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Polyurethane-Based Inhibition for High Flame Temperature Nitramine-Based Composite Modified Double-Base Propellant

(Ms) S. D. Kakade, M. V. Vaidya, D. G. Khangaonkar, P. K. Divekar, U. B. Kadam

and

S.N. Asthana

High Energy Materials Research Laboratory, Pune - 411 021

ABSTRACT

The findings for polypropylene glycol (PPG) and hydroxyl-terminated polybutadiene (HTPB)-based inhibition systems are reported. These findings established that the inhibition system comprising HTPB-IPDI-IDP binder and Sb_2O_3-C black filler is most suitable for advanced nitramine-based composite modified double-base propellants in terms of mechanical properties and processibility. The promising composition was characterised for glass-transition behaviour and propellant-inhibition bond strength. Propellant grains inhibited with selected formulations were subjected to static evaluation at extreme temperatures and limited aging studies to obtain data of practical value.

1. INTRODUCTION

A definite pattern of propellant burning desired for specific applications is achieved by applying inert polymeric materials called inhibitors to restrict propellant combustion. Although a large number of inhibition systems are reported for double-base[1-4] (DB) and composite propellants[5-8], the literature available on inhibition of composite modified double-base (CMDB) propellant is scanty[9-12]. Slurry cast CMDB propellants are comparatively more flexible than conventional DB propellants. This leads to stresses at propellant-inhibitor interface during thermal cycling if rigid inhibitiors commonly used for DB propellants are applied. Another major problem posed by CMDB propellants from inhibition point of view is their higher flame temperature than DB propellants which is due to the presence of oxygen-rich ammonium perchlorate (AP) and energetic nitramines as well as metallic fuel *Al* in DB matrix. Therefore, conventionally used inhibitors for DB propellants, such as cellulose acetate (CA) or ethyl cellulose cannot restrict combustion of CMDB propellants.

Araki,[10] *et al.* have reported a inhibition system based on styrene-butadiene and acrylonitrile-butadiene rubber blend filled with asbestos, silisic acid and carbon black for nitroplastisol propellants. Agrawal[12], *et al.* have developed a inhibition system based on polyester

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resin for nitramine-based CMDB propellant and have recommended barrier coats to overcome the problem of plasticiser migration from propellants to inhibitors. Their inhibition method involved application of a coat of Desmodur R (triphenyl methane tri-isocyanate solution in methylene chloride) followed by barrier coats of fast setting polyester resin and subsequent inhibition by fast setting unsaturated polyester resin containing 30 per cent alumina as filler. In general, polymers with *P-N* linkage (attributable to aziridines used for curing *-COOH* and *-OH* groups) and ester linkage are relatively more prone to hydrolysis during storage. In view of this, a research programme was undertaken to develop thermally-resistant and flexible inhibition system based on polypropylene glycol (PPG), hydroxyl-terminated polybutadiene (HTPB) and their combinations for advanced nitramine-based CMDB propellants.

2. EXPERIMENTAL PROCEDURE

2.1 Materials

The binders used were HTPB (molecular weight, *Mn*: 2300-3000) and PPG (molecular weight, *Mn*: 2300-3000) along with isodecyl pelargonate (IDP), (purity: 99 %) as a plasticiser). The curatives used were toluene-di-isocyanate (TDI) (80 % 2, 4 isomer and 20 % 2,6 isomer) and isophorone-di-isocyanate (IPDI,) (purity: 99 %). The fillers incorporated in the formulations were (antimony trioxide (Sb_2O_3), purity: 99 %, particle size : passing 200 BSS) and carbon black (rubber grade N-774, particle size: 0.8 μm). Ferric acetyl acetonate (FeAA, iron content: 15.8 %) was incorporated as curing catalyst and pyrogallol (purity: 98 %, m.p. 131-134 °C) was added as an antioxidant-cum-crosslinking agent in the polyurethane formulations.

All the liquid ingredients/polymers were deaerated under vacuum (< 10 mm of *Hg*) for minimum six hr and all the solids were dried in air oven at 100 °C for six hr to ensure moisture content < 0.1 per cent (Karl Fischer method).

