Solid Propellant Chemistry

Condensed Phase Behaviour of Ammonium Perchlorate-Based Solid Propellants

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K Kishore & K Sridhara

Foreword by

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FOREWORD

Despite rapid growth and developments in different areas of advanced solid rocket propellants such as composite modified double base (CMDB), fuel rich propellants (FRP) for IRR applications, ammonium dinitramide (ADN) and hydrazinium nitroformate (HNF) based propellants, during last few decades, composite propellants (CP) are still widely used for different military and space applications. A number of research groups are engaged in the basic and applied research on the combustion of composite solid propellants. Although the literature on various aspects of combustion of CP is enormous, but it is scattered. There has been considerable interest in understanding the role and importance of condensed phase and flame zone reactions in controlling the burning process. The combustion behaviour of CP is characterised by the steady linear regression rate of the burning surface and is regarded as the most important and critical performance parameter for the rocket designer.

While Chapter 1 of the present monograph introduces the subject of combustion of CP, Chapter 2 deals with the effect of particle size and its distribution on condensed phase reactions, measurement of burning rates, and the factors affecting the burning behaviour. In addition, the combustion of CP in low, medium and high pressure domains has also been discussed. The effect of other variables affecting burning rate like oxidizer, shape, size, size distribution and purity, fuel and metal content, shape and particle size of metals, type and ratio of binder-plasticizer and total solid content (solid loading), influence of catalysts and additives, initial pressure and initial temperatures, effect of processing parameters, and ageing behaviour are also discussed. The oxidizer content not only affects the energy in terms of specific impulse ($I_p$), but also the mechanical properties of the resultant propellant, safety and cost. While comparing the properties of the various oxidizers namely, ammonium perchlorate (AP), cyclo-1,3,5 trimethylene-2,4,6 trinitramine (RDX), octahydro-1,3,5,7-tetranitro-1,3,5,7 tetrazocine (HMX), ADN, ammonium nitrate (AN), one must look for higher performance, good compatibility and stability, adaptability to tailor a wide burning rate range, and relative insensitivity, low cost and availability.

Chapter 3 essentially reviews the thermal decomposition behaviour of AP (proton transfer, electron transfer) and effect of pressure on the thermal decomposition behaviour. Various binders (polyesters, polyethers, polyurethanes, polybutadienes, etc.) have been used in CP formulations. Chemical and structural characteristics of the binder and its role in the overall combustion of CP is very important. This aspect has been brought out in Chapter 4.
including salient features of fuel-binder pyrolysis and condensed phase and gas phase combustion behaviour of fuel-cum-binder. The authors have also covered the modelling studies in each subchapter, the importance of which does not need overemphasis. Ferrocene compounds, which have been used to increase burn rates (100-150 per cent) of CP are prone to migration and affect the ageing process. The authors have covered these aspects in Chapter 5. Ageing is a very important aspect that has to be considered when formulating propellants for various missions. Various factors that affect the safe and useful life of the propellants, kinetics and mechanism of ageing, estimation of safe-life, and ways and means to increase the life of CP are considered by the authors in Chapter 6.

To obtain higher energy ($L_e$), superior mechanical properties, new and more energetic binders and oxidizers are being searched continuously. Oxetanes—bis-azidomethyl oxetane (BAMO) and azidomethyl methyl oxetane (AMMO)—and their derivatives are attracting considerable attention due to their low polydispersity, low glass transition temperature ($T_g$), higher energy and easy handling characteristics. Glycidyl azide polymer (GAP) is finding applications in CP, low vulnerability ammunition (LOVA) propellants for guns, and plastic bonded explosives (PBX). Chapter 7 is therefore devoted to high energy binders, oxidizers and advanced propellants. To overcome the limitations of AP-based propellants, various other environment-friendly oxidizers like ADN and HNF are being evaluated. The properties of these two oxidizers are explained in detail in Chapter 7. The authors’ views on the future directions of research in the area of combustion of composite propellants are covered in Chapter 8.

