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Hydrazine rocket fuels*

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Abstract

This paper reviews the work carried out by the author on hydrazine fuels. The major aspect relates to the solid derivatives of hydrazines, which have been conceived as fuels for hybrid rockets. The hypergolicity of these fuels with commonly used oxidizers like white- or red-fuming nitric acid (WFNA or RFNA) has been examined. The dependence of the ignition delay on the chemical make up of the fuel has been explored. The preignition reaction process has been examined to pin point the nature of chemical reactions, by isolating the reaction intermediates, and by examining transient temperature profiles. Other studies on hybrid systems include calculation of theoretical performance parameters, thermal decomposition, determination of heats of combustion in WFNA, synergistic ignition and development of metallized fuels, etc. Investigations pertaining to anhydrous hydrazine as a monopropellant involve catalytic decomposition and catalyst development studies. For solid rockets, the use of oxonium salts of hydrazine, namely, hydrazinium mono- and diperchlorates, have been considered as oxidizers. On the synthesis side, considering the problems associated with the prevailing aqueous processes, an anhydrous process, wherein hydrazine and substituted hydrazines could be synthesised in non-aqueous solvents, has been evolved.

Key words: Hydrazines, rocket fuels and propellants, hybrid systems, hypergolic ignition, hydrazones, thiocarbonohydrazones.

1. Introduction

Hydrazine, although discovered a hundred years ago, remained only a laboratory curiosity for over the first fifty years or so. Its potential as a rocket fuel was first recognised during World War II. Since then it has been produced on an industrial scale and used widely for a variety of applications[1]. Of the various storable liquid rocket fuels, hydrazine, monomethylhydrazine (MMH) and unsymmetrical dimethylhydrazine (UDMH) have been most often used. These fuels were largely responsible for the success of the most spectacular space program in history—the Apollo manned lunar-landing mission. Much of the credit for landing on the moon and bringing the astronauts back safely actually goes to monomethylhydrazine which was in the command service and lunar excursion modules in

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the descent and ascent stages, respectively. Of the other important missions one might mention the soft-landing of the Viking spacecraft in the first experimental search for extra-terrestrial life on Mars which was achieved by using hydrazine (N_2H_4) as fuel. The Voyager spacecraft I and II which are still cruising in the vast expanses of the solar system are also propelled by hydrazine fuels. Apart from the deep-space missions the ones closer to earth namely, the communication, weather and surveillance satellites, invariably use hydrazine in attitude and altitude control rockets. As is well known today, the satellites relay telephone calls, transmit television programs, monitor the weather, survey the Earth's surface for minerals and gather sensitive military information. All these benefits could not be readily achieved without the use of hydrazine.

In a rocket, burning propellant (fuel-oxidizer combinations) gives off hot gases which are expelled through a nozzle to produce the thrust that lifts the vehicle off the ground. The simplest classification of rockets is by the physical state of the propellants used[2]. Thus, the three basic types are, biliquid, hybrid or solid-liquid and solid rockets (fig. 1). Gases are not normally used because of the large tanks required for storage. At times, monopropellant systems are also employed[3]. A monopropellant is a single fluid capable of undergoing exothermic decomposition to yield gaseous products. As a matter of fact, anhydrous hydrazine has most often been used in the monopropellant mode.

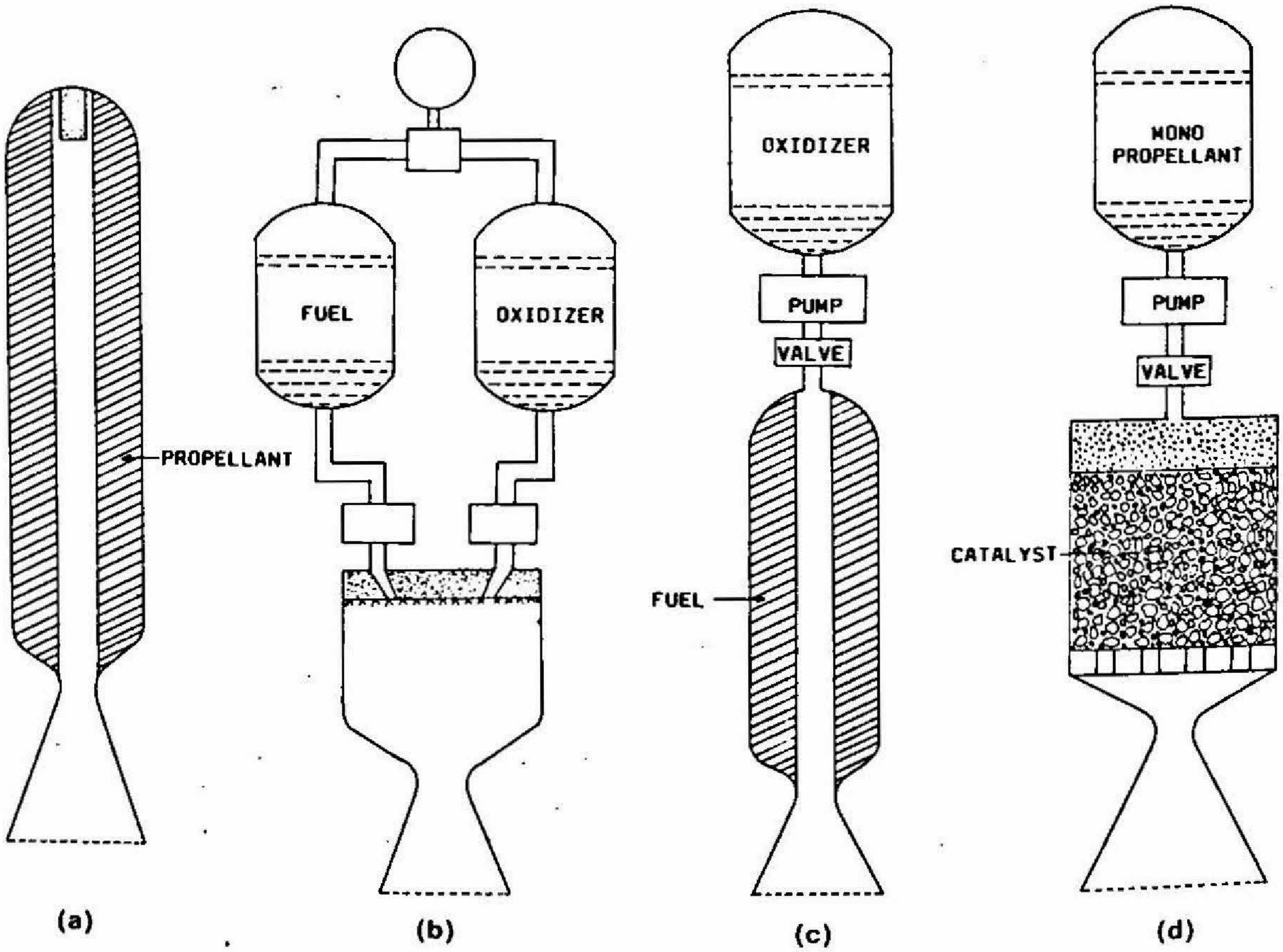


FIG. 1. Schematic diagrams of rocket engines, (a) Solid, (b) Biliquid, (c) Hybrid, (d) Monopropellant.

This paper summarises the work carried out by the author and his coworkers on various aspects of hydrazine fuels.

2. Biliquid propellant systems

Rocket development in this century has focused on biliquid propellants. Not only do they liberate more energy weight for weight than do the solid fuels, but also allow better control of the rocket. In liquid propellant rockets, the fuel and oxidizer are stored separately, and pumped into the combustion chamber where they burn producing hot gases that are ejected through a nozzle. The thrust is controlled by varying the rate at which fuel and oxidizer are pumped into the combustion chamber.

