Journal of Energetic Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713770432

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To cite this Article Khire, Vrushali , Bhide, N. M. and Kurian, E. M.(1998) 'Thermal, combustion and luminosity studies on magnesium-strontium nitrate pyrotechnic system', Journal of Energetic Materials, 16: 1, 45 — 67
To link to this Article: DOI: 10.1080/07370659808216093
URL: http://dx.doi.org/10.1080/07370659808216093

THERMAL, COMBUSTION AND LUMINOSITY STUDIES ON MAGNESIUM-STRONTIUM NITRATE PYROTECHNIC SYSTEM

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ABSTRACT

Magnesium-strontium nitrate compositions with and without binder have been investigated by thermal analysis, x-ray diffraction, hot-stage microscopy, infrared spectroscopy and radiophotometer as regards their thermal behaviour and combustion. Binary magnesium-strontium nitrate compositions with more than seventy percent oxidant showed a broad combustion exotherm in differential thermal analysis (DTA). In compositions with less than seventy percent strontium nitrate the combustion peak was very sharp. In thermogravimetry (TG), weight changes with composition have been interesting and suggestive of the combustion reactions involved. Hot-stage microscopy revealed gas evolution during the combustion. Addition of binder influenced the combustion remarkably and made it stronger and brighter and thus suitable for tracer application. The possible combustion reactions are discussed and kinetics of combustion attempted. The solid products of combustion have been characterised by XRD and IR. Interesting correlation has been observed between the extent of exothermicity in DTA and luminosity which could help optimisation of the composition for pyrotechnic applications.

Journal of Energetic Materials Vol. 16, 045-068 (1998)
Published in 1998 by Dowden, Brodman & Devine, Inc.

INTRODUCTION

Pyrotechnics involves the technology of utilising exothermic redox reactions which are self-sustaining and relatively slow. Oxidation of metallic fuel by oxygen rich compound is the main reaction underlying the pyrotechnic combustion. Fuels commonly used are metals like tungsten, tantalum, zirconium, magnesium and aluminium. Oxidants used are nitrates, chromates, dichromates, perchlorates, chlorates and peroxides. Binder in the pyrotechnic combustion plays an important role by increasing the cohesion between the particles of ingredients and also controls the burning rate and in certain cases protects the metal powder from corrosion[1]. Particle size, internal and external surface area, degree of homogeneity of the mix and chemical history of oxidisers and fuels affect the general combustion pattern. Stoichiometry, heat of reaction and burning rate are interrelated[2]. Thermal analysis has lately been found to be an effective tool in the study of pyrotechnics as a test facility and also more significantly in the understanding of pyrotechnic combustion mechanism, evaluation of hazard potential and ignition characteristics[1,2]. Many delay and smoke compositions have been studied by thermal analysis[3-8] and also some illuminating compositions[9-11]. Charsley et al. have studied magnesium-sodium nitrate and titanium-strontium nitrate mixtures as regards the role of certain binders in pyrotechnic combustion[12].

Though magnesium-strontium nitrate have been evaluated extensively for pyrotechnic applications, data on characteristics of ignition, combustion, kinetics and other related aspects like the effect of phenolic binder on combustion are lacking. Hence in the present paper magnesium-strontium nitrate system with and without

binder has been studied using thermal methods of investigation like differential thermal analysis, thermogravimetry coupled with polarising microscopy, infrared spectroscopy, x-ray diffraction and radio photometer.

EXPERIMENTAL

Magnesium powder was of Gr. V, JSS 1044, having the sieve spectrum between 75 to 63 μ. Strontium nitrate was of Gr. I-IS 5671-1984 specification, with average particle size of 53 μ. The phenolic resin HSR 6312 from M/s. Bakelite Hylam, Hyderabad, was used as binder.

Compositions were prepared taking the requisite safety precautions. Sieves conforming to IS specification were used for sieving the dry compositions. Camel hair brushes were used. Strontium nitrate sieved to the required size was dried separately in an oven at 100°C for nearly five hours and stored in a desiccator.

