RFNA. However, when mixed with magnesium powder, it ignites readily with WFNA. The ignition delay data of epoxy resin 1 cured systems, presented in Table 3, show that most of them are nonhypergolic in the pellet form with WFNA although they have good mechanical strength. Many of these compositions are, however, hypergolic when examined in the powdered form. These results clearly show that hypergolicity of a system in the powdered form does not necessarily mean that it will be hypergolic in the pellet form also.

The vanillin based epoxides (resin 2 and 3) were chosen since the presence of two electrophilic groups (OH and OCH_3) in the benzene ring helps in reducing the ignition delay with WFNA[2,3]. All of the metallised fuel compositions processed using epoxide resin 2, are found to be hypergolic, both in the pellet as well as powdered form, with WFNA, although the resin alone is non-hypergolic. As shown in Table 4, depending upon the composition, the average ignition delay varies from 176 to 630 m sec. This variation is narrow considering the composition differences of the casts. In order to ascertain the effect of composition variables, the ignition delay data were obtained on casts having the same amount of magnesium powder and curing agent (TCH or ACTCH). A comparison of the ignition delays of various cast pellets, reveal no clearcut trend with the variation in composition. Even the change of fuel, from FRPH to DBA in the composition have no significant effect on the ignition delay. Similarly, replacing the curator TCH with ACTCH also deos not affect the ignition delay significantly. However, it is noticed that the shortest ignition delay of a system is obtained when the resin to curator ratio is 1 : 1 by weight.

The ignition delay and compression strength data of the various metallised compositions processed using epoxide resin 3, are presented in Table 5. These data are akin to those obtained on compositions having resin 2, as binder. The various compositions are hypergolic both in the pellet as well as in the powdered form. The ignition delay with WFNA, vary from about 200 to 1430 m sec depending upon the amount of the resin and the fuel used. Here again, apparently little change is observed in the ignition delays on changing one fuel (FRPH) with the other (DBA). However, changing the curator, from TCH to ACTCH, results in longer ignition delays. Coincidentally perhaps, in this case also, the minimum ignition delays are obtained when the resin to curator ratio is 1 : 1. It is also noticed that the ignition delays observed with RFNA are much longer than those with WFNA.

From the results presented in Tables 4 and 5, it is apparent that the overall performance of the compositions cast using resin 2 and 3, are comparable. In both cases, the cast compositions have good compression strength, as well as, short ignition delays. Some of the compositions have ignition delays as short as 200 m sec, in the pellet form, and even shorter in the powdered form. However; there appears to be no strict one-to-one correlation between the delay data on the powders and the pellet forms, of various fuel compositions, although a rough correlation seems to exist, in some cases. For example, the delay data reported in Table 4 (systems 1 to 3) show a clear decrease with increase in the fuel loading from 20 to 30 per cent when the composition is taken in the powdered form, a trend which is not apparent from the data on the cast pellets. On the other hand, the data presented in Table 5 (systems 1 to 3) do indicate the possibility of a correlation between the ignition delay data on the powdered and the pellet forms. These results, once again, emphasise the role of surface characteristics in determining the ignition delays.

A comparison of the ignition delays of the three epoxide cured systems having the same fuel composition viz., epoxide, 25; Mg, 40; curator, 15; and organic fuel, 20 per cent (by weight), has been carried out in Table 6. It is seen that compositions processed with resin 1, ignite with WFNA only in the powdered form. The cast-pellets

Table 4. Ignition delay and mechanical strength data of cured systems using epoxy resin 2

Sl. No.	Binder			Mg powder (%)	Fuel (%)		Average ignition delay (m sec)		Compression strength (kg/cm^2)	Density (g/cm^3)
	Epoxy resin 2	TCH	ACTCH		FRPH	DBA	Pellet	Powder		
		15		40	20		401	84	>15	1.4
	20	15		40	25		579	78	>15	1.1
3.	15	15		40	30	–	427	41	>15	1.1
4.	25	15		40	–	20	570	126	>15	
5.	20	15		40		25	294	116	>15	1.1
6.	15	15	–	40	–	30	400	106	>15	
7.	25		15	40	20		547	206	>15	–
8.	20		15	40	25		557	273	>15	0.9
9.	15		15	40	30	–	176	90	>15	0.9
10.	25		15	40	–	20	355	322	>15	1.0
11.	20		15	40		25	416	155	125.7	
12.	15		15	40		30	630	116	104	

