

EVALUATION METHOD FOR THE EFFECT OF SALTS ON THE ELIMINATION OF SECONDARY FLAMES OF ENERGETIC MATERIALS BY DIFFERENTIAL SCANNING CALORIMETRY

SHIN-MING SHEN

School of Defence Sciences, Chung Cheng Institute of Technology, Tachi 33509 (Taiwan)

AN-LU LEU * and HSI-CHENG YEH

Department of Applied Chemistry, Chung Cheng Institute of Technology, Tachi 33509 (Taiwan)

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ABSTRACT

The effect of LiF, KCl and KHCO_3 on the thermal decomposition of HTPB/RDX energetic composite (where HTPB is hydroxyl-terminated polybutadiene and RDX is cyclotrimethylene trinitramine) was studied and a method suitable for the evaluation of the inhibitory behavior of alkali metal salts on the secondary flame combustion reaction of HTPB/RDX composite was developed, utilizing thermogravimetry-derivative thermogravimetry differential scanning calorimetry (DSC) and a multi-channel recorder. It was found that the addition of salts not only limited the extent, but also changed the mechanism, of the decomposition reaction of HTPB/RDX composite. The original one-stage exothermic reaction was found to be split into two, three or even more stages by the addition of salts. DSC results proved that the decomposition reaction species are different for the various stages. The mixture of LiF and KHCO_3 had a stronger effect as a retardant of the secondary flame than pure compounds such as LiF, KCl or KHCO_3 alone. The maximum peak temperature (T_m) decreased as KHCO_3 concentration increased, at a concentration of KHCO_3 lower than 35%. A relationship between the DSC data and secondary flame intensity was also found.

INTRODUCTION

Alkali metal salts have been used as combustion inhibitors in various applications. Qualitative interpretations of the effects of alkali metal salts as combustion inhibitors have been given by many investigators. Mchale [1,2] reported that the addition of potassium salt to rocket propellant suppressed afterburning of solid propellant. Habersat [3] reported that the addition of potassium sulfate to internal rocket motor components, inhibited secondary combustion in the exhaust plume, and the visible signature was reduced.

* Author to whom correspondence should be addressed.

Agrawal et al. [4] reported an overall cooling effect on the burning polymer as alumina trihydrate (Al_2O_3) is added to semiflexible unsaturated polyester resin-4 as flame retardant. Thermally dispersible solids consisting of a crystalline alkali metal halide and an encapsulated inorganic salt which decompose at moderate temperature were used by Gozalishivili et al. [5] as flame inhibitors. The effects of a series of ammonium and potassium salts on the thermal degradation of polyacetals has been reported by Tompa [6]. It was found that the more acidic the character of the cation and anion moieties, the more effective the additive was in lowering the decomposition temperature of the polyacetals.

Chin et al. [7] found that the composition of smoke containing flame retardant showed a very small exotherm on differential thermal analysis (DTA), which was an indication that the fuel/oxidizer in the colored smoke was desensitized prior to the normal ignition point.

The purpose of the present study was to investigate the effect of alkali metal salts, such as LiF, KCl and KHCO_3 , on the thermal decomposition of HTPB/RDX composite (where HTPB is hydroxyl-terminated polybutadiene and RDX is cyclotrimethylene trinitramine) and to evaluate the inhibitory effect of alkali metal salt additives on the decomposition of HTPB/RDX by means of differential scanning calorimetry (DSC), thermogravimetry (TG), and derivative thermogravimetry (DTG) techniques. A multi-channel recorder was also employed in order to characterize the retardant behavior of additives on the secondary flame of HTPB/RDX composite.

EXPERIMENTAL

Mixtures of HTPB prepolymer, salts such as KCl, LiF, KHCO_3 , bonding agent, plasticizer, RDX powder and curing agent were mixed together according to the compositions listed in Table 1. Composition A is a reference standard without any salts. Mono-salt such as KCl, LiF or KHCO_3 was added to series B energetic materials to evaluate the flame inhibiting

TABLE 1
Composition of energetic materials tested

Ingredients	Composition (wt. %)								
	A	B-1	B-2	B-3	C-1	C-2	C-3	C-4	C-5
Binder (HTPB)	14	14	14	14	14	14	14	14	14
RDX	86	45	45	45	45	45	45	45	45
LiF	—	41	—	—	6	10	20	26	35
KCl	—	—	41	—	—	—	—	—	—
KHCO_3	—	—	—	41	35	31	21	15	6

