

HISTORICAL EVOLUTION OF NASA STANDARD MATERIALS TESTING WITH HYPERGOLIC PROPELLANTS AND AMMONIA (NASA STANDARD 6001 TEST 15)*

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ABSTRACT

The NASA Johnson Space Center White Sands Test Facility (WSTF) has performed testing of hazardous and reactive aerospace fluids, including hypergolic propellants, with materials since the 1960s with the Apollo program. Amongst other test activities, Test 15 is a NASA standard test for evaluating the reactivity of materials with selected aerospace fluids, in particular hydrazine, monomethylhydrazine, *uns*-dimethylhydrazine, Aerozine 50, dinitrogen tetroxide oxidizers, and ammonia. This manuscript provides an overview of the history of Test 15 over a timeline ranging from prior to its development and first implementation as a NASA standard test in 1974 to its current refinement. Precursor documents to NASA standard tests, as they are currently known, are reviewed. A related supplementary test, international standardization, and enhancements to Test 15 are also discussed. Because WSTF was instrumental in the development and implementation of Test 15, WSTF experience and practices are referred to in this manuscript.

BACKGROUND

Materials and processes (M&P) control specifications, such as NASA-STD-6016, "Standard Materials and Processes Requirements for Spacecraft,"¹ are used to define minimum requirements for incorporation in NASA program/project hardware procurements and technical programs. For example, NASA-STD-6016 requires materials exposed to hazardous fluids to be evaluated or tested for compatibility. Appropriate long-term tests are conducted for materials with long-term exposure to spacecraft fuels, oxidizers, and other hazardous fluids. Test conditions must simulate worst-case use environments that would enhance reactions or degradation of materials or fluids. Material degradations in long-term tests are characterized by posttest analyses of the materials and fluids to determine the extent of changes in chemical and physical characteristics, including mechanical properties. The effect of material condition is also addressed in the compatibility determination. Test 15 is a screening test for short-term exposure to fuels and oxidizers.

NASA-STD-6001.B Test 15, "Reactivity of Materials in Hydrazine, Monomethylhydrazine, Unsymmetrical Dimethylhydrazine, Aerozine 50, Nitrogen Tetroxide, and Ammonia"² is the current NASA standard test for the short-term exposure to fuels and oxidizers. Test 15's development, implementation, and improvement over the years since its inception in 1974 have required significant experience and efforts. Standards promulgated by the International Organization for Standardization (ISO) as earlier equivalents of Test 15 and recent enhancements to Test 15 developed and implemented at WSTF are summarized and discussed in this manuscript.

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OBJECTIVE

This manuscript examines the evolution of Test 15 and its enhancements from inception. A historical perspective on Test 15 for the reactivity of materials with the hypergolic propellants (hydrazine, monomethylhydrazine, unsymmetrical dimethylhydrazine, Aerozine 50, nitrogen tetroxide)[†] and ammonia is presented. Anecdotal information from WSTF experience is provided for knowledge capture.

STANDARD TEST DEVELOPMENT

A chronology of Test 15[‡] is outlined in order as follows:

NHB 8060.1A (1974) Test 15 – Constant Temperature Immersion of Materials in Type J Fluids³
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NHB 8060.1B (1981) Test 15 – Compatibility of Materials with Type “J” Fluids⁴
↓
NHB 8060.1C (1991) Reactivity of Materials in Aerospace Fluids (Test 15)⁵
↓
NASA-STD-6001 (1998) Reactivity of Materials in Aerospace Fluids (Test 15) (verbatim with NHB 8060.1C)⁶
↓
NASA-STD-(I)-6001.A (2008) Reactivity of Materials in Hydrazine, Monomethylhydrazine, Unsymmetrical Dimethylhydrazine, Aerozine 50, Nitrogen Tetroxide, and Ammonia (Test 15)⁷
↓
NASA-STD-(I)-6001.B (2009) Reactivity of Materials in Hydrazine, Monomethylhydrazine, Unsymmetrical Dimethylhydrazine, Aerozine 50, Nitrogen Tetroxide, and Ammonia (Test 15)⁸
↓
Supplemental Test A.7 Reactivity and Penetration of Materials due to Incidental Exposure to Hydrazine, Monomethylhydrazine, Unsymmetrical Dimethylhydrazine, Aerozine 50, Nitrogen Tetroxide, and Ammonia was incorporated into NASA-STD-(I)-6001.A (2008), NASA-STD-(I)-6001.B, (2009), and NASA-STD-6001.B (2011)^{7,8,2}
↓
NASA-STD-6001.B (2011) Reactivity of Materials in Hydrazine, Monomethylhydrazine, Unsymmetrical Dimethylhydrazine, Aerozine 50, Nitrogen Tetroxide, and Ammonia (Test 15)² replaced NASA-STD-(I)-6001.B,⁸ incorporating comments from NASA agency-wide review.
↓
The “Enhanced Test 15” (described below) is not a standard test but is a natural extension of NASA-STD-6001.B² and more closely resembles that described in NHB 8060.1A³ Test 15 and NHB 8060.1B⁴ Test 15.

MSC-PA-D-67-13

Literature dated from the Apollo program to the present was reviewed for the development of this manuscript.¹⁻¹⁴ Standard procedures and requirements for the evaluation of spacecraft nonmetallic materials for the Apollo program were developed and mandated in MSC-A-D-66-3, *Procedures and Requirements for the Evaluation of Spacecraft Nonmetallic Materials*,⁹ MSC-PA-D-67-13, *Apollo Spacecraft Nonmetallic Materials Requirements*,¹⁰ and Addendum No. 1 to MSC-PA-D-67-13, *Apollo Spacecraft Nonmetallic Materials Requirements*,¹¹ which were issued by the Manned Spaceflight Center (MSC). There were 12 standard tests and supplementary tests and each was numerically identified (Test 1, Test 2, etc.), and this numbering system is consistent throughout the succession of revisions to NASA standard

[†] The chemical names nitrogen tetroxide (NTO) and dinitrogen tetroxide are used interchangeably as appropriate for N₂O₄.

[‡] Despite revision and supersession as applicable, requests for any of these test revisions are still considered valid and may still be required by contracts or projects.

materials testing protocols, though there have been some test title changes, addition and deletion of tests, and redesignation of tests to “supplemental.” The Apollo program material test requirements in MSC-PA-D-67-13¹⁰ and MSC-PA-D-67-13 Addendum No. 1,¹¹ however, did not identify Test 15 or any form of equivalent testing of materials with hazardous fluids of other than oxygen. The focus was primarily on fire, flammability, ignition, combustion, offgassing, and odor testing.

