Role of Silicon in Boron-Potassium Nitrate System

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ABSTRACT

To examine the possibility of improving the ignition characteristics of the commonly used pyrotechnic ignition system based on B-KNO_3—Binder (30:70:10), B was gradually replaced by Si in its composition. The addition of Si was found to reduce the maximum pressure and increase the ignition delay. Maximum dp/dt value was observed with the composition containing 5 per cent Si. The differential thermal analysis results showed single sharp peaks for ignition in the temperature range 500-570 °C. The heat of combustion and burning rate decreased with increase in Si content. Impact sensitivity of the compositions increased with increase in the percentage of Si, whereas no change was observed in the friction sensitivity in comparison with the base composition.

1. INTRODUCTION

Ignition of the rocket motor is an important and vital parameter. For the ignition of solid rocket propellants, wide use of B-KNO_3-based pyrotechnic ignition compositions has been reported. De Yong, et al[1] studied the reaction mechanism using the differential scanning calorimeter technique. Heat of explosion and adiabatic flame temperature data were reported by Volk, et al[2]. Brassy and coworkers[3] studied the thermal diffusivity of B-KNO_3-based pyrotechnic ignition compositions. A series of compositions containing 5-70 per cent B were studied by Charsley, et al[4,5] employing differential thermal analysis (DTA), combustion calorimetry and time-to-ignition techniques.

Laye and Charsley[6] have reviewed the information available on thermal analysis of pyrotechnics. Si-KNO_3 system was studied for temperature profiles. The temperature profile showed a smooth rise to a maximum temperature in the range 1000-1300 °C, except for the

composition with low (< 30 per cent) Si content[7]. From thermal analysis and temperature profile measurements, these workers estimated the kinetic parameters for the processes occurring during controlled heating and combustion of binary Si-fueled pyrotechnic systems[8].

Studies on the combustion of Si-KNO_3 system were extended to examine the behaviour of ternary systems. The effect of substituting calcium silicide ($CaSi_2$) by ferrosilicon ($FeSi_2$) for some or all the Si present in the systems was examined[9].

B-KNO_3 igniter composition was, however, found ineffective for ignition of fuel-rich type propellants which need a prolonged heat flux. Si containing pyrotechnic compositions are known to form slags which could provide the necessary supply of prolonged heat flux. Hence, it was considered of interest to examine the effect of partially substituting B by Si. A composition containing 30 per cent B was chosen as the base composition, to which Si was added gradually in increments of 5 per cent. The effect of adding Si
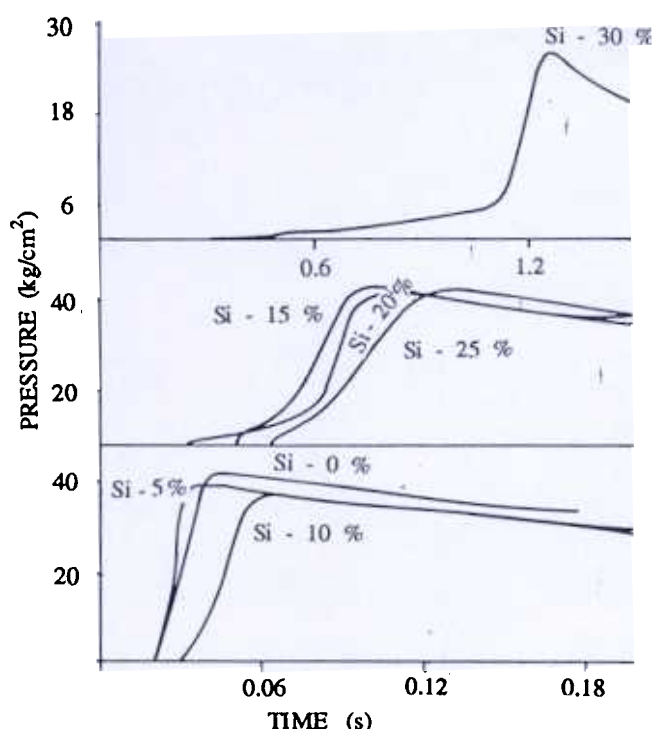
Figure 1. P-T curves for *B/KNO₃/PEC* system

was studied by DTA, Fourier transform infrared (FTIR), X-ray diffraction (XRD) techniques and by determining the calorific values burning rate and pressure-time (P-T) profiles.

2. EXPERIMENTAL DETAILS

2.1 Materials

The materials used were KNO_3 (laboratory grade, particle size 90 · μ), B powder (average particle size 0.7 μ), Si powder of high purity (average particle size 4 μ) and plasticised ethyl cellulose (PEC) (Hercules Co., type N-200).

