Central European Journal of Energetic Materials, **2012**, *9*(3), 237-249
ISSN 1733-7178

Studies on High Burning Rate Composite Propellant Formulations using TATB as Pressure Index Suppressant

MEHILAL*, Shekhar JAWALKAR, Ramesh KURVA, Nandagopal SUNDARAMOORTHY, Ganesh DOMBE, Praveen Prakash SINGH and Bikash BHATTACHARYA

High Energy Materials Research Laboratory,
Sutarwadi, Pune-411021, India
**E-mail: drmehilal@yahoo.co.in*

Abstract: High burning rate propellant compositions are generally used in gas generators to eject missile from canister. Because of high burning rate, pressure index of the composition increases during burning. To reduce the pressure index, a high burning rate composite propellant formulations (~20 mm/s) based on AP/HTPB/Al have been prepared by incorporating TATB and studied in detail for viscosity build-up, thermal and mechanical properties, sensitivity as well as burning rate and pressure index (n). The data indicate that there is a decrease in end of mix viscosity on increasing the percentage of TATB. The same trend was also observed with mechanical properties while significant improvement in overall thermal stability was clearly observed. The sensitivity data indicate that impact and friction values show decreasing trend infer better safe to handle. The burn rate data reveal that on addition of TATB from 0.5 to 2% decrease in burning rate was not observed while on addition of further TATB up to 5% and beyond this significant decrease in burning rate was observed. The data on pressure index (n) also reveal that TATB is very effective in reducing the 'n' value up to 2% and beyond this 'n' value increases close to standard composition. The data on 'n' value reveal that it reduces from 0.47 to that of standard composition to 0.36 for the compositions containing TATB up to 2.0% in the pressure range of 60-90 kg/cm^2.

Keywords: composite propellant, ammonium perchlorate, TATB, pressure index suppressant

Introduction

Composite propellant is the most important class of solid rocket propellants being used in space as well as in missile programmes [1]. It basically contains ammonium perchlorate (65-70%) as an oxidizer, metallic fuel such as aluminum powder (15-20%) and hydroxyl terminated polybutadiene (HTPB) as a prepolymer binder (10-15%) along with isocyanate based curatives and process aids. The mechanical properties of the propellant grains are governed by the nature and quantity of binder as well as other process aids used and to some extent on the morphology of fillers particle. Moreover, the ballistic properties are mostly governed by size and shape of ammonium perchlorate and metallic fuel.

The burning rate is one of the major propellant characteristics, which measured on standard ballistic evaluation motor, based on Saint Robert and Ville's burning rate law, i.e., $r = a \cdot P^n$
where,
r is the burning rate;
a is the variable which depends on initial grain temperature, chemical composition and gas velocity of combustion gas along the surface of the grain;
P is the pressure in combustion chamber;
n is the pressure exponent.

It is understood that the pressure exponent 'n' of a propellant is a measure of the increase in burning rate of a propellant which occurs as the chamber pressure is increased. The pressure exponent is the tangent to the curve which can be drawn when the burning rate is plotted against chamber pressure. The pressure exponent of a propellant is zero when burning rate is totally independent of pressure. However, when it is substantial positive, the rocket will over pressure and may explode. A pressure exponent of less than 0.5 is necessary for a propellant to be acceptable for use in propulsion sub-systems. The exception is pressure sensitive propellants which are intended for use in controllable motor.

The well-known method for effecting some reduction of pressure exponent is to reduce ammonium perchlorate content or resort to the use of ammonium perchlorate of larger weight mean diameter. However, these approaches are unacceptable because they adversely affect the burning rate. Burning rate promoters have been found to have little effect on pressure dependence of burning rate. Literature survey also reveals that method of reducing pressure exponent of a composite propellant using certain copper salts and their chelates [2] such as copper thiocyanate, copper chromite, copper ferrocyanide and tetrachloro-m(bis) dimethyl glyoxamato copper(II) dicopper, copper(II) [(salicylaldehyde) (2,4-pentanedione)], copper phthalocyanine [3], respectively have been studied in detail. However, these ingredients not only reduces pressure exponent but also responsible for reduction in burning rate and thus effectiveness of pressure exponent suppressant is lost.

