NASA HYDROGEN PEROXIDE PROPELLANT HAZARDS TECHNICAL MANUAL*

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ABSTRACT

The *Fire, Explosion, Compatibility and Safety Hazards of Hydrogen Peroxide* NASA technical manual was developed at the NASA Johnson Space Center White Sands Test Facility. NASA Technical Memorandum TM-2004-213151 covers topics concerning high concentration hydrogen peroxide including fire and explosion hazards, material and fluid reactivity, materials selection information, personnel and environmental hazards, physical and chemical properties, analytical spectroscopy, specifications, analytical methods, and material compatibility data. A summary of hydrogen peroxide-related accidents, incidents, close calls, mishaps and lessons learned is included. The manual draws from an extensive literature base and includes recent applicable regulatory compliance documentation. The manual may be obtained by United States government agencies from NASA Johnson Space Center and used as a reference source for hazards and safe handling of hydrogen peroxide.

BACKGROUND

After green propellant and improved propulsion systems performance initiatives identified hydrogen peroxide (HP) as a candidate propellant for propulsion and power systems, NASA Johnson Space Center (JSC) White Sands Test Facility (WSTF) began to develop a hydrogen peroxide reference document. The purpose of this document was to provide a central source of information to enable the user to assess HP hazards. While there are several excellent sources of HP hazards assessments documents, they are dated before 1970, and therefore may not utilize data and other information necessary for modern materials selection processes or adequately address recent concerns and current regulatory requirements.[1-5] Recognizing these issues, an effort was initiated to produce a more up-to-date HP hazards manual. Earlier presentations discussed the status of this program in 2003 and 2004.[6,7]

OBJECTIVE

The objective of this paper is to describe the HP hazards manual, its use, and its availability.

APPROACH

LITERATURE SURVEY

First, representative literature was obtained and reviewed. Next, several key-word search engines were used, and relevant papers were found and obtained. Much of the literature came from journals, books, conference proceedings, Department of Defense (DoD) agencies, NASA, other government agencies including the Department of Transportation (DOT) and the Occupational Safety and Health

* Approved for public release, distribution is unlimited.

Administration (OSHA), the Chemical Propulsion Information Agency (CPIA), advisory agencies including NIOSH and ACGIH, NFPA, and HP manufacturers. The literature was cataloged and organized by subject in the general organization of a draft manual.

PREPARATION, REVIEW, AND ISSUE

WSTF materials scientists, chemists, physicists, and mechanical engineers, knowledgeable in the subject and active in testing and data analysis, participated in preparation of the draft manual. The draft manual was reviewed internally at WSTF, and then reviewed externally. Comments received back were incorporated as appropriate and a signature copy was prepared for NASA WSTF management signature. Once reviewed and approved, the manual was issued internally as a WSTF Reference Document and distributed on-site and to other NASA centers.

The next phase was to issue the document as a NASA Technical Memorandum. This was accomplished through coordination with the Publications section at NASA JSC. JSC provided the support necessary to complete the formatting in accordance with NASA Technical Manual guidelines.

The manual contains material that is restricted to government agencies; it is not available in the public domain.

USE OF THE MANUAL FOR HAZARDS ANALYSIS

NASA's Safety Policy requires the use of an organized and systematic approach to identify and control hazards. Hazards analysis approaches for HP are provided. These analysis procedures are based on a method used successfully to evaluate fire hazards in oxygen components and systems and with hydrazine, MMH, and NTO hypergol systems. Use of the procedures is demonstrated by working through simple scenarios. The procedures can also be used as failure analysis tools.

ASSESSMENT EXAMPLES

Accident avoidance is a primary goal of the assessment examples. Examples are designed to assist the user in evaluating hazards and mitigating risks, using data provided or referenced in the manual.

CONTENT

The *Fire, Explosion, Compatibility and Safety Hazards of Hydrogen Peroxide* NASA Technical Memorandum contains the following primary subjects:

- HP Hazards Introduction
- Fire and Explosion Hazards
- Materials and Reactivity
- Personnel and Environmental Hazards
- Chemical, Physical, and Thermodynamic Properties of HP Propellants
- Analytical Spectroscopy of HP
- HP Specifications
- Quantitative Determination of HP
- HP Accidents, Close Calls, and Lessons Learned
- Compatibility Tables from FMC Bulletin 104

Beginning with a discussion of HP as a propellant, the manual presents a historical review of HP propellant uses and issues. Introductory concepts of HP as a green propellant are addressed. The introduction also outlines the structure of hazard assessment procedures.