FLAMMABILITY, ODOR, AND OFFGASSING REQUIREMENTS AND TEST PROCEDURES FOR MATERIALS IN ENVIRONMENTS WHICH SUPPORT COMBUSTION (DRAFT COPY 1970)

A draft copy of Flammability, Odor, and Offgassing Requirements and Test Procedures for Materials in Environments Which Support Combustion, prepared by the Skylab Intercenter Working Group, was released as NASA-TM-79493¹² in 1970 by the NASA Office of Manned Space Flight. This document was intended as a specification to control selections of materials with respect to flammability and offgassing to be used in and around manned spacecraft during flight and test operations. This document appeared to be a precursor to the NHB standards described below. The material test requirements in NASA-TM-79493,¹² however, did not identify Test 15 or any form of equivalent testing of materials with hazardous fluids of other than oxygen. The focus was primarily on fire, flammability, ignition, combustion, offgassing, and odor testing. This document contained 13 standard tests and appendices information, and may have been a precursor to NHB 8060.1.¹³

NHB 8060.1 STANDARDS

NHB 8060.1

The Office of Manned Space Flight issued NASA Handbook (NHB) 8060.1, *Flammability, Odor, Offgassing, and Compatibility Requirements and Test Procedures for Materials in Environments that Support Combustion* in November 1971.¹³ NHB 8060.1¹³ provided standard requirements for the control of flammability, odor, and offgassing of materials to be used in the design and development of manned space vehicles, guidelines and directions for material selection, and testing procedures for the candidate materials used in and around manned space vehicles during flight and flight operation. The provisions of NHB 8060.1¹³ were applicable to the NASA installations responsible for hardware design and development of manned space vehicles and related hardware, in addition to being included as applicable in all future contracts and programs involving manned space vehicles. NHB 8060.1¹³ was based on the materials technology developed during the Apollo and Skylab programs and it contained a number of tests that were upgrades or additions to those of MSC-PA-D-67-13¹⁰ and MSC-PA-D-67-13 Addendum No. 1.¹¹ The material test requirements in NHB 8060.1,¹³ however, did not identify Test 15 or any form of equivalent testing of materials with hazardous fluids of other than oxygen. The focus was primarily on fire, flammability, ignition, combustion, offgassing, and odor testing.

NHB 8060.1A Test 15 – Constant Temperature Immersion of Materials in Type J Fluids

The Office of Manned Space Flight issued NHB 8060.1A, *Flammability, Odor, and Offgassing Requirements and Test Procedures for Materials in Environments that Support Combustion* in February 1974,³ which superseded NHB 8060.1¹³ and established the Test 15 Constant Temperature Immersion of Materials in Type J Fluids for the first time as a NASA standard test. NHB 8060.1A³ provided standard requirements for control of flammability, odor, and offgassing of materials to be used in the design and development of manned space vehicles, guidelines and directions for material selection, and testing procedures for the candidate materials. The provisions of NHB 8060.1A³ (similar to those in NHB 8060.1¹³) were applicable to the NASA installations responsible for hardware design and development of manned space vehicles and related hardware, in addition to being included as applicable in all future contracts and programs involving manned space vehicles. NHB 8060.1A³ also required the NASA Manned Space Flight Centers (George C. Marshall Space Flight Center, Lyndon B. Johnson Space

Center, and John F. Kennedy Space Center) to use the document and to develop implementation plans for Center-peculiar operations to ensure the disciplines specified in the document were standardized.

The summary and scope of NHB 8060.1A³ Test 15 required that materials used or considered for use in hazardous fluid systems other than oxygen, whether in direct contact with the fluid or as a result of a single barrier failure, were tested according to the guidelines of the Test 15 (Constant Temperature Immersion of Materials in Type J Fluids) procedure. Test 15 determined the gross compatibility of materials in Type J fluids and did not preclude the use of other tests to determine critical compatibilities. The data from other tests were used for information purposes.

The materials usage category "Type J", which did not appear in the NHB 8060.1,¹³ was introduced and defined as "Materials in Combustion Supporting Environments Other than Oxygen." The category "Type J Materials for Combustion Supporting Environments Other Than Oxygen" included all materials exposed to fluids other than oxygen such as nitrogen tetroxide, hydrazine, and other oxidizers and fuels that are theoretically capable of undergoing reactions with the environment in which used. The materials usage category Type J established compatibility of materials as materials shown to be compatible with the environment in question at 160 °F. A material was considered compatible if its exposure to that environment at 160 °F (under maximum use pressure) for a period of 48 h did not result in chemical or physical changes such as tackiness, flaking, complete dissolution, etc. (Data obtained according to general guidelines similar to that of Test 15 were included in the Titan II Storage Propellant Handbook¹⁴ and were considered directly applicable.) Materials shown to be incompatible with Type J fluids at temperatures less than 160 °F were considered incompatible. All materials for which no compatibility data existed required evaluation by Test 15. Additionally, if the materials were exposed to a source of energy such as mechanical impact, pneumatic impact, heat source, or other, then a configuration test or a special test applicable to the unique conditions was to be devised and performed to ensure the material's compatibility, or a configuration analysis was to be performed to ensure adequate compatibility.

A very serious injury occurred at WSTF in 1972, prior to the issue of NHB 8060.1A,³ when an incompatible material tested with a mixed oxides of nitrogen (MON) oxidizer caused the test fixture to explode (Appendix A). Mechanical impact testing was required for post-Test 15 materials exposed to MON-oxidizers at WSTF because of the potential for shock-sensitive product formation. Ironically, posttest screening or beaker-tested materials were not routinely analyzed for chemical changes nor were they subjected to thermal or mechanical testing; rather, a focus on caution was placed on the post-Immersion Test samples. Although a beaker test can provide an indication of gross incompatibility, it may or may not provide information about chemical changes that can occur at elevated temperatures at extended durations.

NHB 8060.1A Test 15 Test Conditions and Procedures

The purpose of the NHB 8060.1A³ Test 15 was to determine the gross compatibility of materials with Type J fluids and was applicable to all materials being considered for use in all Type J fluids. The test technique was hazardous in nature and required remote propellant handling and control. The criteria for acceptability was based on exposure of a material to a test environment consisting of a 48-h conditioning period in the test fluid at a temperature of 160 °F at the material's maximum use pressure. A material was considered compatible with the test fluid if exposure of a minimum of three test specimens to these conditions resulted in no obvious changes in the material, such as dissolution or separation. Materials shown to be incompatible at test fluid temperatures less than 160 °F were also considered incompatible and testing at 160 °F was not required.

To perform the test, the test pressure was adjusted to simulate maximum applied system use pressure of 160 °F + 5.5 °F, - 0 °F. The temperature was raised at a rate of 9 to 18 °F/min, and the samples were continued to be immersed for 48 ± 1 h after the test temperature was reached. The samples were then removed for posttest observations. The test fixture was constructed of 300-series stainless steel (or equivalent) and contained a rupture disc suitable for

protecting personnel and test equipment in the event a sample ignition occurred. The fixture had penetrations for filling, pressurization, and pressure and temperature measuring devices. The test fixture volume was a minimum of 1.5 L with a minimum of two-thirds of this volume as ullage. A minimum of three samples were prepared in lengths of two inches. The normal sample size was 2 x ¼ x ¼ in. (the standard sample size for NHB 8060.1C,⁵ NASA-STD-6001,⁶ NASA-STD-(I)-6001.A⁷ and B⁸, and NASA-STD-6001.B² is 25 cm² (based on surface area rather than dimension)).

Helium was used as a pressurant gas (helium is the most frequently used pressurant gas for hypergolic propellants on spacecraft), while nitrogen was used to purge the test fixture following the test. All observations were recorded on a data sheet.

The NHB 8060.1A³ Test 15 criteria for compatibility was based on exposure to a test environment consisting of a 48-h conditioning period in the test fluid at a temperature of 160 °F at the material's maximum use pressure. A material was considered to be compatible with the test fluid if exposure of a minimum of three test specimens results in no obvious changes to the material (such as dissolution and separation). Materials shown to be incompatible at test fluid temperatures of less than 160 °F were also considered incompatible and testing at 160 °F was not required.

The test procedures in NHB 8060.1A³ Test 15 did not address carbon dioxide contamination. Carbon dioxide has been reported to increase the corrosivity of the propellant hydrazines.¹⁵ Test data acquired under variable carbon dioxide contamination concentrations in propellant hydrazines may not be comparable if variable carbon dioxide contamination is a factor. NHB 8060.1A³ Test 15 also did not impose any specific quality requirements on the test fluid, nor did it reference any procurement or use specification for the test fluids. Military procurement specification limits as specified in MIL-P-26536C¹⁶ through MIL-PRF specifications for carbon dioxide in the various grades of hydrazine, which is the only Type J test fluid with a carbon dioxide specification, are shown in Table 1.

