

**SYNTHESIS AND CHARACTERIZATION OF  
NOVEL OXIDIZER FOR COMPOSITE  
PROPELLANTS**



**By**

**Tariq Zaman**

**Submitted to the Department of Chemical Engineering,  
School of Chemical and Materials Engineering (SCME),  
in partial fulfillment of the requirements for the degree of  
Masters in Energetic Materials Engineering**

**National University of Sciences and Technology NUST,  
ISLAMABAD  
June, 2008**

**IN THE NAME OF ALLAH  
THE COMPASSIONATE  
THE MERCIFUL**

**Praise to be Thee; we do not know  
anything except What Thou hast made  
known to us: indeed Thou art the best  
knower, the wisest.**

(Al-Quran 2-32)

# **DEDICATION**

**To**

**All Those Who Sacrifice Their  
Present for the Better Future of  
Pakistan!**

## ABSTARCT

Enhanced performance of propellants and explosives is the most sought-after attribute for ambitious research progress in the field of high energy materials. Defense and space sector priorities have always kept research and development efforts active in the area of propellants and explosives. The use of chlorine free high performance oxidizers in solid rocket propellants may reduce launch cost while producing less polluting exhaust products. Considerable effort has been expended in the search for high energy oxidizers that are useful in rocket propellant formulation. These oxidizers should be dense, thermally stable and relatively shock insensitive. It has now been found that hydrazinium nitformate (HNF) has the required properties. Nitroform is a very valuable compound for use in the preparation of HNF due to its high oxygen contents and labile hydrogen atom. Many methods have been tried to obtain HNF of desired quality.

Present work deals with a new method of producing trinitromethane (nitroform) by the nitration of isopropyl alcohol with a mixture of fuming nitric acid and concentrated sulphuric acid and the isolation of nitroform with the help of dichloroethane. To the best of our knowledge these two approaches have been employed for the first time. Further the present work relates to a method of preparing HNF by the addition of 96% hydrazine to a solution of nitroform in dichloroethane followed by the purification of the product by means of recrystallization, a solution being made in methanol. Various instrumental techniques have been employed to characterize HNF prepared during the present work, which confirm the purity of the compound.

## ACKNOWLEDGMENTS

In the name of Almighty **Allah**, who gave me the courage and helped me to complete the work. I feel my privilege and pleasure to express my profound and cordial gratitude to my honorable supervisor **Dr. A. Q. Malik** and to my co-supervisor **Miss. Tayyaba Noor** for their valuable guidance, skilled advice and ever-encouraging attitude throughout the work. Under their kind and scholastic guidance and consistent encouragement this work got its present shape. Special thanks to **Dr. K. Sanauallah** and **Dr. M. Bilal Khan** for their encouraging attitude. I am thankful to **Dr. Javed H. Zaidi**, Department of chemistry, Quaid-I-Azam University, Islamabad for helping me in the mechanism of the reaction. I am thankful to all my classmates especially **Khalid Nawaz, Manager (NDC)**, **Nadeem Ahmad, SE (PAEC)** and **Rahat Rasool, (PAEC)** for their co-operation and help.

## **TABLE OF CONTENTS**

	<b>Page</b>
Abstract	i
Acknowledgements	ii
List of Tables	iii
List of Figures	vi
Abbreviations	v
<b>CHAPTER 01    <i>Introduction</i></b>	<b>1-21</b>
1.1 Rocket propellants	1
1.2 Types of rocket propellants	1
1.3 Solid propellants	1
1.3.1 Double base propellants	1
1.3.2 Modified double base propellants	2
1.3.3 Composite propellants	2
1.4 Ingredients of composite propellants	3
1.4.1 Binder system	3
1.4.1.1 Composition of binder system	3
(i) Pre-polymer	3
(ii) Crosslinking agent	7
(iii) Curing agent	7
(iv) Plasticizers	8
1.4.2 Additives	9
(i) Burning rate modifiers	9
(ii) Surface agents and binder	11
(iii) Antioxidants	11
(iv) Catalysts	12
1.4.3 Oxidizers	13
1.4.4 Solid fuels	13
1.5 Chronological development of composite rocket propellant	14
1.6 Conventional oxidizers and their demerits	17
1.6.1 Nitronium perchlorate or NP [NO <sub>2</sub> ClO <sub>4</sub> ]	17
1.6.2 Lithium perchlorate or LP (LiClO <sub>4</sub> )	17
1.6.3 Hydrazinium diperchlorate or HP [N <sub>2</sub> H <sub>6</sub> (ClO <sub>4</sub> ) <sub>2</sub> ]	17
1.6.4 Potassium perchlorate or KP (KClO <sub>4</sub> )	17
1.6.5 Ammonium nitrate or AN (NH <sub>4</sub> NO <sub>3</sub> )	18
1.6.6 Ammonium perchlorate or AP (NH <sub>4</sub> ClO <sub>4</sub> )	18
1.7 Novel oxidizers	19
1.7.1 Cyclic nitramines	19