In continuation to this work further, difluoroamino plasticizers [4] such as 2,2-bis (difluoroamino) 1,3 bis (difluorodinitrodiethoxy)-propane and 2,2-bis (difluoroamino) bis(5-fluoro-5,5 dinitro) pentylformal have also been tried. However, these plasticizers are not suitable for HTPB based composite propellant and not found eco-friendly. It has also been reported that finely divided aluminum oxide [5] is found effective to suppress pressure exponent of composite propellant, at higher pressure only, i.e., >140 kg/cm^2.

Furthermore, propellant composition containing ammonium nitrate in the weight range of 50-75% along with nitrate ester plasticizer 0-30% with 0-3% aluminum powder and curative having 3.5-8% boron powder found very effective in lowering the pressure exponent not exceeding more than 0.3 in the pressure range of 170-480 kg/cm^2 have also been reported [6]. In the same way, ammonium nitrate, phase stabilized by chemical reaction CuO or ZnO [7] using energetic binder GAP along with burning modifier, viz., vanadium/molybdenum oxide has also been studied and found that these are effective in reducing ‘n’ value to a certain extent. Some researchers have also studied the effect of non-toxic metal oxide, i.e., Fe_2O_3 in gas generator composition containing ammonium nitrate and guanidine nitrate are found that Fe_2O_3 reduces the pressure exponent and enables the composition to sustain combustion at or near atmospheric pressure [8].

Further to this, to suppress pressure exponent of a composite propellant formulation based on more than 50% of HMX as an oxidizer with acrylate − acrylic acid copolymer as binder along with difluoroamino type energetic plasticizer using certain nitroaromic compounds [9] viz., hexanitrostilbene (HNS), triaminotrinitrobenzene (TATB), picric acid and ammonium salt of picric acid in the range of 15-20% by weight has also been studied in detail. Moreover, higher the weight ratio of these nitroaromatics affect the performance of the propellants.

The researchers have also tried to suppress pressure exponent of composite propellant formulations using transition metal fluorides [10] such as cupric fluoride and ferric fluoride. However, these ingredients are not eco-friendly in nature and, therefore, not suitable for application. Also, the study on ‘n’ value suppressants further reveals that composite propellant formulations based on AP/HTPB/Al having 0.3 to 5% refractory oxides [11] such as TiO_2, Al_2O_3, SiO_2, SnO_2 and ZnO are found very effective in reducing the ‘n’ value to some extent.

Moreover, the exhaustive literature survey reveals that most of the studies on ‘n’ value suppressants are mostly in the form of patents and researchers have not divulged/published their work in scientific journals and based on metal oxides or their salts. However, the use of these metal oxides affect the performance of the propellant composition. Therefore, based on limited information, a systematic study has been carried out on different pressure exponent suppressants such as TATB, oxamide and nitroguanidine and based on the results it was found that TATB is effectively suitable for suppressing pressure exponent of composite propellant formulations having high burning rate without affecting the performance of the propellant.

In the following section, we report the effect of TATB on viscosity build-up, thermal and sensitivity properties as well as pressure index ‘n’ value in detail.

Experimental

Materials

1,3,5-Triamino-2,4,6-trinitrobenzene (TATB) in-situ made, having average particle size 10-15 µm with 99.5% purity, was used for this study. Ammonium perchlorate (AP), procured from M/s Pandian Chemicals Ltd.(PCL), Cuddalore, was used in tetramodal distribution having particle size 300 µm, 200 µm, 37 µm and 6 µm, respectively. Hydroxyl terminated polybutadiene (HTPB) having molecular weight (Mn) of 2560 ± 50 and hydroxyl value of 43 mg KOH/g was also procured from M/s Anabond, Chennai. Aluminum powder, having average particle size 15 ± 3 µm was procured from M/s The Metal Powder Company, Madurai and used as such. Dioctyl adipate (DOA), toluene diisocyanate (TDI), N-phenyl-2-naphthylamine (NONOX-D), trimethylol propane (TMP) and 1,4-butanediol (nBD) were also procured from trade and used as such.