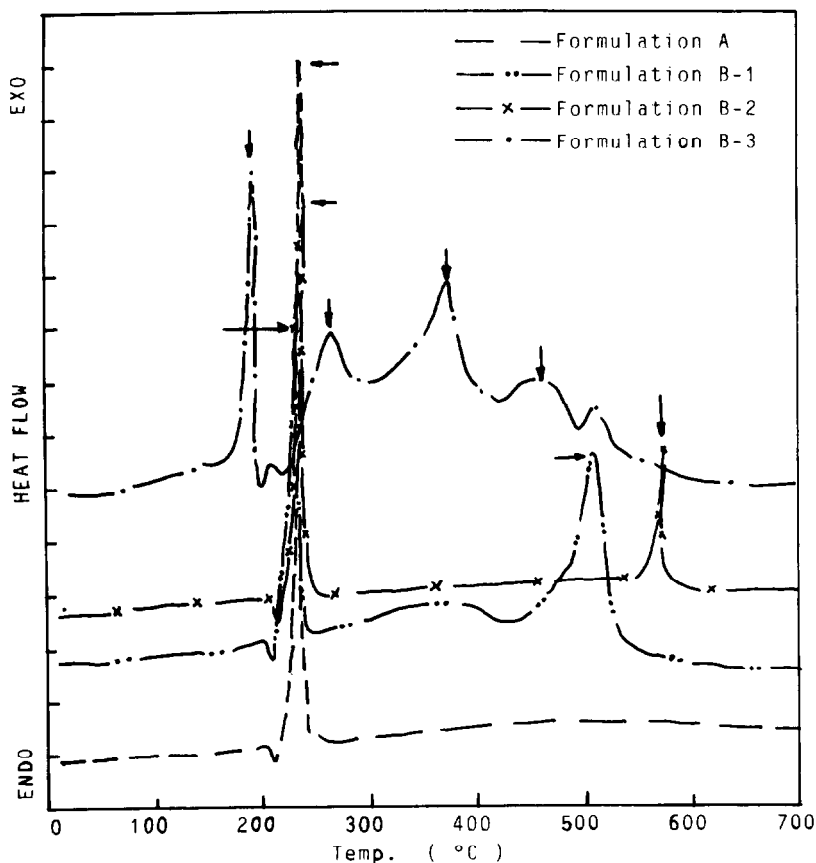


Fig. 1. DSC scans for formulations A, B-1, B-2 and B-3.

effect. Mixtures of KHCO_3 and LiF, of various KHCO_3 :LiF ratios, were added into series C energetic materials to evaluate their combined effect as inhibitors. All the ingredients were blended together in a Baker Perkins 2PX vertical mixer at 60°C . At the end of each blending cycle the slurry mixture was transferred into a casting mold by gravity under vacuum and cured at 60°C for seven days.

To evaluate the inhibitory effects of KCl, LiF, KHCO_3 and the combined effect of various ratios of LiF to KHCO_3 on the HTPB/RDX composite decomposition reaction, DSC measurements were carried out on a Dupont 1090 thermal analyzer. In the DSC measurements, cured samples with a weight of about 1 mg were examined at a heating rate of $20^\circ\text{C min}^{-1}$ in an aluminum crucible under a static nitrogen flow of 50 ml min^{-1} . The results obtained from the DSC measurements are shown in Figs. 1–5 and listed in Tables 2 and 3.

The TG-DTG measurements were carried out on a Perkin-Elmer thermal analyzer. In the TG-DTG analysis, cured samples with a weight of

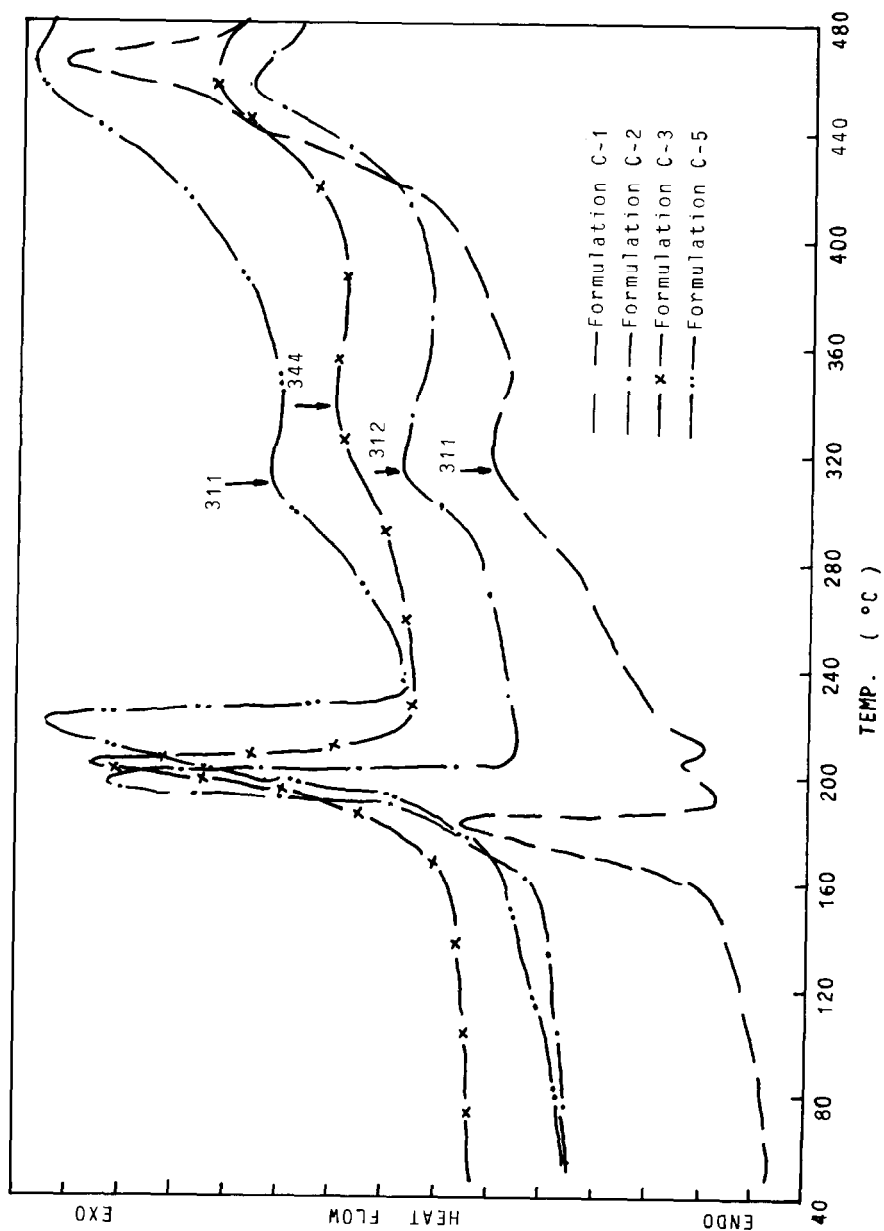


Fig. 2. DSC scans for formulations C-1, C-2, C-3 and C-5.

