JOURNAL OF PROPULSION AND POWER
Vol. 11, No. 4, July–August 1995

High Energy Material Research and Development in India

Haridwar Singh*
Explosives Research and Development Laboratory, Pune 411 021, India

The manuscript presents the research and development (R&D) work carried out by Indian scientists in the various areas of high energy materials (HEM) broadly covering propellants, explosives, and pyrotechnics. While India is self-sufficient in the field of high energy solid propellant, and both science and technology have reached international levels, more exhaustive R&D work is needed in the field of Earth storable liquid and cryogenic propellants. In the field of commercial and military high explosives, slurry/emulsion, cyclotrimethylenetrinitramine/cyclotetramethylenetetranitramine-based compositions have been extensively studied, evaluated, and used. However, to meet futuristic requirements, more powerful (velocity of detonation greater than 9500 m/s, density greater than 2 g/cc) and thermally stable explosives (>350°C) are being synthesized and characterized. Infrared (IR) smoke compositions effective in high IR region (8–14 μ) have been developed. However, the thrust areas in all the wings of HEM are development of more powerful, less sensitive, and environmentally friendly compositions and fully automatic, remote control processing technologies.

I. Introduction

INDIA'S quest for self-reliance started vigorously from the time of independence in 1947. A coherent and comprehensive multipronged thrust guided the plans and programs of the country in almost all the major areas of research and development (R&D) (scientific and industrial research, agriculture, medicine, defense, space, atomic energy, etc.). While the Council of Scientific and Industrial Research (CSIR) labs were created in 1950 to "advance knowledge and to apply science for good of the people," the Defence Research and Development Organisation (DRDO) was formed in 1958 by integrating and consolidating various scientific and technical organizations then existing with the Defence Science Organization. High energy material (HEM) research was no exception to this philosophy, as these materials are well known to play a vital role in the progress and prosperity of human beings and society. In 1972, the government set up the Indian Space Research Organisation (ISRO) to apply space technology for communication, meteorology, and resource management.

Very few civil explosives were being manufactured in India during the 1950s and R&D work in this area was almost negligible. However, since the country was on the threshold of an industrial leap, the mining industry realized the need for the production of a large range of better-performing and cost-effective civil explosives. As a result, there are 30 factories in India manufacturing different types of civil explosives, including nitroglycerin (NG)-based permitted, slurry, and emulsion explosives, and allied items like detonators, detonating cords, safety fuses, etc.

During the last three decades, considerable amount of R&D work has been carried out by academic institutions, DRDO, ISRO, and other scientific organizations in the various branches of HEM. This article attempts to present an overview of the R&D efforts made by Indian scientists/engineers in the areas of HEM, broadly covering propellants, explosives, and pyrotechnics.

II. Solid Propellants

A. Conventional Propellants

Propellant research in India can be divided in two major subdivisions, namely, 1) conventional single base propellants (SBP), double base propellants (DBP), and triple base propellants (TBP); and 2) propellants for rockets/missiles and space vehicles covering extruded double base (EDB), cast double base (CDB), composite propellants (CP), composite modified double base (CMDB), nitramine modified double base (NMDB), metallized and nonmetallized fuel rich propellants (FRP) for integrated rocket ramjet (IRR) applications. In the area of conventional propellants, India has almost achieved world standards (Table 1). Since there is very little scope of improving force constant of SBP due to oxygen deficiency in nitrocellulose (NC), and very limited scope of increasing nitroglycerine (NG) content in DBP and associated higher flame temperature *Tf*, which results in gun barrel erosion problems; further R&D work is being concentrated on TBP and nitramine-based propellants.

To improve force constant by increasing values of moles per gram of product gases, rather than increasing *Tf*, it is essential that the mean molecular mass of product gases should be as low as possible. Hence, product gases (CO_2, CO, H_2O, H_2, and N_2) should have very small proportions of CO_2 and high proportions of H_2. To meet these objectives oxidizers like triaminoguanidine nitrate (TAGN), cyclotrimethylenetrinitramine (RDX) and cyclotetramethylenetetranitramine (HMX) have been studied. In this context, RDX-NC-based propellants by a solvent extrusion technique has been developed to achieve higher muzzle velocity (MV). This propellant has a lower *Tf* (3239 K), but a higher force constant (1200 J/g). In view of a very low burn rate coefficient (0.14), the web size for the same energy level for RDX-based propellant gets reduced, resulting in easier extrusion of the propellant and improvement in loadability.[1]

B. Solid Propellants for Rockets/Missiles and Space Vehicles

1. *EDB and CDB Propellants*

Research work on DBP centers around formulation, processing, and evaluation of both EDB and CDB propellants containing NC, NG, stabilizer, plasticizer, and additives (coolant, ballistic modifiers) for different applications. A large number of EDB/CDB propellants in different dimensions (o.d. 60–200 mm), configurations (tubular, slotted tube, internal star), and weight (5–200 kg) have been developed to meet various requirements (Table 2).

A considerable amount of work has been done on the catalysis and platonization of DBP to obtain pressure- and temperature-insensitive low and high calorimetric value (cal-val) compositions.[2–6] As a result of the studies, it has been possible

Received Aug. 6, 1994; revision received Dec. 1, 1994; accepted for publication Dec. 2, 1994.
*Director. Member AIAA.