Magnesium-strontium nitrate compositions, ranging from 10/90 to 90/10 by weight were prepared and sieved through IS 90 to ensure uniform mixing and to break down the lumps in the compositions if any.

The resin powder was made into solution by dissolving in adequate absolute alcohol (purity 99%) to coat the magnesium powder. Strontium nitrate was then added to the resin-coated magnesium powder and thoroughly mixed. The mixture was then

passed through a sieve and then spread in a thin layer and allowed to dry for 48 hrs. The matured composition was again passed through a 600μ IS sieve, breaking lumps if any formed. Mg/Sr $(NO_3)_2$ / binder compositions, 50/(50-x)/x and 25/(75-x)/x were prepared, where 'x' is binder percent.

The composition was filled in seven equal increments in steel tubes of 14 mm internal diameter and 30mm external diameter with a column length of 45 mm. The empty tubes were fitted with paper liners made from paper craft ammunition to JSS 1209, with a thickness of 0.7 mm. The liners were coated on both the sides with varnish shellac APC 224 to JSS 1-63-11. Each increment of the composition was consolidated at 515 MPa and a total quantity of 12 g of compositions was filled in each case.

The filled tubes were ignited with primed cambric peices and the burning time was recorded with a stop-watch of accuracy within 0.1 second. Luminous intensity of the compositions was measured in candellas using a radiophotometer model 550, supplied by M/s. EG&G Electroptics, USA, kept at a distance of 10 meters from the source of the light. The ambient light was adjusted to zero level and the recordings were done in the visual spectral range. A powerful fan was used to drive away the smoke emitted during combustion so that the flame was not obscured by it.

THERMAL ANALYSIS

A simultaneous thermoanalyser STA 409 of Netzsch was used. For DTA & TG Pt-10 % Rh thermocups and Pt-Pt 10 % Rh thermocouples forming an integral junction with the thermocups were used.

A specially fabricated micro DTA appratus was also used. In this set-up, platinum cups were used. They fit into cylindrical platinum cups with Pt-Pt 13 % Rh thermocouples fused to the bottom of the cups. A Stanton - Redcroft temperature programmer was used with a sensitive and balanced multispan two pen strip chart recorder model "Omniscribe" of M/s. Digital Electronics. Sample was sieved freshly before thermal analysis to avoid seggregation and agglomeration and then just pressed gently in the thermocup, with alumina as the reference material. Thermal analysis curves reproduced in the figures correspond to sample mass 10 mg, heating rate 10°C/min and atmosphere static air.

Perkin Elmer IR Spectrophotometer Model 683 was used to study the residue obtained after thermal analysis, in KBr pellet. Leitz-Orthoplan polarising microscope with hot stage was used under dynamic conditions to characterise the sequence of reaction between fuel and the oxidant. The temperature was programmed through the universal temperature controller of Stanton-Redcroft and the photomicrographs were taken at a magnification of x 300.

A Phillips PW 1390 / PW 1394 diffractometer with nickel filter Cu K_α radiation (40 KV, 20 mA) was used for x-ray powder diffraction study with Debye-Scherrer camera (dia 115 mm).

RESULTS

A number of experiments were carried out on magnesium-strontium nitrate compositions in varying ratios with and without binder at different heating rates and sample mass using micro DTA and simultaneous thermal analysis. DTA curves obtained for compositions at 10 % interval are reproduced in Fig.1. Strontium nitrate melts at about 570 ° C followed by decomposition and magnesium undergoes self-ignition at about 575°C, which gives a sharp exotherm in DTA and marked weight gain in TG, Fig.2. Mg/Sr $(NO_3)_2$ (10/90) gave a prominent exotherm at 575°C 20/80 at 571°C and 30/70 at 566°C and these were broad. But for compositions Mg/Sr $(NO_3)_2$ 40/60 to 90/10 the combustion exotherm occurred around 575°C and was very sharp and increased in intensity with the increase in magnesium content. However Mg/Sr $(NO_3)_2$, 90/10, could be resolved in STA where two exothermic peaks were dominant, the first one attributable to pyrotechnic combustion and the second to the combustion of excess magnesium, Fig.3. Simultaneous DTA-TG studies on these compositions revealed loss in weight corresponding to DTA exotherms upto magnesium content about 70 % and above this magnesium percentage gain in weight. Area of pyrotechnic combustion exotherm was maximum at about 30-40 % magnesium content.

