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Phase-Stabilized Ammonium Nitrate-Based Propellants Using Binders with N–N Bonds

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Phase-stabilized ammonium nitrate- (PSAN-) based solid propellants have been cast using new epoxy resins having N–N bonds in their structures, as binders. The burning rate studies carried out in a strand burner show that significant enhancement in the burning rate, compared with that observed with conventional polybutadiene binders, could be achieved by the use of the N–N-bonded binders. The PSAN-based propellants have a higher burning rate than those based on ammonium nitrate. The enhancement in burning rate cannot be explained in terms of the calorific value of the resin or the ignition temperature of the propellant. The computed performance parameters of the compositions having N–N-bonded resins as binders are superior to those based on polybutadienes. Significantly higher specific impulse and chamber temperature obtained at practical solid loadings appear to be an advantageous feature of the compositions having N–N-bonded resins as binders.

Nomenclature

C^* = characteristic velocity, m/s
I_{sp} = specific impulse, s
M_c = mean molecular weight of product species
P_c = chamber pressure, atm
P_e = exit pressure, atm
T_c = chamber pressure, K
Φ = equivalence ratio

Introduction

ONE of the few serious drawbacks of commonly used ammonium perchlorate- (AP-) based solid propellants is that their products of combustion, which include HCl, chlorine, and chlorine oxides, cause atmospheric pollution. Not only do they affect the launch site surroundings, but these products are also known to cause ozone depletion in the atmosphere. Increasing concern for a clean atmosphere in recent years has resulted in a compelling need for developing chlorine-free, environmentally friendly, smokeless propellant systems. Various attempts made in this direction include the use of nitramines such as cyclotetramethylenetetranitramine (HMX), cyclotrimethylenetrinitramine (RDX), etc., instead of AP; the inclusion of Mg in AP propellants to scavenge HCl; the use of other oxidizers such as ammonium dinitramide (ADN); and ammonium nitrate (AN), etc., in the propellant composition.[1–4] These attempts have led to a rejuvenated interest in AN-based propellants, primarily because of the clean burning nature of AN, its low cost, and easy availability. However, although AN is well known as a low-energy oxidizer in gas generator compositions, its use in large motors is restricted as a result of several of its major adverse characteristics. Its hygroscopicity and near-room-temperature phase transformation resulting in volume expansion cause storage problems and lead to crack formation in the grain. These problems, of late, have largely been overcome. Phase stabilization has been achieved by cocrystallizing AN with K^+ salts and other additives.[5–10] The stabilization of phase also improves upon its hygroscopicity, which can more efficiently be managed by coating the particles with hydrocarbon/polymers, etc. The other major problems in the use of AN as a substitute oxidizer for AP in solid propellants are its low burning rate (BR) and low energy. The AN-based propellants processed with the usual hydrocarbon binders burn at nearly one-fourth the rate of AP-based propellants. Different approaches adopted to enhance the BR of AN-based propellants include the use of catalysts such as chromium compounds,[11] the addition of metals such as Mg[4], the use of a high BR oxidizer such as AP,[12] and energetic binders based on azide polymers.[13] Of these, the approach based on energetic binders seems to be the most promising. However, poor ignitability, combustion instability, and heavy plasticization required for achieving adequate mechanical properties are some of the drawbacks of the azide-polymer-based systems.[13,14]

In our laboratory, a recent development in propellant binders has been the synthesis of hydrazine-based (having N–N bonds in the structure) viscous resins having epoxy end groups.[15] Although initially these resins were synthesized for their use as binders for powder fuel compositions for hypergolic hybrid propellant systems,[16] it was envisaged that these may augment the burning rates of solid propellants. Indeed, the AP-based propellants processed with N–N-bonded binders were found to have enhanced burning rates; almost three- to fourfold higher[17] compared with those processed with the usual carboxyl-terminated polybutadiene (CTPB) binder. A sizable enhancement in the burning rate of AN-based propellants was also noticed in a recent study.[18]

Propellants having a stoichiometric fuel/oxidizer ratio are preferred for the maximization of combustion energy (specific impulse). This, however, is not achieved when a butadiene binder is used because of the solid loading limitation for processing. With the maximum solid loading possibility being limited to about 86% solids, most solid propellants based on polybutadiene binders remain fuel rich and do not yield the expected theoretical specific impulse I_{sp} in practice. In this sense, the binders having N–N bonds could be advantageous because of the higher requirement of the binder (fuel) content for stoichiometric combustion.