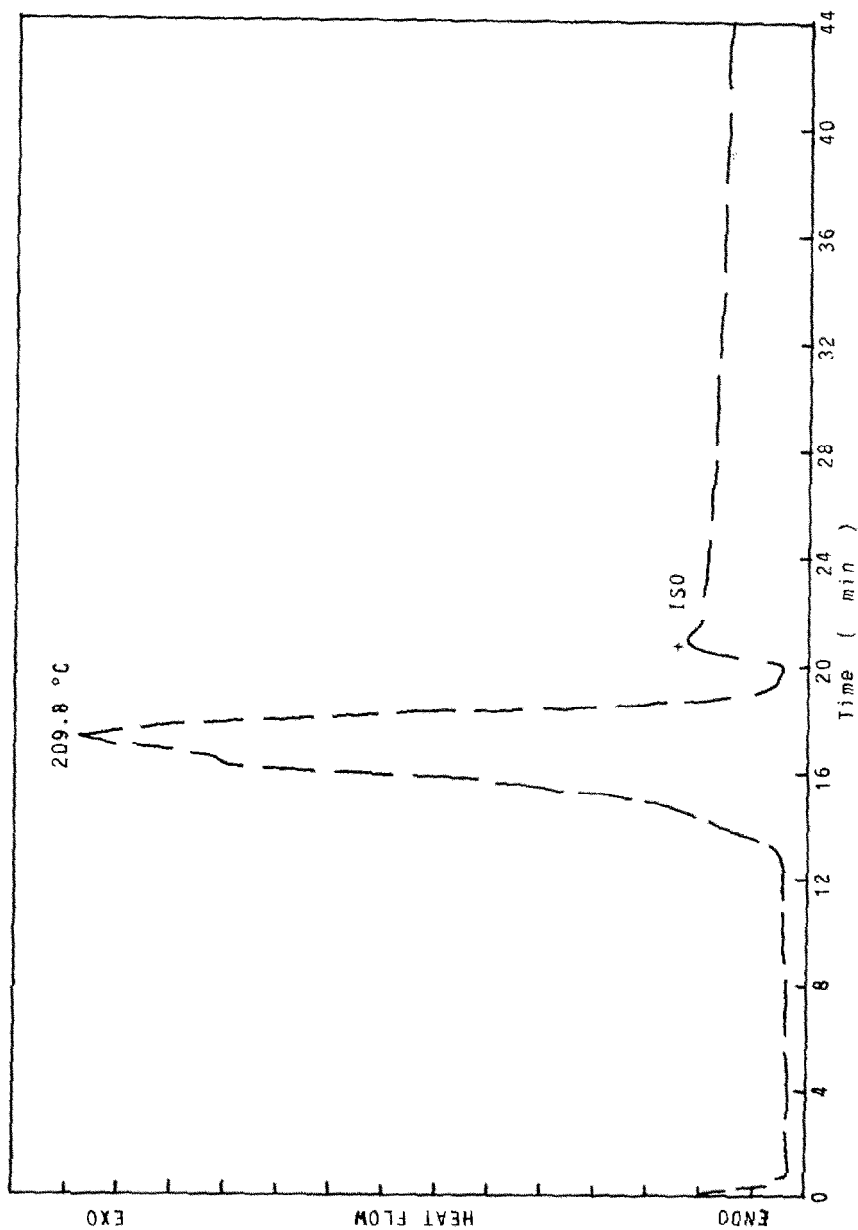


Fig. 3. DSC scans for formulations C-5 according to Process 1 (see text).

