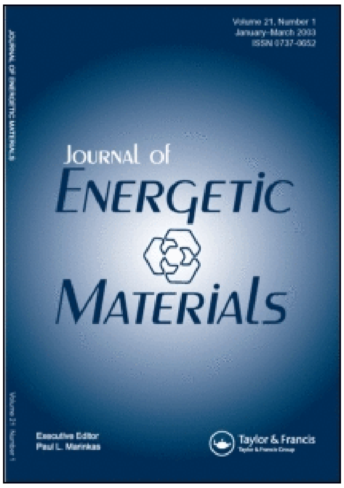

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HEXAMMINE METAL PERCHLORATES AS ENERGETIC BURNING RATE MODIFIERS

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ABSTRACT

Four transition metal hexammine perchlorates namely, $[Cu(NH_3)_6](ClO_4)_2$, $[Co(NH_3)_6](ClO_4)_2$, $[Ni(NH_3)_6](ClO_4)_2$ and $[Zn(NH_3)_6](ClO_4)_2$ have been prepared, characterized and used as ballistic modifiers in the combustion of hydroxy terminated polybutadiene (HTPB)-Ammonium perchlorate (AP) composite solid propellants. Burning rate was considerably enhanced with $[Co(NH_3)_6](ClO_4)_2$ and $[Cu(NH_3)_6](ClO_4)_2$ whereas moderately with $[Ni(NH_3)_6](ClO_4)_2$ and $[Zn(NH_3)_6](ClO_4)_2$ at low concentration (2% by wt.). $[Co(NH_3)_6](ClO_4)_2$ was found to accelerate the burning rate by three fold at two percent concentration and it can be exploited as potential energetic burning rate modifier for HTPB-AP propellants. Further, ignition delay studies showed that the deflagration of propellants and AP was accelerated by these additives.

INTRODUCTION

Preparation, explosive properties and thermal decomposition of transition metal hexammine perchlorates have already been reported[1-4]. However, no details of their role in burning rate modification of composite solid propellants are available in literature. Transition metal salts are known to modify the combustion behaviour of propellants. In continuation of our ongoing research programme on high energetic materials[5-10], hexammine metal perchlorates have been prepared, characterised and their role as burning

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rate modifiers for HTPB-AP solid propellants have been investigated and results are reported in the present communication.

EXPERIMENTAL

Materials

Carbonates of copper, cobalt (BDH), nickel (Thomas Baker) and zinc (Sarabhai), 70% $HClO_4$ (Qualigens), ethanol (Hayman), liquor NH_3 (Ranbaxy), AP (Central Electrochemical Research Institute, Karaikudi, Chennai), HTPB and isophorone diisocyanate (IPDI) (VSSC, Thiruvananthapuram) and dioctyl adepate (DOA) (s.d. fine chemicals) were used as received without any further purification.

Preparation and Characterization of Hexammine Metal Perchlorates

The metal perchlorates hexahydrates were prepared as reported earlier[4] by treating corresponding metal carbonates with 70% $HClO_4$ at room temperature. The metal perchlorates were washed with petroleum ether (Merck), recrystallised from distilled water and dried over fused $CaCl_2$ in desiccator. The hexammine metal perchlorates were prepared by treating ethanolic solution of corresponding metal perchlorates hexahydrates with liquor ammonia in stoichiometric amount at room temperature. The whole reaction mixture was cooled on crushed ice and crystalline complexes of different colours were washed with methanol (Ranbaxy), recrystallised from distilled water and vacuum dried over fused $CaCl_2$. Their purity was cheked by thin layer chromatography (TLC). Moreover, these complexes were characterised by gravimetric method, IR (Impact 400) in KBr pellets and elemental analysis (Fission Instruments DP 200 series 2). Physical, spectral and elemental data are given in Table 1.

