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# Influence of Cellulosic Binders on Sensitivity and Combustion Behaviour of *B-KNO*$_3$ Ignition System

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**ABSTRACT**

Boron-potassium nitrate (*B-KNO*$_3$)-based compositions have been used as an effective igniter system for solid rocket propellants. A systematic study was undertaken to generate exhaustive data on *B-KNO*$_3$ (25:65)-based ignition systems with cellulosic binders, viz., nitrocellulose, ethyl cellulose and plasticised ethyl cellulose. In addition, detailed investigations were carried out with PEC as binder by varying its concentration from 2-10 per cent in the same system. The experimental compositions (*B-KNO*$_3$: binder) were evaluated by closed-vessel firing, thermal analysis, sensitivity, mechanical properties and cal-val determination. The binders significantly influenced the sensitivity and combustion behaviour of *B-KNO*$_3$ compositions. The composition with nitrocellulose as binder produced high flame temperature and cal-val as compared to ethyl cellulose and plasticised ethyl cellulose-based compositions. The data indicated that the calculated flame temperature for all compositions was in the range 2716 K to 2957 K. As the plasticised ethyl cellulose content increased from 2 per cent to 10 per cent, the maximum pressure increased with decrease in heat of combustion.

**Keywords:** Ballistic properties, cal-val, thermal analysis, sensitivity, binders, ignition system, solid rocket propellants, rocket propellants, nitrocellulose, cellulogic binders, combustion behaviour

## 1. INTRODUCTION

The quality and reliability of the performance of pyrotechnic igniter compositions are critical in the ignition of solid rocket motor and gas generators. Earlier research work carried out on igniters focused mainly on metal powders and oxidisers without much attention on the role of binders and their effect on the performance of pyrotechnic compositions[1-3]. Of late, the use and application of binders in pyrotechnic compositions has increased, particularly for magnesium- and titanium-based pyrotechnic compositions, due to their influence on burn rates, cal-val and other performance parameters have been determined for these compositions[4-6]. The behaviour of six different types of binders, namely phenol-formaldehyde resin, shellac, polyvinylchloride, ethylcellulose, nitrocellulose, and fluorel has been studied by Barisin[7], *et al*. with magnesium- boron- and aluminium-based igniter compositions.Their findings indicate that the nature of binder influences burning characteristics of igniter compositions significantly. Kalontarov[8], *et al*. have studied the effect of viton introduction on the chemical reactivity of boron-calcium chromate ignition compositions by thermal analysis and equilibrium thermodynamic calculations. They have found that

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viton induced an additional weight loss and exothermic peak at 490 °C. However, very little or practically no information on comparative effect of binders alone, plasticised binders and their concentration in composition, on heat output, ballistic properties, sensitivity, and processing is available in the literature. In addition, systematic research work is essential to study the effect of degradation of binders on the kinetic and ballistic properties of igniter compositions. Hence, the present work was undertaken to study the above aspects on $B$-$KNO_3$ system. Both energetic and non-energetic cellulosic binders like nitrocellulose (NC), ethyl cellulose (EC) and plasticised ethyl cellulose (PEC) were used in $B$-$KNO_3$ system. During present investigation, data on ballistic performance, sensitivity aspects, mechanical properties, etc were also generated. Since PEC-based compositions were found to be promising, further work was extended to optimise the percentage of PEC binder in $B$-$KNO_3$ system. Thermal studies, ballistic performance evaluation and sensitivity studies along with mechanical property determination were also conducted for pyrotechnic composition.

## 2. EXPERIMENTAL PROCEDURE

### 2.1 Materials

Amorphous boron (purity > 97 % particle size < 1 μm) of Ecka UK, potassium nitrate ($KNO_3$) Gr-1 (particle size < 90 μ), EC (type N-200) from Hercules Co, NC type A (nitrogen content 12 %) and analytical grade of diethylphthalate and toluene were used for processing igniter compositions. The EC was plasticised by diethylphthalate in the ratio of 77.5 : 22.5 using water as the medium.

### 2.2 Preparation of Composition

$KNO_3$ was dried at 110 °C and passed through 90 μm sieve. Boron powder and $KNO_3$ were weighed accurately as per the requirement and passed (three-times) through 600 μm sieve for uniform mixing. To this dry mix, 10 per cent NC or EC or PEC binder solution dissolved in distilled toluene was added. These mixtures were granulated, passing through 600 μm sieve and retained on 300 μm sieve.

