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Burn Rate Studies of a Titanium-Based Pyrotechnic Smoke Composition

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ABSTRACT

A pyrotechnic smoke composition producing titanium tetrachloride ($TiCl_4$) as one of the major reaction products has been studied. The composition consists of titanium metal powder, hexachloroethane (C_2Cl_6), potassium perchlorate ($KClO_4$) and titanium dioxide (TiO_2)/zinc oxide (ZnO). Pyrotechnic aluminium was added in small percentages to tailor the burn rate. The effect of percentage variation of $KClO_4$, TiO_2/ZnO, titanium and aluminium on the burn rate has been investigated. While, the burn rate decreases as the percentage of TiO_2/ZnO increases, it reaches a maximum as the percentage of $KClO_4$ is successively increased, but falls off on further increase. This maximum has been first fixed by studying the tricomponent system containing no oxide. It corresponds to 25 per cent $KClO_4$. Successive additions of C_2Cl_6 and ZnO in 1:3 mol ratio or C_2Cl_6 and TiO_2 in 2:3 mol ratio lead to cooler compositions that burn smoothly without much flame and at lower temperatures. Compositions containing less than 5 per cent titanium is difficult to ignite. Similarly, addition of excess titanium or small quantities of aluminium to the composition is found to increase the burn rate.

1. INTRODUCTION

Smoke is a general term used to denote dispersions of fine solid particles and tiny liquid droplets in air. Many compositions/substances have been developed for the artificial production of smoke. These are extensively used during day time signalling and for obscuring troops and equipment. Another important application is the production of smoke trails in the lower atmosphere for photographic investigations of wind shears needed for dynamic response and control studies of launch vehicles.

Many pyrotechnic mixtures, commonly called HC smokes, are known in literature[1]. These are generally based on zinc chloride ($ZnCl_2$) generation and often contain unburnt carbon as one of the reaction products, thus affecting the quality of smoke. The aim of the present study was to generate smoke based on titanium tetrachloride ($TiCl_4$) as a major reaction product. For this, titanium was used as fuel and hexachloroethane (C_2Cl_6) as chlorinating agent. Potassium perchlorate ($KClO_4$) was chosen as energiser and zinc oxide (ZnO) and titanium dioxide (TiO_2) as moderators. This paper deals with the studies conducted to identify the factors which control the quality of smoke and the rate of burning.

2. EXPERIMENTAL PROCEDURE

2.1 Materials

Titanium metal powder having an average particle size of 60 μm was procured from Metal

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Powder Co. Ltd., Madurai. Both ZnO and TiO_2 were of British Drug House (BDH) origin which had a percentage purity of 99 per cent (minimum) and with an average particle size of 50 µm. These moderators were used as such. C_2Cl_6 was supplied by Prabhex Aids, Pune (differential scanning calorimetry (DSC) m.p. 188 °C), which was sieved and passed through 150 BSS and the fraction retained on 350 BSS (average particle size: 80 µm) was used for further studies. $KClO_4$ with a purity of over 99 per cent was supplied by APEP, Alwaye. The fraction between 150 BSS and 350 BSS was collected by sieving and was used for preparing compositions (average particle size: 70 µm).

2.2 Methods

Mixtures were prepared from accurately weighed ingredients by proper mixing through a 120 BSS five times and paper folding. Charges were press-loaded to a column length of about 50 mm in steel tubes of 2.54 cm (diameter) × 10.16 cm (length) × 0.1 cm (thick) at 450 kg/cm^2 in small increments to minimise formation of density gradients along the charge column. A 24 standard wire gauge (SWG) silver-coated copper wire was inserted across the charge column at approx. 10 mm from the bottom during filling by passing through two-pin holes drilled on opposite sides of the steel tube and this acted as fuse wire. The charge was ignited with a squib and the time from firing of the squib to bridge wire fuse was monitored using an oscilloscope and burn rate computed using these data. All tests were carried out in duplicate and the variation was below 10 per cent. The quoted values are average of the two. For temperature measurements, 3 mm holes were drilled on the steel tubes prior to charge filling at 20 mm and 40 mm from the bottom, holes were suitably covered and after filling, small insertions were made into the charge through these holes, and tungsten-5 per cent rhenium versus tungsten-26 per cent rhenium thermocouples fixed inside ceramic alumina tubes were inserted into the charge at these two locations and bonded to the steel tubes using high temperature Omega ceramic cement. During charge combustion, the output from these thermocouples was given to a digital data acquisition system through an amplifier. The output voltage was converted to temperature, and the average of the two, which generally is well within 50 °C, is reported as combustion temperature.