It is interesting to note that K. Tsiolkovsky, who first conceived the idea of space travel in 1903, also proposed that liquid hydrogen would be a good fuel and liquid oxygen a good oxidizer, and that the pair would make a nearly ideal propellant combination. It was, indeed, found subsequently that not only does this combination gives high-specific impulse—a measure of the power of the rocket, but its combustion product, namely H_2O, being completely innocuous, has been extensively used in modern rocketry. However, it is a cryogenic system, and the fuel and oxidizer need to be refrigerated to remain liquid. The engine, therefore, needs a complicated systems of pipes to carry the refrigerated propellant. These propellants also need an igniter.

The early biliquid rockets, such as Germany's V-2 used in World War II or those developed in USA, were based on storable fuels. Liquid hydrocarbons like kerosene, gasoline, ethyl alcohol, etc., were used as fuels with liquid oxygen as oxidizer. Hydrazine fuels like liquid hydrocarbons, can also be easily stored at ambient conditions requiring no refrigeration. The superiority of hydrazine fuels over hydrocarbons, however, stems from the fact that they ignite almost instantaneously when mixed with liquid oxidizers such as dinitrogen tetroxide (NTO), red- or white-fuming nitric acid (RFNA or WFNA), etc. This makes these propellants ideally suited for repeated firing, providing on and off capability, which is vital for controlling the flight of a rocket. Although hydrazine is about 15–20% less efficient than cryogenic fuels, it is simpler to handle and is more reliable. However, in spite of anhydrous hydrazine (AH) being highly hypergolic with oxidizers like NTO and RFNA, it has virtually never been used as a pure liquid in the biliquid propellant mode. Usually, mixtures of AH with UDMH or MMH are used (Table I), partly because of the inconvenient freezing point of pure hydrazine (+2.0°C) which is lowered significantly by mixing with MMH or UDMH. Many hydrazine fuel combinations are known, *e.g.* Aerozine, which is a 50:50% mixture of AH and UDMH. The most frequently used hydrazine–MMH mixture is the one having 14% (by wt) AH and 86% MMH, which has a freezing point of −54°C. On the other hand, MMH and UDMH have been extensively used as neat liquids. A comparison of the performance parameters of various hydrazines with NTO as oxidizer is given in Table II.

Unlike hydrocarbons, however, hydrazine fuels are not available in nature and have to be synthesised chemically. It is rather surprising that in spite of a long history and large scale use in recent years, the methods for synthesising anhydrous hydrazines are not very

Table I
Hydrazine fuels used in some typical space missions

Mission	Fuel	Application
Bipropellant mode		
Apollo	MMH	Manned lunar landing ascent and descent stages Command service module
Ariane	UDMH	European Space Shuttle I & II stages
Titan II, III & III C	AH(50) + UDMH(50)	US Titan rocket series - all stages
Space Shuttle	MMH	Shuttle Orbiter
Able Star	UDMH	US missile
Monopropellant mode		
Viking I & II	Hydrazine	Soft landing on Mars (Search for extra-terrestrial life)
Voyager I & II	Hydrazine	Jupiter, Saturn, Uranus flyby
Mariner VI & VII	Hydrazine	Mars flyby
Mariner II & V	Hydrazine	Venus flyby
Satellites (Near Earth)	Hydrazine	Communication, weather, navigation, meteorology, etc.

Table II
Performance parameters of four storable fuels with N_2O_4 as oxidizer

Fuel	FP (°C)	Specific impulse I_{sp} (sec)	Density impulse I_d (sec)	Chamber temperature T_c (k)	Oxidizer/Fuel (O/F) wt ratio
Hydrazine	2.0	292	357	3250	1.34
MMH	−52.4	288	346	3385	2.16
UDMH	−51.7	285	336	3413	2.61
RP-1* (H/C = 2)	—	276	345	3446	4.04

*Non-hypergolic.

convenient. On commercial scale, these fuels (AH, MMH and UDMH) are still produced as dilute (1 to 2%) aqueous solutions by the long-known Raschig process. These solutions are converted to the anhydrous product by multiple distillations, extraction, etc. which are cumbersome and expensive processes. Apart from the high cost, some of the methods involve carcinogenic substances as intermediates. For example, UDMH was produced by an economic process, known as the nitrosamine process till about 1974. However, since dimethylnitrosamine is now known to be carcinogenic this process has been abandoned throughout the world.

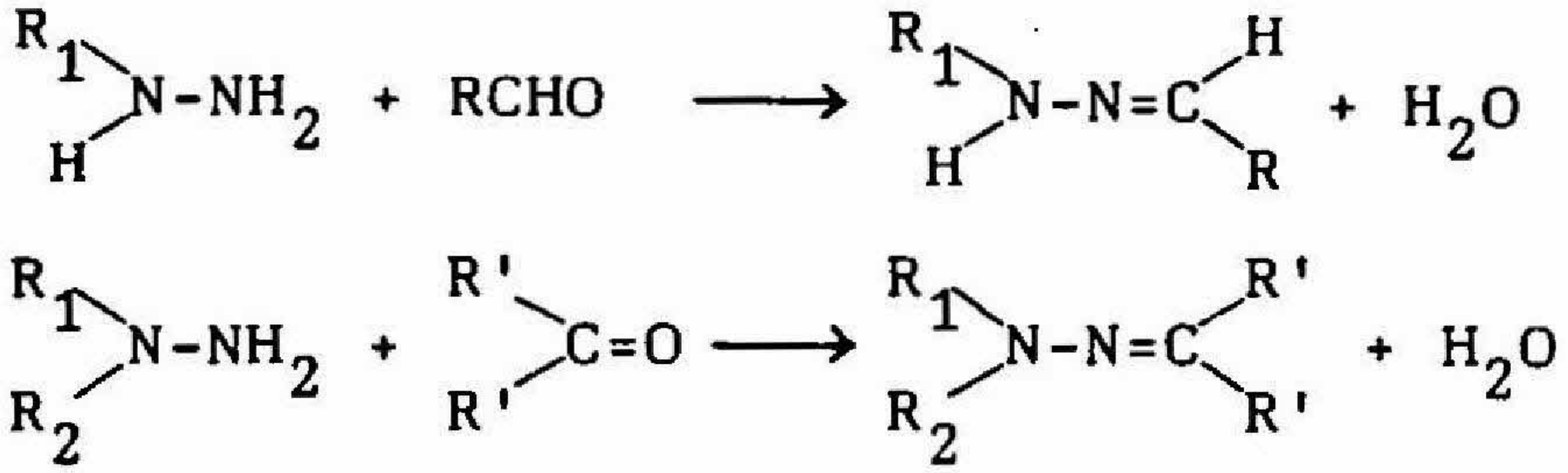
In view of these problems, there has been a renewed interest in the synthesis of hydrazines of late. For effective recovery, synthesis in non-aqueous solvents has been advocated using the anhydrous chloramine process. In this process, also known as Sisler's process, chloramine (NH_2Cl) is produced by the gasphase reaction of ammonia and chlorine and reacted subsequently with an amine/ammonia dissolved in a non-aqueous solvent. A detailed study of this process has been carried out [4,5]. It has been observed that although chloramine does not react with monomethylamine solutions in non-aqueous solvents, it leads to the formation of the corresponding hydrazine, namely, MMH in presence of a fixed base in virtually quantitative yields[6]. Hydrazine and UDMH could also be synthesised in a similar way and recovered simply by single distillation from their alcoholic (ethylene glycol) solutions. These studies have also helped in understanding the mechanism of hydrazine synthesis by the chloramine route. It may be pointed out that water is formed as a product in this process if an hydroxide is used as a base. However, this could be avoided by generating the base, *in situ*, by dissolving, for example, sodium in an alcohol which is used as solvent. Apparently, although this has been shown to be a general method for synthesising a variety of substituted hydrazines[7], it is yet to be explored on a commercial scale.