### 2.3 Evaluation of Igniter Compositions

Thermodynamic parameters of igniter compositions at equilibrium were calculated using REAL program at constant volume[9]. Parr adiabatic bomb calorimeter of 300 cc capacity was used to determine the cal-val of the pyrotechnic compositions in static air.

For ballistic performance evaluation, igniter compositions were fired in 700 cc closed vessel with loading density of 0.01 g/cc and pressure-time profiles were recorded. Linear burn rates of igniter compositions were determined by lead tube method.

Thermal analysis of igniter compositions was carried out on STA Mettler Toledo Star System at a heating rate of 10 °C/min in atmospheric condition. Solid combustion products were analysed using Perkin-Elmer FTIR spectrophotometer (model-1605), in KBr at room temperature. Fall Hammer apparatus was employed to measure impact sensitivity (2 kg drop weight), and sensitivity to friction was measured on Julius Peters apparatus (20 mg sample). Sensitivity to spark was determined by placing 10 mg sample between two electrodes at a distance of 2.0-2.5 mm with 15 mJ to 5 J energy. The mechanical properties of the pellets (20 x 20 mm size) were determined using Instron UTM (model-1185) as per ASTM method[10].

## 3. RESULTS & DISCUSSIONS

### 3.1 Theoretical Calculations

Thermodynamic and chemical equilibrium calculations were carried out using REAL computer program at constant volume and zero internal energy. The results of flame temperature, pressure, enthalpy and entropy are given in Table 1.

It can be seen from the results presented in Table 1 that the flame temperature of binary mixture ($B$-$KNO_3$) and NC-based composition were almost the same, while flame temperature ($T_f$) of EC and PEC-based compositions decreased significantly. With the incorporation of binder, the maximum pressure, however, increased considerably as compared to that of control composition, probably due to the formation of $CO_3$, $CO$ and $H_2$. The impetus of the

**Table 1. Thermodynamic parameter of $B$-$KNO_3$ system with different binders**

| Binder (%) | Flame temp. ($T_f$ k) | Pressure (MPa) | Enthalpy H (kJ $kg^{-1}$) | Entropy S (kJ $kg^{-1}$ K) | Heat capacity (Cp) ($Jg^{-1}$ k) | Impetus ($Jg^{-1}$) |
|---|---|---|---|---|---|---|
| $B$-$KNO_3$ (control) | 2946 | 3.35 | -3195 | 6.2 | 1.4 | 334 |
| NC 10.0 | 2957 | 4.21 | -3028 | 6.7 | 1.4 | 421 |
| EC 10.0 | 2727 | 4.20 | -3107 | 6.9 | 1.5 | 420 |
| PEC 10.0 | 2716 | 4.15 | -3114 | 6.8 | 1.5 | 414 |
| PEC 7.5 | 2799 | 3.98 | -3130 | 6.7 | 1.5 | 397 |
| PEC 5.0 | 2858 | 3.78 | -3149 | 6.6 | 1.5 | 378 |
| PEC 2.0 | 2914 | 3.53 | -3175 | 6.4 | 1.4 | 352 |

binder-containing compositions also increased by 90 units. To study the optimisation of PEC-based binder, the effect of various concentrations was studied. As the binder content decreased from 10-2 per cent, the flame temperature increased gradually, as expected. Proportionately, the impetus values also decreased linearly (414 $Jg^{-1}$ to 352 $Jg^{-1}$).

The predicted combustion species of pyrotechnic compositions and their concentrations at equilibrium are given in Table 2.

With inclusion of binders, gaseous species like $CO$, $H_2$ and $HBO$ were formed. As can be expected, NC-based composition showed a maximum amount of $N_2$, whereas non-energetic binder-based compositions showed higher percentage of $CO$, $H_2$ and $HBO$.

The formation of combustion products like $B_2O_2$, $B_2O_3$ and $KBO_2$ were confirmed by analysing slag using FTIR spectroscopy (Fig.1). The solid combustion products of all compositions showed peaks at 1312 $cm^{-1}$, corresponding to $B$-$O$ linkage, at 1004 $cm^{-1}$ and 3500 $cm^{-1}$ for $OH^{-1}$ group[11](Fig.1). In all the cases, oxides of boron and hydrated salts of boron were identified.

### 3.2 Ballistic Properties

The igniter compositions were subjected to closed-vessel evaluation at loading density 0.01 g/cc to obtain the information on maximum pressure ($P_{max}$), ignition delay, burning time up to maximum pressure ($B_t P_{max}$) and rate of change of pressure ($dP/dt$). The results are presented in Table 3.