This monograph is the most comprehensive review of condensed phase behaviour of AP-based solid propellants and covers all important aspects of AP-based CP. The language is very lucid and easy to understand. Prof. K Kishore is a well known propellant and polymer chemist and a renowned teacher and has incorporated his wide and rich experience both as a researcher and a teacher in the form of this monograph. It was indeed a delightful experience for me to work with Prof. Kishore during the preparation of the monograph. I am confident this monograph will serve as a trustworthy reference book in the field of CP to all scientists/engineers of aerospace engineering.

(APJ Abdul Kalam)
SA to RM and Secretary Defence R&D
Ministry of Defence
PREFACE

There are about half a dozen books dealing with propellant chemistry but much of the information available therein is rather old and none of them discusses the condensed phase combustion chemistry of solid propellants in detail. The present monograph is the first of its kind in which the material accumulated over several decades has been sifted from literature and articulated to highlight the importance of condensed phase chemistry which seems to be vital for understanding the key phenomena like burning rate modulation and ageing. Besides, the subtle roles of binders, oxidizers and catalysts have been brought out. It has also been demonstrated as to how condensed phase chemistry is vital in understanding the commonly observed phenomena in solid propellants like extinction, intermittent, plateau and flameless combustions.

In defence and space laboratories and also in some private companies, a large number of scientists and engineers are involved in work on propellants. This monograph will be extremely useful for this large community, not only in helping them to assess the progress made in AP-based composite solid propellants but also to grasp the key phenomena in an organised manner. It will also serve as a useful information source for those who wish to enter the fascinating field of solid propellant combustion. Besides, there are many academic institutions and universities where propellant chemistry is taught either as an independent subject or under the general courses in combustion or fuel science and technology. This monograph will serve as a good reference book not only for those opting for these courses but also for those engaged in basic research in propellant chemistry. This monograph is aimed at catering to the information needs of readers at postgraduate and research levels. The readers of course are required to have some exposure in propellants.

The authors are extremely thankful to the Indian Space Research Organisation (ISRO), Bangalore and ISRO-Indian Institute of Science-Space Technology Cell for providing funds for writing this monograph. The authors are also thankful to ISRO for agreeing for the open publication of the monograph by DRDO and to have no claim on its copyright from DRDO. They are also thankful to Mr S Vasudeva Murthy for the assistance rendered in the preparation of the manuscript.

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CHAPTER 1

INTRODUCTION

Man's desire to explore outer space and build a strong defense edifice has culminated in the development of space vehicles and missiles in which composite solid propellants (CSP) are the major source of chemical energy\textsuperscript{1,2}. Being complex mixtures, their combustion behavior too is quite complex and is not yet fully understood. CSP\textsuperscript{3-6} are heterogeneous mixtures consisting of a large proportion of oxidizer, usually ammonium perchlorate (AP), and a fuel-cum-binder, generally hydroxy-terminated polybutadiene (HTPB) or carboxy-terminated polybutadiene (CTPB). In addition, they contain curing agents, plasticizers and bonding agents for improving their mechanical properties, and metallic fuel additives and burning rate modifiers for improving specific impulse and burning rate, respectively. A typical CSP composition is given in Table 1.1.

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Weight, %</th>
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<tr>
<td>Ammonium perchlorate</td>
<td>60 - 84</td>
</tr>
<tr>
<td>Butadiene polymer</td>
<td>12 - 16</td>
</tr>
<tr>
<td>Aluminium</td>
<td>2 - 20</td>
</tr>
<tr>
<td>Curing agent(s)</td>
<td>0.2 - 1.0</td>
</tr>
<tr>
<td>Stabilizers</td>
<td>0 - 1.0</td>
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The chemistry of a CSP formulation and its combustion is an engrossing complex phenomenon and has been the subject of many studies\textsuperscript{7-14}. The combustion profile of the propellant can be classified into several zones, such as heated zone, chemical reaction zone, burning surface zone and porous zone, all in the condensed phase, and fragment flowing zone and product zone in the gas phase\textsuperscript{15}. The combustion of CSP occurs to varying degrees in both condensed
and gas phases\textsuperscript{16}. There are two schools of thought regarding the combustion of CSP. According to one school, the gas phase processes are believed to control the burning of the propellant; the gaseous species emanating from the pyrolyzing surface are considered to intermix and react exothermally in the gas phase to form final products, liberating heat and establishing an equilibrium flame temperature. Part of the heat generated in the flame is transferred to the surface to be used up in pyrolyzing and gasifying the surface layer, so that the combustion process recurs steadily. In modelling gas phase combustion processes, the reactions occurring therein are considered to be fast and the heat transfer from the flame to the surface is considered to be the rate-controlling step.