3. Hybrid propellant systems

Hybrid chemical rockets, being inherently safer than the prevailing solid rockets, have received increasing attention in recent years particularly after the failure of the solid booster in Space Shuttle 'Challenger', and have been closely considered as attractive alternatives. In these systems, the propellant is usually a solid fuel and a liquid oxidizer, which are stored separately and brought together only when fired (fig. 1). The hybrid systems composed of hypergolic (igniting on contact) propellants having repeating on-and-off capability are even more advantageous as these could be conveniently used for modulating the thrust, while still maintaining much of the simplicity of the solid rockets. The onset of ignition plays an important role in hypergolic hybrid systems. In order to avoid 'hard start' of the engine, the ignition delay *i.e.* the elapsed time preceding ignition after the liquid oxidizer comes in contact with the solid fuel, must be as short as possible. Since the onset of ignition depends primarily on the chemical reactivity of the fuel and the oxidizer used, it is conceivable that short ignition delays could be achieved by using extremely reactive materials, like fluorine oxidizers and metal hydride fuels. However, most of these systems are highly toxic and present processing and storage problems. Non-toxic systems having high chemical reactivity are, indeed, rare. Apparently, the paucity of suitable hypergolic propellants is the principal reason for non-prevalence of hybrid rockets.

It is generally believed that the main cause of the self-ignition of hypergolic systems is the rapid generation of heat by the exothermic chemical reactions occurring in the preignition stage. The chemistry of these reactions is highly complex, because several types of chemical reactions occur, often simultaneously, in a very short interval of time. The understanding of these reactions being poor, there is no rule of thumb for predicting *a priori* the hypergolicity of a particular fuel-oxidizer system. In an attempt to evolve new hypergolic propellant systems having minimal ignition delays, and to understand the processes leading to hypergolic ignition, a comprehensive programme of research was undertaken in the author's laboratory. Keeping in view that the liquid hydrazines (AH, MMH & UDMH) are highly hypergolic with oxidizers like WFNA, RFNA and N_2O_4, it was envisaged that solid organic compounds having one or more N–N bond/s in the molecule, would similarly ignite on coming into contact with liquid oxidizers. The main emphasis of the study was, therefore, placed on the solid derivatives of hydrazine.

It is well known that hydrazines react readily with aldehydes and ketones giving solid products known as hydrazones.



The hydrazones are non-hygroscopic and thermally stable compounds, and, as expected these were found to be hypergolic with nitric acid[8–10]. The ignition delays were measured using a drop-tester-type device as described earlier[10]. It essentially consists of three parts as shown in fig. 2: (1) a device to receive the 'start' signal when the oxidizer is released, (2) a photodiode circuit to sense the presence of flame and to give the 'stop' signal and (3) an electronic counter. To determine the ignition delay (ID), the oxidizer taken in a graduated pipette is dropped on to the fuel sample held underneath, at a fixed distance, in a porcelain

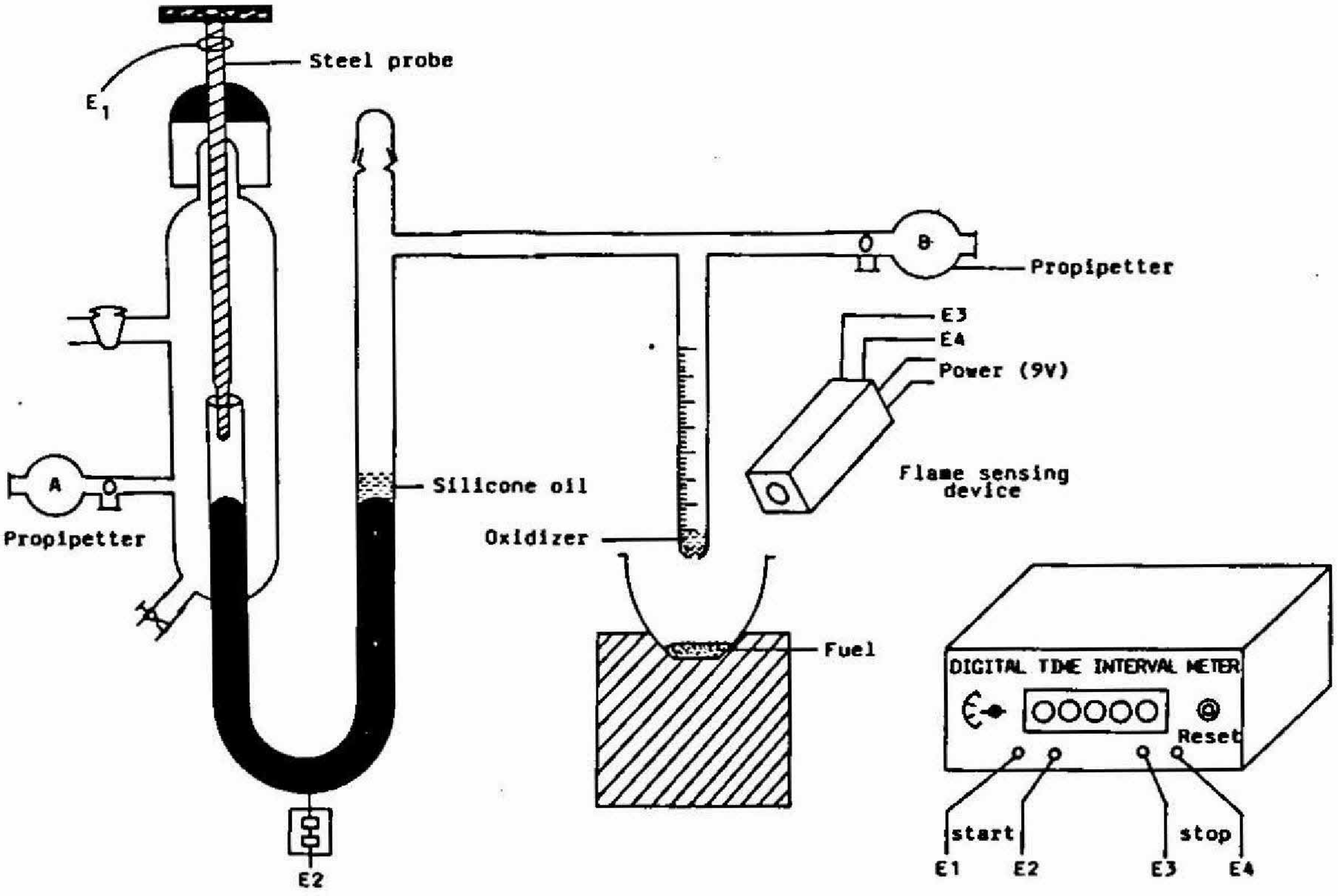
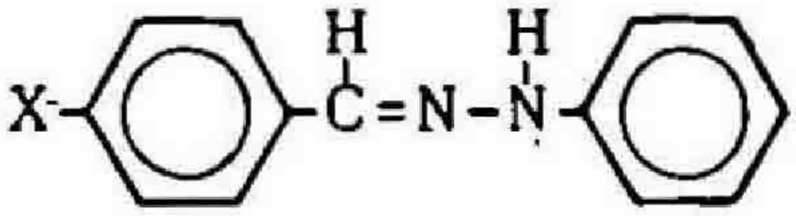


FIG. 2. Sketch of the ignition delay set-up.

cup. The time interval between the 'start' and 'stop' signals includes the oxidizer drop time plus the ignition delay. The drop-time, as obtained by a separate experiment, is subtracted from the total time to get the actual ignition delay. The measured ignition delays of some of the hydrazones with nitric acid, at ambient conditions were found to be of the order of 100 milliseconds (ms).