Descriptions of the fire parameters, hypergolic behavior of HP mixtures, HP explosion parameters, and an expanded guide to HP fire and explosion hazards assessments are presented. Liquid and vapor

detonations, explosive oxidation reactions, and detonations of mixtures of HP with combustible materials are addressed. Selected graphs from the early literature were remastered and are presented with the appropriate references and disclaimers. Example exercises for fire and explosion hazards assessments complete this section.

Next, the manual examines materials reactivity and compatibility issues, including data treatments and stability calculation, active oxygen loss (AOL), and decomposition rates. Materials selection criteria, including that for metals, non-metals, and lubricants, are discussed. Incompatibility topics, such as hazards identifications, contamination, reactivity, analytical and physical testing classification systems (e.g. Class 1-4), and results criteria are then outlined. Stability and reactivity determinations, including AOL and microcalorimetry, are discussed, compared, and contrasted. Considerations are given to the use of historical AOL data and more recent microcalorimetric data to predict decomposition rates in HP systems. Surface effects and passivation are discussed. Compatibility data tables adapted from the literature are also presented. Assessment examples include calculation of HP concentration based on decomposition rate, AOL, and pressure increases in containers.

The manual progresses to a discussion of personnel and environmental hazards associated with exposures to or releases of HP. Exposure rules, recommendations, and guidelines are presented, including those of the American Conference of Governmental Industrial Hygienists (ACGIH), Occupational Health and Safety Administration (OSHA), and the National Institute of Occupational Safety and Health (NIOSH). Exposure routes including contact to the skin and eyes, inhalation, ingestion, and injection and their consequences are discussed, along with general health effects. Handling and storage precautions are reviewed, with guidelines for selection and use of personal protective equipment and monitoring equipment, along with general safety aspects of engineering design. Applicable National Fire Protection Association (NFPA) storage codes and reference to explosive safety standards for quantity-distance relationships are also cited in this section. Passivation procedures for various materials and their intended use with HP are also reviewed. Transportation issues governed by the Department of Transportation (DOT) and regulatory environmental requirements set by the Environmental Protection Agency (EPA), including aspects of waste classification and disposal, are presented and discussed.

The appendices begin with a presentation of HP physical and chemical properties and their reference sources. The content of this section includes:

- General Information for HP Propellants
- Units and Conversion Factors
- Physical Constants
- Thermodynamic Data
- Heats of Reaction of HP Propellants with Fuels
- Temperature Dependency Tables for HP Propellant Properties

The next topic of discussion is the analytical spectroscopy of HP that includes:

- Refractive Index
- Ultraviolet Spectroscopy
- Visible Spectroscopy
- Raman Spectroscopy
- Infrared Spectroscopy
- Spectroscopic Methods for Trace Components in HP

The appendices progress to HP specifications. Topics include:

- Introduction and Background including an informative history of specifications
- Specification Requirements including those from inactive, proposed, industry, and current military specifications including MIL-PRF-16005F "Performance Specification: Propellant, Hydrogen Peroxide" and some of the changes it has undergone.[8] This section is organized

so that future changes to specifications can be documented in subsequent revisions to the manual with minimum effort.

The next topic of discussion is the quantitative determination of HP. Topics include:

- Background
- HP Purity (Assay)
- Trace Methods for Determination of HP in Air and Water
- Common Anions
- Ammonium, sodium, and potassium
- HP Stability
- Evaporation Residue
- Total Carbon
- Metals

Next, a summary of over 80 accidents, close calls, and lessons learned involving HP is presented. These were primarily obtained through the course of the literature review and by sources provided in the peer review process. This section provides an excellent base of examples that can be used to provide increased awareness of HP hazards and the need for appropriate training and controls.

Finally, compatibility data tables are presented that were reproduced from FMC Bulletin 104 by permission.[3]

CONCLUSIONS

Fire, Explosion, Compatibility and Safety Hazards of Hydrogen Peroxide NASA Technical Memorandum NASA/TM-2004-213151 has been prepared. It is intended to be a tool for engineers, chemists, field operators, safety and emergency personnel, and others that should be aware of hazards of working with or around HP or HP systems. The manual is restricted to government agencies. For further information concerning this manual, please contact:

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