2.2 Preparation of Polyurethanes

HTPB/PPG or their combinations were mixed with IDP using mechanical stirrer. The mixture was warmed to 60 °C and FeAA along with pyrogallol were dissolved in it. The mixture was cooled to room temperature, and subsequently fillers (carbon black and Sb_2O_3) were added with continuous stirring. This homogeneous slurry was deaerated in a vacuum desiccator (10 mm of *Hg*) for 30 min. The formulation was allowed to react with isocyanates (*-NCO* : *-OH* ratio, 1:1) at ambient temperature and relative humidity 55 per cent. The slurry was degassed in vacuum and poured in a mould to obtain 2.5-3.0 mm thick sheets. The sheets were cured at ambient temperature for one day and post-cured at 45 °C for five days.

3. CHARACTERISATION

Polyurethane sheets were characterised for tensile strength and per centelongation using Instron universal testing machine. Samples were prepared as per ASTM D-638 M Type M-II. The differential thermal analysis (DTA) was carried out in air on indigenously assembled apparatus at a heating rate of 10 °C/min. The glass transition temperature (*Tg*) was determined by differential scanning calorimetry (DSC) (Mettler DSC-30).

To get an idea of the affinity of plasticisers for selected inhibition system wrt conventional systems, cured samples of standard dimensions (50 x 50 x 2.5 mm) were immersed in desensitised nitroglycerine (NG: 84 %, DEP: 14 %, stabiliser: 2 %) for 10 days. Plasticiser migration was monitored by change in weight of samples after wipe cleaning the samples using filter paper[13]. The bond strength was determined by placing the propellant pieces of dimensions (50 x 20 x 20 mm) in *Al* mould, 10 mm apart and the inhibition material was filled in the gap and cured. It was determined on Instron universal testing machine by holding the propellant ends in the jaws of the machine. The cross-head speed was 50 mm/min.

Peel-off strength was obtained by using propellant pieces of dimensions (50 x 20 x 10 mm), which were inhibited on 10 mm side so as to get a

30 mm flap of inhibitor. The inhibitor was cured and the cured samples were mounted on Instron universal testing machine. The propellant and the inhibitor were held in the lower and upper jaws of the machine, respectively. The lower jaw was moved down at the rate of 50 mm/min. Ten samples were evaluated for each test and an average of the results obtained reported.

3.1 Inhibition & Cured Static Evaluation of Composite Double-Base Propellants

A technology for the use of selected polyurethane formulation as inhibitor to nitramine-based slurry cast CMDB propellant has been developed at the High Energy Materials Research Laboratory (HEMRL). The propellant composition was: spheroidal nitrocellulose (NC: 90, NG: 7.3, Carbamite: 2.7) 41 per cent; casting liquid (NG: 84, DEP:14, 2NDPA: 2) 38 per cent; RDX (25 µm) 12 per cent; AP (10 µm) 6 per cent; *Al* (15 µm) 3 per cent; ballistic modifier (2.5 parts). Propellant grain obtained by casting in moulds was machined after curing to the required dimensions (outer diameter 129.0 ± 0.5 mm, length = 160 ± 0.5 mm). Propellants were positioned in the moulds and inhibited by casting inhibition material over it under vacuum. The inhibitor was cured at ambient temperature for one day and at 45 °C for five days in a water-jacketted oven.

To get realistic data from application point of view, inhibited propellant sets were subjected to static evaluation at ambient as well as extreme temperatures (-30 °C and +55 °C). All the grains were subjected to X-ray radiography for clearance before evaluation.

4. RESULTS & DISCUSSION

Analysis of viscosity profile indicated that PPG-based formulations have long pot life which is advantageous from application point of view. However, these formulations were soft and too flexible (tensile strength 5 kg/cm^2, percentage elongation 325) for practical applications. To improve upon the structural integrity of the formulations, PPG was incrementally replaced by HTPB. Polymeric sheet based on HTPB alone (without PPG) gave tensile strength (TS) of 18 kg/cm^2 and percentage elongation of 120 (Table 1). High flexibility of PPG-based inhibition is attributable to the presence of $-C-O-C-$ bonds in backbone, whereas HTPB contains prominently relatively rigid $-C-C=C-C-$ linkages. On the basis of these findings, HTPB-based composition was selected for further studies.