Because AN as such, cannot be used in a propellant composition as a result of problems associated with the room-temperature phase transformation, phase-stabilized ammonium nitrate (PSAN) was used in the present study. In this paper we report the effects of several typical N–N-bonded resins based on carbono- and thiocarbono-hydrazones with epoxy end groups, on the burning rate of PSAN-based propellants. These data have been compared with propellants based on CTPB rather than a hydroxy-terminated polybutadiene (HTPB) binder, which is known to give slightly better performance. However, the processing of laboratory-scale propellants for burning rate was found to be easier with CTPB. The theoretical rocket performance parameters such as I_{sp}, T_c, C^*, and M_c of these systems have also been evaluated at various compositions to assess the effect of the new binders.

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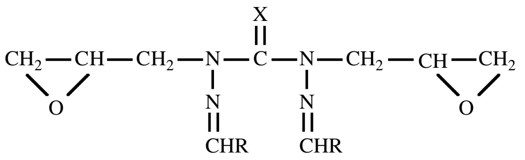
Experimental

Resin Synthesis

The resins, as described next, were prepared by epoxidizing carbono- or thiocarbono-hydrazones following the procedure mentioned earlier.[18] The general structure of the resins could be described as follows:



$X = O$, $R = C_6H_5$; diepoxide of bisbenzaldehydecarbonohydrazone (DEBCH)
$X = O$, $R = C_4H_3O$; diepoxide of bisfurfuraldehydecarbonohydrazone (DEFCH)
$X = S$, $R = C_6H_5$; diepoxide of bisbenzaldehydethiocarbonohydrazone (DEBTCH)
$X = S$, $R = C_4H_3O$; diepoxide of bisfurfuraldehydethiocarbonohydrazone (DEFTCH)

Epoxidation was carried out by refluxing the hydrazone with excess epichlorohydrin and subsequently treating with NaOH. The excess epichlorohydrin was then removed under reduced pressure. The dark-brown resins that were obtained were stored in a refrigerator to avoid self-curing. The resins were characterized by elemental analysis, IR, ^1H NMR spectra, thermal analysis, and viscosity measurements.[18]

PSAN Preparation

PSAN samples were prepared by cocrystallizing AN with various amounts of potassium salts from aqueous solutions.[6] In a typical case, to a solution of AN (50 g) in distilled water (200 ml), the required amount of the K^+ salt powder was dissolved. The solution was subsequently evaporated to dryness in a water bath. The cocrystallized salt separated, was dried in an oven at 80°C, and stored in a desiccator.

Propellant Processing

The propellant ingredients were dried properly before mixing. In a typical batch, about 50 g of the propellant was processed. The required amount of the binder was taken in a beaker and warmed to obtain adequate fluidity to facilitate mixing. Diphenyldiaminomethane (DDM) dissolved in dimethyl sebacate (plasticizer, 2%), in a calculated amount, was then added and mixed thoroughly. The oxidizer (PSAN) was finally added in three portions and mixing continued for more time to ensure a homogeneous mix. Ammonium dichromate (2%) was used as a catalyst in all compositions. The propellant mix was then transferred to a slotted aluminum mold having strand-size slots ($80 \times 5 \times 6$ mm) and was cured at 80°C. While the furfuraldehyde-based systems [diepoxide of furfuraldehyde carbonohydrazone and diepoxide of furfuraldehydethiocarbohydrazone (DEFCH and DEFTCH), respectively] cured in one day, the benzaldehyde [diepoxide of benzaldehydecarbonohydrazone and diepoxide of benzaldehydethiocarbonhydrazone (DEBCH and DEBTCH), respectively] and CTPB-based systems were cured in 5–6 days. The cured propellant strands were removed from the mold and stored in a desiccator. The strands were subsequently coated with a slurry of TiO_2 in Araldite and used for BR measurements.

DTA–TMA Measurements

Differential thermal analysis (DTA) of the resins as well as the propellant samples was carried out on a Schimadzu DT-40 Simultaneous DTA–TG system in nitrogen atmosphere. The thermomechanical analysis (TMA) was conducted using a Schimadzu TMA-40 system to measure the linear expansion of PSAN-based propellant samples when subjected to thermal cycling.

