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Study on Friction Sensitivity of Passive and Active Binder-based Composite Solid Propellants and Correlation with Burning Rate

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ABSTRACT

Friction sensitivity of composite propellants and their ingredients is of significant interest to mitigate the risk associated with the accidental initiation while processing, handling, and transportation. In this work, attempts were made to examine the friction sensitivity of passive binder: Hydroxy Terminated Polybutadiene/Aluminium/Ammonium Perchlorate and active binder: (Polymer + Nitrate Esters)/Ammonium Perchlorate/Aluminium/Nitramine based composite propellants by using BAM Friction Apparatus. As per the recommendation of NATO standard STANAG–4487, the friction sensitivity was assessed by two methods: Limiting Frictional load and Frictional load for 50% probability of initiation (F₅₀). The test results showed that the active binder based formulations were more vulnerable to frictional load as compared to the formulations with passive binders. Examination of a comprehensive set of propellant compositions revealed that the particle size distribution of Ammonium Perchlorate and burn rate catalysts were the most influential factors in dictating the friction sensitivity for HTPB/Al/AP composite propellants. For active binder/AP/Al/Nitramine composite propellants, the formulation with RDX was found more friction sensitive with a sensitivity value of 44 N as compared to its HMX analog (61 N). The correlation studies of friction sensitivity, burning rate, and thermal decomposition characteristics of HTPB/Al/AP composite propellants is described.

Keywords: Friction sensitivity; Composite propellant; Nitramines, STANAG-4487

1. INTRODUCTION

The contribution of composite propellant in the realm of space and defense science is noteworthy. Crystalline oxidizer molecules bound in a three-dimensional matrix of organic polymeric fuel form the composite propellant which is capable of producing high-temperature gaseous products on burning. However, the need of the day demands maximum energy density within a restricted volume to enhance the operational range. It has necessitated the use of oxidiser particles with different granulometric distributions along with burn rate catalysts, incorporation of large amount of high energetic nitramine molecules such as HMX and RDX for a higher specific impulse (I_{sp}) , and substitution of the inert organic binder with an energetic one to minimize the dead weight¹⁻⁵.

The aspiration of attaining desired energy density has resulted in aggravated hazard problems. Some hazard problems with these high energy materials include their very high vulnerability to the friction, impact, shock, spark, temperature stimuli^{6,7}. Hence, negligence in the operations pertaining to these materials may lead to catastrophic accidents with loss of lives and property. Investigation of accidents involving high explosive, pyrotechnics, and propellants by US Army Air Defense Command (US ARADCOM), designated frictional force to be the major cause of inadvertent initiations^{8,9}. The

Received: 05 August 2019, Revised: 01 January 2020 Accepted: 22 January 2020, Online published: 09 March 2020 explosive accident records of UK Health and Safety Executive (HSE) also corroborated with the review of US ARADCOM: 59 per cent of the accidents were attributed to friction stimuli, while only 9 per cent of the accidents were due to impact¹⁰.

In the field of modern warfare, the acceptability of the weapon system to the health, safety, and environment is of prime importance even than the energy density^{11,12}. The hazard evaluation process of a new energetic material, modified propellant formulations or, manufacturing conditions must be qualified with the friction sensitivity measurement^{13–15}.

Propellant processing is a multilayered activity consisting of raw material preparation, mixing, casting, and other post-cure operations. Close inspection of these steps suggests that during the whole processing, the raw materials as well as the propellant are exposed to moderate to high frictional forces. Mixing operation imparts extreme shear forces within the layers of the binder filled with energetic particles, trimming of propellant grain using metallic tools may act as friction stimuli, energetic raw materials also subjected to friction during blending, grinding, and sieving ¹⁶. 'Decoring' of the mandrel and other casting fixtures is also considered to be one of the most hazardous operations due to direct rubbing of propellant with mandrel and fixture surfaces ¹⁷.