The effect of fillers on the mechanical properties and processibility of HTPB-based compositions was evaluated. The Sb_2O_3 was found to be superior to Al_2O_3, lithopone, asbestos as filler, in view of its high heat retardancy, ease in processing and nontoxic behaviour. To determine the reinforcing effect of carbon black quantitatively, the proportions of carbon black and Sb_2O_3 were varied. The T S decreased from 18 to 15 kg/cm^2 on reducing carbon black content from 12 to 5 per cent and increasing Sb_2O_3 content from 33 to 40 per cent. Formulation without carbon black (Sb_2O_3 45 %) gave TS of 13 kg/cm^2 (Table 1). This clearly established the need to incorporate carbon black to augment reinforcement. Further increase in TS was observed with increase in total filler content from 45 to 50 per cent. However, the composition was not found suitable from the point of view of processibility due to limited pot life and high viscosity.

Table 1. Mechanical properties of PPG/HTPB inhibitor formulations

Ingredients	Formulations (g)					
	1	2	3	4	5	6
PPG	50	25	5	-		
HTPB		25	45	50	50	50
IDP	5	5	5	5	5	5
Sb_2O_3	33	33	33	33	40	45
Carbon black	12	12	12	12	5	
Pyrogallol	0.05	0.05	0.05	0.05	0.05	0.05
FeAA	-	0.04	0.04	0.04	0.04	0.04
DBTL	0.04					
Isocyanate ($-NCO$: $-OH$)	1:1	1:1	1:1	1:1	1:1	1:1
TS (kg/cm^2)	5	9	11	18	15	13
Elongation (%)	325	260	210	120	137	165

Regarding curatives, IPDI (pot life 50-60 min) was found superior to TDI (pot life 30 min) as determined by viscosity profile. These findings established that HTPB-IPDI-Sb_2O_3-carbon black formulation is suitable from the point of view of mechanical properties and processibility. Thereby, it was selected for further studies. Characteristics of this system are given in Table 2.

The plasticiser migration, as determined by estimating its content in inhibitor, was lower for polyurethane inhibitior (3-4 %) than that for cellulose acetate (85-100 %) and ethyl cellulose (14-17 %) which are well-known inhibitors for double-base propellants. This property is highly desirable for its use as inhibitor for DB as well as CMDB propellants.

An effective bonding between propellant and inhibitor was established by determining peel-off and bond strength with selected nitramine-based CMDB propellants. Different pre-coats were tried to establish chemical bonding between propellant and inhibition system by crosslinking residual *-OH* groups of the NC (constituent of nitramine-based CMDB propellant) and HTPB (constitutent of inhibition). Two pre-coats (one of IPDI and the other of polyurethane formulation with higher *NCO* ratio without filler) applied 24 hr prior to inhibition of the propellants were found to be effective in this regard. The excellent bonding was shown, as in no case, the bond between inhibitor and propellant cleaved during propellant-inhibition bond strength testing. On the basis of these findings, it was inferred that the bond strength between propellant and inhibitior is more than TS of the propellant (15 kg/cm^2).

Table 2. Characteristics of promising formulation (formulation 4)

Tensile strength (kg/cm^2)	18
Elongation (%)	120
Shore hardness (A)	55-60
Plasticiser migration (%)	3-4
Bond strength (kg/cm^2)	> 15
Peel-off strength (kg/cm^2)	4
Viscosity (27 °C) cps	70,000
Pot life (min)	50-60
Glass transition temperature by DSC (°C)	-75
Endotherm by DTA (°C)	450
Exotherm by DTA (°C)	515

The *Tg* obtained for the composition was -75 °C, indicating its high strain capability even at subzero temperature which is an important requirement for practical applications. DTA of the inhibition system exhibited an endotherm in the range 400-460 °C with maxima at 450 °C and an exotherm in the range 460-530 °C with maxima at 515 °C. Thermograph (TG) of the sample also revealed two-stage decomposition in the temperature range 350-490 °C. The initial decomposition in the range 350-450 °C observed in TG corresponds to the endotherm in DTA while decomposition in the range 450-490 °C corresponds to the exotherm in DTA. This suggests two-stage decomposition for the inhibition system which is in line with the findings of Chen and Brill[14] during thermogravimetric studies. They have suggested initial endothermic cleavage of urethane crosslinks and depolymerisation of HTPB, followed by exothermic cyclisation and crosslinking process of HTPB (that has not undergone depolymerisation). The weight loss in these processes may be attributed to volatilisation of degradation products like 1,3-butadiene and vinyl cyclohexene.