Table 1. Military Procurement Specification Limits for Carbon Dioxide in Hydrazine

Specification	Date Issued	Standard Grade	Monopropellant Grade	High Purity Grade
MIL-P-26536C ^a	May 23, 1969		N/A ^b - no grade specified	
MIL-P-26536C Amendment 1	July 25, 1974	Limit not specified	0.02 max (percent by weight)	N/A – grade not specified
MIL-P-26536C Amendment 2	February 1, 1982	Limit not specified	0.003 max (percent by weight)	0.003 max (percent by weight)
MIL-P-26536D	July 27, 1987	Limit not specified	0.003 max (percent by weight)	0.003 max (percent by weight)
MIL-P-26536D Amendment 1	June 5, 1995	Limit not specified	0.003 max (percent by weight)	0.003 max (percent by weight)
MIL-PRF-26536E	September 24, 1997	Limit not specified	0.003 max (percent by weight)	0.003 max (percent by weight)
MIL-PRF-26536E Amendment 1	January 10, 2000	Limit not specified	0.003 max (percent by weight)	0.003 max (percent by weight)
MIL-PRF-26536F	April 1, 2011	Limit not specified	0.003 max (percent by weight)	0.003 max (percent by weight)

^a Hydrazine (no grade specified) had no limit for carbon dioxide.

^b N/A = not applicable

Note that the first military procurement specification with a limit for carbon dioxide in hydrazine (MIL specifications for MMH (MIL-PRF-27404)¹⁷ and for UDMH (MIL-PRF-25604)¹⁸ do not have limits on carbon dioxide. Throughout the progression of military procurement specifications for hydrazine, the maximum limit for carbon dioxide concentration of monopropellant and high purity grades remained primarily at 0.003 maximum percent by weight.

Avoiding the contamination of propellant hydrazine test fluids with carbon dioxide during Test 15 loading and unloading was an evolutionary process at WSTF. Procedures ranged from transferring “as fast as possible”, to transferring in completely carbon dioxide-free atmospheres using inert purge gases and test systems designed to preclude atmospheric contamination.

NHB 8060.1A³ Test 15 was performed in concrete test cells in the WSTF Hazardous Fluids Test Area. Test personnel wore full encapsulating protective suits with supplied breathing air.

The reporting forms for Test 15 in NHB 8060.1A,³ B,⁴ C⁵/NASA-STD-6001,⁶ and NASA-STD-(I)-6001.A⁷ and B⁸ underwent considerable evolution over the nearly 40 years of Test 15 from initiation in 1974 until the present. NHB 8060.1A³ provided minimum requirements and an example form not specific for Test 15. NHB 8060.1B⁴ provided an example of an “acceptable” form for Test 15. Test 15 changed dramatically with the issuance of NHB 8060.1C (and remained identical to NHB 8060.1C⁵ in NASA-STD-6001⁶). In the latter two documents, a reporting form was not provided, but the test directed that reporting be performed in a format that was compatible with the Materials and Processes Technical Information System (MAPTIS).

NHB 8060.1B Test 15 – Compatibility of Materials with Type “J” Fluids

The Office of Space Transportation Systems issued the next revision of Test 15 in NHB 8060.1B⁴ *Flammability, Odor, and Offgassing Requirements and Test Procedures for Materials in Environments that Support Combustion* in September 1981, which superseded NHB 8060.1A.³ NHB 8060.1B⁴ was similar in intent and applicability as its predecessor NHB 8060.1A,³ though it contained changes to existing tests, including Test 15, and an additional test (Test 16 – Determination of Offgassed Products from Assembled Articles).

The category “Type J Materials for Combustion Supporting Environments Other Than Oxygen” was also addressed with slight changes to the requirements as compared with NHB 8060.1A.³

NHB 8060.1B⁴ Test 15 provided more detail than NHB 8060.1A³ Test 15, including elaboration on test materials as to being solids, semisolids, and/or liquids, and provided guidelines for preparation and cleaning prior to testing. For example, solids (including foam materials), were prepared in triplicate, each with an exposed surface area of approximately 2 in². A 300-series stainless steel cup was used to contain a 0.050 ± 0.010 in³ layer of semisolids and liquids such that the test material had an exposed surface area 6.0 ± 0.2 in². Generally, semisolids and liquids would only be exposed to vapor-phase fluid media. Additionally, if test materials were of the same generic class, several materials could be simultaneously evaluated in the same test chamber.

Expanding on the criteria for acceptability from NHB 8060.1A,³ the NHB 8060.1B⁴ acceptability criteria was based on exposure of a material to a test environment consisting of a 48-h conditioning period in the test fluid at the material’s maximum use pressure and temperature. Materials used at ambient temperature and below were tested at 160 °F. A material was considered to be compatible with the test fluid if exposure of the material to these conditions resulted in no deleterious changes in the material such as dissolution, separation, dimensional, or hardness or tensile strength degradation. Materials shown to be incompatible at test fluid temperatures less than 160 °F were also considered incompatible and testing at 160 °F was not required.

A warning note regarding potential hazards of materials exposed to Type J fluids was included. The test data reporting instructions were expanded by the addition of an example of an acceptable form. The example form showed ammonia as a test fluid. The example form also

contained a variety of pretest and posttest bulk, surface, visual, and compatibility characteristics in addition to a field for posttest material's special tests (such as impact test results), photographs, and results. These characteristics were the subject of much scrutiny as Test 15 evolved in subsequent revisions.

The warning note in NHB 8060.1B⁴ Test 15 stated: "WARNING: Handling of materials exposed to Type J fluids may be extremely hazardous due to changes which may have occurred in the material due to exposure to the test fluid media. Procedures such as mechanical impact testing of small posttest samples should be established to evaluate the hazards associated with handling the material after test."

Despite the warning, no requirements for pre-screening of materials or for testing that could lead to nitrated or other energetic, potentially shock sensitive materials were given in NHB 8060.1B.⁴ The emphasis was on safe handling of posttest materials. However, local procedures were developed and implemented by WSTF requiring a screening test (beaker test) as part of the test protocol for dinitrogen tetroxide oxidizers.

It should be noted that an ambient temperature screening test would not necessarily give an indication of whether a material was sensitized or became energetic due to nitration or oxidization because the conditions are not nearly as stringent (2 h exposure at ambient temperature by current protocols) as compared to the Immersion Test (48 h at 160 °F). Other factors such as an evaluation of chemical functional groups could have been used to predict chemical reactivity. However, evidence of gross reactivity may be seen from an ambient temperature screening test.

NHB 8060.1B⁴ Test 15 was performed in concrete test cells in the WSTF Hazardous Fluids Test Area. Test personnel wore fully encapsulating protective suits with supplied breathing air. A special safety device, dubbed the "White Mule" by local WSTF personnel, was fabricated at WSTF and was wheeled up to a test cell (two people were required because of its weight due to steel construction and handling characteristics) and placed between the Test 15 immersion chamber and personnel. The "White Mule" enabled test personnel, while remaining behind a steel protective shield, to unload a grab sample from the immersion chamber immediately after the chamber had cooled following a test, for mechanical impact testing. The grab sample was then transported for mechanical impact testing by hand. If mechanical impact testing was negative for explosion hazards, samples were handled as ordinary posttest specimens. Local WSTF personnel, however, do not recall any positive mechanical impact test results over at least 30 years of immersion tests with dinitrogen tetroxide.