Preparation of HTPB-AP Composite Solid Propellants

The HTPB-AP composite solid propellant samples (non-aluminised and aluminised) were prepared by dry mixing[11] of AP[100-200 and 200-400 mesh (3:1)] with finely powdered additives (2% by wt.) and other solid components. The solid material was mixed with HTPB in the ratio of 4:1. The binder part included the curing agent (IPDI) in equivalent ratio to HTPB and plasticiser (DOA, 30% to HTPB). Aluminium powder (17% by wt.) was used in aluminised propellant samples. The solid content was kept 80% in all the samples. During mixing of solid components with HTPB, a processing temperature of 50°C was mentained throughout and stirring was continued for 1 hour, after complete addition of solid components in small installment.

The propellants of 40 g batches were prepared using these hexammine metal perchlorates as ballistic modifiers and vacuum casted into aluminium plates having dimensions 1×3×10 cm. The samples were cured in an incubator at 60°C for ten days except in the case of propellant containing $[Co(NH_3)_6](ClO_4)_2$ additive (curing time, 25 days). $[Co(NH_3)_6](ClO_4)_2$ was found to be the best additive and hence samples of propellants were also prepared by varying its percentage (1, 2, 3, 4 & 5%).

Measurement of Burning Rate

The cured propellant samples were cut into smaller pieces having dimensions 0.7×0.7×9 cm and burning rate was measured at ambient pressure by fuse wire technique. An average of three measurements was taken which are within experimental error and results are reported in Tables 2, 3 & 4.

Thermal Decomposition Studies

In order to examine the role of these additives in the combustion of propellant samples (non-aluminised and aluminised), non-isothermal decomposition studies on propellants and AP, with and without additives were carried out in static air using indigenously fabricated TG apparatus[12] fitted with temperature indicator cum controller (Model CT 808 T, Century) at a heating rate of 5°C/min taking 20 mg of samples and bucket type platinum crucible (h= 1 cm & dia= 1 cm) as sample holder. The plots of percent decomposition (α) vs temperature (°C) are given in Figs 1, 2 & 3 while data profiles are given in Table 5.

Ignition Delay (t_{id}) and Ignition Temperature (IT) Measurements

These studies on propellants (non-aluminised & aluminised), AP and AP+additive samples were undertaken using tube furnace (TF) technique[13]. The samples were taken in an ignition tube (h= 5 cm & dia= 0.4 cm) and the time between the insertion of the sample tube into the TF and the moment of an ignition, noted with the help of a stopwatch, gave the value of t_{id}. The accuracy of t_{id} values was well within the limit of experimental error. Activation energy was calculated using following equation[14-15] and plots of log t_{id} vs 1/T are given in Figs. 4, 5 & 6 respectively.

$$t_{id} = Ae^{E^*/RT}$$

where t_{id} = ignition delay, E^*= activation energy for ignition and T is absolute temperature. The values of E^* and IT for propellants, AP & AP+additives are reported in Table 6, 7 & 8 respectively.

RESULTS AND DISCUSSION

The hexammine metal perchlorates are known to be explosive in nature and are reported[2,16] to decompose exothermally. The explosivity of these complexes seems to be due to the presence of both the oxidizing (ClO_4^-) and reducing (NH_3) groups in the same molecule and metal ions are acting as catalysts. The oxidation of ammonia can take place by ClO_2 or other oxidizing agent, which are formed by the decomposition of perchlorate groups[5,6]. The estimated values of percentage of each metal are in good agreement with those of theoretical values (Table 1), which confirms beyond doubt the formation of these complexes. Moreover, the characteristic absorption frequencies of metal-nitrogen bond, coordinated ammonia and perchlorate group are similar to those reported in Nakamoto[17]. The burning rate is enhanced in following order when hexammine metal perchlorates were used as burning rate modifiers for HTPB-AP propellants (Tables 2 & 3).

$[Co(NH_3)_6](ClO_4)_2 > [Cu(NH_3)_6](ClO_4)_2 > [Ni(NH_3)_6](ClO_4)_2 \approx [Zn(NH_3)_6](ClO_4)_2$.

