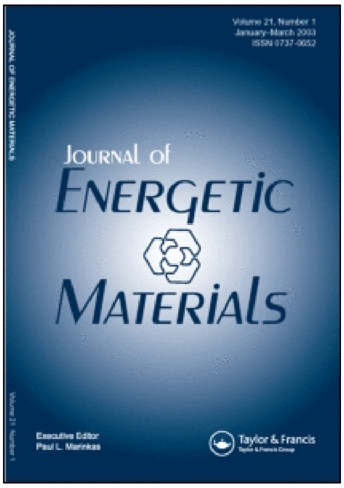

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Studies on energetic compounds part 15 : Transition metal salts of NTO as potential energetic ballistic modifiers for composite solid propellants

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STUDIES ON ENERGETIC COMPOUNDS
PART 15 : TRANSITION METAL SALTS OF NTO AS POTENTIAL ENERGETIC BALLISTIC MODIFIERS FOR COMPOSITE SOLID PROPELLANTS

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ABSTRACT

The combustion of hydroxyl terminated polybutadiene (HTPB) - ammonium perchlorate (AP) composite solid propellants has been studied using transition metal (Mn, Fe, Co, Ni, Cu and Zn) salts of 5-nitro-2,4-dihydro-3H-1,2,4-triazole-3-one (NTO) as energetic burning rate additives. The steady burning rate (r) was considerably enhanced with $Cu(NTO)_2$ and $Fe(NTO)_2$ whereas moderately enhanced with $Zn(NTO)_2$ and $Co(NTO)_2$ at low concentration (2% by wt.). Activity of these salts has been observed during isothermal decomposition of AP at 260 °C. The values of ignition delay (t_{id}), ignition temperature ($T_{igi.}$) and activation energy for ignition (E^*) for AP has also been lowered when these salts are added to it at 2% wt. concentration. The processing parameters as well as mechanical properties of the propellants with $Cu(NTO)_2$ as additive have been studied in detail. The r of the propellants (both highly aluminized and less aluminized) with $Cu(NTO)_2$ as additive at various concentrations, has been determined at high pressures, also shows its activity during combustion. The condensed phase activity of $Cu(NTO)_2$ during propellant decomposition has also been studied using TG-DTG techniques.

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INTRODUCTION

Burning rate of solid propellants is an important parameter because it is directly related to specific impulse (I_{sp}) and hence the performance of the propellant. Burning rate catalysts are essential additives in HTPB-AP composite solid propellant (CSP) due to its low inherent burning rate. Transition metal oxides (TMOs) like Fe_2O_3, copper chromite (CC), MnO_2, Ni_2O_3 etc enhance the burning rate of CSP considerably[1]. However, the effectiveness of these catalysts is concentration dependant[2] and owing to their non-energetic nature, increase in their concentration in the propellant may decrease the total energy. The TMOs affect the processing parameters of the propellant and are incompatible with the propellant constituents. Energetic burning rate modifiers increase the burning rate and at the same time, its use in the propellants does not decrease the total energy of the system. Thus energetic burning rate modifiers have advantages over TMOs.

NTO is an insensitive high explosive[3-5] and is acidic in nature. NTO forms salts with a wide range of metals and the metal salts of NTO are also rather insensitive than other propellant ingredients like AP, RDX etc., and are thus highly useful[6]. The metal salts of NTO have been suggested to be potential energetic ballistic modifiers for solid propellants[7,8]. We have earlier reported[9,10] the preparation, characterization and thermal decomposition of some of the transition metal salts of NTO. Catalytic activity of various additives in the thermolysis and combustion of AP, polystyrene (PS) and their CSPs have also been reported by us[11-19]. In continuation of these studies, some of the transition metal salts of NTO as energetic burning rate modifiers for HTPB-AP composite solid propellants has been studied and the results are reported in this paper.

EXPERIMENTAL

Materials

$Mn(NTO)_2$, $Fe(NTO)_2$, $Co(NTO)_2$, $Ni(NTO)_2$, $Cu(NTO)_2$, and $Zn(NTO)_2$ were synthesized in our laboratory as reported earlier[9]. AP (Central Electro-Chemical Research Laboratory, Karaikudi), HTPB and toluene diisocyanate (TDI) (supplied by VSSC, Thiruvananthapuram) were used as received.