A significant amount of effort has also been given to understand the safety hazards of propellants and the associated factors for sensitivity enhancement. Kubota¹⁸, *et al.* discussed the effect of different catalysts on the friction sensitivity of

non-aluminised AP composite propellants, and their correlation with the burn rate. Lusby¹⁹, et al. reported that HTPB/HMX/ AP based propellants remain relatively insensitive to friction throughout the mixing cycle, and for azido polymeric binder based composite propellant, the incorporation of nitrate ester plasticisers increased the friction sensitivity. Jawalkar²⁰, et al. showed that as the plasticizer (Dioctyl Adepate) content was decreased, HTPB/Al/AP composite propellant became more friction sensitive. Ghosh and coworkers21 demonstrated that with increase in content of ferrocene derivative of HTPB, the propellant compositions became more sensitive towards frictional forces. Pang²², et al. discussed the effect of different metallic fuels on the friction sensitivity characteristic of HTPBbased composite propellants. Considerable amount of work has been carried out to improve the sensitivity of composite propellant by coating the oxidiser particle, Ammonium

propellant by coating the oxidiser particle, Ammonium Perchlorate, with fluorine based polymeric material, or, different functional carbon materials such as graphite, graphene, carbon nano-tubes^{23–27}.

The present study is an effort to provide a technical base to understand the friction sensitivity of composite propellant of HD 1.1 (mass explosion and blast hazard), HD 1.3 (mass fire and heat radiation hazard), and their associated ingredients for the development of zero accident policy and guidance for safe handling. The propellant formulations of hazard division 1.3 were based on pre-polymeric passive binder HTPB, metallic fuel aluminum (Al), and oxidiser Ammonium Perchlorate (AP). Furthermore, we evaluated the propellants of hazard division 1.1 which were based on active binders/AP/Al-Nitramine composite propellant. For these composite propellant systems, the influence of AP particle size distribution and the effect of additives such as transition metal oxide burn rate modifiers, nitramine fillers on the friction sensitivity were evaluated. Additionally, the correlation of friction sensitivity with the decomposition behavior and burning characteristics of composite propellants

2. EXPERIMENTAL

were studied.

2.1 Friction Sensitivity Measurement

The friction sensitivity of various ingredients and propellants was determined using BAM Friction Apparatus FSKM-10 (OZM Research Bliznovice, Czech Republic). The instrument employs frictional force by rubbing the material between static weighted porcelain peg and moving porcelain plate. There are nine different weights to provide frictional forces ranging from 5 N to 360 N.

As per NATO–STANAG 4487²⁸, the friction sensitivity was assessed by using '1-IN- 6' method, and additionally, using Bruceton 'up and down' procedure. The '1-IN- 6' test result was reported as the limiting frictional load at which at least one "explosion" occurs in six trials, when at the next lower loading no-explosion occurs in six trials^{29–31}.

The Bruceton 'up and down' test is based on statistical analysis by determining the frictional load for 50 per cent probability of initiation. For a valid Bruceton result, the standard deviation divided by the load increment (S/D) should

be in the range of 0.5 to 2^{32-35} . The energetic materials have been classified in different sensitivity ranges depending upon their reactivity to friction forces: the friction sensitivity values 6 N - 54 N is considered 'high'; 60 N - 144 N as 'medium', and 144 N - 360 N comes under 'low'²⁹.

2.1.1 Friction Sensitivity of Raw materials of composite propellant

The ingredients of two different hazard classes (HD 1.1, HD 1.3) of composite propellants were tested for friction sensitivity. All the ingredients were dried to limit surface moisture content below 0.05 % prior to friction sensitivity testing. The list of the raw materials along with their source is as given in Table 1.

Table 1. Ingredients of composite propellant

ID	Description	Source	
RM01	Ammonium Perchlorate - Coarse (300 μ)	PCL, Cuddalore, India	
RM02	Ammonium Perchlorate - Fine (50 μ)	Produced by grinding of AP coarse	
RM03	Ammonium Perchlorate - Fine (37 μ)		
RM04	Ammonium Perchlorate - Ultrafine (6 μ)		
RM05	RDX $(X_{50} = 470\mu)$	High Energy Materials	
RM06	$β$ - HMX (Coarse) (X_{50} = 277 $μ$)	Research Laboratory, Pune	
RM07	β - HMX (Fine) ($X_{50} = 15\mu$)		
RM08	Active Binder–I		
RM09	Active Binder-II		
RM10	Diethylene glycol dinitrate (DEGDN)		

Active binders (RM08 and RM09) were used for HD 1.1 propellant formulations. RM08: Active binder–I was prepared by mixing nitrile butadiene rubber with nitrate ester plasticisers: DEGDN and Triethylene glycol dinitrate (TEGDN). RM09: Active Binder–II was based on polyester material plasticised with nitrate ester: Butanetriol trinitrate (BTTN).

