Preface

Encyclopedia of Oxidizers

This is the first set of a series of sets in the *Encyclopedia of Rocket Propellants* summarizing the existing literature on rocket propellants, both liquid and solid rocket propellants. The first set, *Encyclopedia of Oxidizers*, contains information on both liquid and solid oxidizers. The second set to be released shortly after, *Encyclopedia of Liquid Fuels*, is a summary of literature on liquid fuels. The differentiation between liquid fuels and solid fuels was necessary because solid fuels usually are the binders for solid propellants, a topic reserved for a future, planned set in this series. The third set, *Encyclopedia of Monopropellants*, will be a very comprehensive summary of the chemistry of monopropellants. The fourth and fifth sets, planned for the coming years, will describe the performance of hypergolic and nonhypergolic bipropellant combinations, usually combinations of oxidizers and fuels. If time permits, future sets will eventually deal with various aspects of solid propellants, such as “Composite Solid Propellants” and “Double-Base Solid Propellants”, and they would also include gas generants which have found numerous industrial applications such as in airbag inflators in automobile occupant passive restraint systems. “Hybrid Propellants” may find a home in a future set in the distant future.

In spite of the increased capabilities of online search engines like Google Scholar, the current sets of books will be an indispensable tool for scientists and engineers in the rocket propulsion industry and research organizations. The hazards of working with rocket propellants need to be well understood.

Our *Encyclopedia of Rocket Propellants* book series will be the preferred reference source for future generations of rocket propellant chemists. When referring to the profession of rocket propellant chemists, this should not be done without quoting, tongue-in-cheek, the preface written by I. Asimov for J. D. Clark’s landmark book *Ignition!*:

“Now it is clear that anyone working with rocket fuels is outstandingly mad. I don’t mean garden-variety crazy or a merely raving lunatic. I mean a record-shattering exponent of far-out insanity.”

The reader will notice, though, that the correct terminology should have been “rocket propellants” and not just “rocket fuels”. The author of the current book feels that this quote from the literature adequately describes the risks involved for chemists involved with developing more energetic rocket propellants and explosives. The dividing line between powerful rocket propellants and potential explosives is very narrow and rocket propellant development is often treading on a narrow path. Nevertheless, this is one of the most exciting branches of chemistry to be involved with. It is the

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chemistry of rocket propellants that has enabled the dramatic advances in space technology, with many benefits to the common consumer.

Reviewing the recent literature on rocket propellants and other energetic materials, one will notice that the increased capabilities of modern computers have enabled chemists to predict the performance of new molecules even before these compounds were ever made and tested in the laboratory. Numerous publications referenced in our books deal just with theoretical explorations of this type, and that is a difference to previous book publications on this subject.

Rocket propellants generally consist of oxidizers and fuels. The term "rocket fuels" is often misused to describe rocket propellants in general. Correct use of the term "rocket fuel" would only apply to the combustible, fuel-rich part of a propellant combination. Oxidizers for liquid rocket propellants are generally subdivided by physical properties and/or by reactivity. So we differentiate between storable and non-storable (usually cryogenic) propellants. When looking at the reactivity of hypergolic combinations, it is more often the oxidizer and not the fuel that determines if the resulting combination is self-igniting on contact or not. When listing combinations of rocket propellants, we always list the oxidizer first. This is because the properties and the activity of the oxidizer determine the nature of the combination more so than properties of the fuel would. There are fewer oxidizers than fuels in our inventory, so it is easier to organize book chapters on rocket propellant combinations first by arranging them by oxidizers and later by fuels.

A frequently used alternate term for oxidizer, mostly in biologic systems, is *oxidant*. This term is used mostly in life sciences and less frequently in the world of rocket propellants. When conducting literature searches, it may be advisable to search for both terms. A less frequently used term for propellant is *propellent*. And again, when doing literature searches, one may want to search for both variations of the spelling.