Preparation of Propellants

AP (100-200 mesh) was mixed with HTPB, TDI and various finely powdered additives (2% by wt.) using a pestle and mortar, at normal temperature and pressure (NTP). The mixture thus obtained was casted in glass moulds having diameter 1.2 cm and length 12 cm. AP: HTPB ratio was fixed at 3:1 (by wt.) in all samples. The samples were cured in an incubator maintained at 60 ^{0}C for 8 days. The glass moulds were broken and propellant strands were inhibited by applying PVC tape to protect the samples from side burning.

Larger size (1.0 and 1.5 kg) propellant strands were also prepared using AP and HTPB. The other specifications are given in Table 2. Particle size of AP was 215 micron for experiment Nos. 1,2 & 3 and 40 micron for experiment Nos. 4 & 5. Mixing was done for 3 hours under residual pressure of 4 mm of Hg in a micro vertical kneader with twin blade configuration. Isophorone diisocyanate (IPDI) was used as the curing agent. Propellant strands were cured at 60°C for 8 days.

Burning Rate Measurements

The r of propellant strands (diameter 1.2 cm, length 12 cm) was measured manually, at ambient pressure. The propellant strands were held vertically and ignited electrically from the top with the help of an igniter made up of nichrome wire. The time required for the burning of a fixed length was recorded by stopwatch and burning rate was calculated as reported earlier[19]. For each propellant, five strands have been burned and the average values are reported in Table 1. The r of propellant strands (Expt. No. 1-5) was measured by acoustic emission method in which cured propellant strand of 8 cm length having 0.6 cm^2 cross-sectional area was ignited electrically by hot wire and burned under water in a stainless steel bomb. The requisite N_2 pressure (40 or 70 kg/cm^2) was maintained in the bomb. An acoustic transducer was mounted on the side of the combustion chamber and steady burning rates were measured from the acoustic output. For every test pressure, 4 or 5 strands were burned and average value of steady burning rates were taken, which are reported in Table 2.

Isothermal Thermogravimetry (TG) Studies

Isothermal TG data on AP with 2% (by wt.) additives [$M(NTO)_2$] were recorded using our indigenously fabricated TG apparatus[20] in static air, at 60 ^{0}C and thermograms are reported in Fig. 1.

Ignition Delay (t_{id}) Studies

Ignition delay studies on AP+$M(NTO)_2$ were undertaken by tube furnace (TF) technique[12]. The sample (weight = 20 mg, 100-200 mesh) was taken in an ignition tube (4 cm length and 0.4 cm diameter) and the time interval between the insertion of the tube from a fixed point into the TF up to a fixed depth and the moment of audible and/or visible ignition noted with the help of a stopwatch, gave the value of t_{id}. The ignition tube loaded with the sample and clamped in a bent wire was inserted manually into the TF up to a fix depth (8 cm) just above the probe of the temperature indicator-cum-controller (Century, CT 806T). The time taken for insertion of the ignition tube was also kept constant throughout the measurements. Accuracy of temperature measurement of the TF was ± 1 ^{0}C. Each reading was repeated three times and mean of the t_{id} values have been reported in Table 3. The accuracy of t_{id} values was well within the limit of experimental error. The t_{id} data above 400 ^{0}C were found to fit in the following equation[21-23]

$$t_{id} = Ae^{E^*/RT} \text{ ....(1)}$$

where E^* is the activation energy for ignition/explosion and T is the absolute temperature. The plots of ln t_{id} vs 1/T have been given in Fig. 2.

Mechanical properties

The tensile strength, elongation (%) and hardness were measured at VSSC, Thiruvananthapuram using Instron Universal Testing machine with 5 mm thick dumb-bells of ASTM specification D 412 (Die-C) at a crosshead speed of 50 mm min^{-1} at 25 ^{0}C and results are reported in Table 2.

Simultaneous TG/ Differential Thermogravimetry (DTG) Studies

Simultaneous TG/DTG analysis was taken by Dupont 2000 thermal analysis system in conjugation with 951 thermogravimetric analyzer using powder samples of

AP and two of the representative propellants at a heating rate of 10 ^{0}C min^{-1} in static air up to 500 ^{0}C and the thermograms are presented in Fig.3.