2.1.2 Friction Sensitivity of Composite Propellant Samples

In order to process the composite propellant for both the hazard classes, all the solid ingredients were mixed with the liquid binder and plasticiser in a vertical planetary mixture. The propellant slurry thus obtained, was cast into cartons under vacuum and cured at optimum temperature to get the required hardness. After completion of curing, the consolidated propellant samples were cut into uniform small pieces (approximately 10 mm³ of material: maximum 1 mm thick, and 5 mm in diameter) using a non-sparking tool, and subjected to friction sensitivity tests. The summary of the propellant formulations used for this study has been delineated in Table 2.

For both the hazard classes of composite propellants, we examined the effect of physical state on the friction sensitivity. Approximately 10 mm³ of the paste-like uncured slurry was used for each test.

Table 2. Propellant compositions

ID	Description	Propellant class
P01	HTPB/Al/AP (300 μ : 50 μ = 54 : 14)	
P02	HTPB/Al/AP (300 μ : 50 μ = 48 : 20)	HD 1.3
P03	HTPB/Al/AP (300 μ , 50 μ , 6 μ)/IO-CC (0.35%)	пр 1.3
P04	HTPB/Al/AP (300 μ , 37 μ , 6 μ) /IO-CC (2%)	
P05	Active Binder -I/AP/Al/RDX	
P06	Active Binder -I/AP/Al/HMX	HD 1.1
P07	Active Binder -II/AP/Al/HMX	

2.2 Thermal Analysis

Thermal analysis of the propellant samples was carried out in differential scanning calorimeter (DSC) model TA-Q-20 and thermogravimetric analyser (TGA) model TA-Q-600 under nitrogen atmosphere with a heating rate of 10 °C/min. The amount of samples taken for DSC and TGA analysis was approximately 0.4 mg and 4 mg, respectively.

2.3 Burning Rate Measurement of Composite Propellants

The burning rate of the composite propellant was determined in a modified Crawford's bomb using acoustic emission technique³⁶. Solid propellant strands (6 mm \times 6 mm \times 130 mm) were cut from propellant cartons. The burning rate was measured by monitoring the time required for the flame to consume the known length of propellant at a preset pressure.

3. RESULTS AND DISCUSSIONS

3.1 Friction Sensitivity of Raw Materials

The raw materials for the composite propellant manifested a wide spectrum of sensitivity towards friction stimuli. The test results of the raw materials are summarised in Table 3. Irrespective of particle size, Ammonium Perchlorate appeared to be friction insensitive at the maximum available loading of 360 N in the BAM friction apparatus.

The limiting frictional load by 1-IN-6 method for the ingredients: RDX and HMX (Coarse) obtained to be 120 N. In order to get a more precise result, Bruceton-up-down method

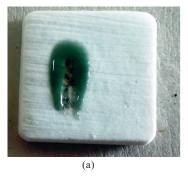
was employed for both the materials. The Bruceton 50 per cent mean for RDX and HMX (Coarse) was derived to be 182 N and 142 N respectively. Friction sensitivity of HMX showed an inverse relation with its particle size.

For the active binder systems (RM08, RM09), it was found that they were insensitive to friction stimuli upto 360 N. At the maximum frictional load of 360 N, both the liquids left black smear (Fig. 1) on the friction surface for consecutive six trials. NATO STANAG-4487 classified this phenomenon as 'Decomposition' which was considered to be a negative response.

The energetic nitrate ester plasticizer Diethylene Glycol Dinitrate (DEGDN- RM10) is commonly used in the formulations of smokeless propellants³. DEGDN, which was extremely sensitive to impact, remained friction insensitive at the maximum available load of 360 N.