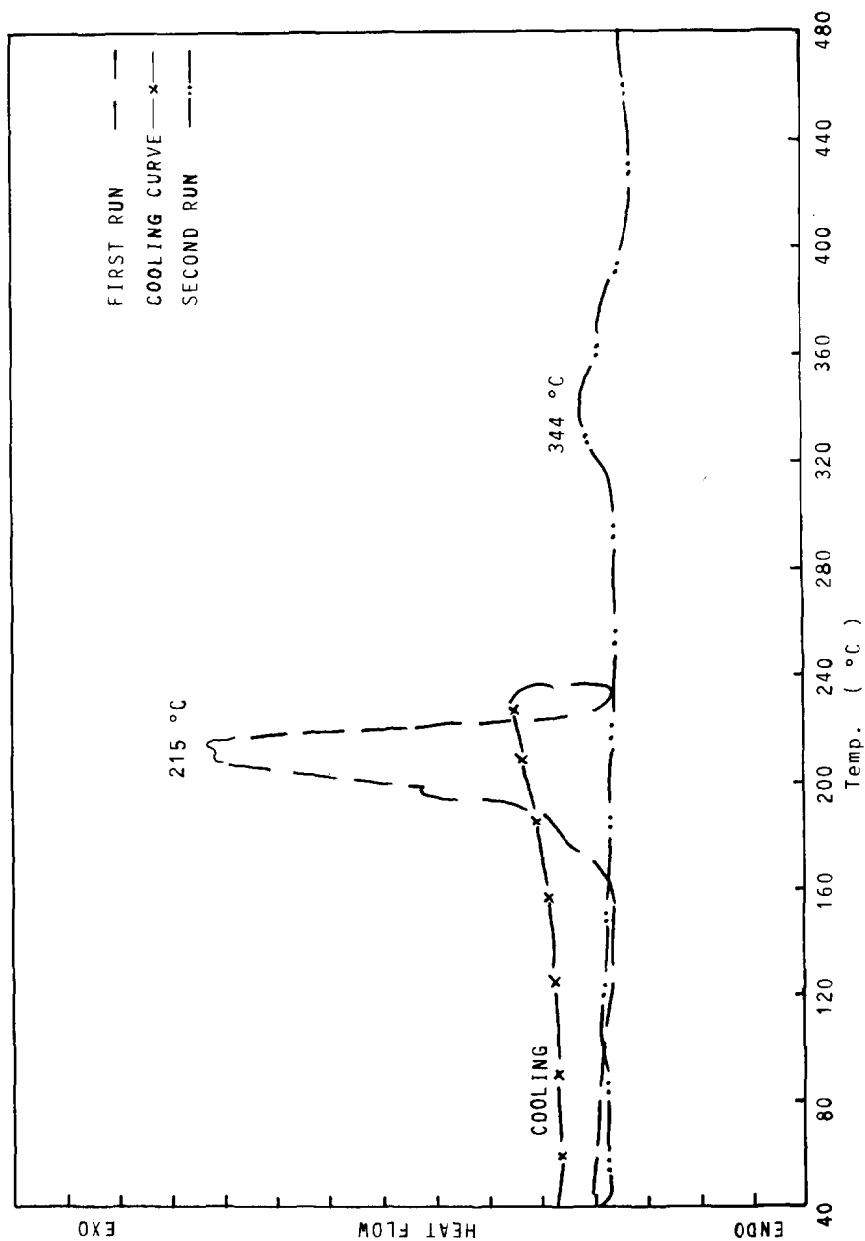


Fig. 4. DSC scans for formulation C-5 according to Process 2 (see text).

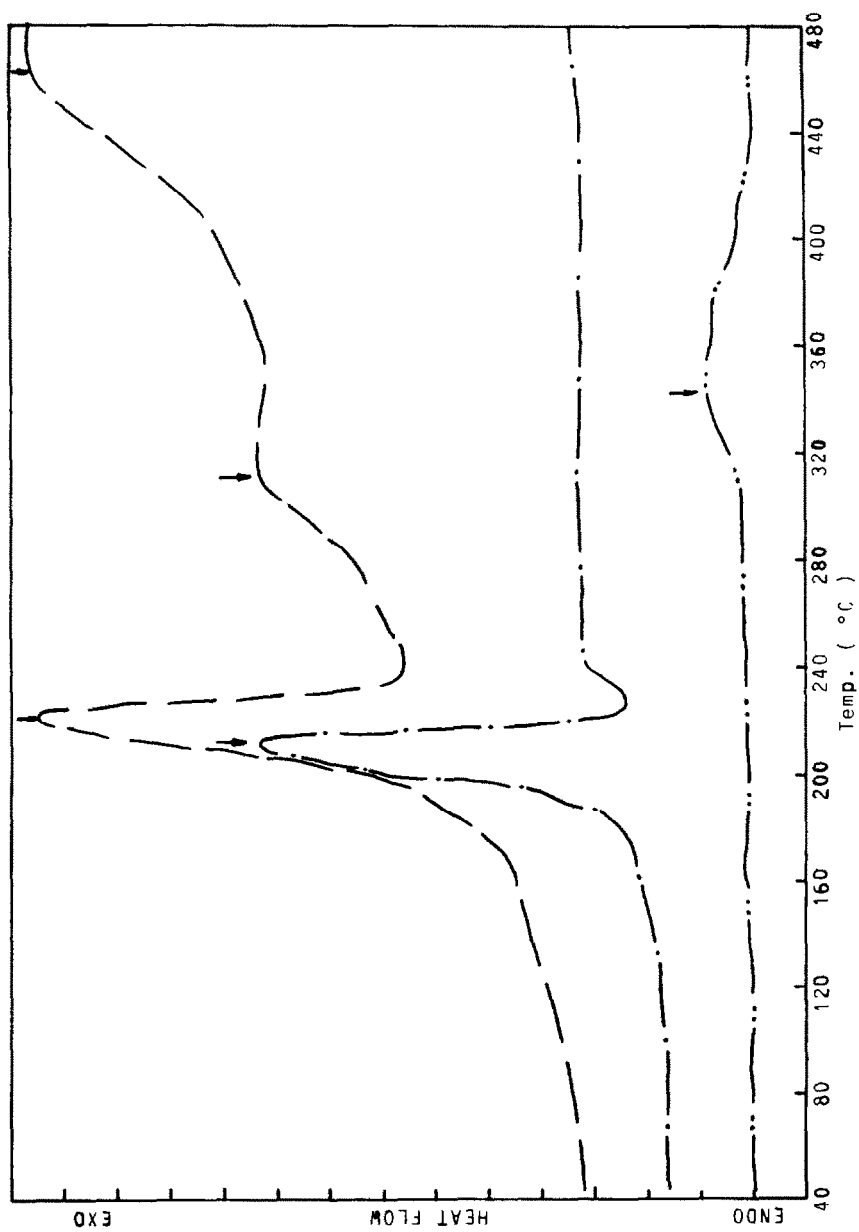


Fig. 5. The combined DSC scans for formulation C-5.