Adduct a homogeneous solution of TMP and nBD where former acts as a cross linker while latter acts as a chain extender during curing of the propellant, was freshly prepared and incorporated in the propellant composition during mixing.

Characterization

a. The particle size of solid ingredients was determined by laser based CILAS particle size analyzer, Model 1064, France, in aqueous and non-aqueous medium. Based on the diffraction angle of laser, particle size of the powder was determined. Generally, smaller the particles, the greater the angle of diffraction and vice versa.
b. The viscosity build-up was determined by Brookfield viscometer, Model

HBT dial type by inserting T-C spindle at a rotating speed of 2.5 rpm.

c. The mechanical properties like tensile strength, percent elongation and E-modulus of cured propellant samples were also evaluated using dumb-bells on tensile testing machine, Hounsfield, conforming to ASTM D638 type IV at a cross head speed of 50 mm/min at ambient temperature.

d. Viscoelastic properties of cured samples was determined on dynamic mechanical analyzer, Model-DSA-10 by taking sample size of 60×12.5×2.5 mm, at ambient temperature and sub zero temperature using liquid nitrogen gas.

e. Solid strand burning rate (SSBR) was determined by acoustic emission technique at 70 kg/cm^2 pressure using N_2 gas. Acoustic emission is defined as a transient wave generated by the rapid release of energy within a material. An acoustic emission sensor converts the mechanical energy carried by the elastic wave into an electrical signal.

f. Calorimetric value (Cal. Val.): Cal. value of any substance is the energy released per gram of sample in absence of oxygen. It was determined by Parr isoperibol-6200 taking one gram of sample in the presence of ultrapure nitrogen at 5 kg/cm^2 pressure.

Methods

All the experimental mixing of composite propellant was carried out at 5 kg batch level in a vertical planetary mixer. A general procedure for the preparation of composition is described in detail.

To a planetary mixer (cap.15 l) 560.0 g of prepolymer resin, i.e., hydroxyl terminated polybutadiene (HTPB), 165.0 g of dioctyl adipate (DOA) as a plasticizer along with 5.0 g of antioxidant, i.e., 2-phenyl naphthylamine (Nonox-D), 6.0 g of bonding agent a mixture of 1,1,1,-trimethylol propane and 1,4-butanediol and 30 g of ballistic modifiers, except curative were charged and the whole system was mixed well for half an hour followed by mixing under vacuum for another half an hour to drive out entrapped air. After this, 900 g Al powder (~15 μm) was added. After complete addition of Al, it was again mixed for another 20 minutes. After this, 75 g TATB was added and mixed for another 10 minutes. After this, 3220 g of ammonium perchlorate (tetramodal size having particle sizes 300 μm, 200 μm, 37 μm, 6 μm) was added and mixed in such a way that homogenous mixing could take place. The overall mixing temperature was maintained at 50 ± 2 °C. After addition of complete solid ingredients, the mixing of composition was further carried out under vacuum for half an hour. In the mean time, the temperature of the mix was brought down at 40 ± 2 °C. At this stage, 39.0 g of toluene diisocyanate (TDI) was added and further mixed for another 40 minutes. After this, the composition was cast into 100 mm (ID) mould by vacuum casting technique and cured at 50 °C for 5 days.

Results and Discussion

TATB with 99.5% purity having average particle size 10-15 µm was used for this study. Initially, TATB was used at 0.5% level and subsequently percentage of TATB was increased up to 5% in composite propellant formulations by replacing coarse AP. The different mixtures prepared using TATB are presented in Table 1 and studied in detail for viscosity build-up, Viscoelastic behaviour, thermal and ballistic properties as well as sensitivity aspects and pressure index 'n'.