1.7.2	Ammonium dinitramide [ADN, $\text{NH}_4\text{N}(\text{NO}_2)_2$ ]	20
1.7.3	Hydrazinium nitroformate, [HNF, $\text{N}_2\text{H}_5\text{C}(\text{NO}_2)_3$ ]	21

**CHAPTER 02      *Synthesis and properties of HNF*      22-42**

2.1	Introduction	22
2.2	Synthesis of HNF	22
2.2.1	Preparation of nitroform (trinitromethane)	23
2.2.2	Separation of nitroform from reactoin mixture	24
2.2.3	Synthesis of HNF	25
2.3	Physiochemical properties of HNF	26
2.3.1	Crystallography	29
2.3.2	Toxicity	29
2.3.3	Sensitivity	30
2.3.4	Stability	30
2.3.5	Thermal decomposition	31
2.3.6	Compatibility	33
2.4	HNF Propellants	34
2.5	Theoretical performance of HNF, ADN & AP based propellants	37
2.6	HNF as Monopropellant	39
2.7	HNF in Hybrid propellants	40
2.8	Further development	41
2.9	Conclusion	42

**CHAPTER 03      *Experimental*      43-54**

3.1	Introduction	43
3.2	Experimental setup	43
3.3	Drying of solvents	44
3.3.1	Dichloroethane	44
3.3.2	Ethyl acetate	45
3.3.3	Pet ether	45
3.3.4	Methanol	45
3.3.5	2-propanol (isopropyl alcohol)	45
3.4	Instrumentation	45
3.5	General synthetic strategy	46
3.5.1	Synthesis of nitroform (trinitromethane)	46
3.5.2	Isolation of nitroform	47
3.5.3	Synthesis of HNF	48
3.6	Procedure	48
3.6.1	Synthesis of nitroform (trinitromethane)	48
3.6.2	Mechanism	49
(i)	Formation of nitronium ion	50
(ii)	Nitration of Isopropyl alcohol	51
3.6.3	Isolation of nitroform	51

3.6.4	Synthesis of HNF	53
3.6.4(a)	Mechanism	53

**CHAPTER 04 RESULTS AND DISCUSSION** **55-64**

4.1	Physical properties	55
4.1.1	Melting point	55
4.1.2	Molar mass	55
4.1.3	Appearance	56
4.1.4	Color	56
4.1.5	Oxygen balance	57
4.2	Elemental Analysis	58
4.3	Spectral properties	58
4.3.1	FTIR spectroscopy	59
4.3.2	UV-Visible spectroscopy	60
4.4	Thermal analysis	62
4.4.1	TG-IR	64

**CHAPTER 05 CONCLUSION AND FUTURE RECOMMENDATIONS** **65-70**

5.1	Energetic oxidizer	65
5.2	Clean oxidizer	65
5.3	Compatibility with energetic binders	66
5.4	HNF as monopropellant	67
5.5	HNF in hybrid propellants	67
5.6	Future of HNF	68
5.7	Conclusions	69
5.8	Suggestions for Future Work	70

