CHAPTER 4

SUMMARY & CONCLUSIONS
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A pyrotechnic composition is an intimate mixture of fuel and oxidizer along with suitable binder. Reactive metals like magnesium, aluminum, zirconium, titanium and nickel find application as fuel. The commonly used oxidizers are nitrates, chromates, perchlorates and chlorates. Infrared (IR) flares are based on pyrotechnic compositions emitting radiations in IR and visible region. IR flares find applications in tracking path of missile and decoying incoming heat seeking missile. Military targets including aircrafts, emitting IR radiations in different transmission wavelengths, can be easily detected and destroyed by IR guided missiles (IRGM). In case of aircrafts, main radiation sources are exhaust plume, hot tail pipe/engine and heated fuselage emitting at 3-5 µm, 2-3 µm and 8-13 µm waveband respectively. Statistics of aircraft losses in hostile actions bring out that ~ 90 % of these losses are due to IRGM. Pyrotechnic decoy flares are the most commonly used countermeasures to lure away incoming IRGM. The decoy flare burns and emits radiation in a manner that simulates the emission radiations from engine of the targeted aircraft. The missile locks on to and destroys the decoys, resulting in escape of the targeted aircraft.

The new generation IRGM are equipped with one or more electronic counter-counter measures (CCM) to discriminate and reject conventional decoy flares. In case, the ratio of IR intensities of the wave bands does not conform to the spectral signature of target aircraft, the countermeasure is recognized and ignored by these modern CCM. The missile seeker uses two different detectors to monitor the energy levels in two bands or a single detector with different band pass filters. Generally, sudden jump in the 1-3 µm band intensity compared to that in the 3-5 µm band reveals the presence of decoy flare in the seeker’s field of view (FOV).

Solid pyrotechnic compositions currently used in decoy flares comprise of magnesium and fluro polymers like polytetrafluoroethylene (PTFE), Viton etc. These compositions are referred as MTV flares. Magnesium reacts with halogenated polymers producing higher heat output due to formation of MgF₂ as the heat of formation of MgO is lower than that of MgF₂. PTFE containing 76% fluorine is a good source of fluorine. PTFE is known for its high stability and chemical inertness. The MTV flares are effective
against missiles of earlier generation capable of seeking heat in a single IR wave band. Present R & D efforts are focused towards spectrally balanced decoy flares capable of producing spectral signature similar to those of aircrafts as MTV based flares have the drawback of higher IR spectral ratio ($\Phi_{2-3}/\Phi_{3-5} > 0.7$). Although minimum required dynamic spectral efficiency is $>3.5$ W.s/sr.g at air speed of 250 kts, minimum static spectral efficiency of $>35$ W.s/sr.g is required because carbon type of payloads undergo degradation in IR efficiencies by a factor of about 10 at such air speed. Static IR spectral ratio of 0.33 is necessary to achieve an appropriate required IR spectral ratio under dynamic conditions due to its degradation to 66% under the dynamic condition.

The IR intensity of pyrotechnic composition is highly dependent on the nature of combustion products, their concentration in the flame, their emissivity, flame temperature and mass burn rate. Generally, there are two ways to achieve spectral adaptation. The first approach involves use of compositions emitting predominantly in 3-5 µm range with minor emission in the 2-3µm range. The second approach is optimization of flame temperature of the composition as $\lambda_{\text{max}}$ is dependent on flame temperature as per Wien’s displacement Law. It can be inferred that temperature of black body should be in the range of 600 to 1000 K for maximum radiation in this region. The promising emitters emitting predominantly in 3-5 µm region are CO$_2$ > FBO > HBO$_2$ > HBO > CO > HCl in descending order of band strength. The most important emitter in the 3-5 µm range is CO$_2$ which is more intense than both CO and H$_2$O by a factor of ~10. HF, CH$_4$ and H$_2$O are the most unfavorable combustion products in this regard. In addition, continuum by condensed matters like carbon soot in the flame causes deterioration of the IR spectral ratio.

Aromatic compounds like anthracene, naphthalene and decacyclene are used as a source of carbon in pyrotechnic IR flare compositions. Thermolysis of these compounds in primary combustion zone yields carbon which readily aggregates producing larger soot particles which have high continuum radiation level due to high emissivity. Entrainment of air in the combustion zone leads to conversion carbon to CO and CO$_2$. Partially oxidized fuels like trioxane, paraformaldehyde, organic anhydrides, anthraquinone, anthraquinone compounds, potassium benzoate, dinitroanisole, bis-2,4-dinitrophenyl
oxalate etc. are preferred choice as oxygen in the vicinity of the aromatic ring alters the decomposition pathway and impedes soot formation.

The present research program is undertaken to carry out the exhaustive study on pyrotechnic compositions based on Mg/NaNO₃/carbonaceous fuels for IR decoy flare applications to arrive at required IR spectral ratio and efficiency. Different carbon sources selected for the present study are high carbon content fuels (HCCF), partially oxidized carbonaceous fuels (POCF) and Fluro polymers (FP).