BR Measurements

The BR measurements were carried out in nitrogen atmosphere using a standard (Crawford) strand burner at different pressures. The BR was determined by direct measurement of the time interval taken for a measured length of the strand to burn. This was done by inserting two fuse wires (tin–lead alloy) in the propellant strand at a measured distance, which send start and stop signals to a digital time interval counter as the flame snaps the fuses. A low-voltage current applied through a kenthal coil connected across two electrodes was used to ignite the strand. The variation in the measured BR was found to be within ±5%.

Performance Parameters

Theoretical performance parameters were computed using a computer program,[19] NASA-SP 273. The parameters were derived assuming equilibrium flow conditions at chamber pressure $P_c = 70$ atm, and exit pressure $P_e = 1$ atm; i.e., $P_c / P_e = 70$. The phase modifier was not accounted for in calculating the performance parameters of AN propellants. It is assumed that the effect will only be marginal, particularly when the relative properties are compared.

Results and Discussion

Although a detailed study on the phase stabilization of AN using K^+ salts is available,[6] it was considered worthwhile to examine the thermal expansion behavior of a few propellant samples processed with the N–N-bonded resins having 80% PSAN solid loading, in a wide temperature range. From the TMA traces given in Fig. 1 it is noticed that the propellant sample having unmodified AN (no phase stabilizer) undergoes a linear thermal expansion to the extent of 2.9% on heating from room temperature onward, whereas the sample having $K_2Cr_2O_7$ (6%) shows no expansion in the heating cycle. It undergoes insignificant (0.3%) expansion, even when subjected to thermal cycling between −50 and 100°C. The inclusion of KF (3%) in AN restricts the expansion to about 0.8%, as also reported elsewhere.[20] Propellants having KNO_3 (3%) or $K_2Cr_2O_7$ (3%) modified AN show a larger expansion than that observed with KF. However, inclusion of an adequate quantity of the salt was found to decrease the extent of expansion.

Propellant compositions having 80 wt% of various PSAN, processed with different resins, were used for BR studies. In the case of PSAN (KNO_3), the percentage of KNO_3 used for phase stabilization was optimized at 3 wt% to avoid performance loss as it replaces AN, although a higher concentration is required for complete phase stabilization. The BR data at different pressures given in Table 1, when plotted against pressure on a log–log scale (Fig. 2), show an approximate linear relationship. It is seen that the BR is dependent on the resin binder as well as the phase stabilizer that is used. In general, the furfuraldehyde-resin-based compositions have higher BRs than corresponding benzaldehyde-based systems. The compositions having DEFCH and DEFTCH resins and PSAN stabilized

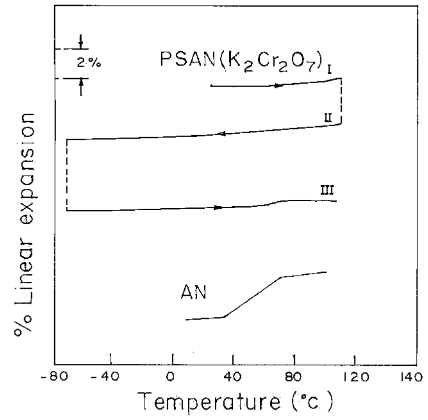


Fig. 1 TMA traces of AN and PSAN ($K_2Cr_2O_7$)-based propellants on thermal cycling.

Table 1 BR data of various propellant systems based on AN at different pressures[a]