Table 1. Formulation details

Sl. No.	Ingredients	Standard composition	Developed composition					
			TATB - 0.5%	TATB - 1.0%	TATB - 1.5%	TATB - 2.0%	TATB - 3.0%	TATB - 5.0%
1	HTPB + TDI	11.98	11.98	11.98	11.98	11.98	11.98	11.98
2	DOA + ADDUCT + Antioxidant	3.52	3.52	3.52	3.52	3.52	3.52	3.52
3	AP	65.90	65.4	64.9	64.40	63.9	62.90	60.90
4	Al(P)	18.0	18.0	18.0	18.0	18.0	18.0	18.0
5	Ballistic modifier	0.60	0.6	0.6	0.6	0.6	0.60	0.60
6	TATB	0.0	0.5	1.0	1.5	2.0	3.0	5.0

Effect of TATB on viscosity build-up

The different composite propellant composition were prepared to study the behaviour of end of mix (EOM) viscosity by varying the TATB content from 0.5 to 5% keeping the solid loading content 84.5% using Brookfield viscometer by inserting T-C spindle at 2.5 rpm and data obtained are presented in Table 2. It is clear from the table that the values of EOM viscosity of the propellant slurry decreases on increasing the percentage of TATB content. The end of mix (EOM) viscosity for optimized TATB content, i.e. ~2% is 960 Pa·s at 40 °C while in the case of 5% of TATB content it is 800 Pa·s at the same temperature confirming infinite plane hydrogen bonded TATB results in a layered structure similar to that observed for graphite and boron nitride, responsible for slippery behaviour which ultimately reduces the viscosity. The slow viscosity build up data indicate that the rate of reaction between -NCO groups of TDI and OH groups of HTPB is affected by addition of TATB because of hydrogen bonding between TATB and OH containing molecules. Further, the slurry viscosity value after three hours at

40 °C was found in the range of 1060-1270 Pa·s for all the studied compositions using TATB. The slow viscosity build-up with TATB is very useful in casting as it increases the pot life of the slurry which yields in flawless grains. However, the viscosity build-up of standard composition is comparatively higher that of TATB content composition where blanketing effect is not there due to absence of TATB.

Table 2. Data on viscosity build-up

Sl. No.	Time (min)	Standard composition (Pa·s) @ 40 °C	Developed composition					
			TATB - 0.5%	TATB - 1.0%	TATB - 1.5%	TATB - 2.0%	TATB - 3.0%	TATB - 5.0%
1	EOM	1120	1072	1056	992	960	848	800
2	60	1184	1120	1120	1072	1024	896	864
3	120	1280	1184	1168	1120	1088	960	912
4	180	1376	1264	1248	1152	1120	1088	1056

Effect of TATB content on Mechanical and Ballistic properties

Mechanical properties of cured propellant were carried out at ambient temperature on Hounsfield at 50 mm/min speed and data obtained are presented in Table 3. It is clear from the table that on increasing the percentage of TATB the value of tensile strength increases marginally in comparison to standard composition, while the value of E-modulus and % elongation decrease on addition of TATB content. The decreasing trend in E-modulus and % elongation may be attributed to the slippery nature of TATB due to infinite planar structure like graphite. The ballistic properties like burning rate of the compositions were also studied by varying the percentage of TATB. The data obtained are shown in Table 3. It is clear from the table that there is no change in burning rate was observed from 0.5% to 1.5% TATB. This seems reasonable because of the solid loading and particle sizes of the ingredients remain constant throughout the present studied compositions. However, on increasing the percentage of TATB content beyond 2% to 5% in place of coarse ammonium perchlorate, a decreasing trend in burning rate was observed. The decrease in burning rate may be attributed to decrease in oxidizer content.

Effect of TATB on pressure index

The pressure index of the studied composition was determined by plotting a graph of ln P Vs ln r_b at different pressures and from the slope of the curve pressure index was calculated and data thus obtained are presented in Table 3. It is clear from the study that TATB is found very effective to reduce the 'n' value at lower concentration. The data reveal that 'n' value starts decreasing on addition of 0.5% of TATB. However, it is found more effective in the concentration range of 1.5% to 2% of TATB only. It is also observed that beyond 2% content of TATB 'n' value starts increasing. In the present study, due to low energetic and insensitiveness of TATB, the content of TATB was not used beyond 2%. However, for optimization of the content of TATB for effective reduction in 'n' value, the content of TATB was studied up to 5% level. Further to this, the other two components, viz., oxamide and nitroguanidine were also tried in the composition; however, 'n' value increases in both the cases in comparison to that of standard composition.