A reporting form for Test 15 was included in NHB 8060.1B⁴ Test 15 (Figure 4-19 Sheet No. 1 (not shown in this paper)), and included blocks for material name and identification, test conditions, material preparation, and test data (including material mass, media volume, test chamber pressure, container volume, media exposure time, media exposure temperature, observations, and pre- and posttest material bulk characteristics, surface characteristics, visual characteristics, and yes/no posttest gross compatibility descriptions: burned, charred, dissolved, fractured, cracked, separated, swelled, shrunk, and remarks). Also included were blocks for posttest material's special tests, photographs, and results; special preparation instructions, material preparation history, special test instructions, and space to record temporary procedure deviations.

NHB 8060.1C Reactivity of Materials in Aerospace Fluids (Test 15)

The Office of Safety and Mission Quality issued NHB 8060.1C,⁵ *Flammability, Odor, Offgassing, and Compatibility Requirements and Test Procedures for Materials in Environments that Support Combustion* in April 1991, which superseded NHB 8060.1B.⁴ NHB 8060.1C⁵ and established requirements for evaluation, testing, and selection of materials that were intended for use in space vehicles, associated ground support equipment, and facilities used during assembly, test, and flight operations.

The provisions of NHB 8060.1C⁵ were to be included (as applicable) in all future contracts and programs involving space vehicles, payloads, and associated support equipment.

The provisions were applicable to the NASA installations; and that application of NHB 8060.1C⁵ must be appropriate to the needs of specific programs. While NHB 8060.1C⁵ superseded NHB 8060.1B,⁴ NHB 8060.1C⁵ also indicated that unless directed otherwise, the use of NHB 8060.1B⁵ could be continued for ongoing contractual programs where currently specified, but it may not be applied to new contracts or requirements. Under these circumstances, NHB 8060.1B⁴ Test 15 was still in effect. In addition, with the numerous changes from NHB 8060.1B,⁴ NHB 8060.1C⁵ encouraged the assessment of the impact of the revised requirements for ongoing work.

NHB 8060.1C⁵ encouraged the selection of materials that had already been shown to meet test criteria in the use environment. Existing test data were compiled in the NASA Marshall Space Flight Center (MSFC) Materials and Processes Technical Information System (MAPTIS) and published periodically as the latest revision of a joint document with Johnson Space Center (JSC), MSFC-HDBK-527 (JSC 09604), *Materials Selection List for Space Hardware Systems*.¹⁹ MAPTIS was also accessible with a computer datalink (the internet as we know it in present times was not established at that time), and eventually became accessible over the internet.

Prior to MAPTIS there was an "Approved Materials List" that was maintained by JSC, and it included data for Test 15. As more data became available, a computer-based system MAPTIS was developed, and has continued throughout the current version of NASA-STD-6001.² The last printed copy of the "Approved Materials List" that WSTF is aware of is dated 1986. There may or may not be an official document number for the "Approved Materials List". MAPTIS has since evolved to MAPTIS II, and is the official repository of materials properties for NASA and NASA-associated contractors and organizations.

NHB 8060.1C⁵ established NASA program requirements for evaluation, testing, and selection of materials to preclude unsafe conditions related to flammability, odor, offgassing, and fluid compatibility. Materials intended for use in space vehicles, specified test facilities, and specified ground support equipment (GSE) must have met NHB 8060.1C⁵ requirements. NHB 8060.1C⁵ *Reactivity of Materials in Aerospace Fluids* (Test 15) described requirements for materials testing with reactive fluids; materials that are exposed to reactive fluids must be evaluated for compatibility with the fluid in their use application. Test 15 was the reactive fluids compatibility test.

NHB 8060.1C⁵ required that materials used in reactive fluids be evaluated for compatibility by meeting the criteria of Test 15. Materials that did not meet the criteria of the required test and were to remain candidates for use required verification to be acceptable in the use configuration by analysis or testing and specifically approved by the responsible NASA Center materials organization.

Along with a change in the Test 15 title to "Reactivity of Materials in Aerospace Fluids (Test 15)", utilization of the Type J materials usage category of fluids, as described in NHB 8060.1A³ and NHB 8060.1B,⁴ was discontinued. The Type J materials usage category was changed to "Reactive Fluid Environment," where "reactive fluids" are fluids that are theoretically capable of reacting with materials in such a way as to create a hazard. Aerospace fuels such as hydrazine and oxidizers such as nitrogen tetroxide were examples of reactive aerospace fluids. Test 15 was identified as a required test for a Reactive Fluids Environment.

Major changes to NHB 8060.1A³ and NHB 8060.1B⁴ Test 15 were made with the issuance of NHB 8060.1C.⁵ These changes are summarized as follows:

- The relatively large scale immersion tests as described in NHB 8060.1A³ and NHB 8060.1B⁴ were not included.
- Definitions were added.
- The "Screening Test" was introduced.
- The "Immersion Test" was introduced along with a diagram of the test system.
- Specific test criteria for compatibility were specified.

- Specific good laboratory practices were established.

The purpose of NHB 8060.1C⁵ Test 15 was to identify changes resulting from exposure of a material to an aerospace fluid that render either the material or the fluid unusable or cause the pressure in a system to rise. Supplemental information on reactivity of materials with aerospace fluids, as specified by the document, could be obtained by other methods such as accelerated rate calorimeters.

The “Criteria for Acceptability” that was described in NHB 8060.1A³ and NHB 8060.1B⁴ Test 15 was replaced with “Test Criteria.” These criteria were as follows:

- Exposure of the material (Screening Test) to the fluid at ambient temperature for 2 h must not have visibly changed either the material or fluid.
- Exposure of the material (Immersion Test) to the fluid for 48 h at the maximum system temperature or 160 °F (71 °C), whichever is higher, must not have caused a pressure rate increase that is 1.5 times the pressure rate increase caused by 304 stainless steel (SS-304) exposed to the identical fluid at those conditions. For fluids that do not decompose into gaseous products at the test temperature (for example, nitrogen tetroxide), a pressure increase greater than the vapor pressure of the fluid must not have occurred.
- After the sample had been decontaminated and dried, no visible change (posttest analysis) in color or texture of the material and test fluid could be apparent after exposure. In addition, the weight of the sample could not change by greater than 2 percent.[§]
- The following changes in the fluid must also not have occurred: (1) the mass of impurities in the fluid after exposure to the material could not be greater than twice the mass of impurities in the identical fluid after exposure to polytetrafluoroethylene (for nonmetals) or 304 stainless steel (for metals); and (2) halide (fluoride (F⁻), chloride (Cl⁻), and bromide (Br⁻) concentrations in the fluid after exposure to the material could not exceed the appropriate military specification for fluid purity.^{**}

NHB 8060.1C⁵ was the first version of Test 15 that required comparison of the posttest fluid to military specifications. The introduction to the Test Methods section stated: “As a minimum, all fluids used for testing must meet or exceed user specifications. U.S. Military Standards for appropriate fluids were listed in Appendix B”; yet no military standards were listed. NHB 8060.1C⁵ also did not provide specific information on determining the surface area of semisolids or liquids, or of test materials such as paints, waxes, lubricants, or coatings on inert substrates. Such determinations were managed at WSTF on a case-by-case basis and the tests were often flagged as non-standard.

For the NHB 8060.1C⁵ Screening Test (commonly referred to as the “beaker test”), the test system for the Screening Test should consist of a glass beaker (WSTF typically used 10 mL borosilicate glass beakers), 1 cm³ of the fluid was applied one drop at a time to 0.25 g of the material at ambient temperature and pressure. After waiting 2 h, the material and the fluid were examined visually for obvious changes caused by the exposure. This procedure was described in minimal detail in NHB 8060.1C.⁵ “Non-standard” tests such as those with samples with mass greater than 0.25 g required prior approval and were flagged accordingly in the report.