Table 5. Ignition delay and mechanical strength data of cured systems using epoxy resin 3

Sl. No.	Binder (%)			Mg powder (%)	Fuel (%)		Average ignition delay (m sec)		Compression strength (kg/cm^2)	Density (g/cm^3)
	Epoxy resin 3	TCH	ACTCH		FRPH	DBA	Pellet	Powder		
	25	15		40	20	–	470	92	>15	1.4
	20	15		40	25	–	384	97	>15	1.0
	15	15		40	30	–	198,342*	74	60.4	0.8
	25	15		40		20	490	145	>15	1.3
5.	20	15		40		25	407	152	>15	1.2
	15	15	–	40	–	30	374,1768*	97	>15	1.1
	25		15	40	20	–	NI	352	>15	1.1
	20		15	40	25	–	450	94	95.58	
	15		15	40	30	–	690	108	>15	1.0
10.	25		15	40		20	1426	187	61.87	
11	20		15	40		25	924	209	194	
12	15		15	40		30	236	125	59.8	

* RFNA (10% NO_2) used as oxidizer

Table 6. Ignition delay data of various binder compositions

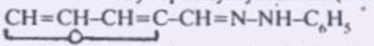
Composition	Average ignition delay (m sec)					
	Resin 1		Resin 2		Resin 3	
(%)	Pellet	Powder	Pellet	Powder	Pellet	Powder
Resin 25, Mg 40, TCH 15, DBA 20	NI	400	570	126	490	145
Resin 25, Mg 40, ACTCH 15, FRPH 20	NI	443	547	206	NI	352

are non-hypergolic irrespective of the kind of fuel and cross-linker used. All compositions processed using resin 2, are hypergolic both in the powdered form as well as the pellet form. Similarly, fuel compositions, processed using resin 3, having DBA and TCH are hypergolic in both the forms. Although the resin 3 compositions having ACTCH (20 per cent) and FRPH (15 per cent) do not ignite in the pellet form, these systems at other concentrations of ACTCH and FRPH, do ignite even in the pellet form, as seen from Table 4. The results show the superiority of the epoxide 2 and 3 systems when considered from the ignition delay point of view and thereby, emphasise the role of the chemical make-up of a binder in determining the ignition characteristics of hybrid propellant system. It may be that of the latter two epoxide resins, better results achieved in the case of resin 2, are related to the presence of a *N-N* bond in the resin structure.

For melt-casting, compounds No. 1 to 6 listed in Table 7, which melt sufficiently below their decomposition temperatures and also have fairly short ignition delays with WFNA in the powdered form, were chosen from an inventory of the hypergolic systems examined earlier[1,2]. As shown therein, it is clear that their ignition delays increase significantly, once they are processed in the cast form. Of these, *p*-chloro- and *p*-hydroxydimethylhydrazones exhibit inconsistent ignition or extremely long ignition delay, and hence were not considered for further study. The ignition delays of FRPH and FMPH in the cast form being relatively shorter, and also since they melt below 100 C, these compounds were mainly used for mixed-cast composition studies.

In order to reduce the ignition delay further, it was considered appropriate to mix the compounds mentioned above with highly hypergolic fuels, such as CHTCH and TMAB, compounds No. 7 and 8 respectively, in Table 7, and then study them in the cast form. The ignition delay data of the mixed melt-casts are given in Table 8. It is noticed that the ignition delays of various compositions of FRPH are decreased on addition of TMAB. Compositions having 10 to 15 per cent TMAB do indeed exhibit short ignition delays both with WFNA and RFNA. Also, the mechanical strength of the fuel casts is good. However, increasing the concentration of TMAB further, spoils the structural integrity of the grain, although the ignition delay becomes desirably short. The addition of another highly hypergolic fuel, CHTCH, to the melt of FRPH also results in decreasing the ignition delay, as compared to that of the grain