3.2 Friction Sensitivity of Composite Propellants

The friction sensitivity of propellant compositions is as shown in Table 4. Active binder and nitramine based propellant appeared to be more sensitive to friction than HTPB/Al/AP propellants. The HTPB/Al/AP composite propellants which consisted almost 68 per cent of AP, got ignited even at a low friction load of 54 N. It implied that relatively insensitive AP particles in conjunction with organic binder and metallic aluminum devised high energy density material sensitive to friction forces.



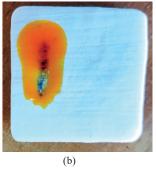


Figure 1. Decomposition of Active binder-I and Active binder-II at 360 N was indicted by the black smear on the friction surface. (a) Active binder – I and (b) Active binder – II

Table 3. Friction sensitivity of raw materials according to 1-IN-6 and Bruceton 'up and down' method

ID	Description	Friction sensitivity		
		Limiting frictional load (N) (1-IN-6)	Frictional load (50% level) (N) (F ₅₀)	
RM01	Ammonium Perchlorate - Coarse (300 μ)	> 360	Bruceton up-down method not required	
RM02	Ammonium Perchlorate - Fine (50 μ)			
RM03	Ammonium Perchlorate - Fine (37 μ)			
RM04	Ammonium Perchlorate - Ultrafine (6 μ)			
RM05	RDX $(X_{50} = 470\mu)$	120	182	
RM06	HMX (Coarse) $(X_{50} = 277 \mu)$	120	142	
RM07	HMX (Fine) $(X_{50} = 15\mu)$	72	132	
RM08	Active Binder –I	>360	Bruceton up-down method not required	
RM09	Active Binder -II	>360		
RM10	DEGDN	>360		

The Limiting Frictional Load of active binder based AP/Nitramine composite propellants (P05 – P07) demonstrated pronounced friction sensitivity; a noisy rapid explosion was recorded at a friction force as low as 36 N (P06). The aggravated friction sensitivity may be the result of higher energy density imparted by oxidiser, nitramine particles, and nitrate ester plasticizers concentrated within a limited domain.

The result obtained from the standard 1-IN-6 method had a narrow difference within the same propellant family; it is around one load above or below. In view of this indistinguishability, Bruceton up-and-down method was employed for a better resolution in the friction sensitivity results. Table 4 shows the Bruceton mean for 50 per cent probability of initiation along with their validation ratio (S/D).

The propellant formulation P01 (bimodal AP) was selected as the standard composition for comparison among the HD 1.3 class, because it was the most basic aluminised HTPB/AP based propellant system without any additives. Although the basic composition of P01 and P02 was same, AP coarse to fine ratio was slightly lowered in P02. For P03 and P04, trimodal (coarse, fine, ultrafine) AP was used with the incorporation of transition metal oxide burn rate catalyst Iron Oxide and Copper Chromite. The differentiating factors between P03 and P04 were the particle size of fine AP, amount of ultrafine AP, and catalyst loading. The amount of ultrafine AP (6μ) and the catalyst was significantly more in P04 as compared

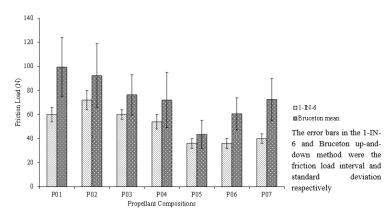


Figure 2. Comparison of friction sensitivity results for composite propellant of both the hazard classes HD1.3 and HD 1.1, obtained from the 1-IN-6 and Bruceton up-and-down methods.

to that of P03. The F_{50} value for the HTPB/Al/AP based HD 1.3 class of composite propellant (P01–P04) indicated that the major influencing factors for the friction sensitivity were the AP particle size and the transition metal oxide burn rate catalysts. The propellant compositions were sensitized with the reduction of the Ammonium Perchlorate particle size and increasing catalyst concentration.

For the HD 1.1 family, the Bruceton mean for 50% probability of initiation revealed that the P05 and P06 formulations exhibited high friction sensitive with a mean value of 44 N and 61 N respectively. The propellant composition P07 is based on a polyester material plasticized with nitrate ester BTTN (Butanetriol trinitrate) and bimodal HMX (240μ, 15μ). The Bruceton mean for 50% probability of initiation was obtained to be 73 N. To determine the friction sensitivity of uncured slurry, the representative compositions P02 and P07 were examined. The test results are described in Table 5.