Table 3. Data on mechanical and ballistic properties

Sl. No.	Composition	TS (MPa)	E-Mod (MPa)	Elongation (%)	SSBR @ 6.87 MPa (mm/s)	Density (g/cm^3)	Pressure index (n)
1	Standard	0.92	3.49	50.5	19.0	1.74	0.47
2	TATB - 0.5%	0.97	3.75	51.0	18.9	1.74	0.45
3	TATB - 1.0%	0.93	3.51	43.7	18.9	1.74	0.41
4	TATB - 1.5%	0.94	3.30	42.5	18.5	1.74	0.36
5	TATB - 2.0%	0.91	3.13	41.0	18.0	1.74	0.37
6	TATB - 3.0%	0.90	2.95	37.3	17.0	1.74	0.39
7	TATB - 5.0%	0.83	2.83	35.4	16.0	1.74	0.42

Effect of TATB on Viscoelastic properties

The Viscoelastic behaviour of TATB based compositions were also studied for glass transition temperature (Tg) and tan δ using Dynamic Mechanical Analyzer (DMA) and results obtained are reported in Table 4. Initially, glass transition temperature (Tg) was determined at three different frequencies namely 35, 11 and 3.5 Hz. The data on glass transition temperature (Tg) infer that on increasing the percentage of TATB content in composition almost no change in Tg values was observed. The table clearly reveal that on increasing the percentage of TATB content, Tg of compositions remains unchanged. However, at lower frequency a slight decrease in Tg values were observed in comparison to higher frequency. To study the structural stabilization of the polymeric material, tan δ value was also determined at 35, 11 and 3.5 Hz and it is clear from the table that on increasing the TATB content the value of tan δ increases. The increase in tan δ value may be attributed to infinite planes of hydrogen bonded TATB molecule in a layered structure. As hydrogen bonding in TATB molecule is all within the plane, with no three-dimensional effect, causes thermal expansion, which is responsible for increase in tan δ value.

Table 4. Data on viscoelastic behaviour

Sl. No.	Composition	Frequency (Hz)	Glass transition temperature (Tg)	tan δ
1	Standard	35 11 3.5	-58.79 -62.82 -66.61	0.5966 0.5862 0.5753
2	TATB - 0.5%	35 11 3.5	-58.64 -62.61 -66.47	0.6266 0.5977 0.5843
3	TATB - 1.0%	35 11 3.5	-58.49 -62.47 -66.31	0.6477 0.6287 0.6161
4	TATB -1.5 %	35 11 3.5	-58.26 -62.32 -66.16	0.6675 0.6578 0.6463
5	TATB - 2.0%	35 11 3.5	-58.11 -62.17 -66.01	0.6261 0.5968 0.5857
6	TATB - 3.0%	35 11 3.5	-58.07 -62.01 -65.60	0.5938 0.5849 0.5741
7	TATB - 5.0%	35 11 3.5	-57.41 -61.25 -65.09	0.5981 0.5898 0.5788

Effect of TATB content on thermal and sensitivity properties

Simultaneous thermal analysis (STA) of the studied compositions was determined on Universal V4.3A TA instrument and results are presented in Figures 1 and 2 for standard composition without TATB and 1.5% TATB, respectively, as optimized content of TATB is 2%, however, thermal studies were carried out in details using 1.5% of TATB. It is clear from the Figure 1 that there is a sharp endotherm observed at 246.32 °C indicating the phase change of ammonium perchlorate for orthorhombic to cubic form followed by decomposition of the mixture appeared with a large exotherm at 329.27 °C. However, thermal decomposition of mixture having 1.5% of TATB content showed that there is a small endotherm (Figure 2) at 248.15 °C followed by a bigger shoulder exotherm at the temperature 302.24 °C and still an exotherm bigger shoulder at 332.87 °C clearly indicates that on incorporation of TATB content the initial thermal stability of the mixture does not alter in comparison to standard composition.