Propellant composition (binder:AN = 20:80)	BR, mm/s 30	40	50	60	70	Pressure index, n
DEFTCH-PSAN (KNO_3)	1.75	——	2.62	——	3.90	>0.8
DEFCH-PSAN (KNO_3)	1.96	——	3.35	——	4.28	>0.8
DEBTCH-PSAN (KNO_3)	1.31	——	2.48	——	2.60	>0.8
DEBCH-PSAN (KNO_3)	1.40	——	2.60	——	3.72	>0.8
DEFTCH-PSAN (KF)	1.71	2.34	3.28	4.21	5.39	>0.8
DEFCH-PSAN (KF)	1.95	2.47	3.90	4.60	5.98	>0.8
CTPB-PSAN (KF)	1.50	——	2.00	2.52	2.70	0.71
DEFTCH-PSAN ($K_2Cr_2O_7$)	2.56	2.96	3.21	3.60	4.04	0.52
CTPB-PSAN ($K_2Cr_2O_7$)	1.74	2.10	2.35	2.64	2.92	0.60
DEFTCH-PSAN ($K_2Cr_2O_7$, 6%)	——	——	——	——	4.20	——
DEFTCH-AN (no AD)	——	——	——	——	1.56	——
DEFTCH-AN[b]	1.58	1.81	1.90	2.20	2.40	0.48
DEFCH-AN[b]	2.05	2.44	2.46	2.68	2.78	0.33
DEBTCH-AN[b]	1.23	1.41	1.70	2.04	2.10	0.68
DEBCH-AN[b]	1.35	1.59	1.86	1.99	2.20	0.57
CTPB-AN[b]	1.23	1.45	1.59	2.09	2.11	0.67

[a] In atmospheres. [b] Data reported earlier.[18]

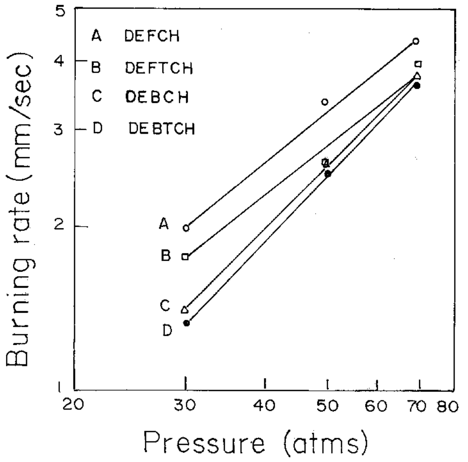


Fig. 2 BR vs pressure plots of PSAN (KNO_3) systems.

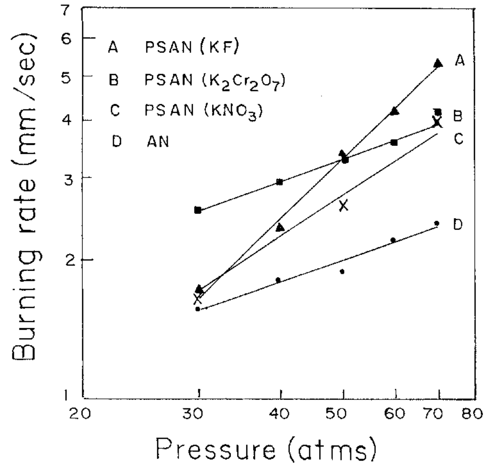


Fig. 3 BR vs pressure plots of AN and PSAN propellants based on DEFTCH.

with KF (3%) have significantly higher BRs (Table 1) than that based on the conventional CTPB resin. The effect of the nature of phase stabilizer on the BR is evident from Fig. 3. Apparently among the various phase stabilizers, KF appears to be most effective, particularly with the N–N-bonded binders. The composition based on DEFTCH and PSAN stabilized with $K_2Cr_2O_7$ (3%) also has a higher BR than that based on CTPB (Table 1). These observations conclusively show the superiority of the N–N-bonded resins over the often-used CTPB binder in enhancing the BR.

Recently, we reported a detailed study of the BR of unmodified (no phase stabilizer) AN-based compositions.[18] A comparison of the BRs of the compositions having unmodified AN and phase-stabilized AN (Table 1) show that the PSAN systems have considerably higher BRs than those based on unmodified AN. The relative trend with regard to the binder used, however, appears to be the same in both cases. For example, the furfuraldehyde-based systems were found to have higher BRs than corresponding benzaldehyde systems in the unmodified propellants. The exact reason for the enhancement of the PSAN systems' BR is not clear. However, similar observations were made by Menke et al.[13] on propellants based on PSAN having azide binders.

All of the compositions discussed thus far had ammonium dichromate (AD, 2 wt%), as the catalyst. To check the influence of AD, the BR of the DEFTCH–AN composition having no catalyst was measured. It was found to be 1.5 mm/s compared with 2.4 mm/s of the catalyzed (with AD) system at the same oxidizer loading. The AN–CTPB composition, on the other hand, does not sustain combustion without AD. This observation supports further the combustion superiority of the N–N-bonded binder systems.