The three times enhancement in burning rate was observed with $[Co(NH_3)_6](ClO_4)_2$ at 2% (by wt.) concentration, and thus it was found interesting to study its effect at various concentrations. The data reported in Table 4 clearly shows the maximum enhancement in burning rate at 2% of $[Co(NH_3)_6](ClO_4)_2$. However, a gradual decrease in the burning rate was observed at higher concentrations of this additive. A lower burning rate was observed in the case of aluminised propellants (Table 3) than the non-aluminised propellant samples (Table 2). This lowering in the burning rate may be due to lower percentage of AP in aluminised propellant samples.

Burning rate might be enhanced on account of acceleration of any of the following:

(i) AP decomposition

(ii) HTPB-AP propellant decomposition.

Non-isothermal TG thermograms reported in Figs 1, 2 & 3 show that incorporation of these additives cause increase in the rate of decomposition of non-aluminised and aluminised propellants and that of AP. This increase may be due to the catalysis of condensed phase and/or gas phase reactions, which inturn the increase of heat flux to the burning surface, and consequently burning rate is enhanced. TG data reported in Table 5 clearly show that decomposition temperatures are lowered when these additives are added to propellant and AP samples. However, $[Co(NH_3)_6](ClO_4)_2$ was found to be the best among all the studied additives in lowering the decomposition temperature.

In order to study the effect of these ballistic modifiers on the deflagration of propellant and AP samples, ignition delay measurements were undertaken by incorporating these additives in all the samples. t_{id}, IT and E* are lowered when 2% of each complex was added to propellant and AP samples (Tables 6, 7 & 8). $[Co(NH_3)_6](ClO_4)_2$ is found to give lowest IT and E* in all the samples. The catalytic activity of metal ions in ignition of propellants and AP is shown to be in order:

$$Co^{2+} > Cu^{2+} > Ni^{2+} \approx Zn^{2+}$$

As all these metal complexes are reported[2,16,21] to decompose to respective metal oxides, the freshly insitu formed metal oxides having finer particle size might be acting as catalyst during decomposition and combustion of propellant. However, metal ammonia complex are also reported[18-20] to facilitate proton transfer reaction during decomposition of AP.

Conclusions

Some of the transition metal hexammine perchlorates are very potential burning rate modifiers for HTPB-AP propellants. $[Co(NH_3)_6](ClO_4)_2$ is the best among them at the tested conditions.

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REFERENCES

1. W. R. Tomlinson, K. G. Ottoson and L. F. Audrieth, *J. Am. Chem. Soc.* 71, 375, (1949).
2. R. A. F. Sherrif and A. K. Galway, *J. Chem. Soc*, 1705, (1967).
3. K. C. Patil and E. A. Secco, *Can. J. Chem*, 49, 3831, (1971).
4. K. C. Patil and V. R. Pai Verneker, *Thermochim Acta*, 15, 257 (1976).
5. G. Singh, I. P. S. Kapoor and S. M. Mannan, *J. Energ. Mater.*, 13, 141, (1995).
6. G. Singh, I. P. S. Kapoor and S. M. Mannan, *J. Therm. Anal.*, 46, 1751, (1995).
7. G. Singh, I. P. S. Kapoor and S. Jacob, *Indian J. Engg. Mater. Sci.*, 5, 140, (1998).
8. G. Singh, I. P. S. Kapoor and S. M. Mannan, *J. Energ. Mater.*, 12, 113, (1994).