The results of closed-vessel firing (Table 3) indicate that binder-containing compositions produced higher peak pressure as compared to control, as theoretically predicted. Ignition delay was invariably much lower for binder-based compositions (13-35 ms) as compared to the control (60 ms). Burn rates were higher for NC-based pyrotechnic compositions (11.6 mm/s) as compared to EC and PEC-based formulations (6-7 mm/s) due to energetic nature of the former. Likewise, cal-val were higher for NC-based formulations and decreased proportionately with inclusion of inert binder (EC and PEC).

The presence of energetic group - $ONO_2$ in polymer gave high energy release as oxygen was weakly bonded to the nitrogen in this group. Therefore, it increased both cal-val and flame temperature.

**Table 2. Concentration of chemical species formed at equilibrium (mol/kg) ($B$-$KNO_3$)-binder**

| Binder % | $B_2O_2$ | $B_2O_3$ | $BO$ | $CO$ | $H_2$ | $HBO$ | $KBO_2$ | $N_2$ |
|---|---|---|---|---|---|---|---|---|
| $B$-$KNO_3$ (control) | 3.95 | 0.27 | 0.27 | -- | -- | -- | 6.15 | 1.86 |
| NC 10.0 | 3.82 | 0.25 | 0.44 | 2.26 | 1.02 | 0.70 | 5.47 | 2.02 |
| EC 10.0 | 2.03 | 0.12 | 0.15 | 4.71 | 3.75 | 0.87 | 5.54 | 0.28 |
| PEC 10.0 | 1.96 | 0.12 | 0.15 | 4.86 | 3.53 | 0.82 | 5.55 | 0.26 |
| PEC 7.5 | 2.42 | 0.15 | 0.22 | 3.64 | 2.52 | 0.81 | 5.65 | 0.55 |
| PEC 5.0 | 2.86 | 0.18 | 0.28 | 2.44 | 1.59 | 0.72 | 5.78 | 0.91 |
| PEC 2.0 | 3.44 | 0.22 | 0.37 | 0.97 | 0.52 | 0.47 | 5.98 | 1.43 |

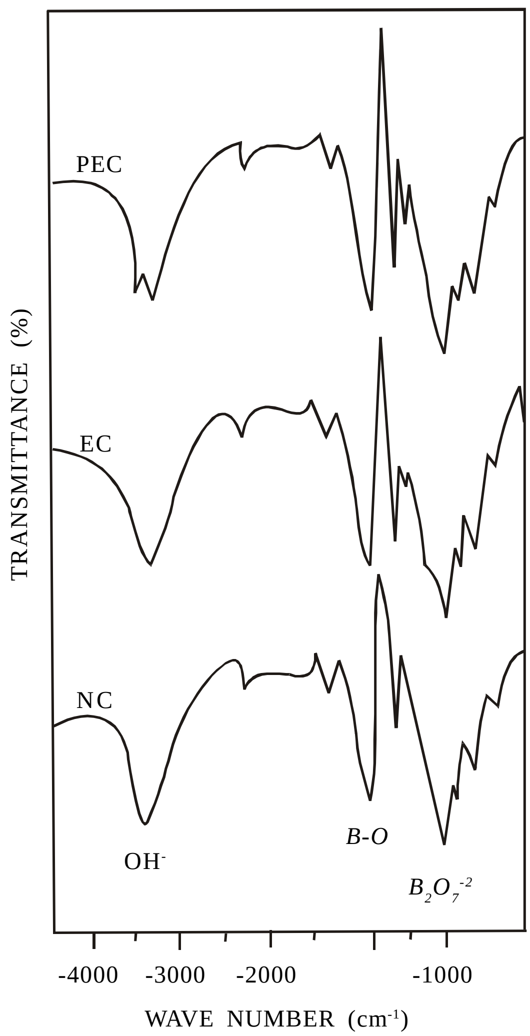


**Figure 1. IR spectra of solid combustion products of *B-KNO*$_3$ system with different binders.**

These results are in agreement with the findings of Russel[13].