The cocrystallization of AN with $K_2Cr_2O_7$ not only results in the phase modification of AN but causes it to decompose exothermically.[6] To ascertain its effect on the BR, two typical uncatalyzed (having no AD) propellant compositions based on DEFTCH and CTPB and AN stabilized with $K_2Cr_2O_7$ (3%) were examined. From the data listed in Table 1, it is apparent that both the DEFTCH–PSAN ($K_2Cr_2O_7$) and CTPB–PSAN ($K_2Cr_2O_7$) systems have higher burning rates than the corresponding systems based on unmodified (no stabilizer) AN, but are catalyzed with AD. This shows that apart from the effect of the dichromate ion, which is common in both cases, the phase modification by K^+ makes the system based on $K_2Cr_2O_7$ burn faster than those based on the AD. Because the use of $K_2Cr_2O_7$ (3%) does not ensure complete phase stabilization, another composition having AN stabilized with $K_2Cr_2O_7$ (6%) and DEFTCH was examined. Only a minor enhancement in the BR was achieved (Table 1). Also, after combustion, a skeleton of chromium oxide is noticed in this case.

From the BR vs pressure plots (Figs. 2 and 3), the pressure exponent n was calculated for all of the compositions in the pressure range of 30–70 atm, and are listed in Table 1. It is seen that AN-based propellants having N–N-bonded resin binders have comparatively lower n values than those based on CTPB binder, particularly for the furfuraldehyde-based resins. In fact, there is hardly a noticeable change in the n value for CTPB-based systems when PSAN is used instead of AN. However, the phase-stabilized AN-based systems, particularly PSAN (KNO_3) and PSAN (KF), having N–N-bonded resin binders, have much higher n values than the CTPB–PSAN system. These results again point to the significant change in the

Table 2 Heats of combustion and heats of formation data of various resins

Resin	Molecular formula	Heat of combustion kcal/gm		Heat of formation kcal/mol	
		Observed	Calculated	Observed	Calculated
DEFTCH	$C_{17}H_{18}O_4N_4S$	6.00	6.15	−39	17.1
DEFCH	$C_{17}H_{18}O_5N_4$	5.74	5.99	−157	−67
DEBTCH	$C_{21}H_{22}O_2N_4S$	6.75	7.31	−136	87.74
DEBCH	$C_{21}H_{22}O_3N_4$	6.20	7.22	−381	5.16
CTPB	C_4H_6	9.70	10.40	−3.0[a]	——

[a] Data taken from literature.[19]

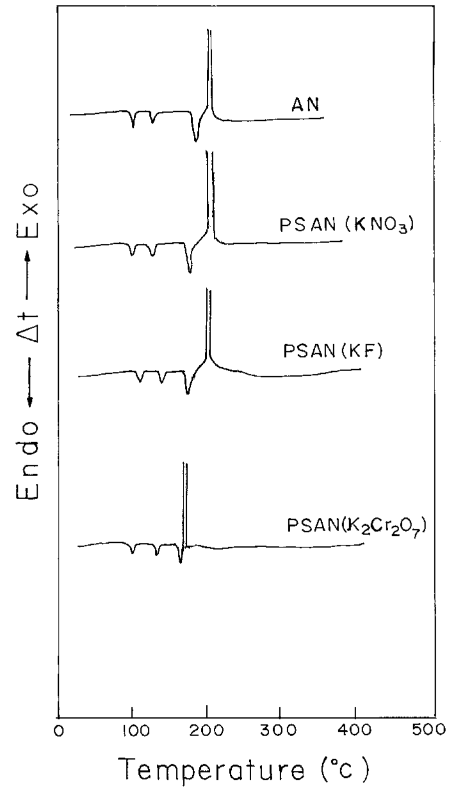


Fig. 4 DTA traces of AN- and PSAN-based propellant samples processed with DEFTCH.

combustion characteristics when the N–N-bonded binders are used and the phase is stabilized. While it could be argued that the change in the BR and *n* values may have been caused by the oxidizing nature of the phase stabilizer used, as in the case of PSAN (KNO_3) or PSAN ($K_2Cr_2O_7$), an inert stabilizer such as KF also causes a similar change both in the BR and *n* values. The cause for the lower BR and *n* value of the AN propellants compared with those on the PSAN system is not clear from these observations.