**REFERENCES** **71-73**



## ***LIST OF TABLES***

<b>Table</b>		<b>Page</b>
Table 1.1	Composition of a typical Cast Double Base propellant	3
Table 1.2	Composition for typical Composite Modified Cast Double Base propellant	4
Table 1.3	Some common inert prepolymers	5
Table 1.4	Properties of the polymers used in composite propellants	6
Table 1.5	Examples of energetic polymers	7
Table 1.6	Crosslinking agents for composite rocket propellants	8
Table 1.7	Crosslinking systems for prepolymers	9
Table 1.8	Major plasticizers for composite propellants	10
Table 1.9	Major ferrocene derivatives used as burning rate modifiers	11
Table 1.10	Commonly used coolants for composite propellants	11
Table 1.11	Binder-solid bonding agents	12
Table 1.12	Catalysts for polyurethane binder propellants	13
Table 1.13	Comparison between different oxidizers	22
Table 2.1	Physical properties of Nitroform or trinitromethane, $\text{HC}(\text{NO}_2)_3$	25
Table 2.2	Physiochemical properties of HNF	29
Table 2.3	IR and Raman absorbance Frequencies of Neat Solid HNF	30
Table 2.4	Sensitivity Data of HNF	32
Table 2.5	Sensitivity Data of HNF and HNF (pressed) Propellant mixtures in Comparison with Typical AP Based Propellant System	38
Table 2.6	Theoretical maximum performance for selected high performance solid propellants	41
Table 3.1	Different properties of the used reagents	47
Table 4.1	Physical data of HNF	59
Table 4.2	Elemental analysis of HNF	62
Table 4.3	FTIR data of HNF	63
Table 4.4	UV-Visible spectrum of HNF	64
Table 5.1	Comparison between AP, AN and HNF	70

## *LIST OF FIGURES*

<b>Figure</b>		<b>Page</b>
Figure 1.1	Chronological developments of double base propellants and composite propellants. Typical HNF Crystals	17
Figure 2.1	Typical HNF Crystals	31
Figure 2.2	Vacuum specific impulse [m/s] for HTPB and GAP based propellants	37
Figure 2.3	characteristic velocities vs. pressure of HNF/Al/GAP and AP/Al/HTPB	39
Figure 2.4	Comparison of HNF, AP, and ADN based propellant	40
Figure 3.1	Reaction between nitric acid and isopropyl alcohol	52
Figure 3.2	Formation of nitronium ion	53
Figure 3.3	Extraction of nitroform	54
Figure 3.4	Mechanism for nitration of isopropyl alcohol	55
Figure 3.5	Reaction between hydrazine and nitroform	56
Figure 4.1	HNF	60
Figure 4.2	FTIR spectra of HNF	63
Figure 4.3	Reported FTIR spectra of HNF	64
Figure 4.4	UV-visible spectrum of HNF	65
Figure 4.5	Reported UV-visible spectrum of HNF	65
Figure 4.6	Decomposition of HNF	66
Figure 4.7	Thermo gravimetric analysis of HNF	67
Figure 4.8	TG-FTIR spectra of decomposition products of HNF	68

## ABBREVIATIONS

ADN	ammonium dinitramide
Al	aluminium
AN	ammonium nitrate
AP	ammonium perchlorate
BAMO	poly 3,3-bis(azidomethyl) oxetane
CMDB	composite modified double base
CTPB	carboxyl-terminated polybutadiene
DCE	dichloroethane
DTA	differential thermal analysis
DOA	dioctyl adipate
DSC	Differential Scanning Calorimeter
FTIR	Fourier transform infrared spectroscopy
GAP	Glycidyl Azide Polymer
HAN	hydroxylammonium nitrate
HAP	hydroxylammonium perchlorate
HMDI	hexamethylene diisocyanate
HMX	tetraethylene tetranitramine
HNF	Hydrazinium Nitroformate
HNIW	Hexanitrohexaazaisowurtzitane, (CL-20)
HTPB	hydroxy-terminated polybutadiene
$I_{sp}$	specific impulse
$I_{vac}$	specific impulse in vacuum
IDP	iso decyl pelargonate
IPDI	iso phoron di-iso-cyanate
LD <sub>50</sub>	Lethal Doses for 50% of the cases
NG	nitroglycerine
NC	nitrocellulose
NF	nitroform (trinitromethane)
NIMMO	nitramethylmethoxetane
NP	nitronium perchlorate
PBAA	polybutadiene-acrylic acid
PBAN	acrylic acid, acrylonitrile, and butadiene terpolymer
PGN	polyglycidal nitrate
PolyGlyn	polyglycidal nitrate
PLN	polynitromethyl oxetane
RDX	Cyclotrimethylene trinitramine
$T_{gl}$	glass transition temperature
$T_{mp}$	melting point temperature
TGA	thermogravimetric analysis
TMD	Theoretical Maximum Density
TMETN	trimethylolethane trinitrate