3. RESULTS & DISCUSSION

It is known that titanium metal can react with chlorine to form $TiCl_4$. Similarly TiO_2 can be chlorinated if a reducing agent like carbon or aluminium is present. From the heat of formation values, the equations can be written as

$$Ti + 2Cl_2 \rightarrow TiCl_4 + 179\,\text{kcal} \quad (1)$$

$$TiO_2 + 2C + 2Cl_2 \rightarrow TiCl_4 + 2CO + 14\,\text{kcal} \quad (2)$$

So, if a source of chlorine is available, it should be possible to generate $TiCl_4$ according to the above reactions. For this, C_2Cl_6 was chosen as the chlorine source, since it can thermally decompose to liberate chlorine[2]. To carry out this reaction between C_2Cl_6 and oxide/metal, exothermicity of the reaction between Ti and $KClO_4$ was utilised. Thus the reactions are:

$$2Ti + KClO_4 \rightarrow 2TiO_2 + KCl + 436.6\,\text{kcal} \quad (3)$$

$$3TiO_2 + 2C_2Cl_6 \rightarrow 3TiCl_4 + 2CO_2 + 2CO + 16.8\,\text{kcal} \quad (4)$$

Adding, Eqns (3) and (4), one gets:

$$6Ti + 3KClO_4 + 4C_2Cl_6 \rightarrow 6TiCl_4 + 3KCl + 4CO_2 + 4CO + 1343.4\,\text{kcal} \quad (5)$$

From Eqn (5), the theoretical heat of reaction is 814 cal/g. This has been checked by carrying out ignition in an isoperibol Parr bomb calorimeter in argon atmosphere, which yielded a calorimetric value of 770 cal/g. The match is reasonably good and substantiates the theoretical prediction. Presence of $TiCl_4$ in the vapour/smoke was indirectly confirmed by H_2O absorption and precipitation as TiO_2 (identified by IR spectroscopy). The smoke generator was also flown in sounding rocket and smoke traced by ground station.

From the above, it can be inferred that heat liberated by reaction between *Ti* and $KClO_4$ [Eqn (3)] will be sufficient to carry forward reaction between titanium metal and C_2Cl_6 [Eqn (4)] and by adding extra oxide and C_2Cl_6 in the above ratio, it should be possible to moderate the reaction. These inferences have been verified by subsequent studies.

3.1 Effect of Potassium Perchlorate Percentage

For the tricomponent system ($Ti/KClO_4/C_2Cl_6$), the influence of the percentage of $KClO_4$ on burn rate has been determined. This has been done by varying the percentage of $KClO_4$ keeping the ratio between *Ti* and C_2Cl_6 constant (6:4 mol ratio). The results are presented in Fig. 1. It is seen that the rate shows a maximum value of 1.60 mm/s for 25 per cent $KClO_4$. This ratio corresponds to Eqn (5) when carbon is oxidised to *CO* and CO_2 in a 1:1 ratio.

When the ratio of $KClO_4$ is further increased, there is a gradual decrease in burn rate and as the ratio exceeds 31 per cent, the smoke becomes yellowish due to incomplete utilisation of chlorine. This is due to the competition between oxygen from excess of $KClO_4$ and chlorine to react with the metal. The reaction becomes sluggish due to the sharp decrease in heat of reaction and starts spurting. On the contrary, when the percentage of $KClO_4$ is on the lower side, the smoke becomes greyish due to incomplete oxidation of carbon and the burn rate falls down on account of lower heat of reaction.