9. G. Singh, I. P. S. Kapoor, S. M. Mannan and S. K. Tiwari, *J. Ener. Mater.*, 16 (1) 31, (1998), 16 (2), 101, (1998).

10. G. Singh, I. P. S. Kapoor, S. M. Mannan and S. K. Tiwari, *J. Hazard. Mater.*, A, 68, 155, (1999).

11. S. Krishnan and R. D. Swami, *J. Propulsion and Power*, 13, (2), 207, (1997).

12. G. Singh and R. R. Singh, *Res. Ind.*, 23, 92, (1978).

13. G. Singh, S. K. Vasudeva and I. P. S. Kapoor, *Indian J. Tech.*, 29, 589, (1991).

14. N. Semenov, "*Chemical Kinetics and Chain Reactions*" (Clarendon Press, Oxford), chap. 18, (1935).

15. S. Freeman and S. Gardon, *J. Phys. Chem.*, 60, 867, (1956).

16. K. C. Patil and V. R. Pai Verneker, *Combust. Flame*, 25, 387, (1975).

17. K. Nakamoto, "*Infrared Spectra of Inorganic and Coordination Compounds*" Wiley and Sons, New York, p 163, (1962).

18. L. Dauerman, *AIAA J.*, 5, 192, (1967).

19. P. W. M. Jacobs and A. Russel Jones, *AIAA J.*, 5, 829 (1967).

20. G. Keenan and R. F. Siegmund, *J. Solid State Chem.*, 4, 362, (1972).

21. G. Singh and D. K. Pandey, *J. Energ. Mater.*, In Press (2002).

TABLE 1

Physical, Spectral and Elemental Data of Hexammine Metal Perchlorates

Compound	Mol. weight	Colour	TLC*		Elemental analysis (%) Observed (calculated)			IR					
			Mobile Phase	R_f	H	N	Metal	$\nu(NH_3)_{asym}$	$\nu(NH_3)_{sym}$	$\nu(Cl{=}O)$	$\nu(Cl{-}O^-)$	$\nu_{M\text{-}N}$	ClO_4^-
$[Cu(NH_3)_6](ClO_4)_2$	364.5	Blue	a:b:c (1:1:2)	0.907	4.47 (4.90)	22.77 (23.04)	15.89 (17.42)	3500w	2940s	652s	1060w	428s	618s
$[Co(NH_3)_6](ClO_4)_2$	359.9	Brown	a:b:c (2:1:1)	0.887	4.50 (5.00)	22.80 (23.33)	14.98 (16.40)	3500m	3200w	626s	1090w	450s	620s
$[Ni(NH_3)_6](ClO_4)_2$	359.7	Violet	a:b:c (2:1:1)	0.937	4.90 (5.00)	22.80 (23.33)	15.12 (16.31)	3380s	3300s	650s	1100w	442s	620s
$[Zn(NH_3)_6](ClO_4)_2$	366.4	White	a:b:c (1:1:2)	0.825	3.90 (4.90)	21.84 (22.90)	16.32 (17.74)	3347s	3281s	525s	1125w	448s	624s

*where : a = ethanol, b = dimethylformamide, c = butanol-1, w =wide, m =medium & s = sharp.
Locating reagent: iodine

TABLE 2

Burning Rate of Non-aluminised HTPB-AP Propellants in Presence of Additives (2% by wt.)

S.No.	Additive	Burning rate (mm/s)	r_c/r*
1.	Nil	1.62	1.00
2.	$[Cu(NH_3)_6](ClO_4)_2$	2.77	1.88
3.	$[Co(NH_3)_6](ClO_4)_2$	4.93	3.35
4.	$[Ni(NH_3)_6](ClO_4)_2$	1.99	1.35
5.	$[Zn(NH_3)_6](ClO_4)_2$	2.03	1.38

*r_c = Burning rate of propellant in presence of additive
r = Burning rate of propellant in absence of additive

TABLE 3

Burning Rate of Aluminised HTPB-AP Propellants in Presence of various Additives

S.No.	Additive	Burning rate (mm/s)	r_c/r
1.	Nil	1.11	1.00
2.	$[Cu(NH_3)_6](ClO_4)_2$	1.72	1.56
3.	$[Co(NH_3)_6](ClO_4)_2$	1.78	1.61
4.	$[Ni(NH_3)_6](ClO_4)_2$	1.34	1.22
5.	$[Zn(NH_3)_6](ClO_4)_2$	1.32	1.20

TABLE 4

Burning Rate of HTPB-AP Propellants (non-aluminised) at Various Concentrations of $[Co(NH_3)_6](ClO_4)_2$

S. No.	Percent Additive	Burning rate (mm/s)	r_c/r
1.	Nil	1.62	1.00
2.	1%	3.77	2.33
3.	2%	4.93	3.35
4.	3%	3.09	1.91
5.	4%	2.73	1.69
6.	5%	2.53	1.57