The data show clearly, however, that the use of N–N-bonded resin binders results in increasing the BR of both AN- and PSAN-based propellants. These results parallel those obtained on AP-based propellants, where a three-to-fourfold enhancement in the BR was noticed with N–N-bonded resin binders compared with CTPB.[17] On the other hand, virtually no enhancement in the BR was noticed when $KClO_4$ was used as an oxidizer instead. It is therefore apparent that the BR enhancement is related to the reactivity of N–N-bonded resin with acidic species, HNO_3 or $HClO_4$, generated from the decomposition of AN or AP, respectively.[17]

The heats of combustion of all the N–N-bonded resins are much lower than that of CTPB (Table 2). Of the N–N-bonded resins, the benzaldehyde-based resins have higher heats of combustion than those based on furfuraldehyde. Furthermore, the thiocarbono hydrazone-based resins have higher calorific values than the carbono hydrazone-based systems. The calorimetric values[21] calculated for AN propellants having N–N-bonded binders at stoichiometric composition are also lower. For example, the DEFCH–AN system has a calorimetric value of 1.158 cal/g compared with 1.2 cal/g for the CTPB–AN system. The BR of these systems, on the other hand, shows a reverse trend. It is thus apparent that the BR cannot be correlated with the heats of combustion of these propellants. It may be pointed out that the BRs of the double-base propellants are largely determined by their heats of combustion.[22]

The thermal ignition characteristics of some typical AN and PSAN propellants are presented in Fig. 4. The DTA traces of propellant samples based on DEFTCH show most of the expected endothermic phase transformations of AN and also the terminal ignition exotherm in each case. A comparison of the terminal exotherms shows that the ignition temperature of the AN propellant (185°C) is not very different from the corresponding PSAN (KF) (185°C) and PSAN (KNO_3) (187°C) systems. The composition based on PSAN ($K_2Cr_2O_7$) ignite at 172°C, showing marked sensitization that is perhaps caused by the catalytic effect of dichromate ion. On the other hand, the BR of all the PSAN systems are significantly higher than those based on AN. It therefore appears that no clear-cut relationship exists between the lowering of the ignition temperature and the enhancement in the BR of the PSAN systems. These results seem to be in contrast to AP-based systems, where an inverse correlation between the BR and the ignition temperature has been suggested to exist.[23]

For performance parameters' evaluation, the most important input data required, viz., the heats of formation of various new resins, were derived from the heats of combustion values obtained experimentally. Table 2 shows that the experimental heats of combustion of the resins are lower than those calculated using a method developed earlier.[21] While the difference is marginal in the case of furfuraldehyde resins, the benzaldehyde-based resins, particularly DEBCH, show large differences. The low values could be attributed to the incomplete combustion, as shown by the brownish film formed on the walls of the bomb calorimeter after combustion in these cases. Because the heat of formation is calculated from the heat of combustion data, even a slight difference in the experimental values could result in a major difference in the heat of formation, as seen from Table 2. The performance parameters discussed here, however, have been computed using the heat of formation values derived from the experimental heats of combustion for various resins, although the calculated value could provide more favorable results.

The four main parameters for AN propellants, namely, I_{sp}, T_c, M_c, and C^*, were calculated at various equivalence ratios Φ, which represents the fuel richness or leanness of the propellant composition, and are given in Table 3. The I_{sp} and T_c plots against a percentage of oxidizer of the various propellant systems are shown in Figs. 5 and 6, respectively. From these data it can be seen that the furfuraldehyde-resin-based AN compositions give higher specific impulses than the remainder of the systems. It is additionally apparent that by using the DEFTCH resin, the maximum I_{sp} (227.1 s) could be achieved at about 90% ($\Phi = 1$) AN solid loading, compared with CTPB, which gives 219.6 s with the same solid loading. In fact, even at stoichiometric loading, which occurs at 95% AN loading for CTPB-based systems, the calculated I_{sp} is only 223.6 s. It is also observed that, in general, the stoichiometric compositions are achieved at much lower solid loading when N–N-bonded resins are used as binders. Except for DEBCH, all three N–N-bonded resins are found to be superior to CTPB. The low performance obtained for DEBCH is caused by the unusually low experimental heat of the