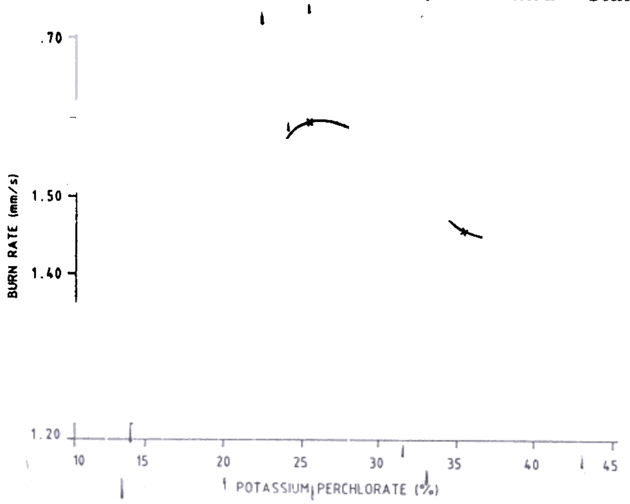

Figure 1. Effect of $KClO_4$ percentage on the burn rate of $Ti/KClO_4/C_2Cl_6$ smoke composition.

3.2 Effect of Addition of Titanium Dioxide to Tricomponent Smoke System

As was earlier stated, it could be possible to moderate the reaction rate and bring down the temperature and flame length by adding extra TiO_2 to the tricomponent ($Ti/KClO_4/C_2Cl_6$) smoke system. C_2Cl_6 should also be added along with the oxide so as to completely chlorinate all the oxide as per Eqn (4). This has been proved by successive additions of the bicomponent system in the mol ratio 3:2 (oxide:C_2Cl_6) to the smoke composition $Ti/KClO_4/C_2Cl_6$ (17.4:25:57.6). The results are shown in Fig. 2.

As was expected, there is a steady decrease in the burn rate as the percentage of TiO_2 was increased. A corresponding reduction in flame length was also observed. The quality of the smoke in terms of whiteness improved as the percentage of TiO_2 was increased. Thus compositions containing more than 13.5 per cent TiO_2 are white. This could be due to complete utilisation of all the chlorine because of lower reaction rate and temperature.

3.3 Effect of Addition of Zinc Oxide to Tricomponent Smoke System

Since normal HC-type smoke formulations are based on $ZnCl_2$ evolution, it was thought beneficial to study the effect of addition of *ZnO* to the tricomponent smoke composition. The reaction between *ZnO* and C_2Cl_6 can be written as

$$3ZnO + C_2Cl_6 \rightarrow 3ZnCl_2 + CO + CO_2 + 115\text{kcal} \quad (6)$$

Since this reaction is much less exothermic than the reaction between *Ti*, $KClO_4$ and C_2Cl_6 [Eqn (5)], addition of this mixture to the tricomponent system should be effective in bringing down the rate of overall reaction and