The other school of thought\textsuperscript{16-18}, which also includes the Bangalore group\textsuperscript{19-26}, believes that the condensed phase reactions occurring at or just below the burning surface are important. The decomposition/degradation in addition to the gas phase reactions of the oxidizer and the binder, and the cross-reactions between their products are exothermic in nature and contribute significantly to the total energy of the propellant. Condensed phase processes also include melting and gasification phenomena at the surface. Knowledge about the chemistry of condensed phase reactions, which is a key process, will facilitate understanding of vital phenomena like burning rate modulation and ageing. An organized comprehension of the condensed phase chemistry will also provide a better insight into the extinction phenomenon and intermittent, plateau and flameless combustion.

Kishore and coworkers\textsuperscript{19-27} demonstrated both qualitatively and quantitatively the existence of condensed phase reactions. In AP/polystyrene (PS) model propellant\textsuperscript{19-26}, mass spectroscopic analyses have indicated that the mass spectrum of CSP is different from the additive spectra of AP and PS individually. Likewise, the enthalpy of propellant decomposition, which is a nucleation-controlled phenomenon\textsuperscript{28}, is larger compared to the additive enthalpies of the individual components\textsuperscript{29,30}. This excess enthalpy of the condensed phase is about one third of the calorimetric value (total heat of combustion)\textsuperscript{18,23,24,31}. This is corroborated by a master plot of the thermal decomposition rate against the burning rate of propellants, which suggests that the burning rate increase/decrease is about one third of the order by which the rate of thermal decomposition increases/decreases in the presence of additives\textsuperscript{21,22,25}. Separation of the binder portion from the quenched
propellant surface and analysis by thin layer chromatography have shown a number of spots, suggesting complex nature of the condensed phase reactions\textsuperscript{25,32}. The largest proportion of the intermediate was found to have peroxo linkages in the polymer backbone. Spectral and chemical analyses confirmed the existence of poly(styrene peroxide) (PSP) in AP/PS propellant system\textsuperscript{32,33}. Both partially decomposed propellant residue and an aged propellant show the presence of this intermediate, which was later used as a natural catalyst for burning rate modification\textsuperscript{34,35}. This has led to detailed investigations on the syntheses of several polyperoxides of styrene\textsuperscript{36-43}, methyl methacrylate\textsuperscript{44}, vinyl naphthalene\textsuperscript{45}, divinylbenzene\textsuperscript{46}, vinylacetate\textsuperscript{47}, \(\alpha\)-methyl styrene\textsuperscript{48,49}, copolyperoxides\textsuperscript{50,51}, terpolyperoxides\textsuperscript{52} and on several aspects of their physicochemical behaviour\textsuperscript{53,54}.

Thermochemical calculations of exothermic degradation of polymeric peroxide have led to the unique discovery that polymers of this class undergo "autopyrolysis" and these are highlighted as special fuels\textsuperscript{55}. The critical AP concentration in CSP for just sustaining its combustion is considerably reduced in the presence of PSP due to its high pyrolytic exothermicity\textsuperscript{56} not only in the combustion of propellant but also in the ageing process. It has been demonstrated that the condensed phase reactions are important. In this laboratory, the rate controlling step for the ageing process has been shown to be proton transfer in oxidizer decomposition, which has led to the use of ammonium salts for increasing the longevity of propellants\textsuperscript{57-66}.