Some WSTF personnel recalled the origin of the 0.25 g quantity used for the Screening Test was the maximum amount of a foam material that could be stuffed into a 10 mL beaker. Others recalled tests were performed with a 0.25 g trinitrotoluene (TNT) equivalent in a fume

[§] The posttest mass was obtained after the sample has been decontaminated and dried, but the time from immersion to obtaining sample post-test masses was not specified nor was there a requirement to document the time. Consequently, the meaning of the 2% mass change was subject to debate, as time was a critical factor especially with respect to absorbed propellant evaporation.

^{**} The appropriate military specifications were not referenced, leaving the test open to a wide variety of types and grades of fluids, which were often not specified on the test request. For example, a test request for hydrazine may indicate only “hydrazine” as the test fluid, leaving the final selection of the specific fluid (standards grade, monopropellant grade, high purity grade, or even Space Shuttle Orbiter grade) open to agreement between the customer and the test organization.

hood using the normal configuration for a screening test, such as behind a safety shield. The results of these tests were believed to indicate a 0.25 g TNT equivalent explosion was safely contained in the fume hood; a 0.25 g TNT equivalent is approximately equal to ¼ that of the old commercially available "cherry bomb," which typically contained up to 1 gram of TNT equivalent explosive.

The test system for the Immersion Test, as specified in NHB 8060.1C,⁵ consisted of one reference and one sample chamber and temperature and pressure monitoring devices. NHB 8060.1C⁵ also specified that differential pressure transducers must be used for fluids such as hydrazine or MMH that decompose into gases at the test temperature, and that absolute pressure transducers (on the sample and reference sides of the test system) should be used for those fluids that do not decompose into gases or undergo wide pressure fluctuations.

The test conditions for the NHB 8060.1C⁵ Screening Test as specified in the procedure should be the ambient temperature and pressure of the test facility. The test conditions (total pressure, test temperature) must have simulated the worst-case use environment that would enhance pressure-producing reactions or degradation of the material or fluid. The minimum temperature must have been 160 °F (71 °C). The test pressure must have been equal to the vapor pressure of the fluid at the test temperature plus the initial pressure in the test system. The test duration must have been at least 48 h (unless testing was halted because of significant pressure rise). Samples for the Immersion Test should have had a surface area of $25 \pm 5 \text{ cm}^2$; otherwise, the test was considered "non-standard" and was flagged appropriately.

The Immersion Test may have been described as a laboratory test employing pressure measurements to determine the pressure difference between a sample and a reference material, each exposed to the same fluid for the same time at the same temperature in the same device. A diagram of the Immersion Test system is shown in Figure 1. The dotted line along the perimeter indicates a water bath, into which the sample and reference arms containing test fluid and material were immersed and kept at the required test temperature for the required time. The water bath also served as a containment barrier in the case of a leak, explosion, or over-pressurization event. The entire apparatus was located in a fume hood.

During the development of the Test 15 Immersion System, an explosion occurred during a test with an incompatible material (believed to be Nylon 6,6) with dinitrogen tetroxide. The developmental system was a glass water bath, which fully contained the explosive force, shrapnel, and the test fluid without rupture of the water tank itself. A metal-clad water bath was finally adopted, in part to provide a further margin of safety than glass and also to more readily accommodate appurtenances.

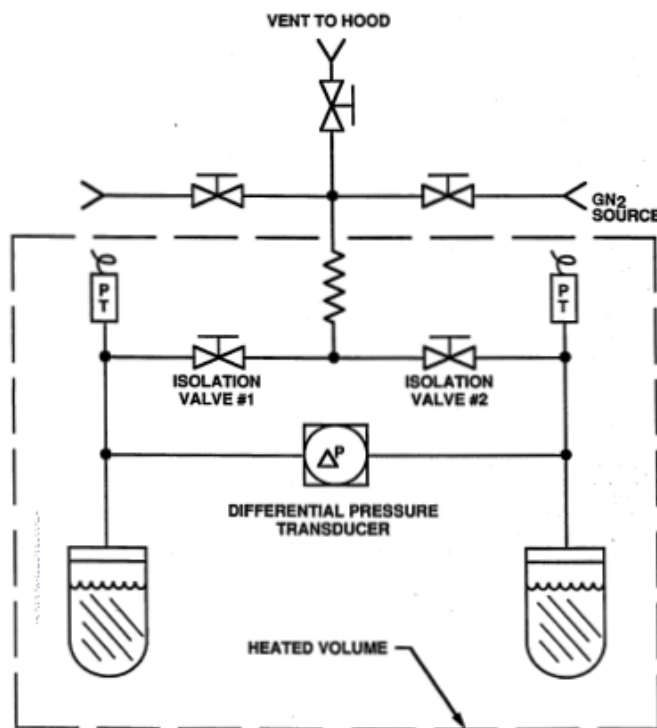


Figure 1. NHB 8060.1C Immersion Test System for Test 15.

For the NHB 8060.1C⁵ Immersion Test, the sample is placed in a sample chamber and sufficient fluid (approximately 10 mL) added to completely cover the sample for the duration of the test. The sample chamber must be sealed onto the sample side of the test apparatus. Sufficient fluid must be added to the reference chamber to obtain the same ullage as in the sample chamber. The reference chamber must be sealed to the reference side of the test apparatus. The pressure and temperature monitoring devices are activated. Both chambers are heated at a rate less than 3 °F (1.7 °C) per minute until the required test temperature is reached. The test is continued for 48 h or until the differential pressure has exceeded the vapor pressure of the fluid plus 20 psi (140 kPa). The conditions in the chamber are then lowered to ambient and the posttest sample, reference material, and fluids are removed for analysis and photography.

A reporting form (Figure 4-19 Sheet No. 1), or a variation thereof, similar to that in NHB 8060.1B⁴ Test 15 was not included in NHB 8060.1C.⁵ This prompted serious discussions by personnel at WSTF. An electronic reporting form that, where practicable, was consistent with the standard terminology used in used in the NHB 8060.1B Test 15 reporting form, and included additional terminology, was developed and implemented at WSTF. This allowed standardized data to be reported to MAPTIS. Eventually, with the development of NASA-STD-(I)-6001.A,⁷ the electronic data form used at WSTF was refined and added in hard copy form to the revised Test 15.

Considerable efforts were expended in designing and implementing the NHB 8060.1C⁵ Immersion Test System. Teams of design engineers, programmers, chemists, and technicians collaborated into what ultimately manifested itself as an operational rather than a developmental system. While NHB 8060.1C required the use of differential pressure transducers ("Differential pressure transducers must be used for fluids, such as hydrazine or monomethylhydrazine (MMH), that decompose into gases at the test temperature"), they were found to be inadequate and absolute pressure transducers were used along with software that allowed calculation of the differential pressure. Some of the problems with differential pressure transducers were that they did not allow absolute leak checks, relatively small pressure differentials were subject to error and misleading results, they had an inability to acquire absolute pressure data, and potential system and safety problems were associated with actual pressures. Other challenges occurred in

developing a good seal between the glass sample and reference arms to the system, and developing means of loading and unloading the systems without contaminating them with air (atmospheric carbon dioxide in particular). Nitrogen purges, selected equipment such as cannulas (small diameter tubing allowing fluid transfers), septa-capped containers, and procedures were used to minimize or eliminate carbon dioxide contamination during various steps in the hydrazine fuels Immersion Test including loading the filling bottle, purging the system, transferring the fuel to from the filling bottle to the system, and unloading the fuel from the system.