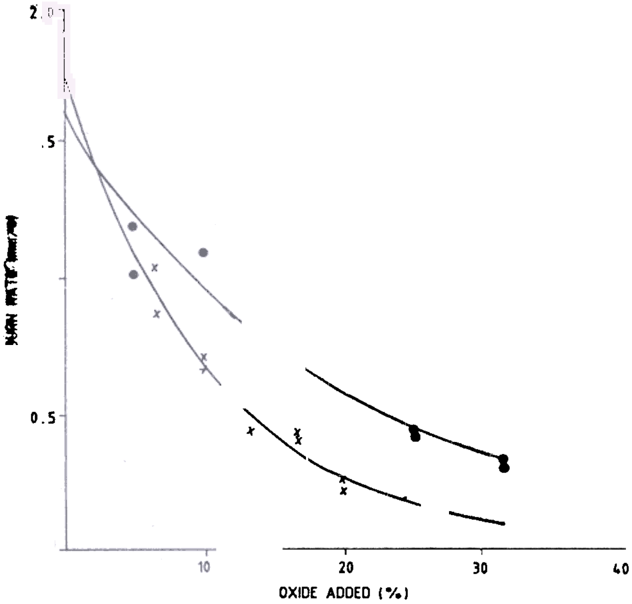

Figure 2. Effect of addition of • ZnO/C_2Cl_6 (3:1 mol ratio) and ×TiO_2/C_2Cl_6 (3:2 mol ratio) to the smoke composition $Ti/KClO_4/C_2Cl_6$ (17.4 : 25 : 57.6 wt per cent).

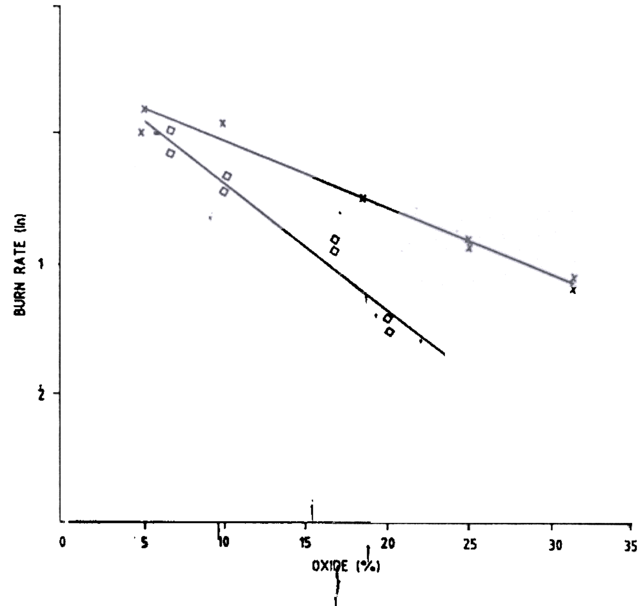

Figure 3. Plot of (burn rate) *vs* oxide percentage for $Ti/KClO_4/C_2Cl_6$/oxide smoke composition □ TiO_2 and × ZnO.

reducing flame length. The results are shown in Fig. 2.

As with TiO_2, there is gradual reduction in flame length and burn rate with successive addition, till it becomes almost flameless. The smoke is also quite white and copious. However, for the same percentage, effect of addition of ZnO is not as high as that of TiO_2 (Fig. 2). This can be explained on the basis of difference in exothermicity induced by both the systems. While a 10 per cent addition of TiO_2/C_2Cl_6 brings down the exothermicity of the total reaction from 814 cal/g to 735 cal/g, ZnO/C_2Cl_6 reduces it to 756 cal/g only.

From Fig. 2, it is clear that the effect of addition of ZnO and TiO_2 on the burn rate of the tricomponent smoke system is not linear, but falls in an exponential fit. So, it can be expected that the dependence of burn rate on ZnO or TiO_2 follows a general equation of the type

$$\text{Burn rate, } r = a.e^{-b.(\text{percentage of oxide})} \qquad (7)$$

where, a and b are constants.

Now

$$\ln r = \ln a - b.[\text{percentage of oxide}] \qquad (8)$$

Equation (8) predicts a linear plot between $\ln r$ and (percentage of oxide). This has been verified and is plotted in Fig. 3. From this plot, the values of a and b have been calculated and the equation assumes the following form:

For ZnO composition, one gets:

$$r = 1.59 \,.\, e^{-0.05.(\text{percentage of } ZnO)} \qquad (9)$$

For TiO_2 composition

$$r = 1.72 \,.\, e^{-0.09.(\text{percentage of } TiO_2)} \qquad (10)$$

3.4 Effect of Addition of Excess Titanium

It is known that excess metal fuel increases the burn rate of many delay compositions[3]. So, it was attempted to increase the burn rate of the slow burning, low flame composition $Ti/KClO_4/C_2Cl_6/TiO_2$ (7:10:63:20) by further addition of Ti powder. The results are presented in Table 1 and Fig. 4. From the plot, it is clear that there is an almost linear dependence between the burn rate and the percentage of excess metal powder added. However, beyond 6 per cent limit, the quality of smoke is reduced due to reduction of oxides of carbon by the excess metal (whiteness of the flame diminishes and the colour becomes greyish), showing that the increase in burn rate is not due to

Table 1. Effect of addition of excess *Ti* on the burn rate of $Ti/KClO_4/C_2Cl_6/TiO_2$ (7:10:63:20) smoke composition

Percentage of excess *Ti* metal added	Actual percentage ($Ti/KClO_4/C_2Cl_6/TiO_2$)	Burn rate (mm/s)		
		1	2	Mean
0.0	7.0/10.0/62.8/20.2	0.25	0.23	0.24
2.0	8.8/9.9/61.6/19.7	0.34	0.36	0.35
3.8	10.5/9.7/60.4/19.4	0.47	0.50	0.48
5.7	12.2/9.5/59.2/19.1	0.58	0.62	0.60
7.4	13.9/9.3/58.1/18.7	0.69	0.71	0.70
9.1	15.4/9.2/57.1/18.3	0.83	0.84	0.83

higher thermal conductivity alone, but also due to higher exothermicity induced by chemical reaction as well.

From the linear fit of the graph, one gets:

$$r = 0.065.(Ti\,\%) + r_0 \qquad (11)$$

where, r_o = 0.23 is the burn rate of the starting composition.

3.5 Effect of Addition of Aluminium

Since *Al* has a higher heat of combustion (7.4 kcal/g), it was decided to establish the influence of addition of small amounts of *Al* to smoke compositions containing both TiO_2 and *ZnO*. Results are shown in Tables 2 and 3 and Fig. 4. Here also, as with excess *Ti*, addition of *Al* increased the burn rate and all the compositions yielded intense smoke with longer flame as the percentage of *Al* was increased. This is in keeping with the higher exothermicity of *Al* oxidation compared to the oxidation/chlorination of *Ti*. Here also beyond 6 per cent limit, the smoke started turning greyish due to incomplete oxidation of carbon.

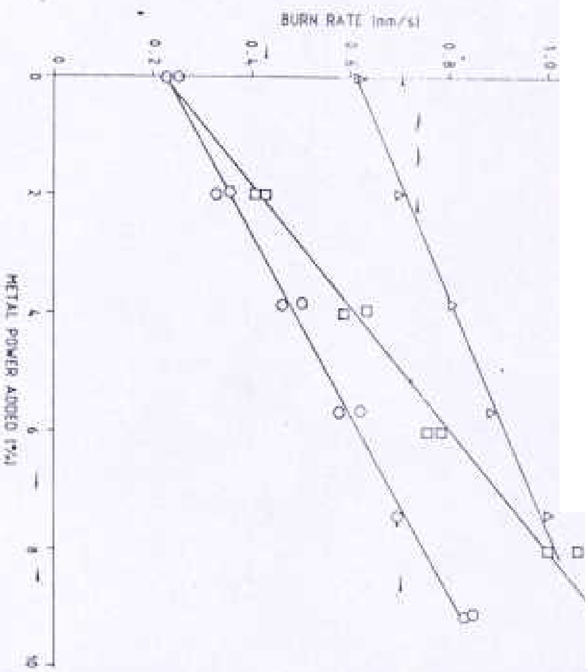

Figure 4. Effect of addition of *Al* and excess *Ti* on the burn rate of smoke composition: Δ *Al* to $Ti/C_2Cl_6/KClO_4/ZnO$ (11.0/54.3/16.0/18.7), □ *Al* to $Ti/C_2Cl_6/KClO_4/TiO_2$ (7.0/63.0/10.0/20.0), o Excess *Ti* to $Ti/C_2Cl_6/KClO_4/TiO_2$ (7.0/63.0/10.0/20.0).