TABLE 2

 T_m and ΔH for the thermal decomposition of the energetic materials of Table 1

Material	1st exothermic reaction		2nd exothermic reaction		3rd exothermic reaction	
	T_m ($^{\circ}\text{C}$)	ΔH (J g^{-1})	T_m ($^{\circ}\text{C}$)	ΔH (J g^{-1})	T_m ($^{\circ}\text{C}$)	ΔH (J g^{-1})
A	225	1552	–	–	–	–
B-1	222	806	500	1316	–	–
B-2	229	1532	562	283	–	–
B-3	183	281	259	184	367	423
C-1	184	397	311	220	465	782
C-2	197	1022	312	506	456	656
C-3	203	1072	344	281	455	574
C-4	212	948	340	179	475	2384
C-5	220	933	311	208	462	355

about 7 mg were examined at a heating rate of $10^{\circ}\text{C min}^{-1}$ under a static nitrogen flow of 50 ml min^{-1} . The testing temperature program was from 30°C to 700°C for each sample. The results obtained by TG–DTG measurement are shown in Fig. 6 and listed in Table 4.

TABLE 3

DSC measurement results by various test methods

Material	Test method	Reaction occurrence					
		1st exothermic		2nd exothermic		3rd exothermic	
		Occurred?	T_m ($^{\circ}\text{C}$)	Occurred?	T_m ($^{\circ}\text{C}$)	Occurred?	T_m ($^{\circ}\text{C}$)
C-1	1 ^a	yes	220	yes	311	yes	462
	2 ^b	yes	210	no	–	no	–
	3 ^c	no	–	yes	344	no	–
C-2	1 ^a	yes	197	yes	312	yes	456
	2 ^b	yes	191	no	–	no	–
	3 ^c	no	–	yes	339	no	–
C-3	1 ^a	yes	203	yes	344	yes	455
	2 ^b	yes	200	no	–	no	–
	3 ^c	no	–	yes	336	no	–
C-5	1 ^a	yes	220	yes	311	yes	462
	2 ^b	yes	197	no	–	no	–
	3 ^c	no	–	yes	346	no	–

^a Test temperature was increased continuously as DSC measurements were carried out.

^b The DSC temperature was raised to the first exothermic reaction temperature T_m , (as Method 1) then kept there.

^c The DSC temperature was raised to the first exothermic reaction temperature T_m (as Method 1), and then cooled to room temperature before being raised again to observe whether any reaction had occurred.

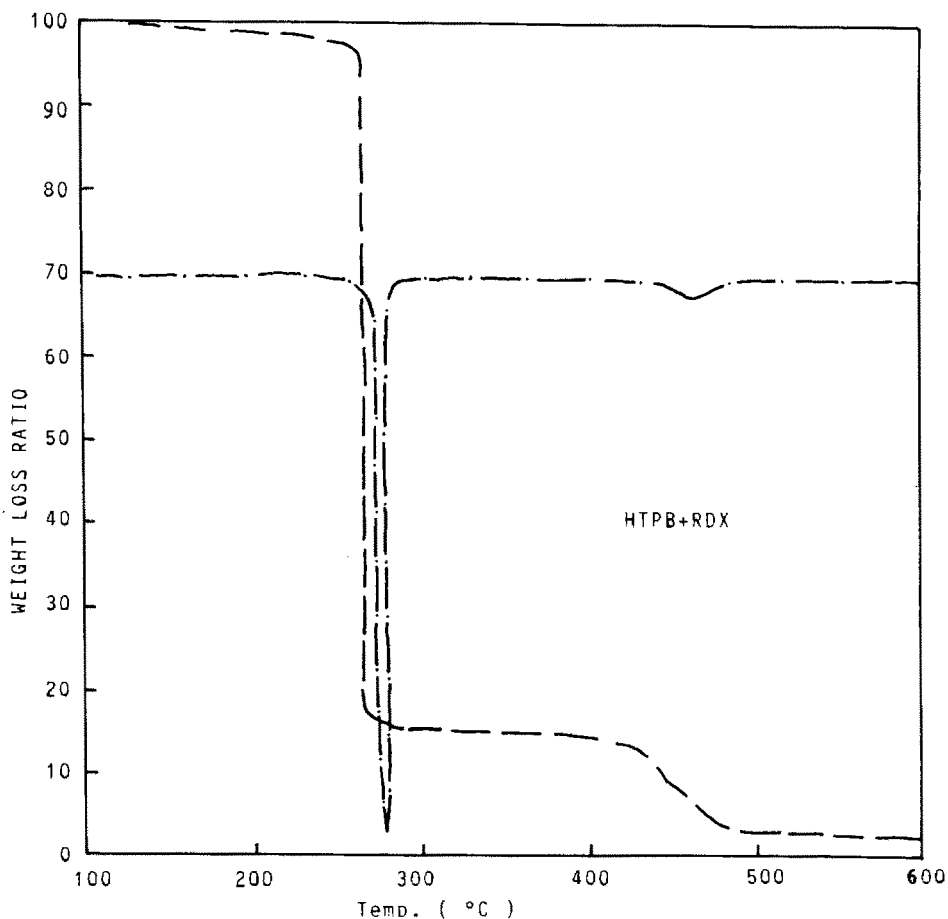


Fig. 6A. TG-DTG results for formulation A.

In order to evaluate the inhibitory effects of additives KCl, LiF and KHCO_3 on HTPB/RDX composite, the dependence of flame intensity on time was recorded on a multi-channel recorder (MCR-80). Typical results are shown in Fig. 8.