Figures 2 through 5 refer, respectively, to WSTF procedures^{††} for loading a filling bottle with propellant hydrazines, purging the system free of air with nitrogen, transferring the propellant hydrazines from the filling bottle to the Test 15 Immersion Test system, and unloading posttest propellant hydrazines from the system.

Figure 2 depicts various steps in a sequence whereby a propellant hydrazine is loaded from a pressurized cylinder equipped with a filling needle through the septum into a nitrogen-purged filling bottle.

Figure 3 depicts the use of a cannula and a gaseous nitrogen purge needle inserted into the filling bottle containing the propellant hydrazine, through its septum, without immersing the cannula in the propellant hydrazine in such a manner that residual air in the cannula is displaced by nitrogen before the propellant hydrazine is introduced into the Test 15 Immersion System.

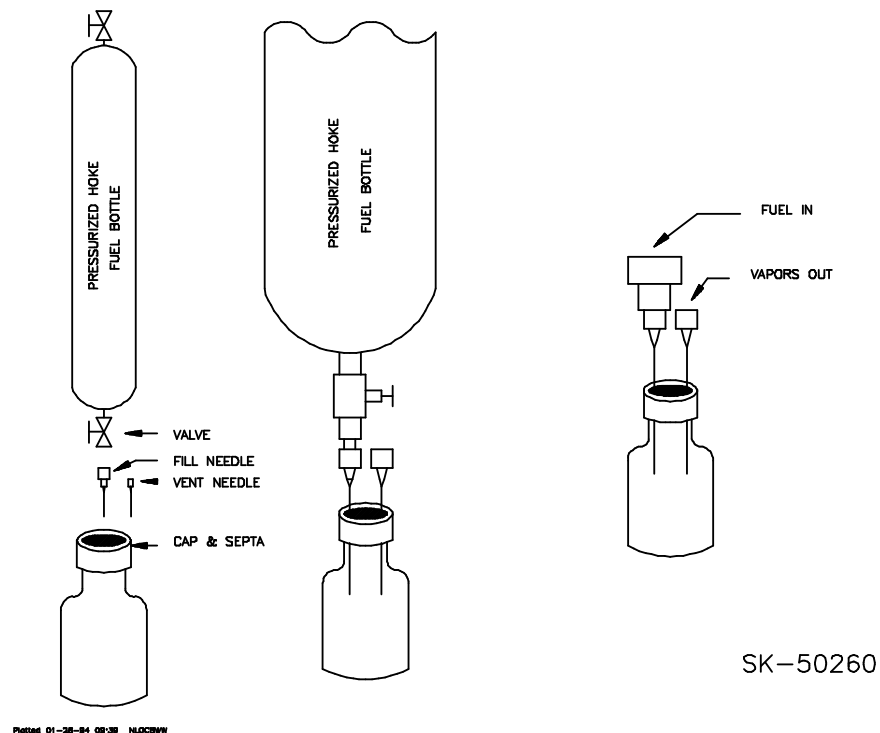
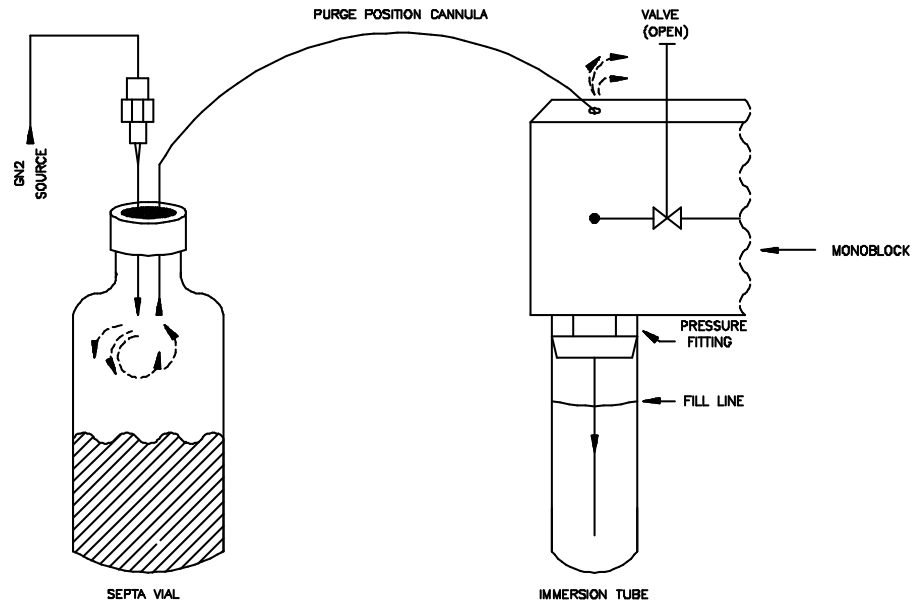


Figure 2. Loading the Filling Bottle

^{††} In-house document. WSTF Job Instruction WJI-320-31-0189, *NASA Technical Standard 6001/ (Formerly) NHB 8060.1C, Test 15 Differential Pressure Immersion Test with Aerospace Fuels*. 2006.



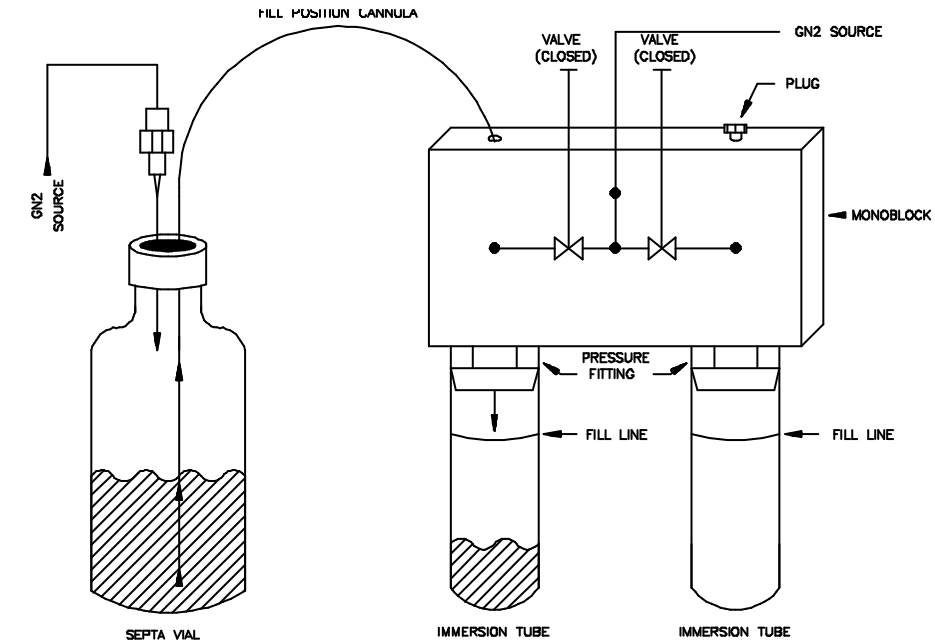
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Figure 3. Purge Step

Figure 4 depicts the transfer of propellant hydrazine from a nitrogen-purged filling bottle through a nitrogen-purged cannula into the Test 15 Immersion System. A metering valve controlling the gaseous nitrogen is slowly opened to transfer the propellant hydrazine to an immersion tube. Before the propellant hydrazine reaches the fill line, the metering valve is closed and residual pressure is allowed to transfer additional propellant hydrazine to fill the immersion tube to its fill line. When the propellant hydrazine reaches the fill line in the immersion tube, the end of the cannula above the propellant hydrazine in the filling bottle is raised to stop the transfer. A filling plug is installed and the process is repeated to fill the other immersion tube and seal the system before performing leak checks and proceeding with testing.