For TiO_2 compositions, the effect of *Al* on burn rate can be represented as

$$r = 0.097\,.\,[\text{percentage of } Al\,] + r_o \qquad (12)$$

where r_o = 0.23 is the burn rate of the starting composition.

For *ZnO* composition, one gets:

$$r = 0.051[\text{percentage of } Al\,] + r_o \qquad (13)$$

Table 2. Effect of addition of *Al* on the burn rate of $Ti/KClO_4/C_2Cl_6/TiO_2$ (7:10:63:20) smoke composition

Percentage of *Al* added	Actual percentage ($Ti/KClO_4/C_2Cl_6/TiO_2$)	Burn rate (mm/s)		
		1	2	Mean
0.0	7.0/10.0/62.8/20.2/0.0	0.25	0.23	0.24
2.0	6.8/9.9/61.5/19.8/2.0	0.42	0.41	0.41
4.0	6.7/9.7/60.3/19.3/4.0	0.63	0.59	0.61
6.0	6.5/9.5/59.0/19.0/6.0	0.76	0.78	0.79
8.0	6.4/9.3/57.8/18.5/8.0	1.00	1.06	1.03

Table 3. Effect of addition of *Al* on the burn rate of $Ti/KClO_4/C_2Cl_6/ZnO$ (11:15.9:54.4:18.7) smoke composition

Percentage of *Al* added	Actual percentage ($Ti/KClO_4/C_2Cl_6/ZnO/Al$)	Burn rate (mm/s)		
		1	2	Mean
0.0	11.0/15.9/54.4/18.7/0.0	0.63	0.62	0.62
2.0	10.8/15.6/53.3/18.3/2.0	0.69	0.72	0.70
3.8	10.6/15.3/52.3/18.0/3.8	0.79	0.83	0.81
5.7	10.4/15.0/51.3/17.6/5.7	0.88	0.91	0.89
7.4	10.2/14.7/50.4/17.3/7.4	0.98	1.03	1.00

where, $r_o = 0.61$ is the burn rate of the starting composition.

From the above, it is also clear that the influence of addition of *Al* to TiO_2 containing composition is more than that of *ZnO* composition. This must be due to lesser fuel percentage in the former since the addition of excess metal powder enhances the reaction rate by increasing the thermal conductivity as well as the exothermicity. The slightly higher influence of *Al* percentage over *Ti* percentage can be explained by the difference in their exothermicity.

3.6 Temperature Measurement

From the above experiments, it was evident that addition of either *ZnO* or TiO_2 reduces the burn rate and at the same time improves the smoke quality. Similarly, addition of extra fuel increases the burn rate. The decrease in burn rate was also associated with shorter flame and, therefore, an attempt was made to find out whether there exists any correlation between the temperature of the burning front and the burning rate. For this, samples containing *ZnO*, TiO_2 and excess *Ti* have been utilised and the results are shown in Table 4 and Fig. 5.

Though the values are somewhat scattered, it appears that *ZnO* containing compositions have a higher burn rate compared to either excess *Ti* containing or TiO_2 containing compositions. Thus for the same burn rate, *ZnO* composition has a lower temperature than either of the two.