RESULTS AND DISCUSSION

Results reported in Table 1 clearly show that r of HTPB-AP composite propellants are enhanced considerably by some of the metal salts of NTO. The order of activity for metal salts of NTO is as follows:

$$Cu(NTO)_2 > Fe(NTO)_2 > Zn(NTO)_2 > Co(NTO)_2 > Ni(NTO)_2 \approx Mn(NTO)_2$$

In case of TMOs, attempts have been reported[24-26] to be made to ascertain whether the catalysts act in the condensed phase or in the gas phase. But there is no definitive report on the regime of the catalyst's action during propellant combustion. Some of the studies proposed that action of the catalyst takes place primarily in the gas phase[27]. However, most of the studies suggest that ballistic modifiers are active mainly in the condensed phase, at the AP-binder interface[28,29], where electron transfer is important[24]. Thus, we found it appropriate to study the effect of these additives during the thermal decomposition of AP, in the condensed phase using TG. The TG thermograms shown in Fig. 1 clearly show that the additives considerably affected the decomposition of AP. AP underwent ignition, when $Mn(NTO)_2$, $Co(NTO)_2$ and $Zn(NTO)_2$ have been used as additives and the time to ignition has been very-very short in the case of $Mn(NTO)_2$ and $Co(NTO)_2$. Fe, Ni and Cu salts of NTO have also increased the rate as well as extent of decomposition of AP. The order of rate enhancement among the NTO salts has been as follows:

$$Mn(NTO)_2 \geq Co(NTO)_2 > Zn(NTO)_2 > Ni(NTO)_2 > Cu(NTO)_2 > Fe(NTO)_2$$

Thus, the isothermal TG results clearly show that $Cu(NTO)_2$ is not the best additive, during the condensed phase thermal decomposition of AP at the temperature studied. Thus the efficiency of the additives during the isothermal decomposition of AP cannot be correlated with the efficacy of these NTO salts as burning rate modifiers.

Ignition delay measurements and kinetic analysis of the data there from is very much useful to study the catalytic effect in high energetic materials[9-12, 21-23]. The ignition delay data presented in Table 3 shows that the values of t_{id}, T_{ign} and E^* all for AP has been lowered by the additives. Ignition in the case of pure AP occurs only at 400 ^{0}C and above, but in the case of modified AP samples it occurs even at temperatures as low as 300 ^{0}C. The order of values of E^* is as follows:

$$Ni(NTO)_2 < Zn(NTO)_2 < Fe(NTO)_2 < Mn(NTO)_2 < Cu(NTO)_2 < Co(NTO)_2$$

The t_{id} data below 400 ^{0}C does not fall in the straight line with the data above it in Eq. 1. This indicates that the mechanism of ignition is different above and below 400 ^{0}C. The mechanism of AP deflagration is reported[30] to be consisting of formation of NH_3 and $HClO_4$ molecules on the surface, their desorption into the gas phase and their reaction there. These gas-phase reactions are exothermic and heat conducted back to solid AP results in rise in temperature, accelerated decomposition and eventually deflagration. The reaction between NH_3 and $HClO_4$ appears to be catalyzed by the NTO salts or more appropriately the corresponding TMO formed by the thermal decomposition of metal salts. However, further work is necessary to confirm this. It is also notable that the decomposition of these NTO salts is highly exothermic[9] and thus they also contribute towards the rise in temperature. The order of energy release during exothermic decomposition of these NTO salts[9] as determined by DSC is as follows:

$$Ni(NTO)_2 > Co(NTO)_2 > Zn(NTO)_2 > Mn(NTO)_2 > Cu(NTO)_2 > Fe(NTO)_2$$

Thus, the higher heat release during the thermolysis of $Ni(NTO)_2$ may be the reason for lowering of E^*, when it is used as additive in AP.