Table 1 Ballistic properties achieved for conventional gun propellants

Propellant type	Density, g/cc	Flame temperature, K	Force constant, J/g	Cal-val, cal/g	Linear burn rate coefficient, b	Mean mol wt of product gases, g/mol
SBP	1.58	2500–3000	940–1020	700–800	0.19	24.4
DBP	1.61	2600–3600	940–1180	720–1200	0.16–0.20	25.6
TBP	1.62	2400–3300	950–1140	750–900	0.12–0.20	22.4
Nitramine based propellant	1.65	2900–3200	1200	800–1100	0.14	22.4

Table 2 Energetic solid propellants, ballistic properties

Propellant	Burn rate, mm/s	Operating pressure, kg/cm^2	Pressure index, η	Temperature sensitivity, %/°C	*Isp*, s (delivered)	Density, g/cc
DBP[a]						
CDB	3–20	30–140	0.02–0.4	0.15	220	1.55
EDB	5–25	30–140	0.01–0.3	0.15	220	<1.6
CP	2–40	15–150	0.1–0.4	<0.2	245	1.8
CMDB	5–30	35–150	0.2–0.5	<0.3	260	1.7
Nitramine	3–20	35–150	0.4–0.5	0.3	235	1.65
FRP[b]						
Metallized	8–30	10–20[b]	0.1–0.2	0.2	600	1.6
Unmetallized	1–5	10–20[b]	0.1–0.2	0.2	—	—

[a]Zero or low pressure index values between 50–140 kg/cm^2 pressure range.
[b]Primary motor.

to offer EDB/CDB compositions having a catalytic activity (ratio of catalyzed burn rate to uncatalyzed burn rate) of 2–2.5. A 100–200% increase in burn rate with low pressure index values (0–0.2) in any pressure region of 35–140 kg/cm^2 are the unique features of these compositions.

By and large, the catalyzed/platonized EDB/DBP formulations are both temperature and pressure insensitive, and are therefore, highly suited for a tropical country like India (−30 to +55°C). Since most of the lead/copper salts of aliphatic and aromatic acids studied earlier pose toxicity problems, studies on the effect of barium and cobalt salts of organic acids have been carried out on the burning rate-pressure relationship of DBP.[7] The results of these studies have revealed that barium β-resorcylate and cobalt salicylate are an effective burn rate catalyst and platonizer.

To explain the site and mode of action of ballistic modifiers in the combustion of DBP, a new mechanism, essentially based on carbon/carbonaceous matter formation, has been proposed,[8] which explains most of the observed facts satisfactorily. According to this mechanism, catalysis and platonization are dependent on the C/NO ratio in the fizz zone (foam, fizz, dark, and luminous flame zone reported in the combustion of DBP). When the C/NO ratio exceeds 1, it results in super rate burning; when it equals 1, a plateau effect is observed, and when the C/NO ratio falls below 1, a post-plateau effect takes place. Thermal analysis and kinetics of decomposition are the other areas, where a good amount of R&D work has been carried out at the Explosives R&D Laboratory.[9]

Cigarette burning propellants of more than 200 mm diam, having a burn rate of 9 mm/s (at 70 kg/cm^2 pressure), in CDB composition have been successfully test fired up to a 180-s burning duration, thereby establishing technology for flawless homogenous propellant charge of about two m length and an associated inhibition and ignition system. Most of the practical formulations developed for different applications broadly cover specific impulse *Isp* of 200–225 s, a burn rate r_b of 5–30 mm/s, a pressure exponent η of 0–0.4, a tensile strength (TS) of 100–140 kg/cm^2, and a percent elongation %*E* of 20. Based on aging studies at elevated temperatures, a life of 15–20 years has been stipulated for this class of propellants.

Table 3 Low-temperature properties of the ISRO polyol propellants

Solid loading, %	Temperature, °C	Mechanical properties TS, kg/cm^2	*Eb*,[a] %	*E*,[b] kg/cm^2
84	27	25.8	18	200
	0	32.6	20	280
	−20	37.3	18	350
87	27	7.3	40	45
	0	9.0	46	50
	−15	17.3	36	112
	−30	36.0	28	210

[a]Percent elongation. [b]Modulus of elasticity.

Thus, the country is self-sufficient to meet any requirement of EDB/CDB propellants in terms of size, energy, burn rates, and mechanical properties.

2. Composite Propellants (CP)

The development of CP during the last three decades has followed generally a pattern of continuing change dictated by requirements of higher ballistic performance coupled with better mechanical integrity under extreme operating conditions. In India, the rocket propellant grain size has grown during this period from 75 mm diam, weighing 4.5 kg, to the first stage of the Polar Satellite Launch Vehicle (PSLV) weighing more than 128 tonne. Correspondingly, the propellant technology also has moved from free-standing to case-bonded propellant grains for improving the performance. Keeping pace with this growth, the polymeric binders used in the propellants have undergone changes from the conventional polyvinyl chloride (PVC), to polybutadiene acrylic acid acrylonitrile terpolymer (PBAN), to carboxy terminated polybutadiene (CTPB), and hydroxyl terminated polybutadiene (HTPB). Both DRDO and ISRO are working on HTPB-based propellant systems for different applications. ISRO has developed three more new polymeric binders, in addition to the above binders, for use in solid composite propellants. The high energy fuel (HEF 20) is a substitute for CTPB and has