### 3.3 Thermal Analysis

Results of thermal analysis are presented in Table 4 and are depicted in Figs 2 to 7. TG/DTA of all pyrotechnic compositions were carried out to understand their combustion behaviour. DTA curve of binary mix $B\text{-}KNO_3$ (Fig. 2) registered two endothermic peaks, first at 136 °C for crystalline transition of $KNO_3$ from orthorhombic to trigonal, while second at 333 °C for melting of $KNO_3$. A small exothermic peak was observed at 496 °C, which may be attributed to surface oxidation of boron into $B_2O_3$, *BO*, etc. which further enhanced into a single sharp exothermic peak at 518 °C for ignition of boron in the presence of oxidiser. The TG of the binary mix showed a continuous weight gain of about 12 per cent up to 487 °C due to oxidation of boron. As the temperature increased, the oxide layer of boron was separated, resulting into a highly exothermic reaction with a weight loss of 7.5 per cent in the range 489–587 °C. The activation energy calculated for weight loss of binary mix was 113 kcal/mol.

TG curve of $B\text{-}KNO_3\text{–}NC$ (Fig. 3) composition showed single-stage weight loss of about 10 per cent in the temperature range 462–547 °C. The activation energy, as calculated from TG curve, was 37 kcal/mol. The DTA curve (Fig. 3) of this mix had a sharp exothermic peak at 515 °C with a shoulder at 484 °C due to oxidation of fuel.

Fig. 4 shows DTA curves of $B\text{-}KNO_3$ compositions containing 10 per cent EC and PEC. These compositions registered two exothermic peaks, first at 225 °C

**Table 3. Results of ballistic properties, burn rate, and cal-val of *B-KNO*$_3$ system with different binders**

| Binder % | $P_{max}$ (MPa) | $BtP_{max}$ (ms) | Ignition delay (ms) | $dP/dt$ (kg/cm$^2$/s) | Burn rate (mm/s) | Cal-val (cal/g) |
|---|---|---|---|---|---|---|
| $B\text{-}KNO_3$ (control) | 3.06 | 27.0 | 60.0 | 3274 | -- | -- |
| NC 10 | 3.53 | 13.0 | 13.0 | 5940 | 11.6 | 1966 |
| EC 10 | 4.37 | 15.6 | 26.6 | 3558 | 5.9 | 1768 |
| PEC 10 | 4.40 | 14.3 | 21.6 | 3624 | 6.5 | 1772 |
| PEC 7.5 | 3.88 | 11.0 | 31.4 | 3822 | 6.7 | 1801 |
| PEC 5 | 3.78 | 12.0 | 34.6 | 4239 | 6.9 | 1881 |
| PEC 2 | 3.54 | 13.0 | 23.3 | 4453 | 10.0 | 1920 |

**Table 4. Results of thermal analysis *B-KNO*$_3$ system with different binders**

| Binder % | Stage | Wt. loss (%) | Temp. range (°C) | Activation engery (kcal/mol) | Endothermic peak (°C) | Exothermic peak (°C) |
|---|---|---|---|---|---|---|
| *B-KNO*$_3$ | I | 12 % Wt. Gain | Up to 487 | -- | 136 | 496 |
| (control) | II | 7.5 % | 489-587 | 113 | 333 | 518 |
| NC 10.0 | I | 10.7 | 462- 547 | 37 | 137 | 484 |
| | | | | | 334 | 515 |
| EC 10.0 | I | 6.2 | 239-342 | 15 | 137 | 255 |
| | II | 15.1 | 482-531 | 169 | 334 | 496 |
| | | | | | | 515 |
| PEC 10.0 | I | 6.3 | 238-347 | 14.0 | 137 | 255 |
| | II | 14.9 | 477-528 | 194 | 334 | 495 |
| | | | | | | 527 |
| PEC 7.5 | I | 5.3 | 240-362 | 15.0 | 136 | 257 |
| | II | 14.6 | 472-528 | 140.0 | 334 | 496 |
| | | | | | | 527 |
| PEC 5.0 | I | 5.0 | 239-360 | 15.9 | 136 | 255 |
| | II | 14.4 | 475-544 | 128 | 334 | 495 |
| | | | | | | 517 |
| PEC 2.0 | I | 13.6 | 477-537 | 114 | 136 | 487 |
| | | | | | 333 | 514 |

followed by main peak at 527 °C with a small shoulder at 496 °C. The TG curve showed two regions of weight loss (Fig. 5). Initially weight loss of 6 per cent was observed in the temperature range 238–347 °C, with activation energy 14–15 kcal/mole. The second weight loss was approx. 15 per cent in the temperature range 477–531 °C. Plasticisation of EC by diethylphthalate increased the activation energy of second-stage weight loss by 25 kcal/mole.