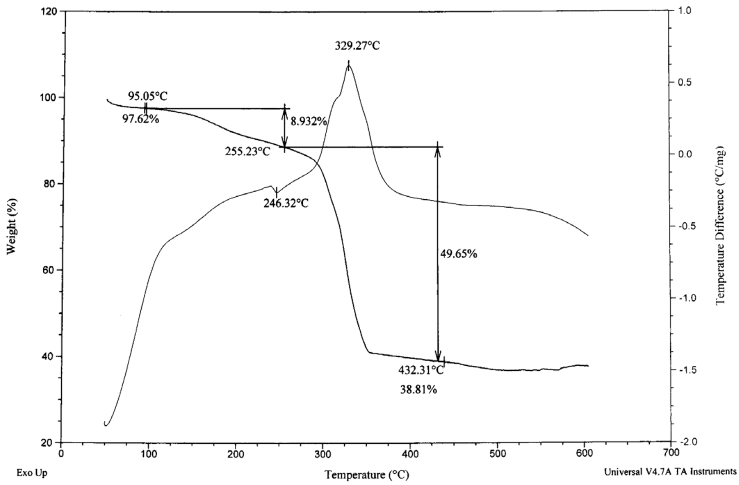

Figure 1. Thermal decomposition of standard composition.

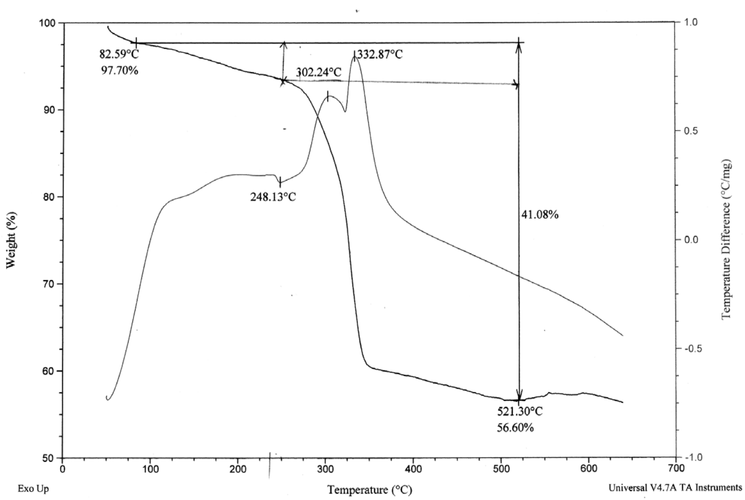

Figure 2. Thermal decomposition of composition with 1.5% of TATB.

Thermogravimetric analysis data indicate that on incorporation of TATB content in the mixture up to 1.5%, the loss in weight percentage of mixture decreases. Thus, at 1.5% TATB based mixture (Figure 2) the weight loss initiates at 82.59 °C, which accounts 4% up to 250 °C and then 36.08% weight loss in the temperature range of 255-521 °C, after that it remains contact up to 650 °C without further weight loss, while in the case of standard composition, its initial weight loss is 8.93% in the temperature range of 95.05 °C to 255.23 °C (Figure 1), which further continued in weight loss to 49.65% in the temperature range of 255.23 to 432.31 °C. It is clear from the above study that even smaller % of TATB content, i.e. 1.5%, also affects the thermogravimetric data towards better stabilization because of its inherent nature of thermal stability further confirms the advantage of incorporating of TATB in the composition.

The data on calorimetric value shown in Table 5 indicates that the studied compositions show a slightly decreasing trend in calorimetric value as compared to TATB free mixture. The decreasing trend in calorimetric value may be negative heat of formation of TATB, which requires slightly higher energy for its decomposition. Moreover, TATB being a negative oxygen balance molecule, the incomplete combustion also attributes to low energy output.