Table 4 Motor details and performance characteristics of PSLV

First Stage, HTPB-based propellant	
OD	2.8 m
Length	20.3 m
Material	maraging steel
Propellant weight	128 tonne
Insulation	Rocasin
Nozzle	Convergent divergent with 15 CDV 6 steel backup and silica/carbon phenolic composite liner
Igniter	Pyrogen with remotely mounted safe arm system
Action time, s	93.4
Burn time	89.4
Maximum pressure, MPa	5.33
Maximum sea level thrust, kN	4,622
Specific impulse S/L, N s/kg	228.5
Total impulse S/L, kN s	294,186
Third Stage, HTPB-based propellant	
Overall length, mm	2,442
Maximum diameter, mm	2,006
Case	Kevlar epoxy composite
Propellant weight, kg	7,293
Nozzle	Submerged flex type
Igniter	Pyrogen type
Burn time, s	73.1
Action time, s	78.3
Maximum pressure, MPa	5.819

been used in the upper stages of the satellite launch vehicle (SLV-3) and the augmented satellite launch vehicle (ASLV), and as apogee kick motor to put the "Apple" satellite into orbit. HEF-20 (lactone-terminated polybutadiene) has a molecular weight of 3000–4000, a density of 0.98 g/cc, and a viscosity of 200–300 P, and has far superior mechanical properties than CTPB at the same solid loading.[10,11] The propellants for launch vehicles are case-bonded and have high mass fraction (>0.90). They have low modulus (<45 kg/cm^2) and high elongation. Another new propellant binder (ISRO polyol) is a substitute for the HTPB binder. ISRO polyol-based propellants are used in sounding rockets, and the binder was considered as a candidate for the booster stages of PSLV. ISRO polyol, based on castor oil, is a saturated ester with low molecular weight (~2000), nearly bifunctional prepolymer, having a viscosity of about 2000 cps at 30°C. The hexyl-pendent group impart good low-temperature properties in addition to making it a self-plasticized system (Table 3). It is cured with isocyanates, and trihydroxy compounds may be added to tailor the mechanical properties.[12] The third new binder is hydroxyl-terminated natural rubber (HTNR), and propellants based on this binder are at present under development.

The largest solid motor booster to be developed by ISRO up to the present time has been the first-stage motor of PSLV, which has been designed for launching the Indian Remote Sensing Satellite of 1000 kg class. The PSLV has a four-stage configuration with the first stage using 2.8 m diam and 128 tonne of HTPB solid propellant in a maraging steel motor case (Table 4); a second stage (2.8 m diam and 11.5 m length) with Viking liquid engine having 37.5 tonne of unsymmetrical dimethyl hydrazine (UDMH) and N_2O_4 propellant; the third stage is a Kevlar® composite motor (2 m diam) with 7 tonne of HTPB-based propellant; and finally a liquid fourth stage uses a twin engine of 700 kg thrust with two tonne of N_2O_4 and monomethyl hydrazine (MMH) propellant contained in a titanium alloy tank. Recently, the development of HTPB-based propellant incorporating around 20% HMX at 88% solid loading has been completed by ISRO. Some of the ongoing programs of ISRO include metallized gel propellants, based on UDMH and phase-stabilized ammonium nitrate (AN)-HTPB propellants. AN-based propellants are being developed to take care of environmental problems, as ammonium perchlorate (AP)-based compositions generate huge amounts of HCl.

DRDO (ERDL) has developed a series of HTPB and polyoxy propylene glycol (PPG)-based polyurethane compositions to meet wide and varied requirements of rockets/missiles. Most of these charges are cartridge-loaded and inhibited with either filled HTPB or filled flexible epoxy resin. Gas generator compositions having high burn rates (42 mm/s) at low pressures have also been developed, using HTPB as binder, fine AP as oxidizer, and butyl ferrocene derivatives as ballistic modifier. The broad spectrum, which practical compositions cover, include burn rates of 2–40 mm/s, *Isp* of 230–245 s, density of 1.8 g/cc, pressure exponent of 0.1–0.3, and tensile strength of 25 kg/cm^2 (Table 2). Epoxy resins, diglycidyl ether of butanonecarbonohydrazone (DGBuCH), diglycidyl ether of butanonethiocarbonohydrazone (DGBuTCH), tetraglycidyl ether of vanillincarbonohydrazone (TGVCH), and tetraglycidyl ether of vanillinthiocarbonohydrazone (TGVTCH) have been synthesized, characterized, and evaluated in propellant compositions. Burn rate data of propellants based on AP/N-N-bonded epoxy binder at various pressures show significant enhancement, some of the order of 400%, over the conventional AP/CTPB systems with the same amount of AP loading.[13,14]

While DRDO and ISRO are engaged in application-oriented research, academic institutions conduct research on the role of boron, ferrocene, and *n*-butyl ferrocene on the burning behavior of HTPB-AP composite propellants, the use of preheated AP and AP + Fe_2O_3 (1 g/100 g of AP) of a given particle size distribution, and the burn rate inhibitors for AP/PS composite propellants. Interest in a systematic study of the characteristics of thermal decomposition of substituted ammonium perchlorates thrives due to the fact that the nitrogen-based salts of inorganic acids like $HClO_4$ and HNO_3 find application in explosive compositions. A large number of perchlorates having ring substituents such as o,m,p-CH_3; o,m,p-NH_2; o,m,p-OCH_3; o,m,p-Cl; m,p-COOH; m,p-NO_2; and p-OEt have been studied for their burning behavior and explosive properties.

3. *Composite Modified Double Base (CMDB) Propellants*

CMDB propellants containing both AP, Al, and nitramines have been investigated and used for the boost phase of a surface to air missile, using the IRR propulsion system. One of the major contributions of Indian scientists in this area has been the development of crosslinked CMDB (XLCMDB) propellants of high mechanical properties (TS and compressive strength) and high energy (delivered *Isp* 246 s). CMDB propellants, both by advanced casting powder (ACP) route and slurry cast technique (SCT), using spheroidal nitrocellulose (SNC) have been developed. High TS of CMDB propellants was obtained by crosslinking unnitrated hydroxyl groups of NC with toluene diisocyanate (TDI) and coating of the oxidizer (AP) with phloroglucinol or trimethylol propane (TMP). While crosslinking reduces the burn rates, a coating of oxidizer with silicone oil along with other additives enhances the burning rates of CMDB propellants.[15–20]

Table 5 Characteristics of hydroxy-terminated block copolymer of polycaprolactone and polybutadiene (HTBCP)