Table 7 Ignition delays of some organic compounds with WFNA

Sl. No.	Compound	M.P./Decom. Temp. (°C)	Average ignition delay (sec)	
				Pellet
1.	2-Furfuraldehydephenylhydrazone (FRPH)  $\underbrace{CH{=}CH{-}CH{=}C}_{O}{-}CH{=}N{-}NH{-}C_6H_5$ *	98/258	0.115	22
2.	p-Dimethylaminobenzaldehydephenlhydrazone (DBPH) $(CH_3)_2NC_6H_4{-}CH{=}N{-}NH{-}C_6H_5$	144/295	0.108	3.25
3.	Formaldehydephenylhydrazone (FMPH) $CH_2{=}N{-}NH{-}C_6H_5$	70/210	0.302	0.704
4.	p-Dimethylaminobenzaldehydedimethylhydrazone (DBDMH) $(CH_3)_2NC_6H_4{-}CH{=}N{-}N(CH_3)_2$	70/307	0.164	2.38
5.	p-Chlorobenzaldehydedimethylhydrazone (CBDMH) $ClC_6H_4{-}CH{=}N{-}N(CH_3)_2$	64/248	0.060	inconsistent flame
6.	p-Hydroxybenzaldehydedimethylhydrazone (HBDMH) $OHC_6H_4{-}CH{=}N{-}N(CH_3)_2$	150/235	0.080	11.94
7.	Monocyclohexanonethiocarbonohydrazone (CHTCH) $(CH_2)_5C{-}NH{-}NH{-}C:S{-}NH{-}NH$	169/179		
8.	Trimethylamineborane (TMAB) $(CH_3)_3NBH_3$	93/173		
9.	N-Benzylideneaniline (BA) $C_6H_5{-}CH{=}N{-}C_6H_5$	52/	No ignition	No ignition
10.	N-p-Dimethylaminobenzylideneaniline (DBA) $(CH_3)_2NC_6H_4{-}CH{=}N{-}C_6H_5$	98/	No ignition	No ignition

* Boiling point.

Table 8. Ignition delays of melt-cast compositions

Sl. No.	Fuel composition	Oxidizer	Average ignition delay (sec)	Mechanical strength
	FRPH (95%) + TMAB (5%)	WFNA	1.264	good
	FRPH (90%) + TMAB (10%)	WFNA	0.698	good
	FRPH (85%) + TMAB (15%)	WFNA	0.149	good
	FRPH (80%) + TMAB (20%)	WFNA	0.149	poor
	FRPH (90%) + TMAB (10%)	RFNA	0.438	
6.	FRPH (80%) + TMAB (20%)	RFNA	0.064	very poor
7.	FRPH (95%) + CHTCH (5%)	WFNA	0.916	good
8.	DBPH (95%) + CHTCH (5%)	WFNA	2.115	good
9.	DBPH (95%) + TMAB (5%)	WFNA	no ignition	good
10.	DBDMH (95%) + TMAB (5%)	WFNA	2.554	good

Table 9. Ignition delays of melt-cast compositions

Sl. No.	Fuel composition	Oxidizer*	Average ignition delay (sec)	Mechanical strength
1.	FMPH (10%) + CHTCH (90%)	WFNA	0.067	very poor
2.	FMPH (15%) + CHTCH (85%)	WFNA	0.096	poor
3.	FMPH (20%) + CHTCH (80%)	WFNA	0.261	fair
4.	FMPH (25%) + CHTCH (75%)	WFNA	0.238	fair
5.	FMPH (30%) + CHTCH (70%)	WFNA	0.242	fair
6.	FMPH (25%) + CHTCH (75%)	RFNA	1.253	good
7	FMPH (25%) + FRPH (75%)	RFNA	2.828	good
8.	FMPH (25%) + CHTCH (65%) + TMAB (10%)	RFNA	0.374	poor
9.	FMPH (25%) + CHTCH (55%) + TMAB (20%)	RFNA	0.159	good
10.	FMPH (30%) + CHTCH (65%) + Al (5%)	WFNA	0.943	good
	FMPH (30%) + CHTCH (60%) + Al (10%)	WFNA	1.068	good
12.	FMPH (30%) + CHTCH (55%) + Al (15%)	WFNA	1.212	good
13.	FMPH (30%) + CHTCH (60%) + Mg (10%)	WFNA	0.598	good
14.	FMPH (30%) + CHTCH (55%) + Mg (15%)	WFNA	0.666	good