The data on impact and friction sensitivities are presented in Table 5. It is clear from the table that as percentage of TATB increases, mixture becomes less sensitive to impact. This may be attributed to unique insensitiveness of TATB due to presence of inter and intra hydrogen bonding in TATB. This insensitiveness of TATB is responsible for higher values for impact and friction.

Table 5. Data on thermal and sensitivity properties

Sl. No.	Composition	Cal. Val. (Cal/g)	Impact sensitivity (Nm)	Friction sensitivity (N)
1	Standard	1327	3.5	128
2	TATB - 0.5%	1323	3.5	144
3	TATB - 1.0%	1317	4.0	160
4	TATB - 1.5%	1311	4.5	160
5	TATB - 2.0%	1305	4.9	160
6	TATB - 3.0%	1280	5.5	180
7	TATB - 5.0%	1256	6.3	192

The prime aim to study the high burning rate composite propellant formulation using TATB was to reduce pressure index value in a acceptable range without affecting burning rate and the performance. We succeeded in our efforts by incorporating TATB from 0.5% to 5.0% and findings reveal that composition containing not more than 2% of TATB is found more effective in reducing the ‘n’ value without affecting the performance of the composition and burning rate.

Conclusion

High burning rate composite propellant compositions having different percentage of TATB has been prepared successfully and evaluated for pressure index. Mechanical and ballistic properties, viscosity build up, Viscoelastic behaviour as well as for sensitivity properties. It is clear from this study that lower content of TATB, i.e. 1.5% to 2%, was found to be very effective in reducing the pressure index value and beyond this the pressure index increases towards standard composition. Furthermore, on increasing the percentage of TATB content overall thermal stability of the mixture increases. The impact and friction sensitivity of the mixture also decreases, indicating safe handling of the mixture.

References

[1] Boyars C., Klager K., *Propellants, Manufacturing, Hazards and Testing*, American Chemical Society, Washington D.C, **1969**, pp. 67-187.

[2] Corley R.C., Myess F.F. Jr., *Copper Containing Ballistic Additives*, US 4391660, **1983**.

[3] Minn-Shong Chi, *Composite Propellants Containing Copper Compounds as Ballistic Modifiers*, US 4971640, **1990**.

[4] Sayles D.C., *Composite Rocket Propellant Composition with a Controllable Pressure Exponent*, US 5059260, **1991**.

[5] Hightower J.O., Hammer J.W., Matthews R.L., *Solid Propellants with Alumina Burning Catalyst,* US 4084992, **1978**.

[6] Minn-Shong Chi, *Low Pressure Exponent Propellants Containing Boron,* US 5074938, **1991**.

[7] Menke K., Bohnlein-Mauss J., Schmid H., Bucerius K.M., Engel W., *Solid Propellant Based on Phase-Stabilized Ammonium Nitrate*, US 5589661, **1996**.

[8] Wheatley B.K., *Metal Oxide Containing Gas Generating Composition*, US 6274064 B1, **2001**.

[9] Sayles D.C., *Pressure Exponent Suppressants*, US 3953259, **1976**.

[10] Roberto F.Q., Crelier A.M., Lium G.D., *Burning Rate Modifiers for Solid Propellants*, US 4000024, **1976**.

[11] Taylor R.H. Jr., Hinshaw C.J., *Aluminized Plateau-Burning Solid Propellant Formulations and Methods for Their Use*, US 5771679, **1998**.

Chemicals

HTPB	Hydroxyl terminated polybutadiene
DOA	Dioctyl Adipate
AP	Ammonium Perchlorate
Al	Aluminum
TDI	Toluene Diisocyanate
nBD	Butane-1,4-diol
TMP	Trimethylol Propane
Nonox-D	N-Phenyl-β-naphthylamine
TATB	1,3,5-Triamino trinitrobenzene

Acronyms

SSBR	Solid strand burning rate
DMA	Dynamic mechanical analyzer
Tg	Glass transition temperature
EOM	End of mix
n	Pressure index