It may be recalled at this stage that the magnitude of ignition delay of a hypergolic hybrid system depends both upon physical as well as chemical parameters. It depends upon diffusion-controlling parameters, such as particle size and compactness of the fuel, as well as compositional factors, such as concentration of the oxidizer, fuel oxidizer ratio, additives, etc. However, more basically the delay depends upon the chemical reactivity between the fuel and the oxidizer and the rapidity of the heat generation, as stated earlier. If the reactivity of the fuel is changed simply by substituting one of the reactive groups in the molecule it is probable that the magnitude of ignition delay measured under identical experimental conditions, will reflect this effect. This was indeed found to be the case when the IDs of various substituted phenylhydrazones (I)-WFNA systems, were measured[10]. It was observed that the IDs depend upon the nature of the substituent on the aldehyde benzene ring.



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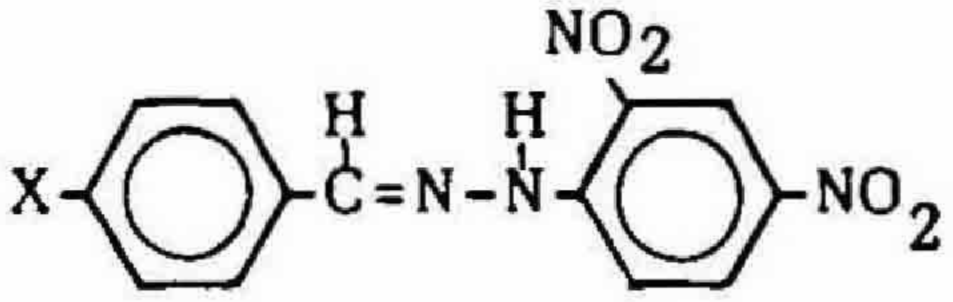

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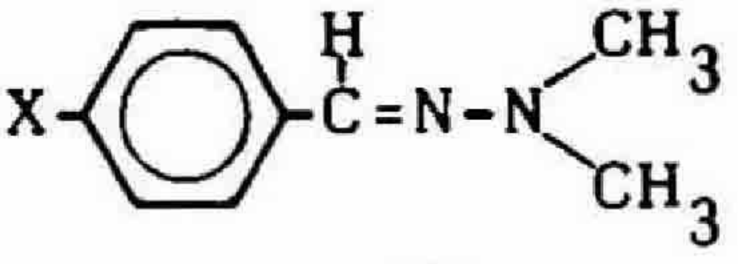


III

Shorter ignition delays with WFNA are obtained when X is an electrophilic group as shown in Table III. On the other hand, when the substituent is an electron-withdrawing group, like NO_2, the hydrazone does not ignite at all. Similarly, it was found that 2, 4-dinitrophenylhydrazones (II) having two nitro groups in the molecule, of various aromatic

Table III
Ignition delays of hydrazones with nitric acid[10]—Average ignition delays (ms)

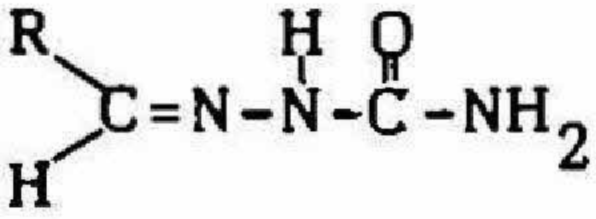
—X	Phenylhydrazone (I)		Dimethylhydrazone (III)		2,4 dinitrophenylhydrazone (II)
	WFNA	*RFNA*	*WFNA*	*RFNA*	*WFNA/RFNA*
H	102	1280	—	—	NI
OH	297	1730	37	103	NI
$—N(CH_3)_2$	108	181	164	195	NI
Cl	420	NI	60	218	—
$—NO_2$	NI	NI	69	230	NI

NI: No ignition.

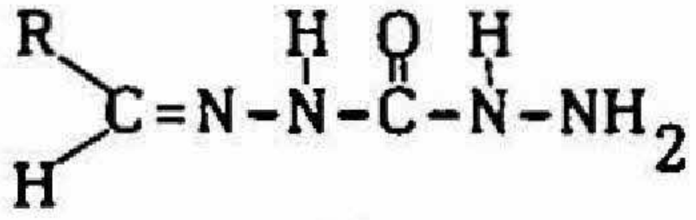
aldehydes, were all found to be non-hypergolic with WFNA. It was also observed that, in general, almost all of the condensed products of phenylhydrazine with aldehydes ignite with relatively longer ignition delays with RFNA than with WFNA. The derivatives of dimethylhydrazine with aldehydes (III) are highly hypergolic with WFNA and ignite with shorter delays than phenylhydrazones. The magnitude of ignition delay of substituted benzaldehydedimethylhydrazones, however, does not display a clear-cut effect of the nature of the substituent group. Since the ignition delay is known to be affected by various parameters, the effect of variables, such as oxidizer/fuel ratio, composition of the oxidizer and compactness of the fuel was evaluated.

In a related study the products of combustion of hydrazones with nitric acid were analysed by mass spectrometry[12]. The heats of combustion and other thermochemical parameters were also determined to assess the applicability of these systems.

Besides the hydrazones, the search for hypergolic solid fuels was extended to other series of hydrazine compounds. The derivatives of semicarbazide, thiosemicarbazide, carbohydrazide and thiocarbohydrazide with various aldehydes and ketones were examined. It was found that whereas the semicarbazones (IV) and

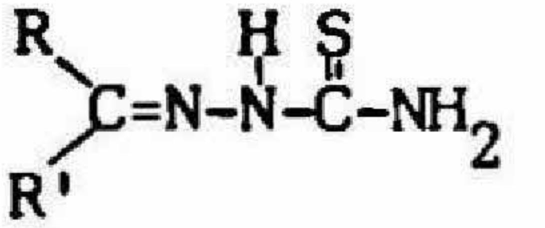


IV

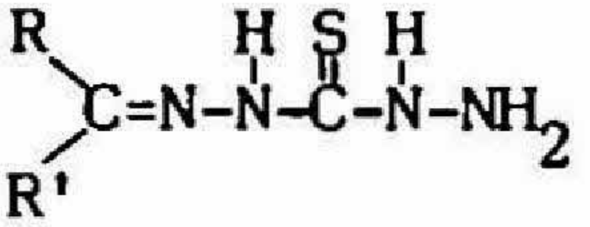


V

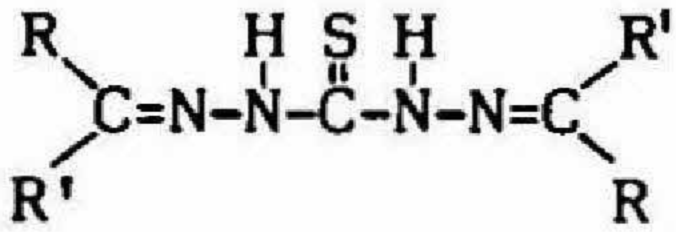
carbohydrazones (V) were found to be all non-hypergolic, the corresponding thio compounds (VI), (VII) and particularly the monothiocarbonohydrazones[13](VII) (Table IV) were extremely hypergolic with WFNA.