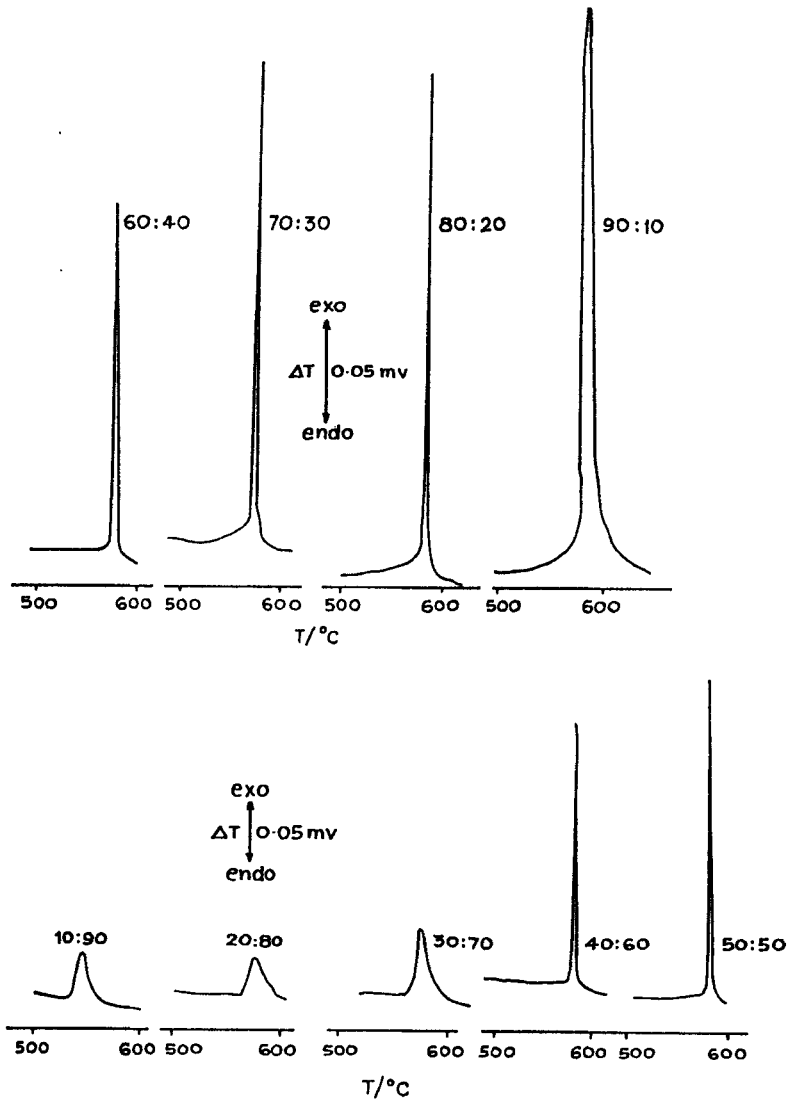


Fig.1 : DTA of Mg/Sr $(NO_3)_2$ (10/90 to 90/10)