TABLE 5

Decomposition Temperature (obtained from TG plots given in Figs 1, 2 & 3) for HTPB-AP Propellants (non-aluminised and aluminised) and AP with and without additives

Sample	$T_{30\%}$	$T_{75\%}$
Non Aluminised Propellants		
1. Control	360	455
2. $[Cu(NH_3)_6](ClO_4)_2$	335	425
3. $[Co(NH_3)_6](ClO_4)_2$	270	315
4. $[Ni(NH_3)_6](ClO_4)_2$	360	425
5. $[Zn(NH_3)_6](ClO_4)_2$	325	422
Aluminised Propellants		
1. Control	365	465
2. $[Cu(NH_3)_6](ClO_4)_2$	342	430
3. $[Co(NH_3)_6](ClO_4)_2$	315	349
4. $[Ni(NH_3)_6](ClO_4)_2$	375	430
5. $[Zn(NH_3)_6](ClO_4)_2$	380	425
AP & AP+Additive		
1.AP	300	369
2. AP + $[Cu(NH_3)_6](ClO_4)_2$	280	340
3. AP + $[Co(NH_3)_6](ClO_4)_2$	270	320
4. AP + $[Ni(NH_3)_6](ClO_4)_2$	285	339
5. AP + $[Zn(NH_3)_6](ClO_4)_2$	275	345

$T_{30\%}$ and $T_{75\%}$ = Decomposition temperature at 30% and 75% mass losses respectively

TABLE 6

Ignition Delay (t_{id}), Ignition Temperature (IT) and Activation Energy for Ignition (E*) of Non-aluminised Propellants

Additive	t_{id} (s) at various temperatures (°C)								IT (°C) for t_{id} of 29 s	E* ($kJmol^{-1}$)
	325	350	375	400	425	450	475	500		
Nil	DNI	116.3	65.0	56.3	47.3	43.0	37.6	30.3	421	31.3
$[Cu(NH_3)_6](ClO_4)_2$	93.3	59.7	54.4	38.0	37.3	29.0	28.0	22.0	422	28.9
$[Co(NH_3)_6](ClO_4)_2$	80.0	67.0	50.6	47.3	38.3	35.3	30.3	27.0	425	25.6
$[Ni(NH_3)_6](ClO_4)_2$	DNI	81.0	60.0	58.0	49.6	38.3	30.3	29.0	420	28.1
$[Zn(NH_3)_6](ClO_4)_2$	DNI	76.0	59.6	58.5	53.3	42.5	33.3	29.3	422	27.7

TABLE 7

Ignition delay (t_{id}), ignition temperature (IT) and activation energy for ignition (E*) of aluminised propellants

Additive	t_{id} (s) at various temperatures (°C)								IT (°C) for t_{id}	E*
	325	350	375	400	425	450	475	500	of 36s	(kJmol^{-1})
Nil	DNI	164.0	87.3	70.0	59.6	44.3	31.3	30.0	466	42.6
$[Cu(NH_3)_6](ClO_4)_2$	107.6	90.3	62.6	54.6	47.0	37.6	30.0	27.0	471	33.9
$[Co(NH_3)_6](ClO_4)_2$	92.0	71.6	55.6	52.0	47.0	37.2	32.3	28.0	465	26.7
$[Ni(NH_3)_6](ClO_4)_2$	DNI	129.3	76.0	65.3	61.0	39.0	31.0	26.3	462	40.9
$[Zn(NH_3)_6](ClO_4)_2$	DNI	142.3	67.3	63.0	58.7	40.6	34.3	29.0	461	41.4

TABLE 8

Ignition Delay (t_{id}), Ignition Temperature (IT) and Activation Energy for Ignition (E*) of AP and AP+ Additive.