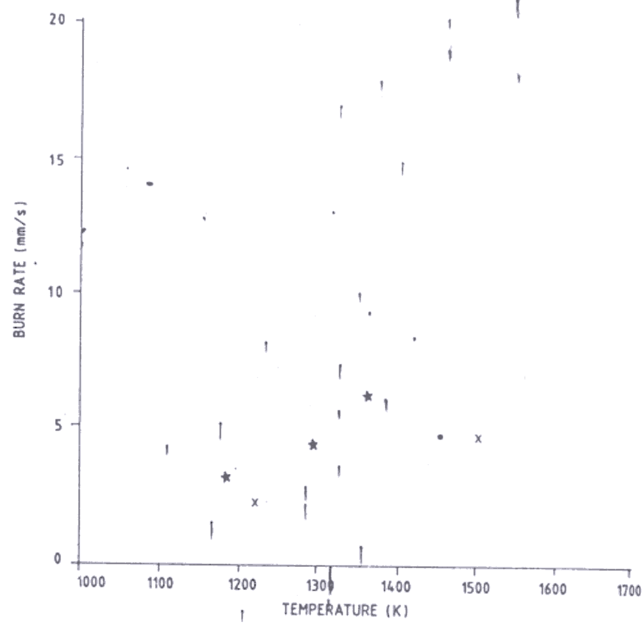

Figure 5. Plot of burn rate of different smoke compositions as a function of its temperature compositions containing × TiO_2, • excess *Ti* and ★*ZnO*.

4. CONCLUSIONS

- Tricomponent smoke system ($Ti/KClO_4/C_2Cl_6$) is a good system for pyrotechnic release of $TiCl_4$.

  The burn rate depends on the percentage of $KClO_4$, with approx. 25 per cent giving the optimum performance.

Table 4. Temperature/burn rate dependence of different smoke compositions

Composition	Percentage	Temp. (K)	Burn rate (mm/s
$Ti/C_2Cl_6/KClO_4$	17.4/57.6/25.0	1670	1.60
$Ti/C_2Cl_6/KClO_4/TiO_2$	13.9/59.2/20.2/6.7	1610	0.96
$Ti/C_2Cl_6/KClO_4/TiO_2$	10.4/61.0/15.1/13.	1500	0.47
$Ti/C_2Cl_6/KClO_4/TiO_2$	7.0/62.8/10.1/20.1	1220	0.23
$Ti/C_2Cl_6/KClO_4/ZnO$	11.0/54.4/15.9/18.7	1360	0.62
$Ti/C_2Cl_6/KClO_4/ZnO$	8.8/53.4/12.7/25.1	1290	0.44
$Ti/C_2Cl_6/KClO_4/ZnO$	6.6/52.4/9.5/31.5	1180	0.32
$Ti/C_2Cl_6/KClO_4/TiO_2$	10.5/60.4/9.7/19.4	1450	0.48
$Ti/C_2Cl_6/KClO_4/TiO_2$	13.9/58.1/9.3/18.7	1560	0.70
$Ti/C_2Cl_6/KClO_4/TiO_2$	15.4/57.1/9.2/18.3	1590	0.83

It is possible to reduce the reaction temperature and improve the smoke quality by successive additions of ZnO/C_2Cl_6 and TiO_2/C_2Cl_6 to the tricomponent system in the mole ratio 3:1 and 3:2, respectively.

- TiO_2/C_2Cl_6 has greater influence in reducing the burn rate than ZnO/C_2Cl_6 due to the lower exothermicity of this mix compared to the latter.

The dependence of burn rate reduction on the percentage of ZnO and TiO_2 percentage is exponential and using the appropriate equation, it is possible to predict the burn rate of a similar composition having different oxide content.

Both excess Ti and addition of extra Al in small percentages enhance the burn rate and the dependence is linear.

- ZnO containing compositions appear to have a lower reaction temperature for the same burn rate compared to TiO_2 containing compositions.

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Mr CB Kartha obtained his MSc (Chemistry) from the University of Kerala in 1968. He joined VSSC, Thiruvananthapuram, in 1969. His area of research includes: explosives. He has participated in almost all the sounding rockets, launch vehicles and satellite programmes of Indian Space Research Organisation. He has published his papers in national/international journals. He is a member of many professional bodies like High Energy Materials Society of India, Aeronautical Society of India and Indian Society for Advancement of Materials and Process Engineering.