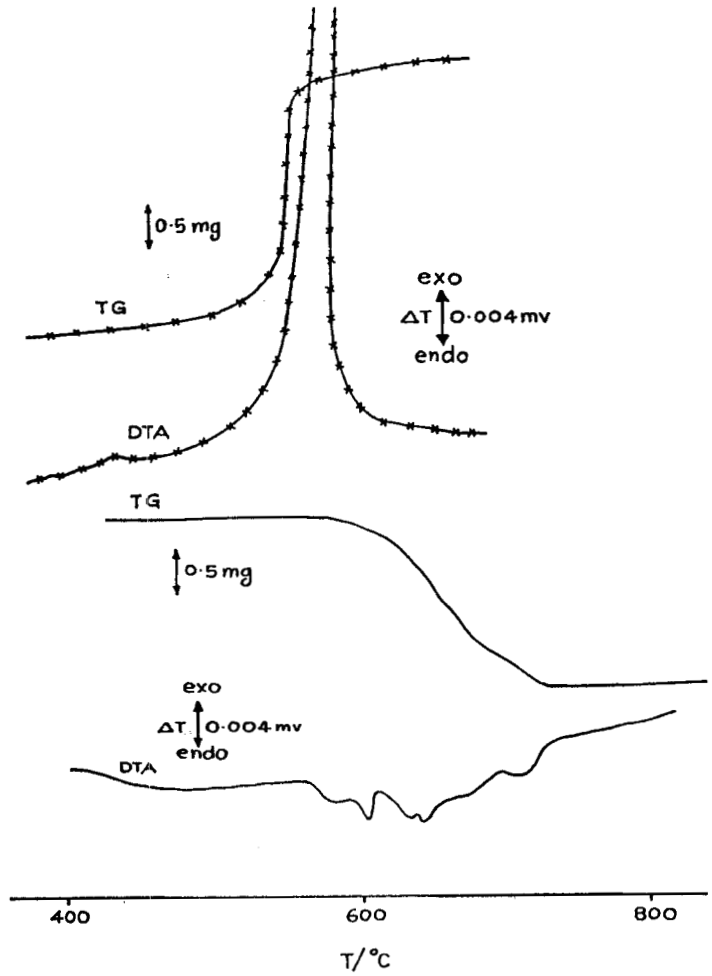


Fig.2 : Simultaneous TG / DTA of Mg and Sr $(NO_3)_2$

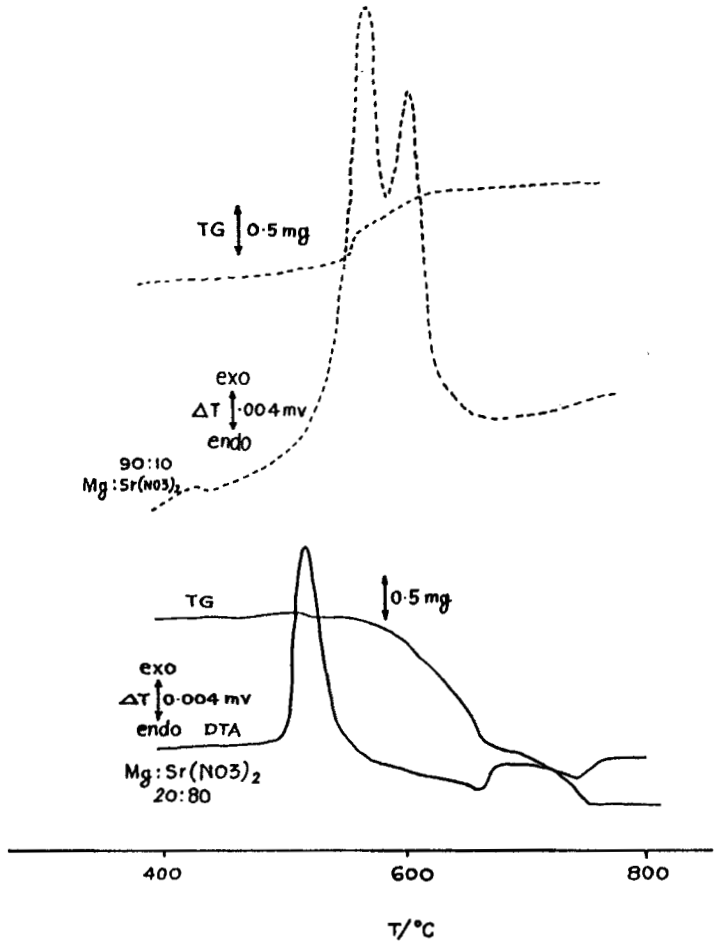


Fig.3 : Simultaneous TG/DTA of Mg/Sr $(NO_3)_2$ 20/80 and 90/10.

