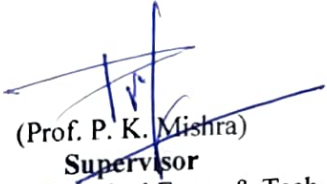


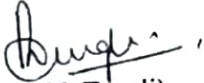
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&
My beloved wife
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loving sons (Tanishq & Avik)

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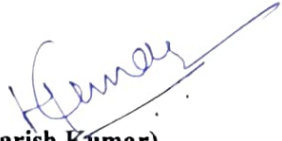
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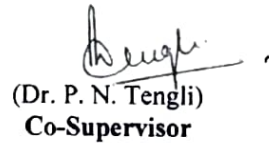
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LIST OF ABBREVIATIONS

A	:	Anatase
AL (P)	:	Aluminum Powder
AP	:	Ammonium Perchlorate
CNT	:	Carbon Nanotube
DTA	:	Differential Thermogravimetric Analysis
EDAX	:	Energy dispersive X-ray Analysis
FTIR	:	Fourier Transformation Infrared
GR	:	Graphene Sheet
HTD	:	High Temperature Decomposition
HTPB	:	Hydroxyl Terminated Polybutadiene
LTD	:	Low Temperature Decomposition
R	:	Rutile
rGO	:	Reduced Graphene Oxide
rGO	:	Reduced Graphene Oxide
SAED	:	Selected Area Electron Diffraction
SCP	:	Solid Composite Propellant
SEM	:	Scanning Electron Microscopy
SRMs	:	Solid Rocket Motors
SVs	:	Space Vehicles
TDI	:	Toluene Diisocyanate
TEM	:	Transmission Electron Microscopy
TGA	:	Thermogravimetric Analysis
XPS	:	X-ray Photoelectron Spectroscopy
XRD	:	X-ray Diffraction

PREFACE

The burn rate modifiers enhance the burn rate of solid composite propellants (SCPs). The burn rate of a SCP can be enhanced by reducing the particle size of ammonium per-chlorate (AP), the work horse oxidizer. High burn rate with less pressure index is one of the prime requirements to achieve the stable and better performance of space vehicles and solid rocket motors. Higher burn rate of propellant reduces the ignition delay and consequently provides the perfect utilization of solid composite propellant. Due to the explosive nature of ammonium per-chlorate below 40μ and higher viscosity of the propellant slurry with the decreased particles size $< 40\mu$ of AP, leads to the limitations for propellant processing. That is why additional additives, known as burn rate modifier, became one of the important and essential ingredients of SCPs and attracted the focus of propulsion researchers to develop a suitable burn rate modifier to increase the burn rate and reduce the pressure sensitivity.

The researchers have synthesized burn rate modifiers of different types starting from powdered transition metals, transition metal oxides, mixture of transition metal oxides, ferrites, chromites, composites, graphene oxide based transition metal oxides, etc. with different particle sizes and surface morphology. The published literature reveals that the catalytic activity of the burn rate modifier has been evaluated by enhancing the thermal decomposition pattern of ammonium per-chlorate, which consequently enhances the burn rate of solid composite propellant.

In the work presented in the thesis, efforts are made to synthesize the effective composites of transition metal oxides (Cu-Cr-Ti oxide) in order to reduce the thermal decomposition of ammonium per-chlorate. In this study the focus was on the action of utilize the large energy band gap of TiO_2 , by introducing the copper chromite of small energy band gap through heterogeneous coupling of the compounds. This heterogeneous coupling has revealed the synergistic effect of the components of synthesized composition of Cu-Cr-O.0.nTiO_2 on the

PREFACE

catalytic activity. Cu-Cr-O.TiO₂ with different molar ratios of Cu-Cr-O:TiO₂ were synthesized and effect of the synthesized catalyst on the thermal decomposition of said oxidizer was evaluated. The best composition of the catalyst thus obtained was further modified with incorporation of the reduced graphene oxide and its effect on the thermal decomposition of AP as well as on the burn rate of solid composite propellant was studied. This thesis is organized in four different chapters

In Chapter1, the introduction to the solid composite propellant (SCP), ingredients of SCP, burn rate of SCP, factors affecting the burn rate, physical and chemical properties of ammonium perchlorate, structure of AP and thermal decomposition behavior of AP are described.

Chapter2 presents the detailed literature review on the enhancement of thermal decomposition of ammonium per chlorate and desirable improvement in burn rate of solid composite propellant (SCP).

Chapter 3 presents the materials and methods used for the synthesis of Cu-Cr-O.nTiO₂ and reduced graphene based (rGO) Cu-Cr-O.0.7TiO₂ composites.

Chapter 4 presents the details of results on the characterization, evaluation of Cu-Cr-O.nTiO₂ and rGO based Cu-Cr-O.0.7TiO₂ on the thermal decomposition of ammonium perchlorate and incorporates a critical discussion. The kinetic study of the thermal decomposition is also discussed in this chapter. In the study, effect TiO₂ molar composition with Cu/Cr molar ratio, calcinations temperature, effect of reduced graphene oxide on the catalytic activity of Cu-Cr-O.7TiO₂, weight % loading of synthesized catalyst with ammonium perchlorate and its effect on the burn rate of synthesized solid composite propellant were studied.

PREFACE

Chapter-5 Summaries the overall conclusions arrived at from the results obtained through this study. The future scope of the work in the related area of research is also briefly outlined at the end of this chapter.