RESULTS AND DISCUSSION

Fig. 1 shows the DSC scans of formulations A, B-1, B-2 and B-3. At about 210°C an endothermic reaction for RDX melting is apparent. At 225°C there is an exothermic reaction peak for HTPB/RDX composite decomposition with a reaction heat of 1.552 kJ g^{-1} . The results show that the thermal decomposition of HTPB/RDX composite is affected by the addition of LiF and KCl. As shown in Table 2, splitting of the original

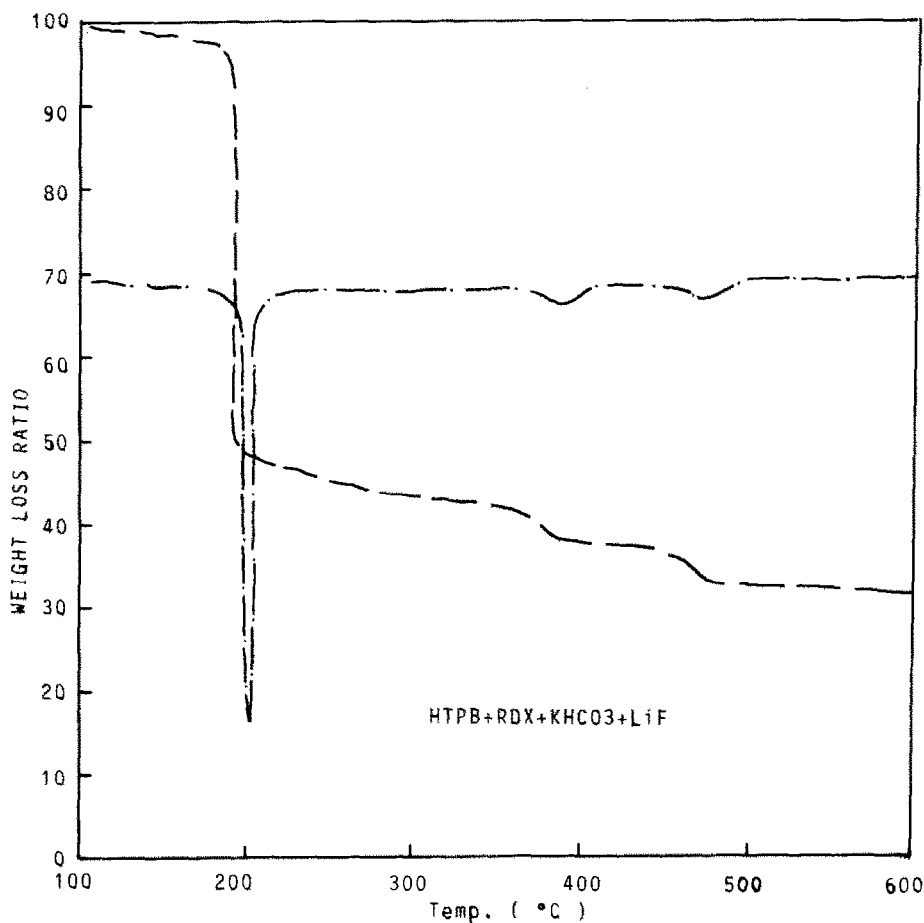


Fig. 6B. TG-DTG results for formulation C-5.

one-step exothermic decomposition reaction into two steps by LiF and KCl, and LiF alone, are more effective inhibitors than KCl in the decomposition of composite. Remarkable differences exist between KHCO_3 and LiF or

TABLE 4

The TG results of energetic materials

Formulation			Weight loss (%)				Total weight loss (%)	Residue (%)	
	Material	KHCO_3 (%)	LiF (%)	1st	2nd	3rd			4th
C-1		35	6	52	9	4	4	69	31
C-2		31	10	20	33	13	4	70	30
C-3		21	20	13	35	11	4	62	38
C-5		6	35	10	40	9	2	61	39

KCl on the thermal decomposition of HTPB/RDX composite material. The decomposition of HTPB/RDX composite is changed from the original one-step to a multi-step exothermic reaction and the decomposition temperature T_m is decreased to an extent of about 50° by the addition of KHCO_3 . The enthalpy change, ΔH , of the first stage decomposition reaction of the composite system with KHCO_3 is decreased by about 80% compared with that of the basic formulation (A).

A mechanism for the inhibition of the combustion of propellant by inorganic salt has been proposed by various investigators [1,8,9]. They suggested that the addition of salt as a flame suppression agent scavenges the active species of H, OH and CO. Therefore the flame is extinguished and the secondary combustion of H_2 and CO is quenched. In this study, LiF and KHCO_3 were added as an ingredient to the HTPB/RDX composite. It might be suggested that the chain reactions of radicals of H, OH and CO are affected by the addition of LiF and KHCO_3 , and therefore H or OH is scavenged and the combustion reaction terminated. Owing to the fact that