Simultaneous DTA-TG curves recorded for Mg/Sr $(NO_3)_2$ / binder, 50/(50-x)/x compositions are reproduced in Fig. 4. The composition with 2 % binder content gives an overall dominant combustion exotherm setting in at about 500 °C showing that the ignition occurs at a much lower temperature with binder. A corresponding sharp loss in weight is also manifest in the TG curve. At 4 % binder content a precombustion exotherm in the range 450 to 515° C is discernible, in conformity with the reported results on other similar systems and may be attributed to partial binder-oxidant interaction prior to the main combustion exotherm starting later at about 550 ° C. Both the precombustion and combustion exotherm, interestingly enough revealed loss in weight in TG. The precombustion exotherm as well as the main pyrotechnic combustion exotherm were more pronounced for 6 to 8 % binder compositions. Compositions with 10 and 12 % binder content also showed more or less the same behaviour pattern, but the exothermicities were, surprisingly, considerably lower and the ignition temperature for the main combustion exotherm was higher.

To substantiate these results further studies were carried out on Mg/Sr$(NO_3)_2$ /binder 25/(75-x)/x compositions. DTA-TG results are analogous to those observed for 50 / (50-x)/x Mg/Sr(NO3) $_2$ / binder compositions and gave both precombustion and

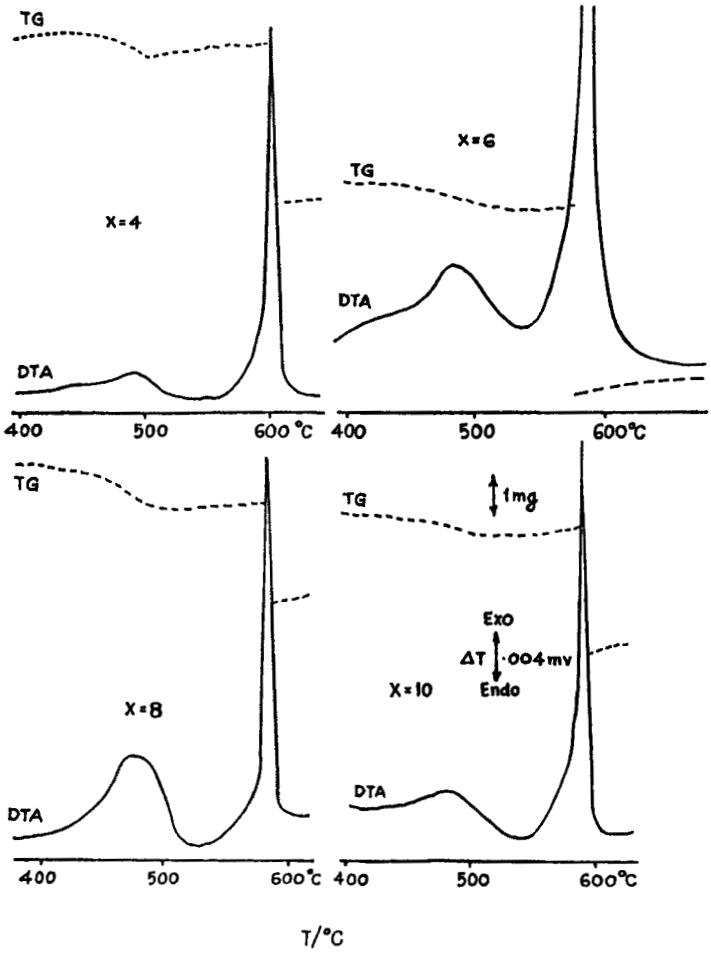


Fig.4 Simultaneous TG/DTA of $Mg/Sr(NO_3)_2$ /binder 50/(50-x)/x