All these salts during their thermolysis give their corresponding metal oxides as the final product, has been reported[9]. Thus the TMO that formed *insitu* in the system seems to be the active species during the combustion. The metal oxides formed *insitu* in the system from different metal salts are more active than the corresponding aged samples of TMO has been evident from our previous studies also[12,13,17,19]. This may be attributed to the fact that the *insitu* formed oxides will be having finer particle size, hence higher surface area and more defects in their lattices. The fact that the transition metal salts of NTO are high energetic and they explode during thermolysis yielding metal oxides is notable. Because the TMOs thus formed are deemed to be having finer particle size than that formed by the non-energetic salts.

$Cu(NTO)_2$, which imparts a two fold enhancement in r of HTPB-AP composite propellants has been selected for further studies. Thus, five different formulations (both highly aluminized and less aluminized) were made in bulk quantities at the propellant processing facility available in VSSC Thiruananthapuram. Solid loading of 86 % is easily achieved in the case of highly aluminized formulations and 81 % for less aluminized ones. The slurry viscosity of the formulations has been determined both after the addition of all the constituents as well as after 3 hours of mixing at 50

^{0}C using Brookfield viscometer. The results of the viscosity measurements show that a slight build up in viscosity is observed when $Cu(NTO)_2$ was used as additive. However, amount of the additive has a low bearing on the viscosity build-up, rather than its presence. Thus, viscosity build-up is negligible for $Cu(NTO)_2$ even at a 2 % concentration. The values for tensile strength, elongation and shore A hardness summarized in Table 2 also show that the mechanical properties are also affected by the additive, but only to a negligible extent.

The values of r reported in Table 2 show that there is considerable enhancement in r of HTPB-AP propellants when $Cu(NTO)_2$ was used as additive, at various concentrations. The activity is enormous, even at a very low concentration as 0.1 % by weight. However, a comparison of the r_a/r_0 values ($r_a = r$ of propellant with additive and $r_0 = r$ without additive) of experiment No. 2 & 3 shows that the activity is concentration dependant. Of all the variables, pressure is the most important parameter on which r depends[30], is a well-established fact. A comparison of the values of r at 40 kg/cm^2 and 70 kg/cm^2 shows that the addition of $Cu(NTO)_2$ does not have much a bearing on the inherent pressure exponent of the HTPB-AP-Al propellant system. Thus $Cu(NTO)_2$ as a ballistic modifier does not affect the combustion stability of the propellants.

In order to get an idea about the events that are occurring in the condensed phase during propellant combustion, TG-DTG studies have been done on two representative propellant formulations (expt. No. 3 & 5). The corresponding thermograms shown in Fig. 3(b) & (c) respectively indicate that the condensed phase behaviour is predominantly determined by AP, which is the major constituent. Thus, to have a comparison of the thermal behaviour of the propellants with that of pure AP, TG-DTG studies of the pure AP used in the experiments has also been shown in Fig 3(a). AP has a two step decomposition is well established[31], namely low temperature decomposition (LTD) and high temperature decomposition (HTD). However, two-step decomposition is observed in the case of one of the formulations (expt. No. 3), which may be attributed to the LTD and HTD of AP. A comparison of the DTG peak values for pure AP with that for propellant (expt. No. 3) shows that the activity of the additive is not evident in this case. Whereas in the case of propellant formulation (expt. No.5), the thermal decomposition occurs in a single stage, clearly indicating the activity. The difference of the two formulations (expt. No. 3 & 5) being in the amount of AP as well as concentration of the additive and Al powder is an inert constituent, it may be inferred that the activity is mainly on the thermolysis of AP and it is dependant on the concentration of the additive.

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CAPTION OF FIGURES

FIGURE 1

Isothermal TG thermograms of AP and AP + additives (2 % by wt.) at 260 ^{0}C.

FIGURE 2

Plots of ln t_{id} vs 1/T for AP with and without additives (2% by wt.)

FIGURE 3

Simultaneous TG/DTG thermograms of (a) AP (b) Propellant (Expt. No.3) (c) Propellant (Expt. No.5)

TABLE 1

Steady Burning Rate of HTPB/AP (1/3) Propellants in Presence of Various Additives (2% by wt.)