Table 5. Comparison of limiting frictional load of propellant slurry and cured consolidated propellant

Dhysical state	Limiting frictional load (N) sensitivity		
Physical state	P02	P07	
Slurry	48	40	
Consolidated	72	40	

It was found that the uncured propellant slurry of the HTPB/Al/AP composite propellant composition P02 had higher friction sensitivity than the cured propellant; the Limiting Frictional Load for P02 had reduced to 48 N from 72 N of the consolidated form. Hence, more care is to be taken while handling the propellant slurry. The friction sensitivity of Active binder/Al/AP/Nitramine composite propellant P07 remained unaltered, that is 40 N, even in the uncured slurry state.

3.3 Correlation of Friction Sensitivity with Thermal Analysis and Burning Rate of Propellant

When a friction force is applied between the surfaces of an energetic crystalline material or propellant samples filled with energetic materials, it leads to the generation of 'hot-spots', localized in a very small region of $0.1-10~\mu m$ in diameter with a surface temperature of approximately

Table 4. Friction sensitivity of the consolidated composite propellants

Duanellant alogs	ID	Description	Friction sensitivity		
Propellant class			Limiting frictional load (N)	F ₅₀ (N)	S/D*
HD 1.3	P01	$HTPB/AI/AP (300\mu : 50\mu = 54 : 14)$	60	99	1.53
	P02	$HTPB/Al/AP~(300\mu:50\mu=48:20)$	72	92	1.66
	P03	$HTPB/Al/AP~(300\mu,50\mu,6\mu)/IO\text{-}CC~(0.35\%)$	60	76	1.40
	P04	HTPB/Al/AP (300 μ , 37 μ , 6 μ) /IO-CC (2%)	54	72	1.44
HD 1.1	P05	Active Binder -I/AP/Al/RDX	36	44	1.45
	P06	Active Binder -I/AP/Al/HMX	36	61	1.66
	P07	Active Binder-II/AP/Al/HMX	40	73	1.45

^{*}All the propellant formulations resulted in a valid Bruceton mean value ($0.5 \le S/D \le 2.0$)

1000°C, and the action time is in the scale of 10⁻³–10⁻⁵ s. These transient 'hot-spots' leads to thermal decomposition of the solid phase resulting in a tandem phenomenon of reaction among the decomposed gas and finally a 'thermal explosion' ³⁷⁻³⁹.

Considering the thermal origin of friction sensitivity, the thermal properties of the composite propellant were evaluated using DSC and TGA. The HTPB/Al/AP based compositions (P01–P04) were examined for an appropriate comparative study. Figure 3 shows the results obtained from DSC of propellant compositions P01–P04.

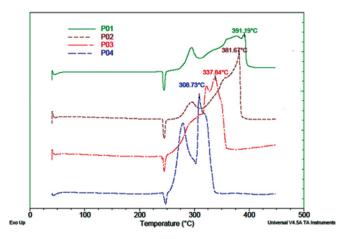


Figure 3. DSC of HTPB/Al/AP based composite propellants illustrated that thermal decomposition of HTPB/Al/AP based composite propellants was accelerated by the addition of ultrafine AP and burn rate modifiers.

The first endothermic peak at 245 °C corresponded to the crystal transformation of AP from orthorhombic to cubic lattice structure. Similar to thermal decomposition of AP, two exothermic decompositions had been observed in the DSC curve of the propellants.

It can be observed that the exothermic peak shifts to lower temperature as we go from P01 to P04. The decomposition of HTPB/Al/AP composite propellant was drastically accelerated by the addition of ultrafine AP and Iron Oxide/ Copper Chromite catalysts (P03, P04). The exothermic peak due to high temperature decompositions originally at 391 °C for the base composition, appeared at 337 °C and 308 °C for P03 and P04, respectively. Shifting of T_{max} of P02 to 381.67 °C revealed that decrease in coarse to fine ratio of AP also affected the decomposition profile. In order to deduce the correlation between the thermal decomposition and the friction sensitivity, the Bruceton 50 % mean value (F_{50}) was plotted against the T_{max} of exothermic high temperature decomposition in DSC (Fig. 5). It showed that as the exothermic peak in propellant decomposition was shifted to the lower temperature, the propellant became more and more prone to initiation by frictional force.