Figure 5 depicts unloading the propellant hydrazine from an Immersion Test system. Clean vials (40 mL) are purged with gaseous nitrogen, labeled, and a vent needle is inserted through the septum cap on each vial for pressure relief. A polytetrafluoroethylene (PTFE)-coated septum cap is threaded onto the cannula; the septum is used to produce a gas seal. The cannula is inserted through the septum cap on the vial labeled for the reference-side propellant hydrazine, the filling plug on the reference side of the system is removed, and the blunt end of the cannula is lowered to the bottom of the corresponding reference immersion tube to ensure that all fluid can be removed. A gaseous nitrogen purge is used to transfer the propellant hydrazine from the immersion tube into the 40 mL vial by pressing the PTFE-coated septum cap onto the top of the filling port. The purge forces the fuel from the immersion tube through the cannula into the 40 mL vial. This process is repeated for the sample side of the Immersion Test system.

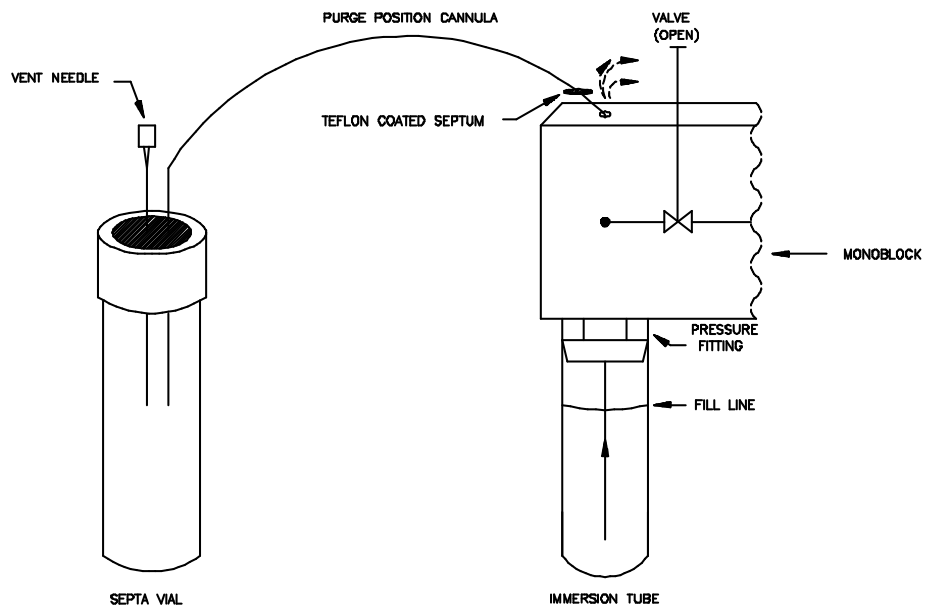


SK-50254

FUEL TRANSFER STEP

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Figure 4. Propellant Transfer Step



SK-50261

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Figure 5. Unloading Posttest Propellant from the Test 15 Immersion Test System

The “Good Laboratory Practices” gave data for the Screening Test and the Immersion Test for selected materials tested with hydrazine (Screening Test: visible reaction; Immersion Test: pressure rate, visible changes to material or fluid, weight change, halide ion concentration, and the ratio of mass of impurities (sample/reference) for SS-304, Rene 41^{®††} (a nickel-based high temperature alloy), PTFE, Nylon 6/6 (a semi-crystalline polyamide), Kynar^{®§§} 460, Kel-F^{®***} 81 (a polychlorotrifluoroethylene formulation), and Rulon^{®†††} J (polymeric reinforced, dull gold colored PTFE compound)) or with dinitrogen tetroxide (Screening Test: visible reaction; Immersion Test: final pressure, visible changes to material or fluid, weight change, and the ratio of mass of impurities (sample/reference) for SS-304, Rene 41, PTFE, Kynar 460, and Flamesafe^{®†††} (a fibrous insulation product)). At least every 2 years, a test facility was required to successfully demonstrate the ability to obtain accurate and repeatable data when testing selected materials.

Unfortunately, the early immersion test data for hydrazine and MMH were acquired under conditions of variable carbon dioxide contamination before the extent of atmospheric contamination was fully understood and measures taken to preclude it, so results were often irreproducible and did not necessarily measure compatibility with pure test fluid, but rather test fluid contaminated with variable amounts of carbon dioxide. These early immersion test data were also, unfortunately and prematurely, incorporated into the “Good Laboratory Practices” data criteria before the test matured enough to fully understand the problem and to preclude carbon dioxide contamination. Consequently, the “Good Laboratory Practices” test data criteria for hydrazine fuels were most often unable to be met.

NHB 8060.1C⁶ Test 15 provided requirements and details for preparing the test samples including receiving and visually inspecting the material, preparing samples to the proper dimensions, cleaning the samples, and inspecting the samples. Pretest procedures included analysis and verification of the test fluid, recording all pertinent information for the test (such as sample identification and pretest information about the sample and fluid), and photography of all unusual samples. The standard practice at WSTF was to photograph all samples, pre- and posttest.

The comparison of recorded visual observations and posttest photographs were sometimes discrepant and became a subject of debate. For example, in one case the test chemist recorded a posttest observation that a white material exposed to a MON-dinitrogen tetroxide appeared orange, but by the time the photograph was taken, sufficient evaporation of the residual test fluid had occurred such that the sample appeared relatively colorless. In another case, the posttest observation was that a clear, transparent rigid plastic material, dissolved in dinitrogen tetroxide, changed to a gelatinous green semisolid. However, by the time the photographs were taken the sample had sufficiently dried that it was a yellow material crystalline material. These apparent discrepancies led to changes in local procedures at WSTF instructing that posttest photographs be taken with every effort to reduce or eliminate inconsistencies noted when comparing pretest or comparison samples with posttest samples and their respective photographs. This usually entailed improved coordination with the photography department to obtain photographs in the same time frame as the posttest observations were made.

Figure 6 shows a sample of Kapton^{®§§§}-insulated wire that was subjected to a vapor phase Screening Test with hydrazine. Samples for vapor-phase Screening Tests are suspended or otherwise supported above the test fluid. Discoloration (yellowing) of the material exposed to the hydrazine vapor is evident.

^{††} Rene[®] 41 is a trademark of General Electric Inc.

^{§§} Kynar[®] 460 is a trademark of Arkema Group, Inc.

^{***} Kel-F[®] 81 is a trademark of 3M Company.

^{†††} Rulon[®] is a trademark of Dixon Corporation, Bristol, Rhode Island.

^{†††} Flamesafe[®] is a trademark of W.R. Grace & Company.

^{§§§} Kapton[®] is a registered trademark of E.I DuPont de Nemours Company.

While widely used because of good electrical insulating properties, Kapton, a polymeric phthalimide compound, readily undergoes chemical reaction with hydrazine to form phthalhydrazides, a completely different class of compounds with different properties.

Figure 7 shows three thermal barrier coatings subjected to the Screening Test and exposed to MON-3 dinitrogen tetroxide for 2 h. As photographed, changes to the posttest samples versus the comparison and are readily and visually observed. Visible changes in the posttest samples are indicative of some level of incompatibility.