without additive. However, the ignition is rather erratic in this case; the ignition stops and restarts again after sometime. The addition of CHTCH to the melt of DBPH also results in decreasing the ignition delay, to some extent. It is further noticed, that the addition of just 5 per cent TMAB to the DBPH melt results in making the casts non-hypergolic with WFNA. This is rather surprising since TMAB being highly hypergolic its addition should have, instead, resulted in a decrease in the ignition delay. On examining the casts closely, it was realised that TMAB actually reacts chemically with DBPH. The yellow casts of DBPH become almost black when TMAB is used as additive. The addition of TMAB to DBDMH casts, on the other hand, had only a marginal effect on the ignition delay.

Formaldehyde phenylhydrozone (FMPH) actually is a low melting thermoplastic polymer and, therefore, was considered as a suitable binder for casting higher loadings of the additive. The ignition delays of the various cast compositions of FMPH having CHTCH as the main fuel ingredient, are given in Table 9. It is noticed that although compositions having 80-90 per cent CHTCH loading have short ignition delays, the mechanical strength of the grains is poor. Compositions having 70-75 per cent CHTCH loading, have ignition delays of the order of 250 m sec. with WFNA, with grains having good mechanical strength. These casts, however, exhibit much longer ignition delays with RFNA. The use of FRPH instead of CHTCH, as additive also results in longer ignition delay with RFNA.

There is a significant improvement in the ignition delays of the casts when TMAB is added as a third ingredient. A cast composition of FMPH having 20 per cent TMAB and 55 per cent CHTCH has a significantly short average ignition delay (159 m sec), as well as good mechanical strength. Introducing aluminium or magnesium powder as a third ingredient to the compositions of FMPH and CHTCH, however, appears to result in an increase in the ignition delay. This effect is more pronounced in the case of aluminium, wherein the ignition delay increases rather steeply with the increase in the concentration of aluminium in the cast.

The oxidizer used also plays an important role in determining the ignition delay. Whereas the melt cast compositions of FRPH with TMAB exhibit shorter delays with RFNA as compared to these with WFNA, the reverse appears to hold good in the case of the compositions of FMPH with CHTCH. This trend apparently seems to be determined by the type of the additive used, since the observed ignition delay of FRPH is longer with RFNA than with WFNA[16].

The addition of magnesium powder in major amounts to various other melt-cast systems results in short ignition delays as reported in Table 10. Significant decrease in the ignition delays of the melt-cast pellets of FRPH is noticed when 40 to 60 per cent magnesium powder is used in the cast. These samples also have good compression strength.

Realising that the mixing of magnesium with organic fuels helps in their ignition with WFNA[11], some of the systems which by themselves are non-hypergolic, were also examined. Non-hypergolic Schiff bases, BA and DBA respectively, were mixed with magnesium powder and cast by melting the base. The cast pellets were found to ignite readily with remarkably short ignition delays with WFNA (Table 10). Furthermore, the pellets also have high mechanical strength in a certain range of mix composition. For example, the melt cast pellets of DBA with 40 per cent magnesium powder have an average ignition delay of 212 m sec and compression strength higher than 15 kg/cm^2. Usually, however, the compression strength decreases with the loading of magnesium powder.

In general, the studies on melt cast compositions show that although the ignition delay of an organic fuel hypergolic with WFNA, increases on melt casting, it could be improved, to some extent, by adding a highly hypergolic fuel. Normally, the effect of using a more hypergolic fuel as additive, results in shorter ignition delays as expected, provided it does not react chemically with the fuel on melt casting. However, the delays can be reduced only to some extent keeping the structural integrity of the grain. It is usually observed that the mechanical strength of the cast is affected adversely on addition of excess amount of the additive. A similar effect is observed in the case of metallised grains (Table 10). The ignition delays show a minimum when the magnesium content is 40-50 per cent in the composition. In some cases a further decrease in the delay observed with increase in magnesium content, may be due to the loss in the structural integrity of the grain rather than as a result of the composition.