Table 3 Performance parameters of AN-based propellant systems

			Performance parameters			
Binder	% Oxidizer	Φ	I_{sp}, s	T, K	M_c	C^*, m/s
DEFCH	75	1.50	200.0	1658	20.99	1234
DEFTCH	75	1.50	205.1	1785	21.36	1271
DEBTCH	75	1.80	187.9	1337	20.25	1135
DEBCH	75	1.70	176.5	1172	20.88	1062
CTPB	75	2.40	191.8	1216	18.57	1147
DEFCH	80	1.30	209.7	1911	21.92	1302
DEFTCH	80	1.30	214.0	2007	22.20	1328
DEBTCH	80	1.50	198.0	1640	21.17	1223
DEBCH	80	1.50	186.6	1393	20.85	1136
CTPB	80	2.00	196.7	1304	18.28	1187
DEFCH	85	1.10	219.2	2156	22.91	1358
DEFTCH	85	1.10	222.0	2197	23.01	1371
DEBTCH	85	1.20	210.4	1945	22.23	1306
DEBCH	85	1.20	200.7	1760	22.01	1246
CTPB	85	1.60	205.5	1622	19.45	1266
DEFCH	90	0.98	224.5	2305	23.81	1388
DEFTCH	90	0.99	227.1	2356	23.92	1402
DEBTCH	90	1.00	222.5	2246	23.45	1373
DEBCH	90	1.00	217.1	2153	23.39	1345
CTPB	90	1.20	219.6	2042	21.42	1363
DEFCH	95	0.81	196.9	1809	23.36	1229
DEFTCH	95	0.82	198.6	1841	23.43	1238
DEBTCH	95	0.80	202.7	1910	23.45	1262
DEBCH	95	0.80	199.3	1848	23.39	1242
CTPB	95	0.90	223.0	2237	23.26	1380

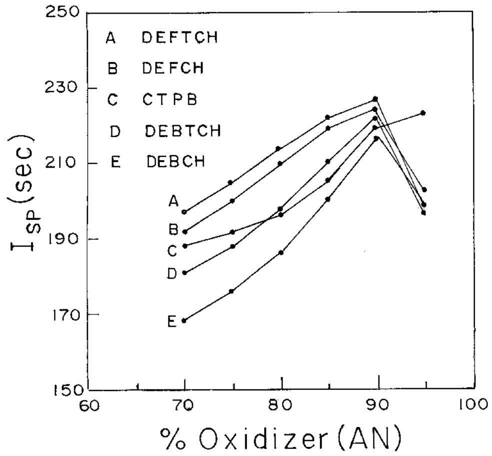


Fig. 5 Variation of specific impulse with percentage of oxidizer.

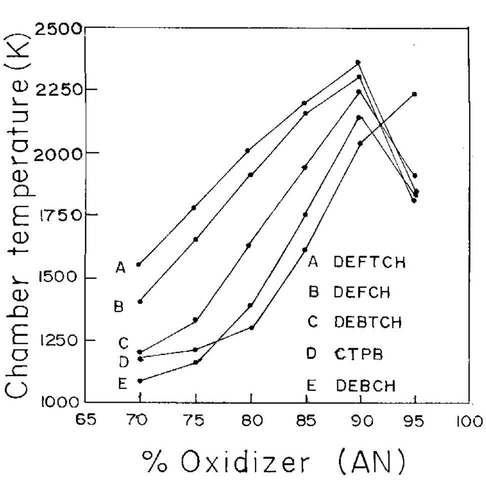


Fig. 6 Variation of chamber temperature with percentage of oxidizer.

combustion value obtained, unlike the other systems. It is important to note that the T_c is significantly higher for all four N–N-bonded resin-based compositions, compared with the CTPB-based system, which is reflected in high I_{sp}. The characteristic velocity C^* usually follows the same trend as I_{sp} (Table 3). The nature of the exhaust combustion products computed at $P_c / P_e = 70$ at $\Phi = 1$ and at 85% AN (practical solid loading) is evident from the product profile given in Table 4. The main combustion products are CO_2, H_2O, H_2, and N_2 at 85% loading. It is interesting to note that the sulfur-containing resins (DEFTCH and DEBTCH) produce H_2S at 85% AN solid loading and SO_2 at stoichiometric ratio ($\Phi = 1$), as combustion products. The M_c values of the N–N-bonded systems are marginally higher than those based on CTPB. In general, the major products of combustion of these compositions are all innocuous.