Anthracene is selected as carbon source among HCCF due to its high carbon content as carbon acts as a black body and emits with more intensity in the IR region of the electromagnetic spectrum. Graphite and charcoal are also studied as carbonaceous fuels. Fluro polymers Viton A (66% fluorine) and Kel-F 800 (50.6% fluorine) are selected as binder as well as carbon source for this study to take advantage of high heat output. POCF like phthalic anhydride, succinic anhydride, benzene tetracarboxylic dianhydride and benzophenone tetra carboxylic dianhydride have combined advantage of high carbon to hydrogen ratio and better oxygen content aiding in conversion of carbon to carbon dioxide leading to increased IR intensity in 3-5 µm wave bands.

Magnesium is selected for pyrotechnic flare compositions due to its high calorific value and low boiling point on line of its applications in illuminating flares/tracers/igniters in combination with inorganic oxidizers (nitrates). High calorific value of magnesium results in high flame temperature. Owing to low boiling point, excess magnesium vaporizes and burns with atmospheric oxygen providing additional heat to flare composition. Sodium nitrate is chosen because of its high active oxygen content, relative ease of ignition due to its low melting point and excellent compatibility with magnesium.

Compositions are prepared by coating the magnesium powder with binder and sieving followed by addition of sodium nitrate and carbon fuels. Subsequently, the ingredients are mixed and sieved six times. Flare composition along with booster and priming composition are loaded into 20 mm dia steel tube at 5 ton load. Booster composition used is 1:1 mixture of flare composition and priming composition. An electric squib is placed on priming composition surface using adhesive tape for initiation of IR flare composition.
Sensitivity of pyrotechnic compositions to impact and friction stimuli are determined by standard methods. The Fall Hammer apparatus is used to determine the impact sensitivity of the pyrotechnic compositions. A 2 kg weight is dropped on the explosive sample from increasing order height and the height for 50 % probability of initiation is computed as measure of impact sensitivity. Friction sensitivity is determined using a Julius Peters Apparatus. The figure of insensitivity of a sample is given as maximum load in kg at which the sample does not deflagrate / detonate in six consecutive tests. Ignition temperature of the compositions is determined using locally fabricated DTA apparatus by subjecting 10 mg sample to heating rate of 40°C /min. Gaseous product analysis is carried out on gas chromatograph (NUKON) using thermal conductivity detector.

Thermo chemical characteristics of the compositions are studied using REAL programme (developed by Belov G.V.). Flame temperature, volume of gaseous products, total number of moles of the products, condensed species etc are predicted by the programme. The performance parameters evaluated in the course of the present investigations are calorimetric value (cal val), linear burn rate (LBR), IR intensity and IR efficiency. Cal val are determined in an adiabatic bomb calorimeter in argon atmosphere. LBR are determined by burning the composition of known length in steel tube and recording the burn time on IR radiometer. The IR intensity of the pyrotechnic compositions is measured using a computerized spectro radiometer. Thermal analysis of the selected compositions is carried out on DSC-TGA. A numerical correlation for prediction of IR intensity of the compositions is also developed.

Friction sensitivity data of compositions indicates that, all the compositions are insensitive to friction stimuli. Results of impact sensitivity tests of compositions reveal that graphite and charcoal based compositions are insensitive to impact upto the maximum limit of test equipment (170 cm). Anthracene based compositions gave figure of insensitivity (FOI) in the range of 70 - 90. In the case of MTV and anhydride based compositions an increase in FOI is observed with increase in magnesium content. MTV, and HCCF based compositions exhibit an increase in ignition temperature on increase in magnesium content. Ignition temperature of magnesium /fluro polymers compositions increases with increase of sodium nitrate content in the range studied.
Cal val and flame temperature of HCCF compositions decreases on increase in high carbon content fuels (graphite, charcoal and anthracene) content. It may be mentioned that the stoichiometric composition for the magnesium sodium nitrate binary system contains around 40% magnesium corresponding to Mg/NaNO₃ ratio of ~ 2:3 whereas the system chosen for this study has 2:1 Mg/NaNO₃ ratio. Among the three systems the mixture containing charcoal show higher flame temperature due to presence of internal oxygen. The burn rate also reduces with addition of more and more carbonaceous fuels. Among the three systems the burn rate is higher for the one containing graphite, probably due to the higher thermal conductivity of the mix. Thermo-chemical calculations bring out that almost all the carbon remains as free carbon under anaerobic conditions whereas formation of CO or CO₂ content is a side. Thus, major emission in the IR region may be due to the solid carbon particles. As the $\lambda_{\text{max}}$ should be at ~ 2µm, background emission should be more in the 2-3 µm compared to 3-5 µm region. However, peak emission in 3-5 µm region is more compared to 2-3 µm. This is perhaps due to the formation of CO/CO₂ in the flame because of the participation of atmospheric oxygen. IR efficiency of HCCF based compositions decreases with increase in graphite content whereas it increases with increase in charcoal content. In case of anthracene based compositions it increases up to 30% anthracene content. Graphite and charcoal based compositions show IR spectral ratio of $\Phi_{2.3/3.5}$ in the range of 0.34 - 0.44. However, charcoal based compositions show lower IR spectral ratio suggesting better performance potential.