Table 10 Ignition delays of metallised compositions

Sl. No.	Compound	Mg powder	Average ignition delay (sec)	Compression strength (kg/cm^2)
	Furfuraldehydephenylhydrazone (FRPH)	30	0.856	
		40	0.331	
		50	0.261	5.0
		60	0.283	1.2
		70	0.298	0.5
	N-Benzylideneaniline (BA)	30	0.332	>15
		40	0.200	15
		50	0.249	3.0
		60	0.337	0.8
		70	0.451	0.3
	N-p-Dimethylaminobenzylideneaniline (DBA)	30	0.596	>>15
		40	0.212	>15
		50	0.116	2.2
		60	0.158	
		70	0.214	

On increasing the loading of magnesium the grain becomes porous because of insufficient fuel melt; consequently, a larger surface area is available for chemical reaction with the oxidizer, thereby, causing a reduction in the ignition delay.

The phenomenon of synergistic ignition exhibited by the cast mixtures of magnesium and organic fuel with WFNA, was observed earlier[10,11], wherein a powdered mixture of the materials were used, instead. This phenomenon is exhibited by a variety of organic fuels and metal powder mixtures[11]. Although the mechanism of this process is not clearly understood, an explanation was attempted by Gune et al.[10] based on their study of synergistic hypergolicity of aromatic primary amines and magnesium mixtures, in terms of the formation of nitramines and their subsequent decomposition. It is, however, not a general mechanism and does not explain the synergistic ignition of metals on non-nitrogen compounds. A general mechanism postulated[11] recently, on the basis of mutual exothermicity of the chemical reactions occurring between the organic fuel, magnesium and nitric acid, appears more reasonable and could be operating in systems of the present study.

ACKNOWLEDGEMENT

[illegible] Ministry of Defence, India. We gratefu
received during the course of this investigation

REFERENCES

Jain, S.R., *Combust. & Flame,* **28** (1977), 101.

2. Jain, S.R., Krishna, P.M.M. & Pai Verneker, V.R., *J. Spacecraft and Rockets,* **16** (1979), 69.

3. Rajendran, G. & Jain, S.R., *Fuel,* **63** (1984), 709.

4. Pitchaiah, K. & Krishna, P.M.M., *J. Spacecraft and Rockets,* **17** (1980), 284.

5. Pugibet, M. & Moutet, H., *La Recherche Aerospatiale,* **132** (1969), 15.

6. Vessel, E.D. & Ebeling, R.W. Jr., *Chem. Abst.,* **77** (1972), 50940.

7. Verdier, C., *La Recherche Aerospatiale,* **137** (1970), 181.

8. Netrochemie, GMBH, *Chem. Abst.,* **78** (1973), 6089.

9. Moutet, A. & Barrere, M., *Proc. Int. Congr. Aero. Sc.* (1960), 465; *Chem. Abst.,* **68** (1963), 585442.

10. Gune, S.D., Kulkarni, S.G. & Panda, S.P., *Combust. & Flame,* **61** (1985), 189.

Jain, S.R., Rao, R. & Murthy, K.N., *Combust. & Flame* **71** (1988), 233.

12. Rajendran, G., *Ph.D. Thesis* Indian Institute of Science, Bangalore, 1984.

13. Beilsteins Handbuch der Organischen Chemie, (Springer-Verlag, Berlin), Vol **8**, 1970, p. 2038.

Potter, W.G., Epoxy Resins (Springer-Verlag, New York), 1970, p. 12.

15. Lee, H. & Neiville, K., Hand Book of Epoxy Resins (Mc Graw Hill Book Co. New York), 1967, pp. 4-38.

16. Jain, S.R., Krishna, P.M.M., Gautam Sai, K. & Pai Vernekar, V.R., *J. Spacecraft and Rockets,* **14** (1977), 573.