The weight loss profile of different propellants in their TG curve (Fig. 4) showed that thermal decomposition of propellant was accelerated by addition of transition metal oxides and increasing the finer AP content. The start of the thermal decomposition (Fig. 4 (inset)) of different propellant followed the same sequence as that of their friction sensitivity.

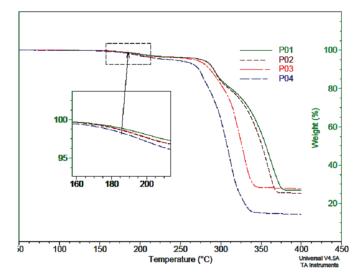


Figure 4. TGA thermogram depicting weight loss profile of HTPB/Al/AP based composite propellants.

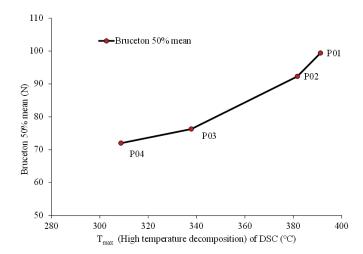


Figure 5. Plot of friction sensitivity (F_{50}) versus T_{max} of DSC. Friction sensitivity was inversely proportional to T_{max} of DSC.

The compositions with comparatively lower thermal stability displayed higher friction sensitivity.

To assess the relationship between the friction sensitivity and the burning rate of HTPB/Al/AP composite propellant, the burning rate measurement of the propellant compositions P01 – P04 was carried out. It was observed that the burning rates were increased with the increase in finer AP content, and by the addition of burn rate modifiers which catalysed the decomposition of AP. From the thermal analysis study, it was known that the friction sensitivity was correlated to the decomposition behaviour of the propellant, which in turn implied that burning rate, friction sensitivity, and the thermal decomposition of propellant are interconnected. The correlation between the friction sensitivity and the burn rate had been demonstrated as shown in Fig. 6. The HTPB/Al/AP composite propellants became more friction sensitive as the burn rate of the propellant increased.

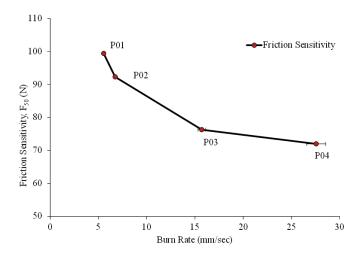


Figure 6. Plot of friction sensitivity versus burning rate of HTPB/AI/AP composite propellant. Friction sensitivity was directly proportional to burning rate.

4. CONCLUSIONS

The study of friction sensitivity of composite propellants and its raw materials revealed several interesting insights. Explicit reduction in ammonium perchlorate particle size, and inclusion of burn rate modifiers, such as iron oxide and copper chromite sensitised the HTPB/Al/AP composite propellant. The active binder/AP/Al/Nitramine composite propellants appeared to be substantially sensitive to frictional forces (F_{50} = 44 N) as compared to their HD 1.3 counterpart.

It was observed that the uncured propellant slurry of the HTPB/Al/AP composite propellant exhibits exceptional increased friction sensitivity (Limiting value: 48 N) whereas the friction sensitivity of Active binder/AP/Al/Nitramine composite propellant remained unchanged in the uncured slurry state. The thermal decomposition study of HTPB/Al/AP composite propellants suggested that propellants were sensitized due to the catalytic effect on the AP decomposition. Furthermore, a direct correlation was observed between the friction sensitivity and the burning rate characteristics of HTPB/Al/AP composite propellants.

To summarise, the friction sensitivity investigations of composite propellants and its raw materials provided critical sensitivity values, and the parameters which altered the reactivity of composite propellant to friction stimuli. This valuable information adds confidence and assurance about safety, and also attenuates the hazard of unintended ignitions during various operations with these propellants.

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