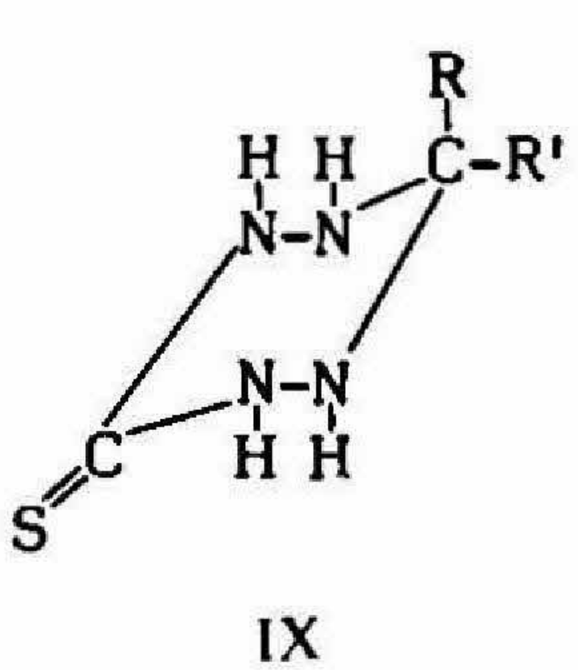
VI



VII



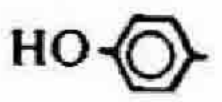
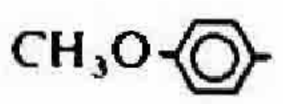
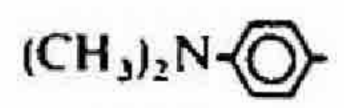
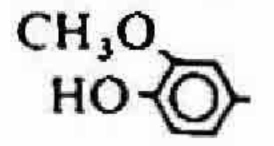
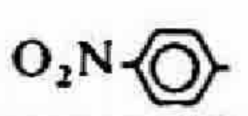
VIII



IX

It is thus apparent that the hypergolicity is primarily related to C=O and C=S bonds in this series of compounds. Incidentally, while characterizing the monothiocarbonohydrazones by ^{1}H NMR spectroscopy[14,15] we found that these derivatives exist in two isomeric

Table IV
Ignition delays of monothiocarbonohydrazones with WFNA[13]

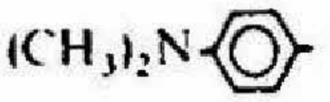
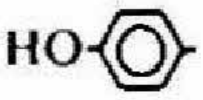
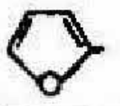
VII			IX		
R	R′	Ignition delay (m sec)	R	R	Ignition delay (m sec)
	H	53	H	H	64
	H	40		H	30
	H	48	CH_3	CH_3	38
	H	15	CH_3	C_2H_5	43
	H	13	$-CH_2CH_2CH_2CH_2-$ (Cyclohexanone)		15
	H	61			
	H	NI			

structural forms—linear (VII) and cyclic (IX)—depending on the nature of the aldehyde. However, it was observed subsequently, that the configuration of the molecule has no significant effect on the ignition delay (Table IV). A comparative study[16] of the hypergolicity of these compunds revealed that the ignition delays of monothiocarbonohydrazones with WFNA are shorter than those of thiosemicarbazones (VI), and bisthiocarbonohydrazones[17] (VIII) (Table V). Within a series, for example, the monothiocarbonohydrazones, the ignition delays of the substituted benzaldehyde-monothiocarbonohydrazones, determined under identical conditions, vary with the substituent group in the order: $N(CH_3)_2 < OH < OCH_3 < H < Cl < NO_2$.

Again, it appears that electron-releasing groups tend to decrease the ignition delay, whereas electron-withdrawing groups increase the ignition delay or make the system non-hypergolic, as observed in the case of phenylhydrazones. These results point to the prominent role of a nitration reaction in the preignition stage. It may be recalled that in nitration reactions with HNO_3 the effect of substitution of various groups in the benzene ring follows a similar trend. The velocity of nitration appears to decrease with the substituents on the ring exactly in the same order.

Nitric acid, however, can undergo a variety of reactions with hydrazine compounds, the principal ones being neutralization, oxidation and nitration. The evidence of the occurrence of these reactions in the preignition stage of the systems discussed above, was obtained by isolating the reaction intermediates in the quenched products. Major products identified[16] among the preignition products of benzaldehyde derivatives of thiocarbohydrazide with WFNA were benzoic acid, p-nitrobenzoic acid, benzaldehyde, sulfur trioxide, nitrogen dioxide and nitrogen. Benzoic and p-benzoic acids were also identified in the preignition reactions of benzaldehydephenylhydrazone[10]. These studies provide

Table V
Ignition delays of thiocarbonohydrazones and thiosemicarbazones[16]

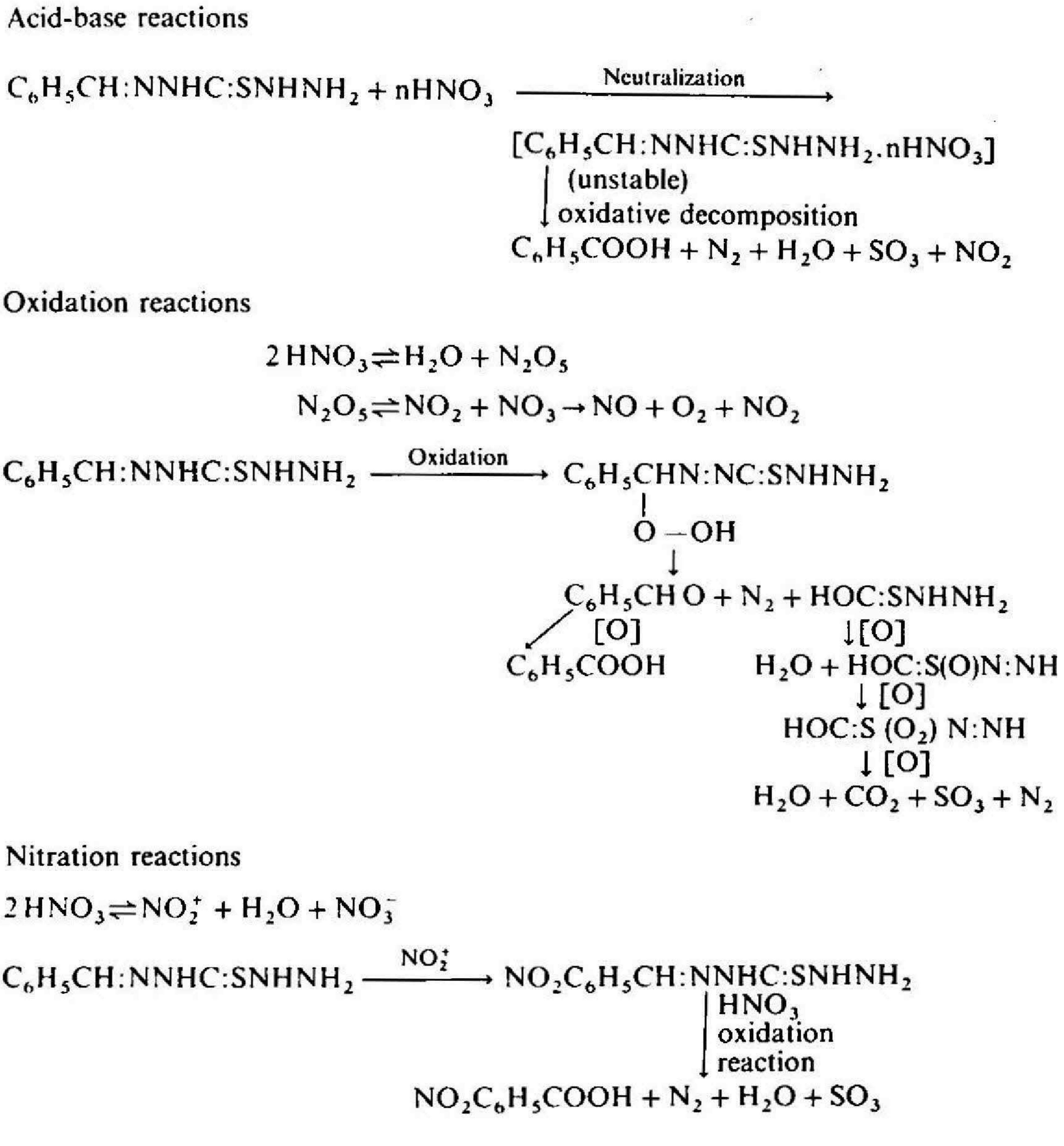
R	R'	Average ignition delays (ms)				
		Monothiocarbono* hydrazone (VII)		Bisthiocarbono hydrazone (VIII)		Thiosemicarbazone (VI)
		WFNA	*RFNA*	*WFNA*	*RFNA*	*WFNA*
H	H	64	82	87	486	—
CH_3	H	48	—	74	140	—
CH_3	CH_3	38	31	70	148	67
C_2H_5	CH_3	43	48	63	162	52
	H	53	68	NI	NI	231
	H	15	92	1360	NI	175
	H	40	91	NI	NI	—
	H	61	–	NI	—	NI
	H	30	69	782	—	76