2.2 Preparation of Composition

KNO_3 was dried at 110 °C and passed through 90 μ sieve. It was then mixed with B and the mixture passed through 600 μ sieve three or four times. To this mixture, 10 parts of PEC in distilled toluene was added. This mixture was further granulated using a' screen. The granules passing through 600 μ sieve and retaining on 300 μ sieve were selected for further work. Further, a mixture

was prepared by substituting β by Si, each batch being about 400 g.

2.3 Measurements of Pressure-Time Profiles

Loose granules (7 g) were burnt' in a closed combustion chamber of 'capacity 700 cc. For this experiment, the sample was loaded in a small cotton bag in which a squib was embedded and desired current was passed for ignition. The pressure produced on combustion, and the ignition delay, were measured as a function of time. The signals were transferred to an oscilloscope and the main computer for recording P-T history. The P-T profile gave values of parameters like maximum pressure, burning time for maximum pressure and ignition delay.

DTA curves of these mixtures were recorded on an indigenously-fabricated DTA apparatus using 5 mg sample with 10 °C/min as the rate of heating. The reaction exothermicities were measured in air at 1 atm by burning these samples in a Julius Peter adiabatic calorimeter bomb. The burning rates of the compositions were determined by the lead tube method.

The combustion products were analysed employing Perkin-Elemer FTIR spectrophotometer model 457 in KBr at room temperature. In addition, X-ray diffraction patterns were recorded on Phillips X-ray · diffractometer at room temperature. Sensitivity to impact was measured using a fall hammer· apparatus fabricated in the laboratory using a 2- kg drop weight and a sample weight of 20 mg. Bruceton staircase method was used to carry out the test from which the height of 50 per cent explosion was determined.

Sensitivity towards friction was determined using a Julius Peter friction sensitivity apparatus.

3 RESULTS & DISCUSSION

3.1 Combustion Pressure in Closed Vessel

The pyrotechnic compositions were subjected to ignition in a closed vessel at 1 atm. The P-T profiles obtained for all compositions along with that for the base composition ($B:KNO_3$:PEC: :30:70:10) are presented in Fig. 1. The values for

Table 1 : Pressure-time data (X % ,Y %, 70 % KNO_3 and 10 parts PEC)

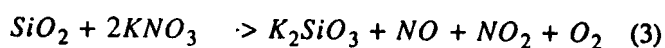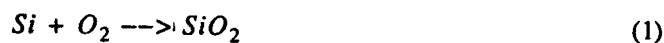| X B (%)	Y Si (%)	P_{max} (MPa)	Ignition delay (ms)	Burning time up to P_{max} (ms)	dp/dt I (kg/cm²/s)	dp/dt II (kg/cm²/s)
30	0	4.25	24	21	2017	
25	5	4.15	22	14	3024	
20	10	3.83	32	28	773	1880
15	15	3.76	58	42	363	
10	20	3.59	6	48	122	
5	25	3.49	75	58	306	
0	30	2.55	955	310	5	11

P_{max} ignition delay, *dp/dt*, eto. are given in Table 1. It is observed that by substituting *Si*, the maximum pressure decreases with increase in *Si* content. The base composition and the composition containing 5 per cent *Si* showed sharp peaks, while the remaining compositions showed two steps in the ignition transient. A composition containing 30 per cent *Si* gave pressure which is nearly half of the base composition. The composition containing 5 per cent *Si* was observed to have the least ignition delay value. Beyond 5 per cent, the ignition delay increased with increase in *Si* content (Fig. 2). The presence of *Si* particles supports the combustion phenomenon for 5 per cent *Si* composition in which combustion of *B* takes place very fast. This is also reflected in the values of burning time to maximum pressure.

The composition having 5 per cent *Si* has the least burning time (14 ms) to maximum pressure after which the burning time to maximum pressure

goes on increasing with further addition of *Si* particles. Krishnamohan, *et al*[10] found the compositions containing more than 40 per cent *Si* to have ignited in lead tube experiments. This indicates that even 30 per cent *Si*—70 per cent KNO_3 composition ignites in the closed vessel testing.

The *dp/dt* value of the base composition is 2017.7 kg/cm²/s, while that for 5 per cent *Si* composition is 3024.3 kg/cm²/s. The latter value of *dp/dt* shows that the reaction rate of the composition with 5 per cent *Si* is faster than that of the base composition. The oxidation of *Si* and *B* takes place simultaneously and hence it has lower ignition delay and burning time values, leading to higher *dp/dt* values. The *dp/dt* values indicate that the first reaction is due to the oxidation of *Si* and the second one due to the oxidation of *B*. With increase in *Si* content in the composition, the reaction is observed to slow down. This can be· explained as follows:

The oxidation of *Si* takes place at 400 °C to give SiO_2 and that of amorphous *B* takes place at 700 °C to give B_2O_3[11]. These reactions are:

$$Si + O_2 \longrightarrow SiO_2 \tag{1}$$

$$4B + 3O_2 \longrightarrow 2B_2O_3 \tag{2}$$

$$SiO_2 + 2KNO_3 \longrightarrow K_2SiO_3 + NO + NO_2 + O_2 \tag{3}$$

The products obtained from these reactions produce hot slag, which strikes on the propellant
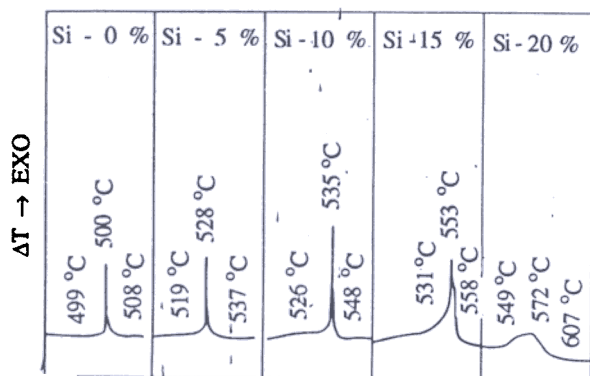

Figure 2. DTA curves for *B/KNO₃/PEC* system

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Table 2. Calorific value, burning rate and sensitivity test (X %, Y %, 70 % KNO_3 and 10 parts PEC)

X B (%)	Y Si (%)	Calorific value (cal/g)	Burning rate (mm/s)	Friction (kg)	Impact (cm)
30	0		7.03	36	122
25	5		6.90	36	84
20	10	1529	5.01	36	93
15	15	1508	3.78	36	90
10	20	1402	.91	36	72
5	25	1382	.73	36	70
0	30	1158	Not ignited	36	63

surface and ignites the propellant even at low temperatures. The pyrotechnic composition containing 5 per cent Si only could ignite a fuel-rich propellant (conditioned at -20 °C for 8 hr), while the base composition failed to ignite this fuel-rich propellant.

3.2 Differential Thermal Analysis

The DTA of amorphous B shows a single broad exothermic peak at 697 °C, which is attributed to the oxidation of B in air. It always forms stable B_2O_3. The DTA of KNO_3 shows an endothermic peak at 130 °C, which is due to phase transition from orthorhombic to triagonal structure. The second endothermic peak at 334 °C is attributed to the melting of KNO_3. It shows a broad exothermic peak in the range 547-647 °C which is due to the decomposition of KNO_3. This is in conformity with the one reported in literature[12].

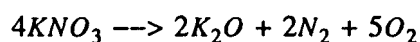$$4KNO_3 \longrightarrow 2K_2O + 2N_2 + 5O_2$$

Figure 2 shows the DTA curves of $B:KNO_3:PEC$ system and the compositions containing varying percentages of Si. The base composition shows a single sharp exothermic peak at 500 °C, which could be due to the ignition reaction. The DTA curves of the main reaction are
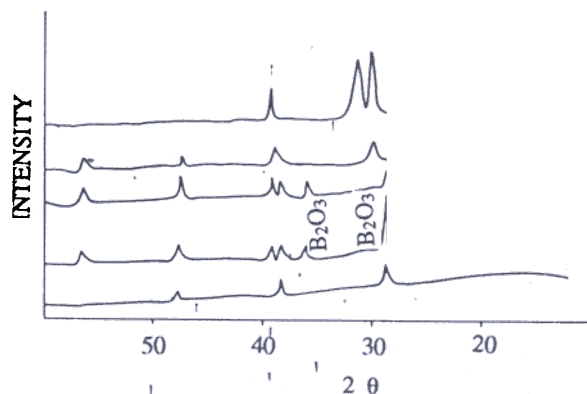

Figure 3. XRD patterns of slag containing % Si in $B/KNO_3/PEC$ system.

shown in Fig. 2; the other peaks at 130 and 334 °C are deleted. It is noted that the ignition reaction occurs at a lower temperature than the air oxidation of B. This is due to oxygen available from KNO_3, which leads to a spontaneous reaction.

The peak temperature is observed to increase with increase in Si content. The reaction of the composition containing 5 per cent Si starts at 519 °C and gets completed at 537 °C. The inception temperature increases with increase in Si content. The peak width also increases and then finally the reaction does not show a spontaneous nature.

4. HEAT OF COMBUSTION

The heat of combustion was determined in air at 1 atm in a bomb calorimeter. The values obtained are given in Table 2. The value of heat of combustion of the base composition is 1696 cal/g, while that of the composition containing 30 per cent Si is 1158 cal/g. Substitution of Si in the base composition lowers the heat content. As the heat of formation of SiO_2 is -202 kcal/mole and that of B_2O_3, -302 kcal/mole, the net heat of reaction for the oxidation of B is higher than that for the oxidation of Si.