ABSTRACT

Solid rocket motors are the simplest form of all rocket motors. The performance reliability, ease of operation, more safe in transportation and storability made them more attractive in propulsion industries. These mentioned unique properties of SRMs are due the solid composite propellant. The chemical composition of solid composite propellant can be tailored to meet the desired mission requirement i.e. mechanical and ballistic properties. These are few reasons due to which SRMs became famous for use in spite of having the less specific impulse over its counter part of liquid engines.

The solid composite propellant (SCP) is a rubbery like material and consist of an inorganic compound of ammonium per-chlorate (AP): an oxidizer, aluminum powder (ALP): a metallic fuel, flow aids and other additives i.e. burn rate modifier into the matrix developed by the polyurethane reaction of hydroxyl terminated polybutadine (HTPB),toluene di-isocyanate (TDI) and cross linking agents. The burn rate of SCP, one of the important mission requirements, depends on the oxidizer weight %, particle size & shape and can be achieved by some extent. Beyond which enhancement in burn rate will be met by incorporation of burn rate modifier in basic composition of SCP on the expense of oxidizer weight %.

The burn rate of SCP can be enhanced by reducing the particle size of ammonium perchlorate, the work horse oxidizer. High burn rate with less pressure index is always the one of the prime requirement to achieve the stable better performance of space vehicles and solid rocket motors. Higher burn rate of the propellant reduces the ignition delay, consequently provides the perfect utilization of solid composite propellant. Due to the explosive nature of ammonium perchlorate below 40μ and higher viscosity of the resultant propellant slurry limits the propellant processing. That is why additional additives, known as burn rate modifiers, became one of the

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important and essential ingredients of SCPs and attracted the focus of propulsion researchers to develop a burn rate modifier which increases the burn rate and reduces the pressure sensitivity.

From the review of the available literature beginning 1960 it is clear that sufficient work on the usage of burn rate modifiers on thermal decomposition of ammonium per-chlorate has been carried out. This work was started in late 1960's and still undergoing for improving the catalytic activity and reducing the particle agglomeration property of the burn rate modifier. Transition metals, different phase of MnO_2 , NiO, ferrites, nitrides, chromites, and carbon based transition metal composites etc. have been attempted to increase the thermal decomposition of ammonium per-chlorate. From the reported literature, three major stages occur during the decomposition of ammonium per-chlorate as listed below.

1. Crystallographic change: The structure of ammonium per-chlorate changes from orthorhombic to cubic. This event is endothermic in nature.
2. Low Temperature Decomposition (LTD): Ammonium per-chlorate get partial decomposition into its intermediates. This event is exothermic in nature.
3. High Temperature Decomposition: This is the final stage of AP decomposition and all the formed intermediate compounds got fully decompose into their smallest molecules. This event is also exothermic in nature.

The reported literature indicates that there is no effect of catalyst on the crystallographic change with temperature where as a significant effect is observed on the low and high temperature decomposition (LTD and HTD) of ammonium per-chlorate. The particle size, shape, compositions, % loading affect the decomposition pattern of the mention oxidizer. The merging of low and high temperature decomposition peaks and appearance at the lowest possible

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Temperature is the prime objective for designing the burn rate modifier. The amine modified carbon nitride, graphene based transition metal oxide composites have delivered the required decomposition pattern of ammonium per-chlorate.

The scientists and researchers of propulsion arena from all over the globe are putting their best efforts for developing the burn rate modifier capable of reducing the ignition delay and increasing the combustion energy in the solid propellant system. In line with this, The researchers have landed up to the carbon based transition metal oxides composites, incorporation of nitride group to the graphene. The motivation behind the development of such a burn rate modifier is probably because of the energetic property of carbon in the form of carbon nanotubes and graphene sheet.

In the present work efforts were made to synthesize the effective composites of transition metal oxides with the aim of reducing the thermal decomposition of ammonium per-chlorate. In this study the focus was on the utilization of the large energy band gap of TiO_2 , by introducing the copper chromites of small energy band gap and made the heterogeneous coupling of the compound. This heterogeneous coupling has revealed the synergistic effect on the catalytic activity of as synthesized composition of $\text{Cu-Cr-O} \cdot 0.0 \cdot \text{TiO}_2$. $\text{Cu-Cr-O} \cdot \text{TiO}_2$ with different molar ratio $\text{Cu-Cr-O} \cdot \text{TiO}_2$ was synthesized and effect of as synthesized catalyst on thermal decomposition of said oxidizer was observed. Thus the best composition of the catalyst thus obtained was further modified with the incorporation of reduced graphene oxide and the effects on thermal decomposition of AP as well as on the burn rate of solid composition propellant were studied. The effects of TiO_2 molar composition on Cu/Cr molar ratio, calcinations temperature, weight % loading of synthesized catalyst with ammonium perchlorate were studied and it was

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found that Cu-Cr-O.0.7TiO₂ calcined at 300°C exhibited excellent catalytic activity over the thermal decomposition of AP. Further the catalytic activity of the optimal catalyst compositions was improved by incorporation of reduced graphene oxide. The catalyst was synthesized using the sol-gel method assisted with the modified Hummer method. The ammonium perchlorate was modified with the different weight% catalyst loading with AP and thermal decomposition study was carried out using the TG/DTA technique. The 5% of catalyst modified AP exhibited the best thermal decomposition pattern in which both LTD and HTD peaks merged together with a faster rate of decomposition. In the study of burn rate evaluation of solid composite propellant, the catalyst has delivered the 175% higher burn rate than the currently used commercial catalyst.