combustion exotherms. TG shows weight loss for both these stages. Here also compositions with about 8 % binder content show the maximum exothermicity. The plot of the area under the combustion exotherms with the binder percentage is given in Fig.5. Burning rate and luminosity studies were also carried out on $Mg/Sr(NO_3)_2$ / binder system under various conditions. Variation of burning rate and luminosity with the binder concentration are also given in Fig.5. The burning rate decreases linearly with the increase in binder percentage in the range investigated. Luminosity increases with the binder percentage upto 8 % and then decreases.

XRD data of the solid products of combustion along with those of the probable products are given in Table 1.

Results indicate that MgO, Mg_3N_2 and SrO may be the main solid products of combustion.

An IR spectrum of the solid combustion products is given in Fig.6. This is in conformity with the XRD data and showed the characteristic asborption bands[13] corresponding to MgO, Mg_3N_2 and SrO.

Photomicrographs taken are given in Fig.7 and these revealed melting and bubbling of gases during combustion.

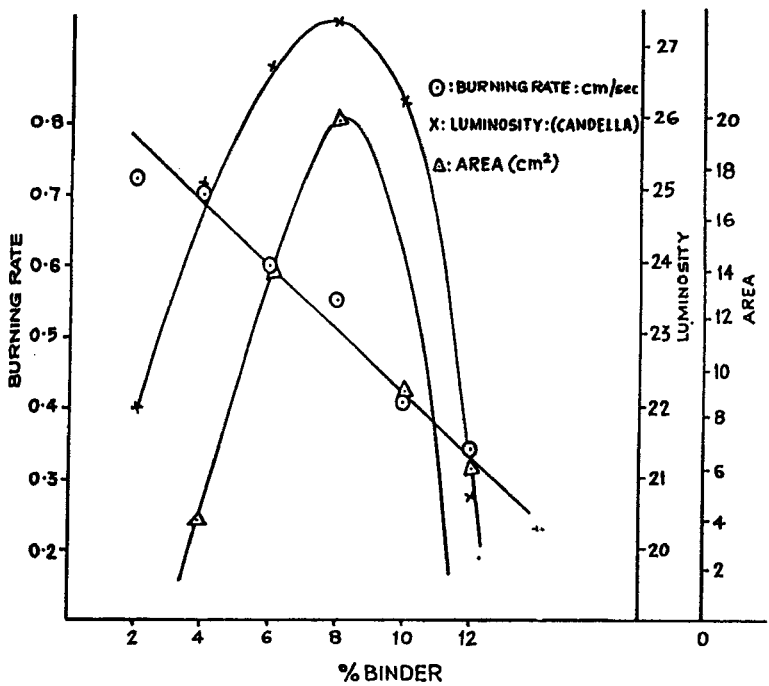


Fig.5 : Variation of burning rate, luminosity and area under DTA peaks with binder.

TABLE 1

XRD results of the solid combustion products of

$Mg/Sr(NO_3)_2$ (50/50)

o d A		I / I o (observed)	o d A (reported)	I/Io Compound
2.970	s	2.97	100	SrO
2.563	m	2.58	86	SrO
2.309	vs	2.34	72	$Sr(NO_3)_2$
1.970	m	2.10	100	MgO
		1.95	50	Mg_3N_2
		1.99	80	SrO_2
1.790	m	1.77	60	SrO_2
		1.80	50	Mg_3N_2
		1.82	71	SrO
1.642	s	1.61	18	Mg
		1.61	50	MgO
1.440	vs	1.43	50	MgO, Mg_3N_2
1.369	m	1.35	100	Mg_3N_2
		1.37	16	Mg
1.296	vs	1.29	80	SrO2
1.245	vs	1.26	100	Mg_3N_2
		1.24	40	SrO2
1.199	vs	1.18	29	SrO
1.062	m	1.06	60	SrO