Polymer characteristics	
mol wt	6000–8000
Softening point	40–50°C
Density	0.9 g/cc
Hydroxyl value	15 mgm/KOH
Functionality	2
Heat of formation	213 cal/g
Cal-val	−1500 cal/g
Decomposition temperature	438°C (inception) 487°C (peak)
Propellant parameters[a]	
Cal-val	1680 cal/g
Isp	263 s
Chamber temp.	3614°C
Burn rate at 50 kg/cm^2	8.7 mm/s
Impact sensitivity	27 cm (height of 50% explosion)
Friction sensitivity	Insensitive up to 9.6 kg/cm^2
Ignition temperature	150°C
Decomposition temperature	160°C (inception) 165°C (peak)

[a]Composition: HTBCP: 10.5, NG: 18, DEP: 2.5, NC: 1, AP: 49, Al: 19, NCO:OH: 1·3:1

A novel block copolymer has been synthesized from caprolactone using HTPB as the ring opening initiator. The polymer has high miscibility with nitric esters and has a high solid loading capability (Table 5).[21] Recently, R&D work on glycidyl azide polymer (GAP)-based propellants has been started, as it offers a unique energetic binder and plasticizer system for advanced propellants to achieve higher performance, superior mechanical properties, and low vulnerability. Its chief advantages are higher density and positive heat of formation as compared to the widely used HTPB. Research work carried out in ERDL has indicated that GAP acts as a high energy desensitizer and is capable of enhancing the energy and burn rates (Table 6). Replacement of DEP by GAP resulted in a 7 s increase in *Isp*. Burn rate enhancement of 75% was obtained for a typical NC-NG-based composition.[22] Thermal decomposition studies of GAP and GAP-based propellants under N_2 atmosphere, suggest that GAP decomposes in two stages, the first stage of decomposition takes place between 127–200°C with a steady slope having an *Ea* of 37 kcal/mole, and the second one between 200–210°C with a higher slope. Below 200°C, the decomposition appears to be based on reactant-product interface, diffusion controlled, while at higher temperatures a nucleation-based diffusion appears to be predominant.[23]

4. *Fuel-Rich Propellants (FRP)*

Both pressed- and cast-type of fuel-rich propellants for IRR applications, based on Mg powder and hydrocarbons, have been studied and evaluated. Burn rates of the order of 27 mm/s in the primary chamber (18–20 kg/cm^2 pressure), and *Isp* of 600 s in the secondary chamber have been achieved for formulations containing Mg powder, naphthalene, and $NaNO_3$ as oxidizer (Table 2). At present, studies are being carried out at ERDL with Ti, Ni, Zr, Mg-Al metal powders with HTPB, and GAP-plasticized DB matrix. Preliminary findings indicate that metallized formulations (Ti, Zr) with HTPB as a binder produce lower (50%) burn rates as compared to corresponding compositions with DB matrix. While the in-

Table 6 Ballistic of GAP-based DBP and CMDB propellants

	I	II	III	IV	V	VI	VII	VIII
				Acoustic/Crawford bomb data				
Composition								
DNC	60	60	60	60	60	60	60	60
NG	32	32	28	24	20	28	24	20
DEB	7.2	—	7.2	7.2	7.2	—	—	—
GAP	—	7.2	4	8	12	11.2	15.2	19.2
2-NDPA	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8
Burn rate, mm/s								
@ 50 kg/cm^2	7.2	11.3	6.9	6.9	8	12.6	10.9	9.8
@ 70 kg/cm^2	8.1	12.9	8	8.1	10.7	15.1	14.8	14.6
@ 90 kg/cm^2	9.8	16.3	9.6	10	12	17.9	17	15.9
Pressure exponent								
η50–70	0.35	0.39	0.44	0.48	0.86	0.54	0.91	1.18
η70–90	0.75	0.95	0.73	0.84	0.42	0.68	0.55	0.34
Theoretical *Isp*, s	228	235	222	214	206	229	222	214

	I	II	III
		Static motor firing data (CMDB propellant)	
Composition			
DNC	55	60	52
NG	37.8	32	37.8
GAP	6.3	7.2	6.3
2-NDPA	0.8	0.8	0.8
RDX	—	—	3
Cu_2O + PbO (1:1)	—	2 (parts)	—
Burn rate, mm/s @ 50 kg/cm^2	11.3	11.6	10.6
Pressure exponent	0.6	0.14	0.67
Specific impulse, s @ 50 kg/cm^2	216	—	220

Grain Dimensions. OD: 67 mm, ID: 20 mm, L: 100 mm.

corporation of metals at the cost of oxidizer (AP) in HTPB-based composite formulations resulted in decreased burn rates, replacement of binder by metal led to an increase in burn rates. In case of composite formulations, all the compositions gave sustained and stable combustion in the entire pressure ranges studied (10–90 kg/cm^2).[24,25] Castable FRP-based on HTPB-AP/AN and a polystyrene system are capable of producing superior mechanical properties without reducing energy (*Isp*) significantly.

5. *Low Vulnerability Propellants (LOVA)*

Research in the field of high impetus low flame temperature (HILT) and LOVA has gained momentum with the objective of achieving reduction in gun barrel erosion and overcoming the problem of initiation of ammunition by spall or hypervelocity impact, respectively, without penalty on energetics. Sensitivity characteristics and energetics of HILT and LOVA propellants based on nitramines and other oxidizers such as diaminotrinitrobenzene (DATB), hexnitrostilbene (HNS), and nitroguanidine (NQ) have been studied. The potential of various binders, namely, cellulose acetate butyrate (CAB), cellulose acetate phthalate (CAP), polyvinyl acetate (PVAc), ethyl cellulose (EC), and GAP as component of LOVA propellants has also been evaluated.[26] Incorporation of DATB and HNS resulted in decreased flame temperature and a marginal drop in impetus. Energetics and sensitivity characteristics of RDX/HMX and CAB/CAB-GAP-based LOVA compositions have indicated that RDX-based compositions produce higher impetus *F* than HMX-incorporated LOVA. Incorporation of 3–6% low molecular weight GAP (mol wt ~ 400) resulted in further increases in *F* by 23–43 J/g[27] (Table 7).