5. STATIC EVALUATION

Inhibited propellant sets were subjected to static evaluation at ambient as well as extreme temperatures (- 30 and + 55 °C) in cigarette burning mode from the point of view of establishing practical value of inhibition system for a wide range of temperatures. A smooth *P-t* profile (Fig.1) was obtained during the combustion of propellant grains at all temperatures, establishing effective bonding between propellant and inhibitor system.

6. AGEING STUDIES

To get an idea regarding the life of bonding between propellant and inhibition system during storage, limited aging trials were undertaken. Inhibited grains were stored at + 50 °C for a period

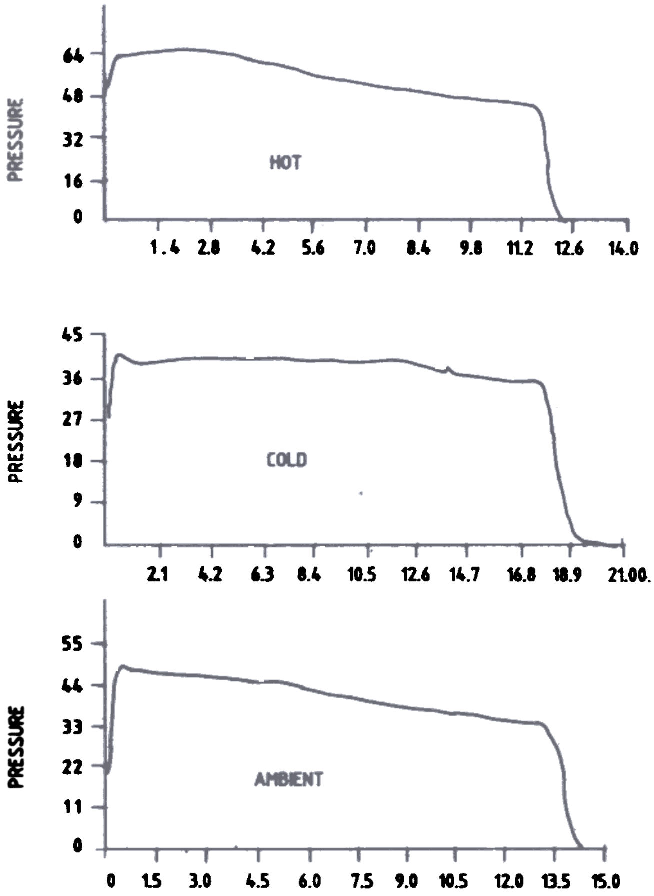


Figure 1. Pressure-time profiles for PU-inhibited nitramine-based CMDB propellant at (a) ambient (b) + 55 °C, and (c) - 30 °C.

ranging from one to three months. The grains were radiographed after aging and no debond was observed. This was further confirmed by static evaluation of aged grains which gave smooth *P-t* profile like unaged grains.

7. CONCLUSION

The results obtained established that inhibitor system based on HTPB-IDP-IPDI binder and Sb_2O_3-carbon black filler is suitable for slurry cast CMDB propellants which are flexible and have high flame temperature as compared to the conventional DB propellants. It also established superior strain capability of the selected composition even at subzero temperature which is an important parameter for practical applications. Effective bonding between HTPB-based inhibitor formulation and nitramine-based CMDB propellant was established by bond strength and peel-off testing. Smooth *P-t* profile obtained for grains evaluated at extreme temperatures (-30 and +55 °C) and after aging at elevated temperatures confirm the suitability of the selected formulation as inhibitor for advanced nitramine-based propellants.

REFERENCES

Stenson, R. The interactions of cellulose acetate and ethyl cellulose inhibitors with double-base propellants, ERDE, U.K Waltham Abbey Essex, 1971. TM-48.

2. Schwartz, A. Aging effects on adhesion of inhibitors to propellant grains. *In* Chemical problems connected with the stability of explosives, National Defence Research Institute, Tumba, Sweden, 1976. 4, pp. 65-72.

3. Sadafule, D.S.; Raghuraman, R.N.; Navale, N.G.; Kumbhar, C.G. & Panda, S.P. A photocrosslinkable vinyl polyesters. *J. Macromol. Sci.,* 1988, **A 25** (1), 121-26.