vs - very strong ; s - strong ; m - medium

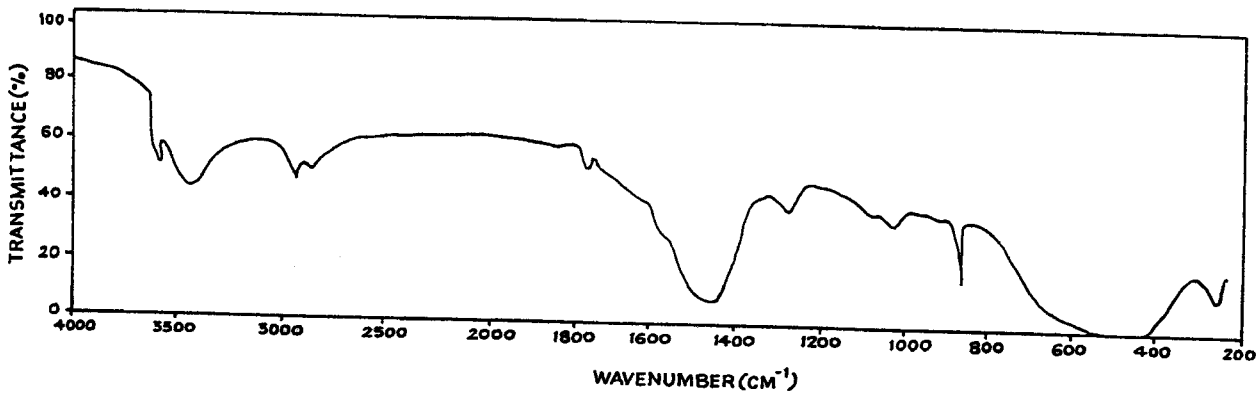
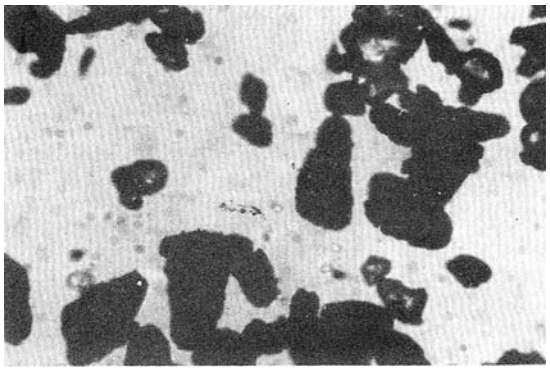
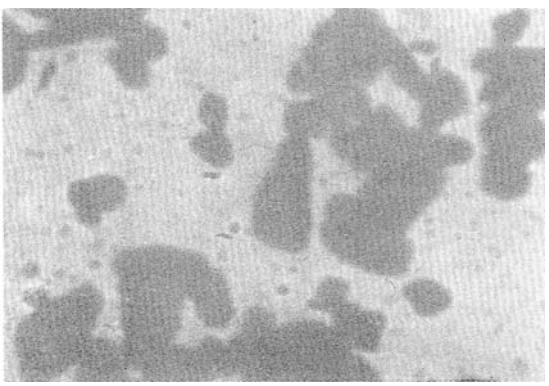


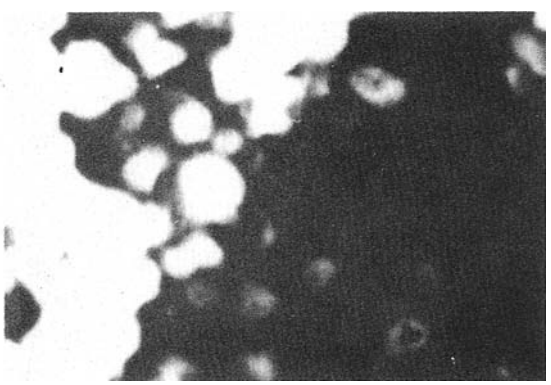
Fig.6 IR Spectrum of the solid combustion products of Mg/Sr $(NO_3)_2$, 50/50.



a : at 25°C (x 300)



b : at 560°C (x 300)



c : at 600°C (x 300)

Fig.7 : Photomicrographs of Mg/Sr $(NO_3)_2$, 30/70.