In case of magnesium/fluoro polymers based compositions teflon shows promising results as revealed by its low IR spectral ratio compared to viton and KeL-F. Substitution of fluropolymer by NaNO₃ results in reduction of the heat output whereas the flame temperature and burn rate increases. Among the three fluropolymer systems the teflon based system shows higher heat output, flame temperature and burn rate because of its higher fluorine content (oxidizer). In case of magnesium/teflon system progressive replacement of teflon by NaNO₃ results in reduction in the IR efficiencies in all wave bands. However, the reduction is more in 2-3 µm wave band compared to 3-5 µm region resulting in decrease of IR spectral ratio. KeL-F and viton based compositions also
indicate similar trends. It may be attributable to decrease in carbon content and increase in content of oxides of carbon in combustion products on increase in NaNO₃.

In the case of systems containing the organic anhydrides, the mixtures studied cover a broader range namely fuel- rich and oxidizer rich compositions. Among four systems studied, heat output and flame temperature are maximum for the Mg (30 %)/NaNO₃ (50 %)/anhydrides (18 %) with 2% viton binder indicating that the composition is near stoichiometry. The thermo-chemical calculations also reveal higher extent of oxidation of the carbon for the oxidizer rich mixtures and presence of more free carbon for the fuel rich mixtures as expected. The burn rate of fuel rich compositions of POCF compositions is higher than those of stoichometric compositions. In the case of compositions containing partially oxidized fuels, increase in IR intensity and IR efficiency is observed with increase in magnesium content in all the wavebands. In case of BPTA and PA based compositions, IR spectral ratio \( \Phi_{2-3/3-5} \) minimum at 20 % magnesium and 30 % magnesium content respectively and further increase in magnesium results in increase in the value of IR spectral ratio. IR spectral ratio of SA and BTDA based compositions reduces up to 40 % magnesium content. The IR intensity curves of all the POCF based compositions in spectral mode show strong peak at 4.0 - 5.0 \( \mu \)m corresponding to oxides of carbon.

Certain interesting observations can be made from the above studies. The total IR output from the flame is from both the background emission due to the carbon particles and the spectral emission of gaseous products like CO, CO₂ and H₂O. The major contribution for the IR output in 2-3\( \mu \)m and 3-5 \( \mu \)m comes form the carbon particles. Thus, total IR output is influenced by the % carbon in the flame products. Extent of formation of CO and CO₂ modifies ratio of IR output in the two regions.

As POCF based compositions gave promising results in terms of IR spectral ratio, thermal analysis of these compositions is also undertaken by applying DSC/TGA technique in nitrogen atmosphere at a heating rate of 10°C/min. Reference data is also generated for individual major ingredients magnesium, NaNO₃ as well as their mixtures with viton binder. It is seen that the increased magnesium content increases the net heat evolution in the exotherms upto 30% magnesium and ignition temperature reduces on increasing magnesium content. It is in line with trends of cal val and flame temperature.
Gaseous combustion products analysis of SA based compositions by GC also exhibited formation of CO$_2$ in larger volume for 30% magnesium containing composition in air. Experimental IR intensity data has been used to develop numerical correlation for prediction of IR intensity.

Following conclusions may be drawn from the present research work for various pyrotechnic compositions studied.

- IR efficiency decreases with increase in graphite content in the composition whereas it increases with increase in charcoal content. IR efficiency of anthracene based composition increases on increase in anthracene content upto 30%.
- The IR spectral ratio $\Phi_{2-3/3-5}$ obtained for the graphite and charcoal compositions is in the range of 0.34 - 0.44. and for anthracene based composition it is about 0.6.
- IR efficiency reduces with increase in NaNO$_3$ content as a replacement of fluropolymer.
- IR spectral ratio of 0.25 is obtained for Mg/teflon/NaNO$_3$ (70/05/25) and 0.36 for Mg/KeL-F/NaNO$_3$ (70/10/20) whereas viton based compositions gave minimum value of 0.42.
- IR efficiency of POCF based compositions increases with increase in magnesium content.
- IR spectral ratio of SA and BTDA based compositions is low as compared to PA and BPTA based compositions.

Following major inferences can be drawn from the present study:

- IR intensity ratio $\Phi_{2-3/3-5}$ of the compositions studied is less than the standard MTV composition.
- SA and BTDA based compositions show low IR spectral ratio $\Phi_{2-3/3-5}$ among all the compositions studied during this work.
- For obtaining low IR spectral ratio the combustion products should have oxides of carbon with no carbon soot.
Incorporation of energetic ingredients like GAP, Poly BAMO, dinitro piperazine will be in step with recent developments that have taken place in the area of propellants, explosives and pyrotechnics. In an innovative approach, double base and composite propellants can be explored for application as decoy flare. There is a scope of application of this class of compositions in spectrally balanced decoy flares.