Additive	**t_{id} (s) at various temperatures (^{0}C)**								
	325	**350**	**375**	**400**	**425**	**450**	**475**	**500**	**525**
Nil	DNI	DNI	DNI	DNI	280.0	233.0	189.5	154.3	103.0
$[Cu(NH_3)_6](ClO_4)_2$	163.0	139.0	114.0	79.2	66.0	54.4	43.0	35.0	30.0
$[Co(NH_3)_6](ClO_4)_2$	157.0	131.5	86.2	75.0	57.3	45.5	33.3	33.0	30.0
$[Ni(NH_3)_6](ClO_4)_2$	DNI	220.5	170.0	120.3	75.0	50.0	44.3	34.6	32.0
$[Zn(NH_3)_6](ClO_4)_2$	272.0	212.0	174.0	99.3	65.2	57.6	50.3	40.6	35.1

DNI= Did not ignite.

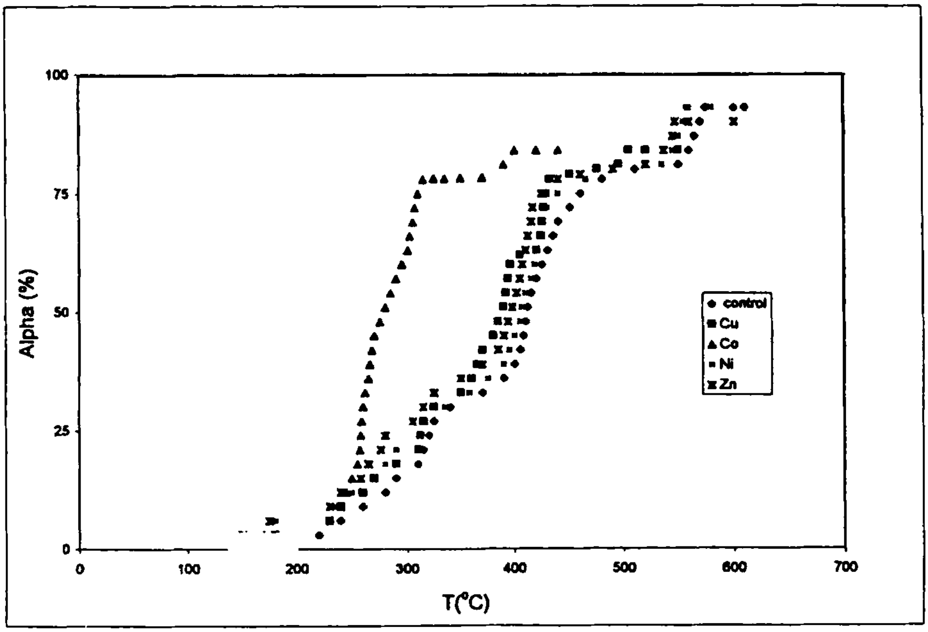

FIGURE 1

Non-isothermal TG Thermograms of Non-aluminised Propellants Containing Various Additives

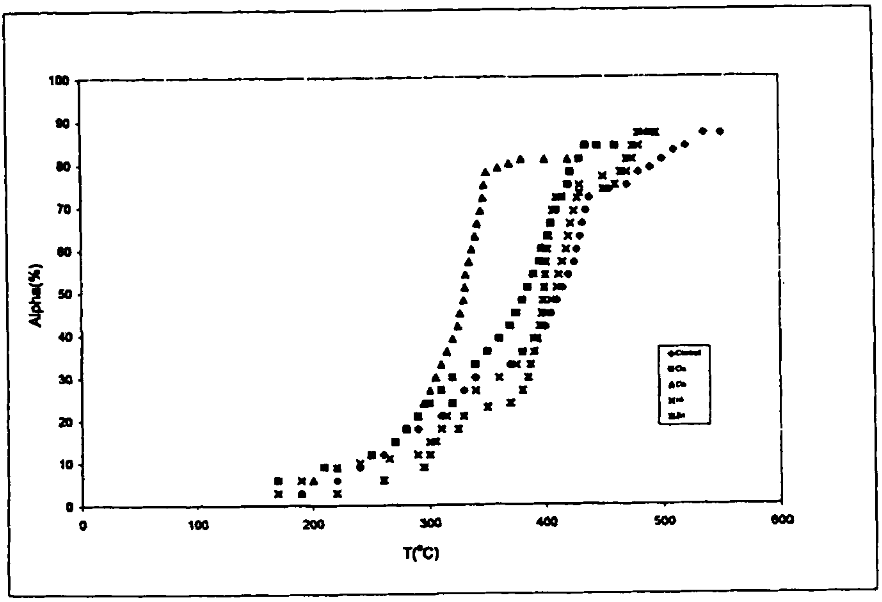

FIGURE 2

Non-isothermal TG Thermograms of Aluminised Propellants Containing Various Additives