The literature on various aspects of the process of combustion of CSP is enormous and fragmentary. In this book, an attempt has been made to present various facets of propellant combustion, focusing attention on the importance of condensed phase reactions, hitherto unattempted in this fashion. The subtle role of the binder, which has so far remained latent, compared to that of the oxidizer, is also brought into prominence and its impact on combustion parameters has been presented. While maintaining the above objectives, this book begins with a brief introduction about CSP in this chapter followed by a discussion on the influence of non-chemical factors, such as pressure and initial temperature in Chapter 2. Chapters 3, 4, 5 and 6 are devoted to CSP, oxidizer, fuel-binder, catalyst and ageing, respectively. Chapter 7 describes recent developments in the area of high performance binders, oxidizers and propellants. These aspects are briefly highlighted below.
Solid Propellant Chemistry

The combustion behaviour of CSP is generally characterized by the steady linear regression rate of the burning surface, known as the burning rate \( \dot{r} \), and is regarded as one of the most important performance parameters. It strongly depends on the nature of the condensed phase and gas phase reactions and on other variables.\(^{2,7}\) But its dependence on pressure \( P \) and initial temperature \( T_o \) is the most important and well recognized aspect.\(^{67,68}\) Although information on these aspects is available in literature, important features of empirical relationships of \( \dot{r} \) with \( P \) and \( T_o \) are discussed in this book to get an overall comprehensive picture as to how \( \dot{r} \) is primarily influenced by the oxidizer, nature of the fuel-binder, catalyst, heat release rate, etc. Some of these features are helpful in understanding plateau and extinction phenomena as well.

The combustion behaviour of CSP also depends on the burning behaviour of its major component—the oxidizer AP—which happens to be the most commonly used oxidizer in CSP formulations. AP is a unique oxidizer, which is capable of supporting its own combustion (i.e., monopropellant) also and has been the subject of vast investigations for a long time to understand its decomposition and deflagration behaviour. AP deflagration has also been used as a prelude to the development of a suitable model for CSP combustion. Despite the existence of extensive literature on AP, its decomposition mechanism is still a matter of debate, while the deflagration process is intriguing in its various facets, making their mechanistic understanding more elusive as much it is pursued. For example, a clear understanding of the low pressure deflagration limit (LPL) has remained an elusive goal. Literature has been organised to clearly comprehend the decomposition and deflagration processes, emphasis being laid on the analysis of LPL. Although the oxidizer happens to be the largest ingredient in CSP, it is the binder which is the key fuel in solid propellant formulations, controlling their energetics, but it has not received adequate attention.\(^70\) The impact of structural and other physical features of the binder has largely been ignored in literature. The subtle role of the binder, which has so far remained latent compared to that of AP, has also been brought into prominence, and its impact on combustion parameters has been discussed. Chemistry of AP decomposition/deflagration and binder degradation/combustion has been presented separately to assess their relative performance in CSP.

A lot has been said in literature about various kinds of catalysts and additives for controlling the \( \dot{r} \) of CSP and AP. The most effective
and commonly used catalysts are transition metal oxides (TMO). The present book overviews the existing knowledge in the field of catalysts and discusses the mechanism of their action on AP and binder decomposition. Currently, ferrocene derivatives are receiving considerable attention and much of the available information is patented. In this book, information on various ferrocene derivatives used in CSP has been consolidated; their advantages and multifunctional role have also been highlighted.

The useful life of a propellant is extremely important from the point of view of its flawless performance during the stipulated usable period. Various chemical reactions that occur and lead to changes in characteristics of the oxidizer and the binder are presented. Strategies for remedial measures, which have emerged from such studies, have been pointed out.

There has always been interest to develop high energy binders and oxidizers which could not only provide high specific impulse but should also be safe to handle and should produce pollution-free combustion plumes. High energy polymers based on oxetanes and their derivatives are attracting considerable attention and appear to be the most suited binders in this regard. A separate chapter has been presented on various high energy binders and oxidizers.