III. Liquid Propellants

A. Liquid Propellants for Space Applications

Unsymmetrical dimethyl hydrazine (UDMH) and N_2O_4-based systems have been exhaustively studied, evaluated, and used by ISRO for the second stage of PSLV (PS-2). PS-2 is the largest liquid propulsion stage developed in the country. The engine operating at a chamber pressure of 52.6 bar, delivers an *Isp* of 293 s (nominal). The motor develops a 60 tonne thrust at sea level and burns for 150 s. The propellants from the tanks are fed to the combustion chamber at the rate of about 251 kg/s (at 65 bar nominal pressure) by a turbopump system, driven by a turbine rotating at 9600 rpm. The turbine is driven by the hot gas from a gas generator, which also works on the same propellant combination as that of the engine. The engine is controlled by a two-stage feedback regulation system. The propellant tank is of a common bulkhead construction with N_2O_4 in the top compartment and UDMH in the bottom compartment.

B. Liquid Gun Propellants (LGP)

Solid gun propellants have almost reached a saturation limit in terms of energy, and higher MV (>2000 m/s) is not possible from a solid system. Hence, LGPs are being investigated for futuristic gun applications. Higher firing rate, variable range, increased operational safety, reduction in barrel erosion, and substantial financial savings are other distinct features of LGP. Hydroxyl ammonium nitrate (HAN)-based monopropellants have been developed by ERDL. These are a mixture of HAN, triethanol ammonium nitrate (TEAN), and water in a stoichiometric ratio with respect to CO_2, N_2, and H_2O. HAN has been prepared by the double decomposition of hydroxyl ammonium sulphate and barium nitrate. At present, the lab scale process is being scaled up to the pilot plant/production level.

IV. High Explosives (HE)

Initiatory explosives are an important subdivision of high explosives and are vital for igniters, cap, and detonators. Thrust of R&D in this field is either by modification of traditional initiatory explosives or by the synthesis and evaluation of new initiatory explosives. Service lead azide (SLA), which has been extensively used in India, has inherent drawbacks such as high friction sensitivity, lesser stability to moisture, and incompatibility with copper and brass used in ammunition. A number of double salts such as lead double salt of 5,5′-diazoaminotetrazolic acid and styphnic acid (LDDS), azotetrazolic acid (LDDA), 5-nitroaminotetrazolic acid (LDAN), and lead double salt of azotetrazolic acid and 5-nitroaminotetrazolic acid (LDDN) were prepared and studied for their initiatory properties (Table 8).[28] Basic lead azide (BLA) has been synthesized and characterized at ERDL, which has better hydrolytic, and thermal stability, flash pickup, high bulk density,

Table 7 Energetics of Lova propellant compositions

Composition					Cal-val,	*F*,	*P*,		
RDX	HMX	CAB	DEP	GAP	cal/g	J/g (delivered)	MPa (delivered)	*Tf*, K	*Ti*, °C
80, 25μ	—	16	4	—	831	1103	125	2822	218
80, 50μ	—	16	4	—	831	1150	125	2822	220
85, 25μ	—	12	3	—	962	1228	138	3189	228
85, 50μ	—	12	3	—	962	1227	138	3189	228
90, 50μ	—	8	3	—	1110	1313	149	3495	226
—	80, 25μ	16	2	—	799	1065	125	2813	250
—	85, 25μ	12	3	—	932	1233	123	3157	262
85, 25μ	—	12	—	3	1011	1251	142	3130	226
85	—	12	—	6	1081	1271	144	3379	226

Table 8 Properties of the various lead double salts and related compounds as initiator

Salt	Explosion temperature, °C	Energy of activation, Kcal/mol	Impact sensitivity, ft lb/in.^{2}
LDDS	290	16.31	4.98
Lead styphnate	255	67.04	9.8
Lead 5,5′-diazoaminotetrazolate	185	12.31	Less sensitive
LDDA	225	27.42	4.2
Lead azotetrazolate	194	12.31	2.1
LDAN	234	18.28	3.83
Lead 5-nitroaminotetrazolate	355	21.71	Less sensitive
LDDN	222	13.32	8.05

Table 9 Comparative properties of LDDS, SLA, and BLA

Property	LDDS	SLA	BLA
Lead percentage	49.5	95.5	70
Bulk density, g/cc	1.35	1.85	2
Impact sensitivity	4.98 ft lb/sq. in	100 cm	100 cm
Friction sensitivity	30–40-g load[a]	50-g load[a]	250-g load[a]
Explosion temperature, °C	290	325	350
Stability in humid air	Stable	Decomposes	Stable
Compatibility with copper and brass	Explodes	Explodes	Explodes producing hole on copper foil

[a]On the beam of Julius Peters apparatus.

and flow property, thereby offering a new generation of safer detonators for various military and civil applications.[29] Comparative properties of LDDS, BLA, and SLA are given in Table 9.

Heavy metal salts of Pb, Hg, Ag, and Ba are generally used in initiatory compositions. Intrinsic properties of metal salts determine explosive properties like heat sensitivity, impact, friction, and explosion temperature, etc. Nitroanilino acetic acid esters have been studied for their plasticizer properties for high-energy propellants and explosives. Studies on metal salts (lead, copper) of trinitroanilinoacetic acid (TNAAA) indicate that they are thermally stable and undergo exothermic decomposition between 160–200°C. The explosion temperatures of these metal salts are in the range of 230–270°C.[30] The effect of Pb and Cu salts of TNAAA as ballistic modifiers in EDB and CMDB propellant formulations is presently being pursued.