*Some of the compounds have cyclic structures; NI: No ignition.

conclusive evidence for the occurrence of oxidation, nitration and possibly neutralization reactions in the preignition stage. A reaction scheme for the preignition process has been proposed (fig. 3) based on the reaction intermediates identified[16].

The preignition process also was examined by monitoring the transient temperature profiles of a hypergolic system[18,19]. The temperature profiles were obtained using a new thin-film thermometric technique. The instrument used consisted of a probe (a glass cup) with a thin platinum film as fast responding temperature sensor and sensitive photodiodes for sensing the flame. Both ignition delay and temperature profiles were recorded and displayed simultaneously on the two channels of a duel trace storage oscilloscope. The fuel reacted with the oxidizer in the probe. Since a temperature change causes a change in the resistance of the platinum film, the probe could be used for monitoring the exothermicity of the chemical reactions occurring on mixing the fuel and the oxidizer, particularly prior to ignition in hypergolic systems. Several fuel-oxidizer systems were studied using this device. An oscillogram of a typical system showing a vertical marking corresponding to the onset of ignition, and progressive temperature build up of the system is shown in fig. 4.

Besides ignition-related studies, thermochemical- and rocket-performance parameters of the proposed propellant systems were also determined. For the first time, calorimetric bomb was designed to determine the heats of combustion of hypergolic propellants[20]. In the device, a liquid oxidizer, hypergolic with the fuel was used instead of the gaseous oxygen used in conventional calorimetric studies. The liquid oxidizer (HNO_3), taken in a specifically designed glass vessel was dropped on the fuel in a closed bomb by a remote control device. The fuel ignites on coming into contact with the oxidizer and the heat produced was



Acid-base reactions

$$C_6H_5CH{:}NNHC{:}SNHNH_2 + nHNO_3 \xrightarrow{\text{Neutralization}} [C_6H_5CH{:}NNHC{:}SNHNH_2.nHNO_3]$$

$$\downarrow \text{(unstable) oxidative decomposition}$$

$$C_6H_5COOH + N_2 + H_2O + SO_3 + NO_2$$

Oxidation reactions

$$2HNO_3 \rightleftharpoons H_2O + N_2O_5$$

$$N_2O_5 \rightleftharpoons NO_2 + NO_3 \rightarrow NO + O_2 + NO_2$$

$$C_6H_5CH{:}NNHC{:}SNHNH_2 \xrightarrow{\text{Oxidation}} C_6H_5\underset{\substack{|\\ O-OH}}{C}HN{:}NC{:}SNHNH_2$$

$$\downarrow$$

$$C_6H_5CHO + N_2 + HOC{:}SNHNH_2$$

$$C_6H_5CHO \xrightarrow{[O]} C_6H_5COOH \qquad HOC{:}SNHNH_2 \xrightarrow{[O]} H_2O + HOC{:}S(O)N{:}NH$$

$$\downarrow [O]$$

$$HOC{:}S(O_2)N{:}NH$$

$$\downarrow [O]$$

$$H_2O + CO_2 + SO_3 + N_2$$

Nitration reactions

$$2HNO_3 \rightleftharpoons NO_2^+ + H_2O + NO_3^-$$

$$C_6H_5CH{:}NNHC{:}SNHNH_2 \xrightarrow{NO_2^+} NO_2C_6H_5CH{:}NNHC{:}SNHNH_2$$

$$\downarrow HNO_3 \text{ oxidation reaction}$$

$$NO_2C_6H_5COOH + N_2 + H_2O + SO_3$$

FIG. 3. Proposed ignition reaction pathways for monobenzaldehydethiocarbonohydrazone + WFNA.

monitored in a manner similar to that used in a constant volume bomb calorimetric technique. The experimental values of heats of combustion of some of the thiocarbonohydrazones with HNO_3 as oxidizer matched well with the theoretical values, which in turn were calculated from the heats of formation data using the heats of combustion values in oxygen[21]. (Table VI).

Thermal analyses of monothiocarbonohydrazones carried out using DTA and TG techniques[22] show that they all decompose exothermally soon after melting around 180°C. The analysis of the products of decomposition of the benzaldehyde derivative show the