4. Rate of Burning

Data on rate of burning determined by the lead tube method are given in Table 2. The burning rate of the base composition is 7.03 mm/s. On adding

Table 3. FTIR data for slags of B-KNO_3 -PEC

Si, %	Frequency cm^{-1} and assignments							
20	3500	2360	1712	1426	1004	832	704	458
	OH	B-H	B-H-B	B-N	B_4O_7	SiO_2	SiO_2	SiO_2
15	3502		1710	1426	1004	832	704	646
	OH		B-H-B	B-N	B_4O_7	SiO_2	SiO_2	SiO_2
				1336	940			
				B-O				
10	3444				1002	834		
	OH				B_4O_7	SiO_2		
				1384				
				B-O				
5	3442			1384	996			
	OH			B-O	B_4O_7			
0	3440			1382	1004			
	OH			B-O	B_4O_7			

Si to the base composition, the burning rate gradually decreases from 7.03 to 1.73 mm/s. This can be correlated with the oxidation processes which are not the same. The oxidation of Si is slow, as compared to that of B.
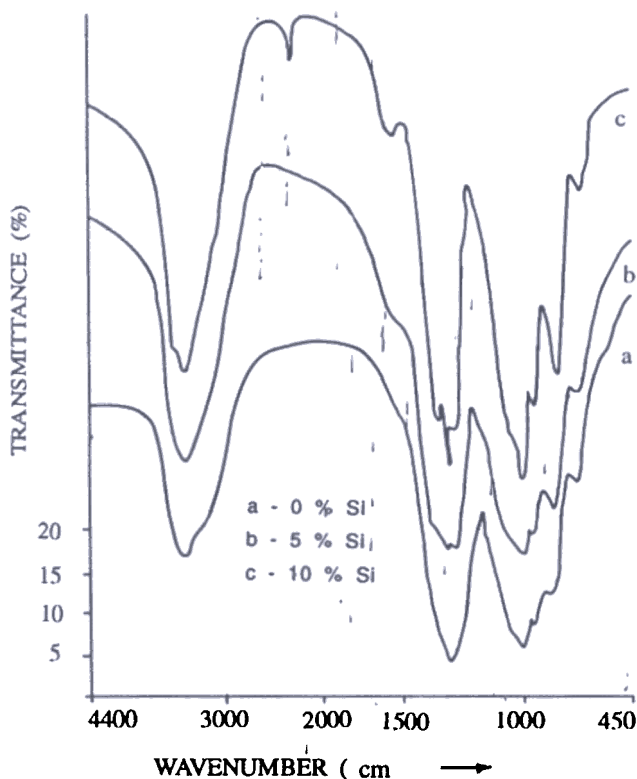
Figure 4. FTIR spectra of slags of B/KNO_3/PEC system containing Si.

5. X-RAY DIFFRACTION & FTIR

The slags obtained in the combustion calorimetry experiment, were analysed by X-ray diffraction to identify the final products of the combustion reactions. X-ray diffraction patterns obtained are shown in Fig. 3. The 'd' values of the corresponding products compared with standard ASTM data cards[13] are:

Compound	d (Å)
B_2O_3	3.2177 and 2.5066
KBO_2	3.0354, 2.8115
KB_5O_8	5.9804, 4.5026, 3.5036, 2.9568
SiO_2	1.515
$K_6Si_3O_9$	6.5053, 3.0335, 3.1291

From these data, only crystalline materials are identified. Further analysis was carried out employing FTIR spectroscopy. FTIR spectra of the same slags are shown in Fig. 4 and the values of frequencies along with assignments are given in Table 3. In all cases, hydrated salts of B and Si were identified. This indicates the formation of compounds like KBO_3 and $SiO_2.K_2O$, B_2NO_2, free-silica and borohydrates. It is to be noted that only qualitative analysis of the products was done[14].

6. SENSITIVITY

The results of impact and friction sensitivity measurements are presented in Table 2. Composition 1 is found to be less sensitive to impact, and addition of Si increases its sensitivity. Composition 7 is highly sensitive in comparison to the other compositions. This is probably due to the hard surface of Si (4-6 μ), which might be behaving as grit. This grit type material might be increasing the sensitivity by generating heat in the composition.

The friction insensitivity of these mixtures was observed up to 36 kg. It can be seen that these compositions are not very sensitive to friction.

7. CONCLUSION

The present study reveals that the addition of Si to the B-KNO_3-based ignition system increases ignition delay, ignition temperature and impact sensitivity, while it decreases maximum pressure, heat of combustion and rate of burning.

A unique feature observed in this study is that the addition of 5 per cent Si causes maximum increase in dp/dt value compared to the base and other compositions.

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