RDX and HMX still continue to be the most widely used HE, because they represent the best compromise between performance, density, heat stability, cost, and processability. A continuous process for the production of HMX, based on the modified Bachmann process, has been developed by ERDL, which can be scaled up easily. Keeping the future requirements in mind, newer high-energy materials having velocity of detonation (VOD) of more than 9500 m/s, density greater than 2 g/cc, detonation pressure of more than 40 GPa, and thermal stability higher than 350°C are being synthesized. To meet the need of thermally stable explosives for oil well shooting charges and space programs, systematic and exhaustive R&D work has been started on dinitrofurazano piperazine (DNP), triaminotrinitrobenzene (TATB), hexanitrostilbene (HNS), diaminohexanitro diphenyl (DIPAM), 3-picrylamino-1,2,4-triazole (PATO), 3-nitro-1,2,4-triazole-5-one (NTO), and 2,5-dipicryl-1,3,4-oxadiazole (DPO). Flexible linear shaped charges (FLSC) having explosive loading of 1–100 g/m have been developed both by DRDO and ISRO for military and civilian applications, including stage separation of space vehicles, cutting of outer casing of warheads, and canopy severance system, etc. One such composition recently tested gave a clean cut of a 7-mm-thick acrylic sheet without any adverse effect (shock, vibration) on other subsystems.

In the area of high explosive anti-tank (HEAT), ammunition usage of HMX-based compositions along with improvement in liner material, wave shapers, and explosive fabrication technology has resulted in a penetration capability of 8–10 times the caliber of modern antitank guided missile warheads. A large number of HMX-based compositions have been developed and evaluated for the fragmentation and penetration type of warheads. The pattern of distribution, shape, and size of explosively formed fragments have been optimized to produce more reproducible and predictable behavior. A number of aluminized high-explosive compositions have been developed to obtain blast effect. These explosives, despite having low brisance, possess high underwater, open air, and underground blast potential. Low brisance is due to lower gas volume and nonreaction of Al in the Chapman–Jouguet (C–J) plane, whereas high blast is due to heat generation and afterburning phenomena and the exothermic oxidation of Al with the detonation products. Some of the compositions, based on RDX/Wax/Al developed for blast effect, produce *Pmax* of high order and have VOD in the range of 8000–8100 m/s.

Table 10 VOD and compression strength of PBX charges

Composition	VOD, m/s	Loading density, g/cc	Compression strength, kg/cm²
RDX/PU: 95/5	8100	1.66	134
RDX/PU: 97/3	8300	1.67	139
HMX/PU: 95/5	8500	1.72	187
HMX/PU: 97/3	8630	1.73	208
RDX/LDPE: 95/5	7900	1.67	66.3
RDX/LDPE: 97/3	8227	1.69	68.3
HMX/LDPE: 95/5	8428	1.72	75
HMX/LDPE: 97/3	8610	1.76	72.3

Conventional explosives, based on RDX/trinitrotoluene (TNT) or HMX/TNT, have disadvantages of poor mechanical property, poor adhesion to metal, higher percentage of shrinkage after melt casting, and are sensitive. Therefore, work on plastic-bonded explosives (PBX) is being carried out to eliminate the above shortcomings. Pressed HMX and low density polyethylene (LDPE)-based formulations have given a VOD of 8600 m/s, with an impact sensitivity of 65 cm and a friction sensitivity of 22 kg. These formulations have density in the range of 1.72–1.76 g/cc. Polyurethane (PU)/HMX-based pressed PBX compositions produce a VOD of 8650 m/s, density of 1.86 g/cc, and compressive strength of 200 kg/cm² (Table 10).

V. Pyrotechnics

In the areas of pyrotechnics, R&D work in the field of pyrotechnic delays, incendiary compositions, IR smoke, tracers, illuminating composition, and IR flares is being carried out. A number of gelled and solid incendiary compositions have been developed by ERDL. For spinning-type ammunition and for applications demanding higher shelf/useful life, solid incendiary compositions are preferred. To meet this requirement, zirconium-based compositions with polymeric base have been developed, which are capable of producing flame temperature of 1800–2000°C and can be tailored to burn for 3–5 min.

Tracer compositions, which are a mixture of an oxidant, a metal fuel, and other additives, are used to observe flight trajectory, and thus, facilitate more accurate aiming at fast moving aerial and ground targets. Additives are mainly added to modify burn rate, color, radiant output, and sensitivity. A number of indigenous tracer compositions, based on magnesium powder, aluminium, strontium nitrate, and polymeric binder, have been developed at ERDL. For a tracer composition containing Mg/strontium nitrate and polyester resin as binder, luminous intensity of 15,000–17,000 cd-s/g was obtained. By and large most of the tracer compositions used in India are based on polylinseed oil, chlorinated rubber, and contain strontium nitrate or barium nitrate as oxidizer and Mg or Mg-Al as metallic fuel.