Additive	Burning rate (mm/s)	r_a/r_0
Nil	1.47 ± 0.13	1.00
$Mn(NTO)_2$	1.50 ± 0.08	1.02
$Fe(NTO)_2$	2.77 ± 0.49	1.88
$Co(NTO)_2$	2.01 ± 0.04	1.36
$Ni(NTO)_2$	1.54 ± 0.02	1.04
$Cu(NTO)_2$	3.03 ± 0.30	2.06
$Zn(NTO)_2$	2.07 ± 0.11	1.40

r_a = Burning rate of propellant in presence of additive

r_0 = Burning rate of propellant without additive

TABLE 2

Physical Parameters, Mechanical Properties and steady Burning Rate of HTPB/AP Propellants

S. No.	Parameters	Experiment No.				
		1	2	3	4	5
1	Mix size (kg)	1	1	1	1.5	1.5
2	Al content (%)	18	18	18	2	2
3	AP content (%)	68	67.9	67.5	79	77
4	Solid loading (%)	86	86	86	81	81
5	$Cu(NTO)_2$ content (%)	0	0.1	0.5	0	2
6	Slurry viscosity (Poises), 50 °C					
	End of mix viscosity	5440	6400	6080	4800	5120
	3 hour viscosity	8320	9600	9600	6080	6080
7	Steady burning rate (mm/s)					
	40 kg/cm^2	4.95 ± 0.05	6.31 ± 0.07	6.91 ± 0.06	8.2 ± 0.00	11.26 ± 0.00
	70 kg/cm^2	6.03 ± 0.06	7.90 ± 0.08	8.70 ± 0.08	10.1 ± 0.00	14.0 ± 0.00
8	r_a/r_o					
	40 kg/cm^2	1.00	1.27	1.40	1.00	1.37
	70 kg/cm^2	1.00	1.31	1.44	1.00	1.39
9	Mechanical properties					
	Tensile strength (kg/cm^2)	7.5	6.8	6.2	5.6	4.4
	Elongation (%)	38	30	30	60	49
	Shore A hardness	75	70	68	60	50

TABLE 3

Ignition Delay (t_{id}), Ignition Temperature (T_{ign}) and Activation Energy for Ignition (E^*) of AP and AP + Additives

Additive	**t_{id} (s) at various temperatures (^{0}C)**									**T_{ign} (^{0}C)**	**E***
	300	**325**	**350**	**375**	**400**	**450**	**500**	**550**	**600**	**25 s**	**(kJ/mole)**
Nil	DNI	DNI	DNI	DNI	100.0	75.0	45.6	37.0	24.0	600	34.7
Mn(NTO)$_2$	216.0	152.0	122.0	51.6	50.0	32.0	25.6	17.0	14.0	498	31.2
Fe(NTO)$_2$	DNI	DNI	217.0	47.0	43.0	33.3	26.0	19.6	13.0	475	28.3
Co(NTO)$_2$	64.6	55.0	44.0	40.6	32.6	20.0	13.6	10.0	8.0	432	34.5
Ni(NTO)$_2$	DNI	DNI	DNI	DNI	43.0	35.6	27.6	21.0	18.0	523	22.1
Cu(NTO)$_2$	DNI	49.0	46.6	41.0	37.3	25.3	16.6	12.0	10.0	452	33.2
Zn(NTO)$_2$	230	57.6	53.6	50.3	38.6	36.0	26.0	16.6	14.0	483	27.1

DNI - Did Not Ignite

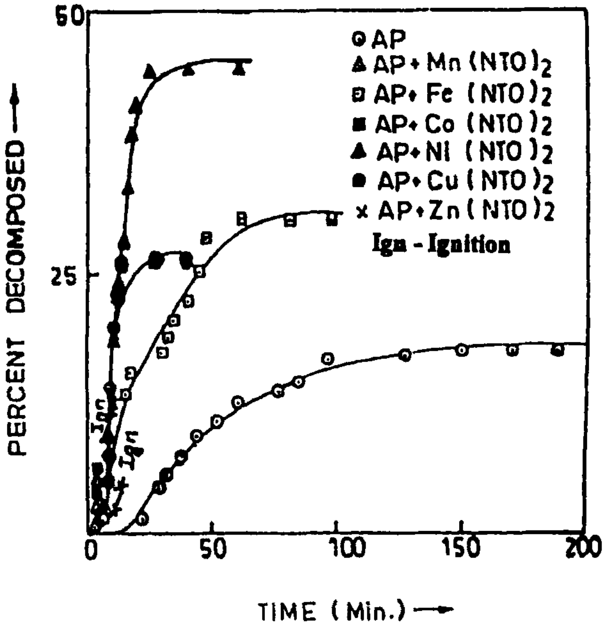
50
25
0
50
100
150
200
PERCENT DECOMPOSED
TIME (Min.)
AP
AP + Mn (NTO)2
AP + Fe (NTO)2
AP + Co (NTO)2
AP + Ni (NTO)2
AP + Cu (NTO)2
AP + Zn (NTO)2
Ign - Ignition
Ign
Ign