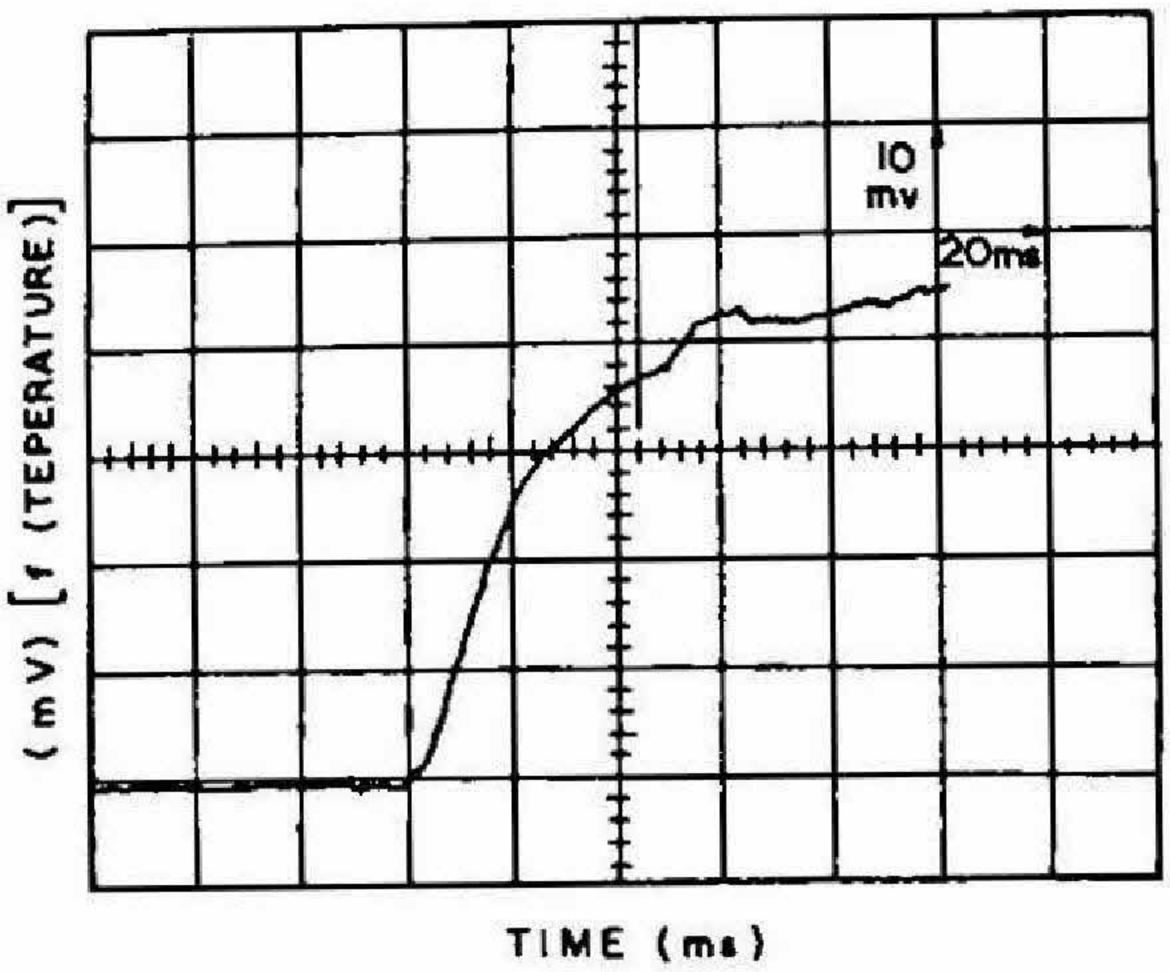


FIG. 4. Transient temperature profile of p-hydroxybenzaldehydethiocarbonohydrazone + WFNA system. Amount of the fuel = 150 mg, O/F ratio = 3, Particle size of the fuel = 230–310 μ, Probe current = 30 mA.

Table VI
Heat of combustion in oxygen (ΔH_c) and in nitric acid (ΔH_{HNO_3}), and formation (ΔH_f) of thiocarbonohydrazones, kcal/mole

Sl no.	Thiocarbonohydrazone	$-\Delta H_c$	ΔH_f	$-\Delta H_{HNO_3}$	
				observed	calculated
1.	Benzaldehyde $C_6H_5CH{:}NNHC{:}SNHNH_2$	1239.2	+6.5	925.4	1179.5
2.	p-Dimethylaminobenzaldehyde p-$(CH_3)_2NC_6H_4CH{:}NNHC{:}SNHNH_2$	1624.1	+31.0	1208.7	1550.0
3.	Furfuraldehyde $C_4H_3OCH{:}NNHC{:}SNHNH_2$	964.0	−11.3	870.3	934.7
4.	Formaldehyde $CH_2NHNC{:}SNHNH$	537.6	+8.6	502.7	515.7
5.	Acetone $(CH_3)_2CNHNHC{:}SNHNH$	856.4	−0.2	792.8	817.6
6.	Cyclohexanone $(CH_2)_5CNHNHC{:}SNHNH$	1236.7	−39.8	1024.8	1179.2

presence of nitrogen, ammonia, hydrogen sulfide, benzonitrile, thiobenzaldehyde, 2, 4, 6 triphenyl-s-triazine and complex condensation products containing C=N linkages. A mechanism of decomposition based on the formation of these products, assuming the homolytic cleavage of the N—N bond as a primary step has been proposed.

The theoretical engine performance parameters of the proposed hybrid systems, such as specific impulse, chamber temperature, characteristic velocity, etc., at various O/F ratios have been evaluated[21] using a computer program (NASA-SP273). High values of specific impulse and chamber temperature, and low values of average molecular weight of the exhaust species (Table VII) are indicative of their superior performance.

A significant development in hybrid systems in recent years has been the discovery of synergistic hypergolic ignition[19]. A variety of hydrazine fuels become hypergolic with WFNA on mixing with metal powders especially with magnesium. In the absence of magnesium powder, these fuels are either non-hypergolic or have longer ignition delays (Table VIII). The observation is significant considering the fact that the metallized solid fuels having short ignition delays are preferred in propellant systems. The performance parameters of some of these systems have been evaluated[23].

Another significant development in hybrid hypergolic systems has been the emergence of hydrazine-based polymeric resins, which could be used as binders without significantly increasing the ignition delays. As is well known, the ignition delay of highly hypergolic fuel powders increases significantly, when they are processed in a 'grain' form using commonly available polymeric binders. However, since in actual practice the fuel is used in the 'grain' form, it is essential that the binder used imparts necessary strength without adversely affecting the ignition delay. For this purpose, based on the experience on the hypergolicity of various fuels, new polymeric binders having N—N bonds in the backbone have been synthesised recently. These have yielded promising results[24] as is shown by a comparison of the ignition delays of fuel grains cast with various resins (Table IX).

Table VII
Theoretical performance parameters of various thiocarbonohydrazones-HNO_3 systems[*]

Parameter	Fuel no.[†]					
	1	2	3	4	5	6
Optimum oxidizer/fuel ratio	2.8	2.8	2.5	1.9	2.5	3.1
Specific impulse, I_{sp}, s	245.5	250.3	240.9	238.9	246.7	246.3
Vacuum specific impulse, I_{vac}, s	267.9	272.7	262.3	260.3	269.0	269.2
Combustion chamber temperature, T, K	3061.0	3081.0	3012.0	2945.0	3002.0	2985.0
Mean molecular weight, M, g mole	28.53	27.41	28.80	28.50	27.52	27.69
Characteristic velocity, C, m/s	1490.0	1526.0	1469.0	1458.0	1500.0	1493.0

[*] Calculated assuming equilibrium flow conditions at Pc = 30 atm and expansion ratio, Pc/P = 60.
[†] Fuel numbers as reported in Table VI.

Table VIII
Ignition delays of organic fuels and their mixtures with magnesium powder (60:40) with WFNA as oxidizer

Sl no.	Compound	Ignition delay (ms)	
		Compound	Compound : Mg (60:40)
1.	Thiosemicarbohydrazide	No ignition	333
2.	Thiocarbohydrazine	Inconsistent ignition	204
3.	p-Hydroxybenzaldehydephenylhydrazone	298	137
4.	Benzaldehydethiosemicarbazone	231	104
5.	bis-Benzaldehydethiocarbonohydrazone	No ignition	1179
6.	bis-p-Methoxybenzaldehyde-thiocarbonohydrazone	No ignition	502
7.	bis-p-Dimethylaminobenzaldehyde-thiocarbonohydrazone	1360	706
8.	bis-Furfuraldehyde thiocarbonohydrazone	782	154

Table IX
Ignition delay data for various binder compositions*

Composition %	Average ignition delay (ms)					
	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

*Resin 1, diglycidylether of bisphenol A; Resin 2, diglycidylether of vanillinazine; Resin 3, diglycidylether of vanillylidene ethylenediamine; TCH, thiocarbohydrazide; DBA, dimethylaminobenzylideneaniline; ACTCH, acetonethiocarbonohydrazone; and FRPH, furfuraldehydephenylhydrazone.

4. Monopropellant mode

A remarkable property of hydrazine is that it decomposes exothermically in presence of catalysts giving completely gaseous products. This property has led to extensive use of anhydrous hydrazine in monopropellant rockets. In the monopropellant mode the liquid hydrazine is simply passed through a catalyst bed, wherein it is decomposed instantaneously, and the gaseous products are exhausted through the nozzle of the rocket. Although hydrazine in this mode does not provide a very high specific impulse, monopropellant devices are preferred for control rockets because of their reliability and simplicity. These rockets have been extensively used in various applications. An account of some of the important missions using liquid hydrazine as propellant is given in Table I.