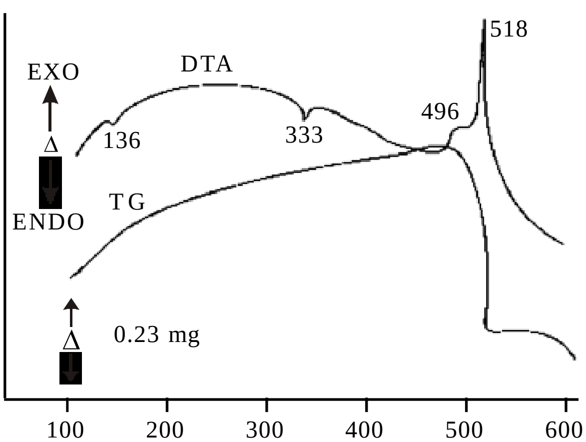


**Figure 2. STA curves of *B-KNO*$_3$ (1:1) atmohpheric static air, HR 10 °C/min.**

The STA curves (Figs 6-7) of all PEC-based compositions indicate that intensity of first exothermic peak (255 °C) and magnitude of first stage weight loss (238–360 °C) were decreased with the reduction in PEC content.

### 3.4 Sensitivity & Mechanical Properties

To ensure safe processing of the pyrotechnic compositions, these were tested for impact, friction,

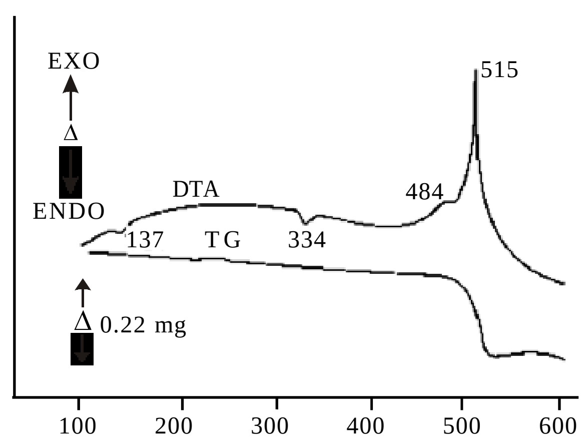


**Figure 3. STA curves of *B-KNO*$_3$–NC composition atmospheric static air, HR 10 °C/min.**

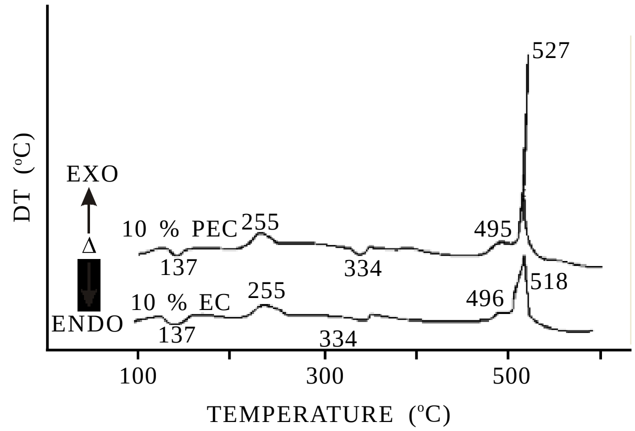


**Figure 4. DTA curves of *B-KNO*$_{33}$ system with different binders, HR 10 °C/min.**

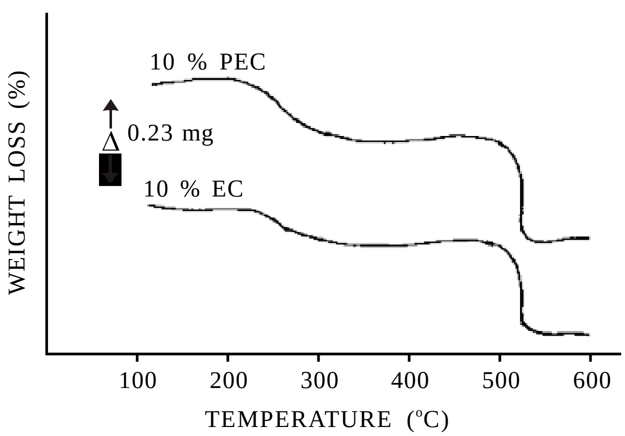


**Figure 5. TG curves of *B-KNO*$_3$ system with different binders, HR 10 °C/min.**

and spark sensitivity. The mechanical properties were determined to obtain information on the strength of pellets, and also to avoid the metalloid segregation problem. The results are given in Table 5.