Figure I

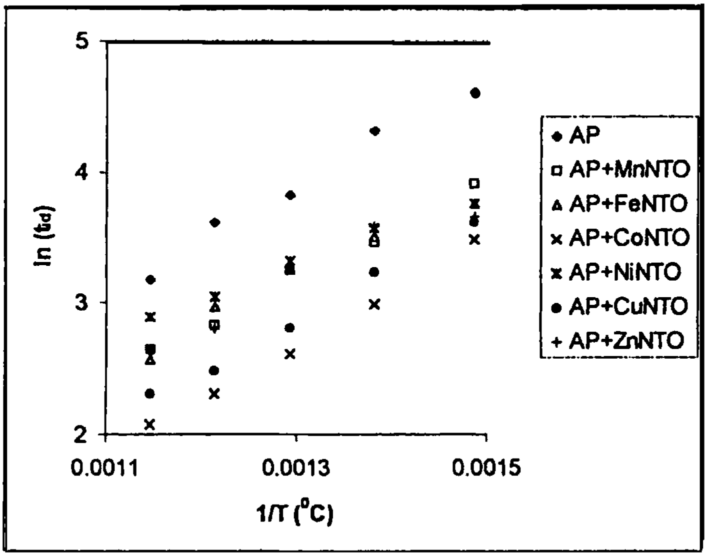
5
4
3
2
ln (td)
0.0011
0.0013
0.0015
1/T (°C)
◆ AP
□ AP+MnNTO
▲ AP+FeNTO
× AP+CoNTO
✱ AP+NiNTO
● AP+CuNTO
+ AP+ZnNTO

Figure 2

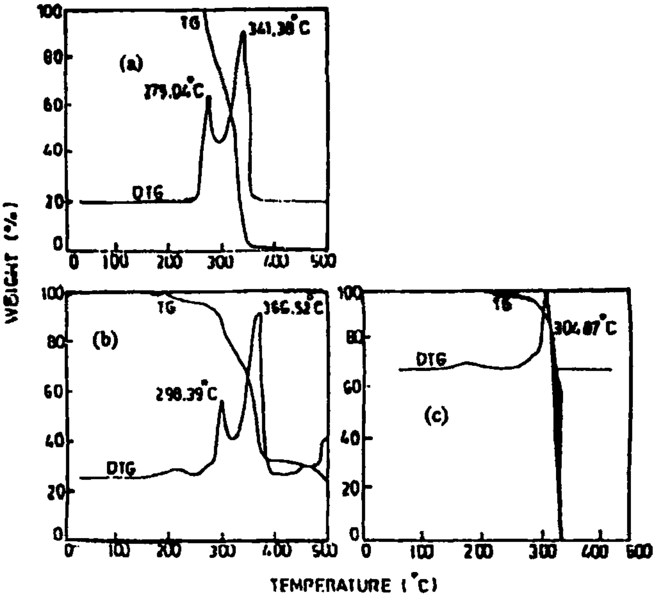
WEIGHT (%)
(a)
TG
341.38°C
279.04°C
DTG
100
80
60
40
20
0
0
100
200
300
400
500
(b)
TG
366.52°C
298.39°C
DTG
100
80
60
40
20
0
0
100
200
300
400
500
(c)
TG
304.87°C
DTG
100
80
60
40
20
0
0
100
200
300
400
500
TEMPERATURE (°C)

Figure 3