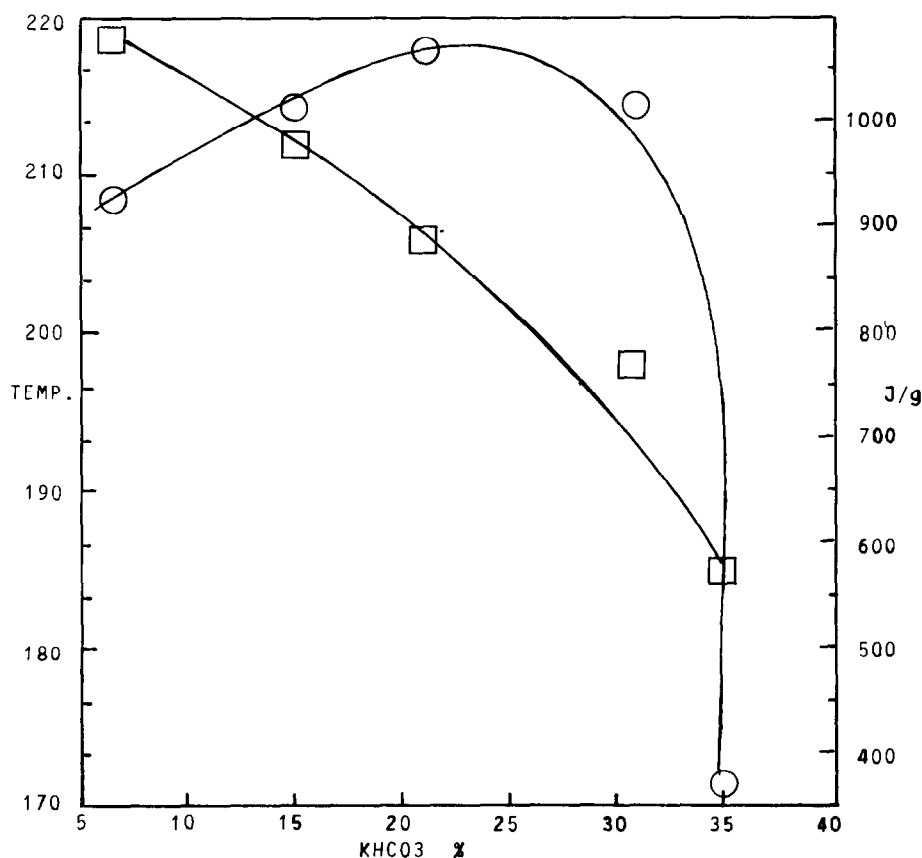


Fig. 7. Dependence of T_m and ΔH on the concentration of KHCO_3 .

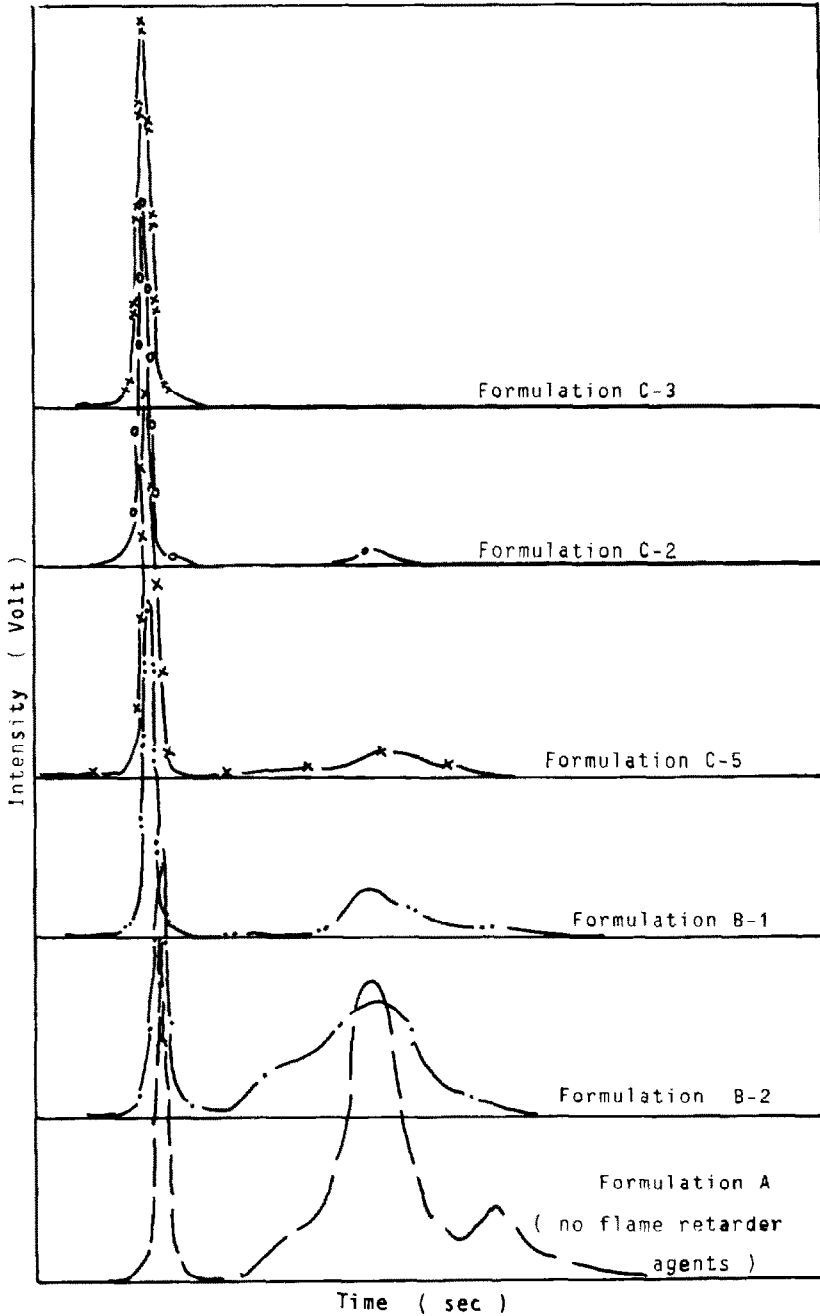


Fig. 8. Dependence of flame intensity on time for energetic materials.

the temperature of the DSC testing environment is increased continuously in the testing process, the residue of the first decomposition product gained heat continuously. If enough heat energy were gained, the combustion

reaction could happen again and the periodic reaction sequence ... combustion—extinction—combustion—... would appear in the DSC scans.

LiF and KCl were added (wt.%) in formulations B-1 and B-2. The mole percentages of LiF are higher than those of KCl. The collision frequency of LiF molecules with the active species of H, OH and CO is higher than that of KCl molecules. Hence the inhibitory effect of LiF on the secondary flame is greater than that of KCl. At 230 °C, a broad endothermic reaction for pure KHCO_3 ($\Delta H = 683 \text{ J g}^{-1}$) exists. At 225 °C there is an exothermic reaction for HTPB/RDX composite decomposition. Therefore, as KHCO_3 is an ingredient in HTPB/RDX composite, the reaction heat of HTPB/RDX composite will be absorbed by KHCO_3 . KHCO_3 is more efficient in inhibiting the decomposition of HTPB/RDX composite than KCl and LiF.