The catalytic decomposition of hydrazine has been studied extensively. The stoichiometry governing the decomposition of hydrazine is given by

$$3N_2H_4 \rightarrow 4(1-x)NH_3 + (1+2x)N_2 + 6xH_2$$

where x is the degree of ammonia dissociation occurring during the reaction. Its value depends upon such factors as pressure, bed loading, dwell time, etc.

The catalyst which has often been used for hydrazine decomposition is Shell 405 patented by Shell Co., USA, which is basically iridium metal deposited on γ-alumina. Recent restrictions on the availability of this catalyst have led to studies pertaining to indigenous development of similar catalysts. In one of our studies[25], decomposition was monitored on a vacuum line by injecting under-vacuum anhydrous hydrazine on to catalyst held on a porous glass frit, and noting the pressure developed as a function of time. Of the various indigeneous catalysts prepared, iridium and rhodium catalysts supported on γ-alumina have been found to be the most effective although cobalt and mixed cobalt-platinum catalysts decompose hydrazine fairly readily. The effects of various factors influencing decomposition, such as activation temperature, impregnation condition, catalyst bed temperature and packing, have been evaluated.

5. Solid propellant oxidizers

Hydrazine salts of oxyacids, especially hydrazinium mono- and diperchlorates, have been considered as high-energy solid oxidizers for solid-composite propellants. From the oxygen balance point of view they are better oxidizers than the often used ammonium perchlorate. These also give completely gaseous products on decomposition. However, these are highly sensitive to shock and friction. The shock sensitivity of hydrazinium monoperchlorate is comparable to that of initiating explosives. In order to make them safely usable in solid propellants, it is necessary to desensitise them by suitable treatment. Attempts to do this by pretreating the samples by doping, pre-irradiation, etc., have been made. Thermal decomposition behaviour[26] of the treated samples has been examined. It has been observed that hydrazinium monoperchlorate is desensitised with respect to thermal decomposition by impurities capable of forming associated complexes[27] with the hydrazinium or perchlorate ion. Hydrazinium diperchlorate, on the other hand, is desensitised by cation vacancies and age, whereas pre-irradiation sensitises the compound. However, these materials still need careful handling and are not routinely used.

To summarise, it is clear that hydrazine fuels have been used extensively in bi- and monopropellant rocket motors. The hydrazine-based solid fuels, being fairly stable in air, non-hygroscopic, and easily storable, are attractive possibilities for use in hypergolic hybrid propellant systems. Though hydrazine perchlorates could give better performance, as oxidizers in solid composite propellants than the commonly used ammonium perchlorate, they are dangerous to handle. The relatively high cost of the propellant-grade hydrazines is a deterrent to their use as rocket fuels. However, it is believed that their costs will be reduced.

References

1. Schmidt, E. W. *Hydrazine and its derivatives*, Wiley-Interscience, 1984.
2. Sarner, S. F. *Propellant chemistry*, Reinhold, 1966.
3. Holzmann, R. T. *Chemical rockets and flame explosives technology*, Marcel Dekker, 1969.
4. Jain, S. R., Mathur, M. A. and Sisler, H. H. Synthesis of methylhydrazine in nonaqueous solvents, *Inorg. Chem.*, 1980, **19**, 2192–2195.
5. Sisler, H. H., Mathur, M.A., Jain, S. R. and Greengard, R. Studies of the chloramination of dimethylamine and 1,1-dimethylhydrazine, *Ind. & Engng Chem.* (Products, Research & Development), 1981, **20**, 181–185.
6. Jain, S. R. *Studies relating to the synthesis of monomethylhydrazine and unsymmetrical dimethylhydrazine*, Final Project Report, Aerospace Engng, Indian Institute of Science, Bangalore, 1985.
7. Jain, S. R. and Chellappa, D. Synthesis of some N-substituted hydrazines by the anhydrous chloramine process, *Proc. Indian Acad. Sci. (Chem. Sci.)*, 1985, **95**, 381–389.
8. Jain, S. R. Ignition and thermal behaviour of solid hydrazones, *Combust. Flame*, 1977, **28**, 101–103.
9. Jain, S. R., Krishna, P. M. M., Sai, K. G. and Pai Verneker, V. R. Ignition delay studies on hybrid propellants, *J. Spacecraft Rockets*, 1977, **14**, 573–574.
10. Jain, S. R., Krishna, P. M. M. and Pai Verneker, V. R. Hypergolic ignition of various hydrazones with nitric acid, *J. Spacecraft Rockets*, 1979, **16**, 69–73.
11. Jain, S. R., Krishna, P. M. M. and Pai Verneker, V. R. Effect of variables on ignition delays of hydrazone/nitric acid systems, *Propellants Explos.*, 1980, **5**, 135–138.
12. Jain, S. R., Krishna, P. M. M. and Pai Verneker, V. R. Studies on the combustion of solid hydrazones with nitric acid, *Propellants Explos.*, 1980, **5**, 119–122.
13. Rajendran, G. and Jain, S. R. Novel solid hypergolic fuels for hybrid propellants, *Fuel*, 1984, **63**, 709–712.
14. Rajendran, G. and Jain, S. R. Structural assignment of monothiocarbonohydrazones by ^{1}H NMR spectroscopy, *Organic Magn. Resonance*, 1984, **22**, 6–10.
15. Rajendran, G. and Jain, S. R. Unusual structural isomerisation of monopropiophenonethiocarbonohydrazone, *Organic Magn. Resonance*, 1984, **22**, 550–551.
16. Jain, S. R. and Rajendran, G. Chemical aspects of the hypergolic preignition reactions of some hybrid hypergols, *Combust. Flame*, 1987, **67**, 207–215.
17. Rajendran, G. and Jain, S. R. Synthesis and characterization of bis-thiocarbonohydrazones, *Indian J. Chem.*, 1985, **24B**, 680–682.
18. Murthy, K. N. and Jain, S. R. Transient temperature studies on hypergolic propellant systems, *Proc. V National Symposium on Thermal Analysis*, IIT, Kharagpur, 1985.

19. Jain, S. R., Rao, R. and Murthy, K. N. Studies on the synergistic hypergolic ignition of hybrid systems, *Combust. Flame*, 1988, **71**, 233–243.

20. Jain, S. R. and Rajendran, G. A calorimetric bomb for determining heats of combustion of hypergolic propellants, *J. Spacecraft Rockets*, 1986, **23**, 120–122.

21. Jain, S. R. and Rajendran, G. Performance parameters of some new hybrid hypergols, *J. Propulsion Power*, 1985, **1**, 500–502.

22. Rajendran, G. and Jain, S. R. Thermal analysis of monothiocarbonohydrazones, *Thermochim. Acta*, 1984, **82**, 311–323.

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

24. Jain, S. R., Murthy, K. N. and Thanoo, B. C. Ignition delay studies on hypergolic fuel grains, *Def. Sci. J.*, 1988, **38**, 273–286.

25. Jain, S. R. and Oommen, C. Catalytic decomposition of hydrazine, *Indian J. Technol.*, 1988, **26**, 145–149.

26. Pai Verneker, V. R., Sharma, A. N. and Jain, S. R. Effect of intentional impurities, aging, particle size and pre-irradiation on the thermal decomposition of hydrazinium diperchlorate, *Propellants Explos.*, 1977, **2**, 45–48.

27. Pai Verneker, V. R., Sharma, A. N. and Jain, S. R. Thermal decomposition of hydrazinium monoperchlorate in the molten state, *J. Thermal Analysis*, 1977, **11**, 277–287.