A significant advantage of using the N–N-bonded resin is that a relatively higher amount of the binder is required for stoichiometric combustion compared with CTPB, thereby making the processing of near-stoichiometric composition possible. Usually 85% solid loading of the powder is about the upper limit for processing grains having a reasonably good mechanical strength. At this loading most solid oxidizer compositions, e.g., those based on AN, AP, or ADN, and having CTPB binder, are fuel rich, and therefore, will result in a lower than expected performance. In other words, although a higher I_{sp} could be obtained at stoichiometric solid loading, in practice, it is not possible because of processing limitations. This restriction becomes less stringent when N–N-bonded binders are used. In fact, the solid loading required for maximum I_{sp} of AP propellants could be easily achieved with N–N-bonded binders. To appreciate this point, it is worthwhile to compare the I_{sp} of propellants having another oxidizer, such as AP, and ADN, using the N–N-bonded resins and CTPB binders. The results are tabulated in Table 5. It is important to note that the performance of DEFTCH or DEBTCH with AN is superior to CTPB–AN systems, unlike that with the other two oxidizers at stoichiometry ($\Phi = 1$). With AP and ADN as oxidizers, higher I_{sp} could still be achieved with a CTPB binder, but at much higher solid loading, which is not possible to achieve in practice without adversely affecting the mechanical properties. At practical 85% solid loadings, the N–N-bonded resins give much higher I_{sp}, with both AP and ADN, than that obtained with CTPB. This emphasizes the importance of the N–N-bonded binders in solid propellants.

Table 4 Combustion products (mole fraction) of propellants at Φ = 1 and at 85% AN loading, at the exit

	Composition (binder/oxidizer)	
Binder	$\frac{15}{85}$, weight ratio	Φ = 1
DEFTCH	CO (0.0192), CO_2 (0.1388) H_2 (0.08766), H_2O (0.4798) H_2S (0.00923), N_2 (0.2651)	CO_2 (0.1118), H_2O (0.5986) N_2 (0.2828), SO_2 (0.0065)
DEFCH	CO (0.0141), CO_2 (0.1438) H_2 (0.10188), H_2O (0.4719) N_2 (0.2628)	CO_2 (0.1197), H_2O (0.5985) N_2 (0.2816)
DEBTCH	CO (0.0234), CO_2 (0.1544) H_2 (0.16206), H_2O (0.3966) H_2S (0.00843), N_2 (0.2643) CH_4 (0.0051)	CO_2 (0.1082), H_2O (0.6030) N_2 (0.2835), SO_2 (0.0051)
DEBCH	CO (0.0166), CO_2 (0.1634) H_2 (0.16626), H_2O (0.3935) CH_4 (0.0055), N_2 (0.2544)	CO_2 (0.1141), H_2O (0.6032) N_2 (0.2826)
CTPB	CO (0.0397), CO_2 (0.1610) H_2 (0.25946), H_2O (0.2937) CH_4 (0.0274), N_2 (0.2184)	CO_2 (0.10), H_2O (0.625) N_2 (0.2750)

Table 5 Performance parameters at Φ = 1 and at 85% solid loading, for AN-, AP-, and ADN-based propellant compositions

	I_{sp} at Φ = 1		I_{sp} at 85%
Propellant	% oxidizer	$I_{sp,s}$	oxidizer loading, s
DEFTCH–AN	89.76	228.3	222.0
DEBTCH–AN	91.65	225.1	210.4
CTPB–AN	94.20	223.6	205.5
DEFTCH–AP	83.73	247.4	244.1
DEBTCH–AP	86.40	244.5	243.5
CTPB–AP	90.00	253.0	242.6
DEFTCH–ADN	87.17	260.6	259.4
DEBTCH–ADN	89.29	258.6	251.8
CTPB–ADN	92.70	265.1	248.6

Conclusions

The use of N–N-bonded epoxy resins based on carbono- and thiocarbono-hydrazones as binders in PSAN propellants results in enhancement of the burning rate. The performance parameters of the systems having N–N-bonded binders at practical solid loadings are superior to those based on the conventional polybutadiene binder.

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