An endothermic reaction peak for LiF and KHCO_3 (LiF/ KHCO_3 = 50 : 50 by weight) mixtures appears at 222 °C. Comparing the endothermic reaction temperature of pure KHCO_3 (230 °C) and the mixtures of LiF/ KHCO_3 (50 : 50 by weight, at 222 °C), it is shown that the endothermic reaction temperature of KHCO_3 was affected by LiF. In order to understand the combined effect of LiF and KHCO_3 on the HTPB/RDX composite decomposition reaction, LiF/ KHCO_3 were added in various ratios as ingredients to the HTPB/RDX composite. As shown in Fig. 7, it is found that T_m for the first step decomposition reaction decreased as the concentration of KHCO_3 increased. But as the concentration of KHCO_3 exceeded 35%, there was no remarkable change in the T_m value. The T_m value of composite material B-3 (40% KHCO_3) is 183 °C. Comparing with composite material C-1 (35% KHCO_3 , $T_m = 184$ °C), this conclusion is proved. In Table 2, referring to the second exothermic reaction temperature of formulations C-1 to C-5, it is found that more effective inhibition is obtained for the second-step exothermic reaction of HTPB/RDX composite and T_m for the second-step exothermic reaction shifts to higher temperature, by 30 °C, as the weight percent ratio of LiF : KHCO_3 approaches one. It is concluded that the occurrence of the second exothermic reaction might be affected by the weight ratio of LiF : KHCO_3 . A suitable LiF/ KHCO_3 ratio supplies more energy required by the second exothermic reaction. In order to prove the correctness of this explanation and to distinguish between the combustion of the first and the second step exothermic reactions, special DSC test processes were designed and performed as follows.

Process 1

When the DSC temperature had been raised to the first exothermic reaction temperature, T_m the DSC testing process was kept at this temperature and the sequential reaction phenomena examined. Typical results are shown in Fig. 3.

Process 2

The DSC temperature was raised to the first step exothermic reaction temperature, T_m , cooled to room temperature and then raised again. Typical results are shown in Fig. 4.

From Fig. 3, it may be concluded that no sequential reaction took place as the first step decomposition reaction occurred. It could be explained that the addition of LiF and KHCO_3 terminated the combustion reaction. Due to the maintenance of isothermal conditions the residue of the components cannot gain enough energy to enable the second step exothermic reaction to occur. From Fig. 4, it is clear that an exothermic reaction happened at 215°C on the first heating run. After quenching, there was no exothermic reaction at 215°C as the temperature was raised again. But at 344°C an exothermic reaction occurred. This result proves that the decomposed materials were different for the first and second steps. Furthermore, it proves that LiF or KHCO_3 , secondary flame inhibitors, can completely extinguish secondary combustion.

Referring to Fig. 5, it is apparent that the second exothermic reaction peak shifts to higher temperature and that the third exothermic reaction peak, which appeared on the first run, became less intense or disappeared. This may be explained by supposing that on cooling, the rearrangement of extinguished species may occur and a new material may be formed. Therefore, the original second and third exothermic reactions are changed. Figure 6 shows the TG-DTG results for HTPB/RDX composites. The TG-DTG trace of HTPB/RDX composite indicates that the composite with inhibitor has one major and two minor weight loss stages. At the minor stage the weight loss rate is low. TG-DTG traces of HTPB/RDX composite without inhibitor indicate that this composite has one major weight loss stage and one minor weight loss stage. Figure 6 shows that during the minor weight loss stage the weight loss rate of composite without inhibitor (1.5 mg min^{-1}) is larger than that of composite with inhibitor (1.2 mg min^{-1}). It can be concluded that the inhibitor retards the decomposition reaction of HTPB/RDX composite.

The typical detonation results for energetic composites, recording the dependence of flame intensity on time during detonation, are shown in Fig. 8. It is found that the flame intensity of HTPB/RDX composite was reduced by adding KCl, LiF or KHCO_3 . In addition, the intensity of the secondary flame of the energetic composite has a good correlation with the secondary exothermic temperature of the same composite in DSC measurements. The retarding effect of a LiF/ KHCO_3 mixture on the second flame reaction is larger than that of a mono-salt such as LiF or KCl only. In studies on the retarding behaviour of a LiF/ KHCO_3 mixture, it was found that the secondary flame intensity decreased as the KHCO_3 percentage was increased. The secondary flame intensity approached zero as the weight ratio

of KHCO_3/LiF approached one. The secondary flame was inhibited completely if a suitable inhibitor was used in the energetic composite.

The results show that KCl , LiF or KHCO_3 retard the secondary flame of HTPB/RDX composite and that the mixture of KHCO_3 and LiF (21:20 wt.%) retards the secondary flame completely. Comparing the flame intensity results with the DSC measurements, it is obvious that the salts inhibit the secondary flame, as the second exothermic reaction peak of the energetic composite shifts to a higher temperature in the DSC measurement. In addition, on DSC measurement, the reaction heat of first, second or other exothermic reaction stages must also be considered.

CONCLUSION

A convenient method for the evaluation of the effectiveness of inorganic salts on the elimination of the secondary flame of energetic composite was found from DSC measurements. If the secondary exothermic peak from DSC measurements is shifted to higher temperature by more than 30°C as inorganic salt is added to the energetic material, then the salt may be judged to be a good inhibitory material.

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