Table 11 IR flares/decoys developed at ERDL for various applications

Type	Weight of composition, g	Burning time, s	IR output, μ	Power, W/sr
Missile tracking	50–160	10–34	1.5–2.4	95–570
Decoy	100–285	3.5–10	1.5–2.5	1000–4500

Table 12 Details of smoke composition and results of attenuation

Number	Composition	% Composition	% Attenuation
1.	Hexachloroethane	15–40	
	Anthracene	15–40	97.8
	Potassium perchlorate	30–50	
2.	Hexachloroethane	15–20	
	Magnesium	15–25	97.3
	Naphthalene	05–30	
3.	Hexachloroethane	15–70	
	Zinc oxide	15–25	
	Calcium silicate	02–10	
	Potassium nitrate	01–05	93.4
	Titanium oxide	01–10	
	Mg/Al	05–15	
	Naphthalene	15–25	
4.	Hexachloroethane	15–40	
	Naphthalene	05–30	
	Zinc oxide	10–25	92.8
	Calcium silicate	01–20	
	Potassium perchlorate	15–40	

A large number of illuminating compositions, based on Mg, sodium nitrate, binder, and calcium oxalate, have been developed to obtain a burning time of 24–45 s, a linear burn rate of 2.5–3.1 mm/s, a luminosity of $2–10.4 \times 10^5$ cd with an efficiency of 20,000–36,000 cd-s/g. IR flares (Table 11) have been used as decoys against heat-seeking missiles and for tracking the path of missiles. The decoy flares generally contain metallic fuels (Mg, Si, Zr) or alloys, oxidizers (BaO_2, Fe_2O_3) and additives, in addition to binders. The effective performance of flare compositions depends on the chemical nature of IR-producing formulations and design. Teflon®-based compositions emit high IR intensity as compared to barium nitrate-based compositions in 3–5- and 8–14-μ regions, and an increase in combustion temperature results in an increase in radiant intensity in near IR region. Particle size distribution of metal powder and oxidizer plays an important role in controlling the burning characteristics of IR flare compositions.

Camouflage has gradually evolved into highly complex technology designed to conceal objects of all kinds. This is a natural consequence of progress made in reconnaissance technology, including thermal, electromagnetic, and photochemical sensors. To balance this progress improved pyrotechnics compositions are required. ERDL-developed smoke compositions (Table 12) are effective against night vision equipment and night fire control systems.[31] A composition containing Mg, hexachloroethane, and naphthalene has been found suitable for more than 97% attenuation of CO_2 laser and was effective in obscuring IR emitting targets for about 140 s.

VI. Conclusions and Plans

India is today self-sufficient and has attained international standard in the field of solid rocket propellants (both conventional and advanced) and has developed high explosive compositions based on RDX and HMX to meet most of the operational requirements. However, R&D efforts are needed to master technology for cryogenic propellants, low vulnerability explosives, and pollution-free pyrotechnic compositions to meet futuristic requirements.

The success of the PSLV mission has put ISRO on the course for building the Geo-Stationary Satellite Launch Vehicle (GSLV), which will orbit an indigenous telecommunication satellite at 36,000 km above the Earth. In order to improve the vehicle performance in terms of reduced gross lift-off weight (GLOW) and higher payload capability, high-energy liquid propellant system (liquid oxygen-liquid hydrogen) assumes importance. Considering the need and potential of this system, ISRO has embarked on the development of the cryogenic system for use in the upper stage of GSLV.

The current composite propellants are based on HTPB with ammonium perchlorate as the oxidizer. The major efforts at present are in increasing the solid content from 86 to 90% by the use of a multimodal distribution of oxidizer, improving the mechanical properties of the propellant by the use of bonding agents, and increasing the burn rate without increasing the pressure exponent. Use of other metallic fuels (Ti, Zr, B) are being studied with a view to use these fuel-rich propellants in air breathing propulsion systems. Research on the use of new energetic binders/plasticizers/additives/oxidizers in solid propellants will continue. Hybrid propulsion systems are attractive from energy, safety, reliability, and low vulnerability aspects, and hence, R&D work with high energy solid fuels and liquid oxidizers is being planned. The promising applications of N-N-bonded epoxides as hypergolic fuels for hybrid propulsion will be exploited. The new emphasis on performance will require the development of low cost composite cases to reduce the weight of the motor.

References

[1]Rao, K. P., Umrani, P. K., Nair, R. G. K., and Venkatesan, K., "Studies on Some Aspects of Propellants for Improving Performance of Tank Guns," *Defence Science Journal*, Vol. 37, No. 1, 1987, pp. 51–57.

[2]Singh, H., and Rao, K. R. K., "Effect of Lead and Copper Methylene Disalicylates on the Combustion Rates of Double Base Propellants," *Propellants, Explosives, Pyrotechnics*, Vol. 7, 1982, pp. 61–65.

[3]Singh, H., and Rao, K. R. K., "Lead Aliphatic Mono and Dicarboxylates as Ballistic Modifiers," *Journal of Spacecraft*, Vol. 19, No. 5, 1982, pp. 478–480.

[4]Singh, H., and Rao, K. R. K., "Ballistic Modification of Double Base Propellants by Lead Salts of Aromatic Acids," *Indian Journal of Technology*, Vol. 24, No. 1, 1986, pp. 26–28.

[5]Singh, H., and Rao, K. R. K., "Mechanism of Combustion of Catalysed Double Base Propellants," *Combustion and Flame*, Vol. 71, No. 2, 1988, pp. 205–213.

[6]Singh, H., and Rao, K. R. K., "Catalytic Effect of Lead Salts—Role of Organic Moiety," *Proceedings of the 7th National Seminar on Advances in Catalysis, Science and Technology*, Indian Petrochemical Co., Ltd., Baroda, India, 1985, pp. 229–232.

[7]Raman, K. V., Singh, H., and Rao, K. R. K., "Effect of Certain Barium and Cobalt Salts on the Burning Rates—Pressure Relationship of Double Base Rocket Propellants," *Combustion Science and Technology*, Vol. 45, 1986, pp. 213–219.

[8]Singh, H., and Rao, K. R. K., "Role of Carbon/Carbonaceous Matter Formation in the Combustion of Double Base Propellant," Max-Planck Inst. Rept. 113, Germany, Dec. 1985.

[9]Singh, H., and Rao, K. R. K., "Thermal Decomposition Studies of Catalysed Double Base Propellants," *Proceedings of the Indian Academy of Sciences (Chemical Sciences)*, Vol. 93, No. 2, 1984, pp. 93–97.