About the Format of the Several Sets in the Encyclopedia of Rocket Propellants

The manuscript for the *Encyclopedia of Rocket Propellants* has evolved through several iterations and modifications, and the terminology in designating sets, volumes, chapters, and sections has changed during this period. The most recent terminology is now referring to *Encyclopedia of Oxidizers* as a set of five volumes and similarly referring to *Encyclopedia of Liquid Fuels* as a set of five volumes. The sequence of volumes in a set and the sequence of chapters in a volume is arranged in alphabetical order, similar to a dictionary.

A critical reviewer might describe the format of the books as not much more than an annotated bibliography. The author is aware of the fact that collecting and reproducing references from the literature is not a very creative job, but to arrange these thousands of references in a systematic manner requires a good understanding of the subject matter, justifying the effort especially in the age of computers and the internet.

Fifty years ago it used to be common practice to cite literature references followed by their Chemical Abstract citation. Providing the Chemical Abstracts citation often allowed the reader to read a more detailed abstract and to decide if it is worthwhile to obtain a complete copy of the original publication. Nowadays that function has been taken over by Digital Object Indentifiers (DOI) in the Internet. Nevertheless, we have continued to carry along a few Chemical Abstract citations in addition to the DOI. Some of those citations are useful because they direct users to the Chemical Abstracts Registry Number which can be used for subsequent, more specific searches in computerized data bases. Some of the books on energetic materials even contain an index of Chemical Abstract Registry Numbers.

Selection of Oxidizers

When selecting combinations of bipropellants, hypergolic or nonhypergolic, it is usually the oxidizer that determines the reactivity of the combination once oxidizer and fuel meet in the rocket engine combustion chamber. The choice of oxidizers has less of an impact on the specific impulse than the choice of fuels with their widely varying hydrogen content. The selection of oxidizers is governed by a number of considerations:

- Specific impulse
- Reactivity with the intended fuel partner (hypergolic or nonhypergolic?)
- Boiling point/critical point temperature
- Storage stability
- Density (important for compact, pressure-fed systems)
- Corrosivity (corrosive oxidizers require exotic materials for tankage and tubing)
- Toxicity
- Availability
- Cost

The same criteria apply also to the selection of fuels.

Until the beginning of the Space Age, liquid oxygen and fuming nitric acid had been used most extensively, primarily because of low cost and relatively easy handling characteristics. In the field of moderate performance, red fuming nitric acid had proved successful with proper modifications for dealing with its corrosive nature and pressure build-up problem of WFNA during storage. For high performance, liquid oxygen has been used satisfactorily, although additional engineering complications arise because of the need for refrigeration and/or insulation. Among the storable oxidizers, hydrogen peroxide and dinitrogen tetroxide have once been considered as close competitors to red fuming nitric acid. In the group of oxidizers containing fluorine, liquid fluorine has generally the highest performance. Nonmetallic fluorides have lower performance, but they are storable at room temperature. A common disadvantage of all the compounds in this group of fluorine oxidizers stems from the fact that elemental fluorine is required for the industrial production of many of these oxidizers. The main disadvantage is the toxicity of the exhaust, hydrogen fluoride. Therefore fluorine oxidizers are now a thing of the past, and we include them here only because of historical interest. Outside the field of rocketry, fluorine and some nonmetal fluorides are still used for chemical lasers.

For solid oxidizers, ammonium perchlorate is the most widely used solid oxidizer. A detailed chapter in *Encyclopedia of Oxidizers* deals with ammonium perchlorate. Other solid oxidizers, actually used or evaluated for future use, are ammonium nitrate, ammonium dinitramide, hydrazinium salts, and hydroxylammonium salts, each represented with their own chapter.

An apology is needed to explain the incorrect display of semipolar bonds in nitro groups. Semipolar bonds are currently shown as N=O double bonds instead of semipolar bonds. Semipolar bonds should have been shown as an arrow $N \rightarrow O$. The chemical formula drawing software used here for creating chemical structures did not have an option for semipolar bonds, so for the time being these bonds were shown as double bonds instead.

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