All compositions studied were found to be insensitive to friction up to 36 kg and to spark up to 5 joule. *B-KNO*$_3$–NC composition was comparatively more sensitive to impact and showed crushing strength of 4.1 kg/cm$^2$. With the incorporation of EC, crushing strength increased marginally from 4.1 kg/cm$^2$ to 4.6 kg/cm$^2$. The compressive strength for EC- based composition was higher than that of NC-based pyrotechnic composition and plasticisation gave higher compressive strength than non-plasticised EC.

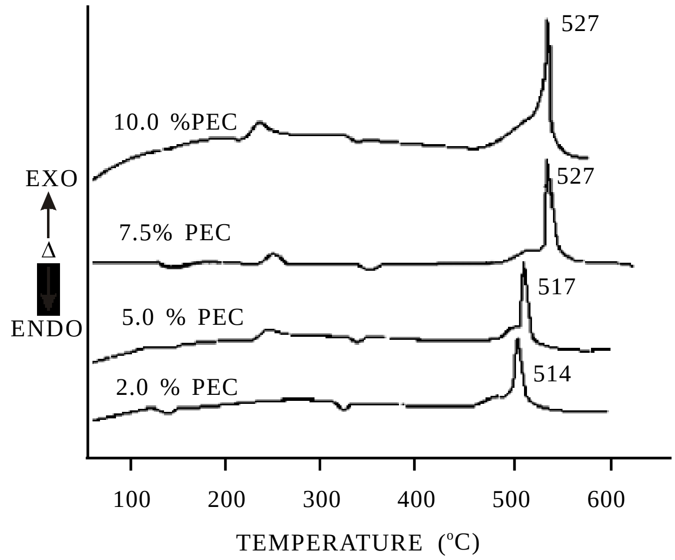


**Figure 6. DTA curves of *B-KNO*$_3$ system with various percentage of PEC binder atmospheric static air, HR 10 °C/min.**

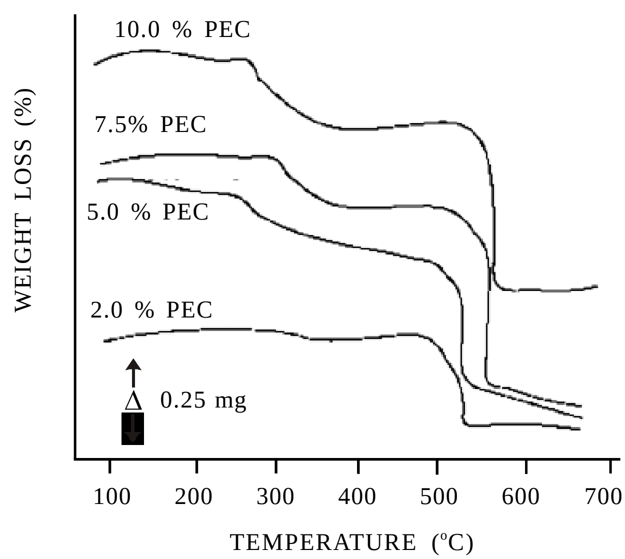


**Figure 7. TG curves of *B-KNO*$_3$ system with various percentage of PEC atmospheric static air, HR 10 °C/min.**

## 4. CONCLUSION

The three cellulosic binders have been studied using *B-KNO*$_3$ system successfully. The following conclusion have been drawn from the data:

- *B-KNO*$_3$-NC composition gave high cal-val and flame temperature with low ignition delay and high burn rates.

**Table 5. Results of sensitivity and mechanical properties of $B$-$KNO_3$ system with different binders**

| Binders % | Height of 50 % explosion (cm) | Crushing strength ($kg/cm^2$) | Compression (%) |
|---|---|---|---|
| $B$-$KNO_3$ (control) | 82 | -- | -- |
| NC 10 | 75 | 4.1 | 204 |
| EC 10 | 100 | 4.6 | 246 |
| PEC 10 | 113 | 5.7 | 269 |
| PEC 5 | 109 | 3.6 | 174 |
| PEC 2 | 84 | 3.1 | 105 |

- Plasticisation of EC improved the sensitivity and 10 per cent PEC produced better mechanical properties.
- All pyrotechnic compositions based on $B$-$KNO_3$– energetic and non-energetic binders, were insensitive to friction and spark.
- The efficiency of binder in wetting mix for granulation can be graded as PEC > EC > NC.

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