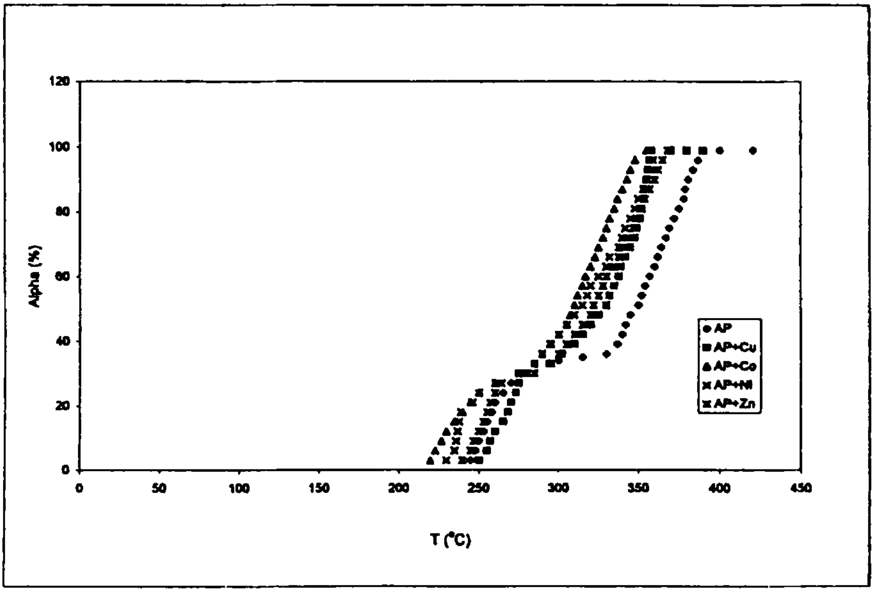

FIGURE 3

Non-isothermal TG Thermograms of AP and AP + additives

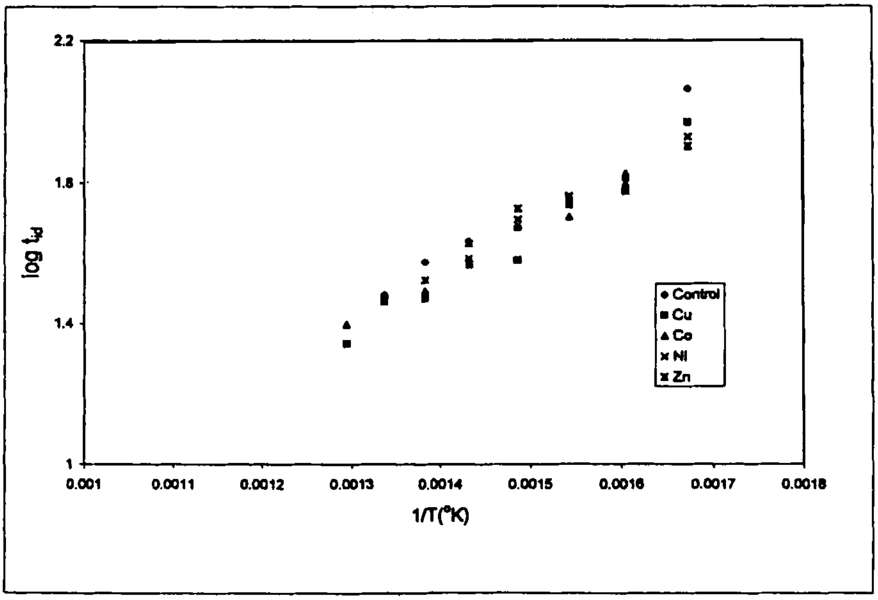

FIGURE 4

Plots of log t_{id} versus 1/T (°K) of Non-aluminised Propellants