4. Hans, B. Polyester resin coating for nitroglycerine propellants. Nitrochemie GmbH. German Patent DE 1,206,340. 2 December 1965. 2 p.

5. Nauflett, George W.; Johnson, Craig E. Nitroester propellant, casing and liner of an epoxy-polyamide copolymer containing a stabiliser. US Department of Navy. USA Patent 3,882, 784. 13 May 1975. 6 p.

6. Agrawal, J.P.; Gupta, D.C.; Chowk, M.P. & Khare, Y. Liquid rubber epoxy systems blends for inhibition of composite propellants. *Prop. Expl. Pyro.,* 1993, **18**, 155-60.

7. Proebster, Manfred; Huebel, Roland. Bayern-Chemie Gesselschaft fuer Flugchemische Antriebe GmbH. Polyurethane liners containing acid amides for propellant adhesion to rocket chamber walls. German Patent DE-3,643,824. 30 June 1988. 3p. (In German).

8. Agrawal, J.P.; Shrotri, P.G. & Gupta, D.C. Fibre reinforced plastics fabrication-based technique for inhibition of composite propellants composites. *Composite Manufacturing,* 1991, **48**.

9. Schaffling, Otto G. Olin Corporation Composition comprising epoxy resin, copolymer of butadiene and acrylic acid, curing agent and inorganic metal salt. USA Patent 3,947,523. 30 March 1976. 6p.

10, Araki, T. & Nakasato, N. Preparation of liner and insulating materials for solid propellants. Japanese Patent JPN-49-25324.. 1974, 5 p.

Gupta, D.C.; Vaidya, M.V.; Raomore, S.S.; Phadke, V.K. & Divekar, P.K. Epoxy resin as inhibitor for nitramine containing composite modified double-base (CMDB) propellants. *Macromolecular Reports*, 1995. **A32** (Supp 8), 1245-55.

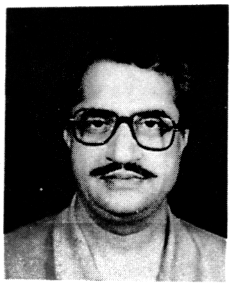
12, Agrawal, J.P.; Chowk, M.P. & Satpute, R.S. Comparative account of properties of novel unsaturated polyesters synthesised by various polyesterification processes. *J. Polym. Sci.*, 1989, **27** (Pt.A), 409.

13 Agrawal, J.P. & Pokharkar, R.D. Inhibition of rocket propellants. *J. Sci. Ind. Res.*, 1980, **39**, 633-40.

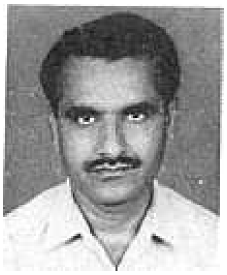
14, Then, J.K. & Brill, T.B. Chemistry and kinetics of hydroxyl-terminated polybutadiene (HTPB) and diisocyanate-HTPB polymers during slow decomposition and combustion like conditions. *Combustion Flame*, 1991, **87**, 217-32.

Contributors

Dr (Ms) SD Kakade received her PhD in Organic Chemistry from University of Poona in 1987. She joined DRDO at the High Energy Materials Research Laboratory (HEMRL), Pune. Her areas of research include polymer synthesis related to military applications. She has published six papers in national/international journals.



Mr MV Vaidya received his BSc in Chemistry from University of Poona in 1964. He joined DRDO at HEMRL, Pune and has been working in the field of solid rocket propellant and their inhibition system for the past 23 years. He has published five papers in national/international journals.



Mr PK Divekar received his MSc in Chemistry from University of Poona in 1997. He joined DRDO at HEMRL, Pune and has been working in the field of solid rocket propellant for the past nine years.

Mr UB Kadam received his BSc in Chemistry from University of Poona in 1984. He joined DRDO at HEMRL, Pune and has been working in the areas of inhibition of solid rocket propellant.

Dr SN Asthana obtained his PhD from University of Poona in 1990. Presently, he is Senior Scientist at HEMRL, Pune. His areas of research include advanced solid propellants combustion sensitivity and ageing studies of futuristic propellant systems as well as establishment of synthesis process of allied high energy materials. He is a recognised guide for PhD and has more than 50 research publications to his credit.