KINETICS OF COMBUSTION

Kinetics of combustion has been evaluated[14] from the DTA data using Coats-Redfern equation[15]. These data are incorporated in Table 2. The rate parameters reported are for global kinetics and intended basically for comparison only. The activation energy for the precombustion in Mg/Sr $(NO_3)_2$ / binder compositions are considerably lower than those for pure Mg/Sr $(NO_3)_2$ compositions as expected in conformity with the more efficient combustion observed for the compositions incorporating binder.

DISCUSSION

The thermal study of strontium nitrate shows that it starts melting at 570°C and then decomposes endothermally in accordance with the equation[16] :

$$Sr(NO_3)_2 \longrightarrow SrO + N2 + 2.5\ O2 + 92\ kcal..... \quad (i)$$

The reaction corresponds to an active oxygen content of 37.7 %.

According to Cackett[1] the basic reaction during combustion is probably,

$$8Mg + Sr(NO3)_2 \longrightarrow 5MgO + SrO + Mg_3N_2 + 754\ kcal... \quad (ii)$$

with stoichiometry at 48 % magnesium content. But the combustion of composition with 48 % magnesium content showed considerable weight loss whereas

TABLE 2

Rate parameters for pyrotechnic combustion of various compositions in Mg/Sr $(NO_3)_2$ / binder system

Composition	Temperature rage (K)	Activation energy (kcal.mole^{-1})
Mg/Sr$(NO_3)_2$ / binder		
10 : 90 : 0	858 - 893	439.0
20 : 80 : 0	833 - 873	426.0
30 : 70 : 0	830 - 855	325.0
25 : 67 : 8	636 - 803	34.0
35 : 65 : 10	708 - 801	65.0
50 : 44 : 6	673 - 791	43.0
50 : 42 : 8	683 - 792	42.0

reaction (ii) does not involve loss in weight. DTA reveals that the composition with Mg about 30-40 % gives the largest combustion exotherm which is normally attained with proportion of fuel around stoichiometry[2]. Hot stage microscopy of the combustion reaction shows the evolution of gas during the reaction. TG showed weight loss corresponding to combustion exotherm in DTA except at very high percentage of magnesium content. These data suggest that an alternate basic combustion reaction,

$$Sr(NO_3)_2 + 5Mg \longrightarrow SrO + N_2 + 5MgO$$

which corresponds to a stoichiometric ratio of magnesium content at 36 % is also plausible. Weight loss during combustion for a Mg/Sr $(NO_3)_2$ (48/52) stoichiometric composition and composition with higher $Sr(NO_3)_2$ (> 52 %) indicate simultaneous thermal decomposition of strontium nitrate also occuring along with the pyrotechnic combustion reaction. Also true is the parallel combustion of magnesium for compositions with higher magnesium content than the stoichiometric one.

Combustion enhancement by the binder in the Mg / Sr $(NO_3)_2$ / binder compositions substantiates that the organic binder interacts chemically with the nitrate and this binder-nitrate reaction appears to be an important factor[11,12]. In Ti/$Sr(NO_3)_2$ systems, the binder was found to promote ignition under conditions where the binary mix failed to ignite and the increase in binder concentration caused greater lowering of ignition temperature.

The heat of combustion represented by the area under the DTA peaks including both the precombustion and combustion exotherm is maximum at about 6-8 % binder content in both the Mg/Sr $(NO_3)_2$ / binder compositions investigated. Luminosity observed in 50/(50-x)/x, Mg/Sr$(NO_3)_2$ /binder composition is also maximum at about 8 % binder content. Thus there is a good correlation between the heat of combustion as obtained in DTA and the luminosity. This corroborates that thermal analysis of pryotechnics can give valuable data in the optimisation of compositions[17-20] for use in pyrodevices.

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