[10]Rao, K. V. C., Jaydev, S., Varghese, T. L., and Gowarikar, V. R., *Journal of Spacecraft*, Vol. 15, 1978, pp. 293–298.

[11]Nema, S. K., Francis, A. U., Nair, P. R., and Gowarikar, V. R., AIAA/SAE 15th Propulsion Conference, Palo Alto, CA, July 1976.

[12]Krishnamurthy, V. N., and Thomas, S., "ISRO Polyol—The Versatile Binder for Composite Propellants for Launch Vehicles and Missiles," *Defence Science Journal*, Vol. 37, No. 1, 1987, pp. 29–39.

[13]Jain, S. R., and Amanulla, S., "Novel N-N Bonded Epoxy Binders for Solid Propellants," *Proceedings of the 7th National Seminar on High Energy Materials*, Vikrann Sarabhai Space Centre, Trivandrum, India, 1994, pp. 49, 50.

[14]Jain, S. R., "Spontaneously Igniting Hybrid Fuel-Oxidizer Sys-

tems," *Defence Science Journal, Special Issue on High Energy Materials*, Vol. 45, No. 1, 1995, pp. 5–16.

[15]Singh, H., Raman, K. V., and Rao, K. R. K., "Ballistic Modification of CMDB Propellants Containing AP," *Propellants, Explosives, Pyrotechnics*, Vol. 12, No. 1, 1987, pp. 13–16.

[16]Bhat, V. K., and Singh, H., "Cross Linked Slurry Cast CMDB Propellants-Mechanical Properties," *Defence Science Journal*, Vol. 37, No. 1, 1987, pp. 39–44.

[17]Bhat, V. K., Singh, H., and Rao, K. R. K., "Processing of High Energy Cross Linked CMDB Propellants," *Proceedings of the 18th International Conference of ICT*, Fraunhofer Inst. for Chemical Technology, Karlsruhe, Germany, 1987, pp. 1–3.

[18]Bhat, V. K., Dhar, S. S., Singh, H., and Rao, K. R. K., "Effect of AP and Al Solid Loading on Mechanical and Ballistic Properties of CMDB Propellants," *Proceedings of the Seminar on Solid Rocket Propellants for Rocketry and Explosives*, Trivandrum, India, 1987, pp. 137–142.

[19]Bhat, V. K., Singh, H., and Rao, K. R. K., "Preparation of CMDB Propellants of High T.S. for Propulsion of Rockets/Missiles," Indian Patent 163,103, 1988.

[20]Asthana, S. N., Divekar, C. N., and Singh, H., "Studies on Thermal Stability, Autoignition and Stabilizer Depletion for Shelf Life of CMDB Propellants," *Journal of Hazardous Materials*, Vol. 21, 1989, pp. 35–46.

[21]Bhat, V. K., Shrotri, P. G., and Singh, H., "A High Performance Binder for EMCDB Propellants," *Defence Science Journal—Special Issue on High Energy Materials*, Vol. 45, No. 1, 1995, pp. 31–34.

[22]Dhar, S. S., Asthana, S. N., Shrotri, P. G., and Singh, H., "Pyrolysis/Combustion Behaviour of GAP Based Double Base Propellants," *Proceedings of the 22nd International Conference of ICT on Combustion and Reaction Kinetics*, Karlsruhe, Germany, 1991, p. 58.

[23]Dhar, S. S., Asthana, S. N., Natu, G. N., and Singh, H., "Thermal Decomposition of GAP and GAP Based Double Base Propellants," *Combustion Explosion and Shockwaves*, Vol. 29, No. 3, 1993, pp. 276–280.

[24]Athawale, B. K., Vaidya, M. V., Asthana, S. N., and Singh, H., "Energetic Solid Fuel for Ramjet/Ducted Rockets," *Proceedings of the 7th National Seminar on High Energy Materials*, Vikrann Sarabhai Space Centre, Trivandrum, India, 1994, pp. 87, 88.

[25]Athawale, B. K., Asthana, S. N., Shrotri, P. G., and Singh, H., "Combustion Studies on Metallized Composite and CMDB Propellants," *Proceedings of the 13th National Conference on IC Engines and Combustion* (Bangalore, India), Tata McGraw Hill, Dehli, India, 1994, pp. 338–345.

[26]Choudhari, M. K., Gautam, G. K., Pawar, S. B., Kulkarni, M. P., and Asthana, S. N., "Studies on High Impetus Low Flame Temperature (HILT) and LOVA Propellants," *Proceedings of the 7th National Seminar on High Energy Materials*, Vikrann Sarabhai Space Centre, Trivandrum, India, 1994, pp. 205, 206.

[27]Choudhari, M. K., Asthana, S. N., and Singh, H., "Studies on High Energy LOVA Compositions," *24th International Annual Conference of ICT*, Karlsruhe, Germany, 1993, pp. 61/1–61/7.

[28]Bahadur, K., "Preparation of New Initiatory Compounds and Study Their Explosive, Physical and Chemical Properties," Ph.D. Dissertation, Univ. of Poona, India, 1972.

[29]Surve, R. N., "Studies on the Preparation and Properties of Basic Lead Azide," Ph.D. Dissertation, Univ. of Poona, India, April 1992.

[30]Rao, K. U. B., Soman, R. R., and Singh, H., "Explosive Properties of Metal Salts of Nitro-Anilino Acetic Acid," *Journal of Energetic Materials*, Vol. 8, 1990, pp. 99–109.

[31]Singh, A., and Singh, H., "Evaluation of Pyro Smokes for Anti-IR and Anti-Laser Roles," *Propellants, Explosives, Pyrotechnics* (to be published).