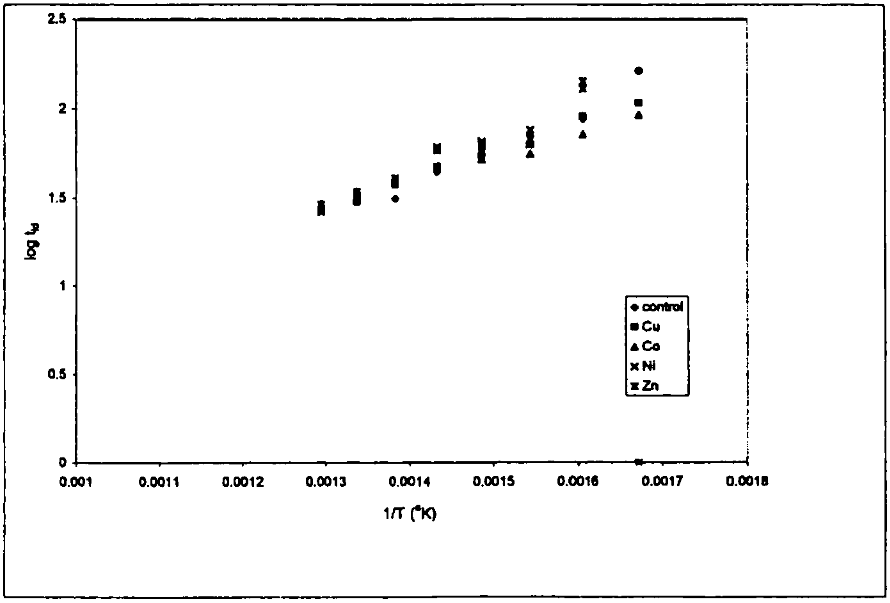

FIGURE 5

Plots of log t_{id} versus 1/T (°K) of Aluminised Propellants

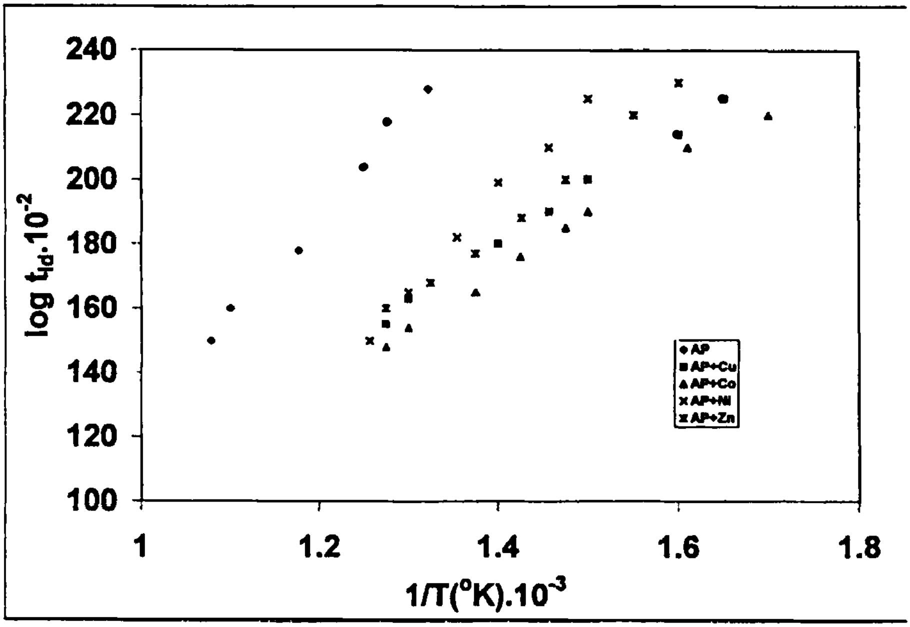

FIGURE 6

Plots of log t_{id} versus 1/T (°K) of AP and AP + additives