Figure 6. A Beaker Test Vapor Phase Exposure of a Kapton-Insulated Wire with Hydrazine

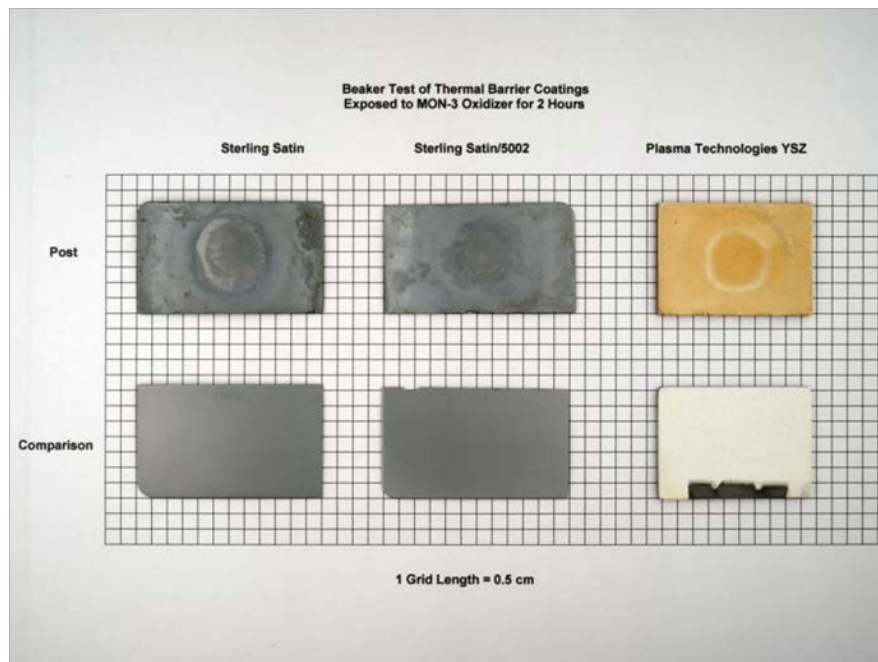


Figure 7. Three Thermal Barrier Coatings Exposed to MON-3 for 2 h; Posttest and Comparison Samples Shown

Additional efforts made to reduce or eliminate sources of inconsistencies included development of a “photo standard” with color/sizing to match all samples, development of a custom grid for samples, establishing magnification requirements, identifying and resolving problems associated with photography of reflective surfaces, emphasizing importance to the customer of providing comparison samples to achieve an accurate representation of pretest and posttest samples, and including original photos in all copies of the final report (color copies were found sometimes not to be of photographic quality).

Figure 8 is a photograph of pre- and posttest gypsum taken from the landing strip at White Sands Space Harbor, which was tested with MON-3 dinitrogen tetroxide. The pretest sample may be more accurately described as a comparison sample.

Figure 9 shows a comparison and posttest Immersion Test sample of a blue-reinforced PTFE. No changes between the posttest PTFE and the comparison sample are evident by visual observation.

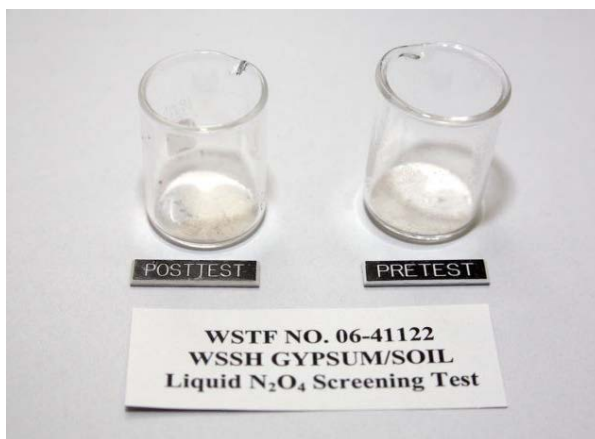


Figure 8. A Screening Test Photograph

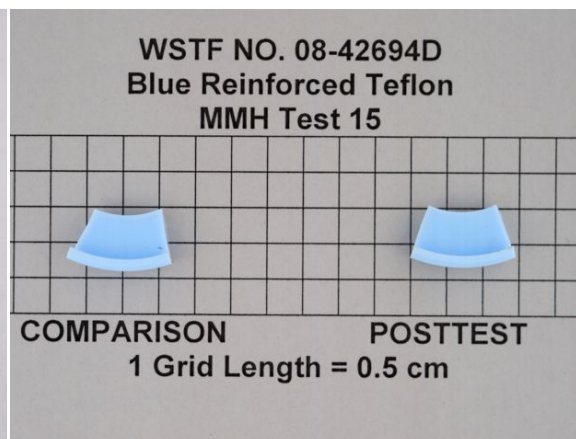


Figure 9. An Immersion Test Photograph

In cases where only one sample was available, such as when the sample was submitted as a unit or there was insufficient sample for reserve to compare with posttest sample (reserve sample used for photographic purposes to compare pre- and posttest material was referred to as a “comparison” sample), a pretest photograph of the same sample that was tested was used to compare with the posttest sample photograph. Occasionally, the pre- and posttest samples were taken under conditions that led to problems in comparing them. For example, occasionally the photograph of a pretest photo was not comparable to a posttest photo due to variables in photographic or processing conditions (e.g., different shades of paper or minor lighting differences), or the photographs occasionally did not facilitate an accurate comparison and were inconsistent with the visual observations made in the report. Other details such as the size (so as not to overwhelm the photograph), consistency of appearance and orientation (font, angle, location with respect to the sample(s), and accuracy of sample labels (identification scheme (name and/or number) were addressed to avoid visual discrepancies and potential discrepancies with the report. Occasionally, a photograph did not capture the observations of the test conductor, leading to inconsistencies with the report. Protocols were established at WSTF to ensure the test conductor directed the photographic instructions and to prioritize timely review of photographs in case other shots were necessary.

Immersion Systems at WSTF were designed for the fuels (hydrazine, MMH, and ammonia), and for dinitrogen tetroxide oxidizers. Hydrazine fuel and dinitrogen tetroxide oxidizer Immersion Systems were not interchanged (WSTF had one system devoted to hydrazine, one system devoted to MMH, one system devoted to ammonia, and one system devoted to dinitrogen tetroxide oxidizers. One series of tests with Aerozine 50 (A-50) and one test with UDMH were performed in the hydrazine or MMH fuel systems. Figure 10 shows an ammonia Test 15 Immersion System in a laboratory fume hood. All Test 15 Immersion Systems at WSTF are located in fume hoods appropriate for the test fluid.



Figure 10. A Test 15 Ammonia System in a Laboratory Fume Hood

Recommended analytical instruments for the posttest analysis include a differential scanning calorimeter, gas chromatograph, ion chromatograph, and high-performance liquid chromatograph. Routine procedures were employed to analyze the posttest fluid for purity to compare with its original specification. For non-metal test materials, posttest halides (typically fluoride, chloride, and bromide) or other halides and anions in accordance with the non-metal composition were analyzed; for metal test materials (typically iron, nickel and chromium for steels) or other metals in accordance with the metal composition, the samples were analyzed after dissolution of the non-volatile residue from the remaining fluid. Posttest analysis of the material was done on a case-by-case basis. Infrared spectroscopy was found to be very convenient for identifying changes in material composition, such as identification of nitrated functional groups following dinitrogen tetroxide fluid tests. The thermal properties of the posttest materials are reliably determined by differential scanning calorimetry, which measures the heat flow from a material as a function of temperature. Typically, energetic materials, such as nitrated materials, give exothermic events (such as energetic decomposition) when they decompose.

WSTF uses a protocol for the analysis of posttest immersion fluids and materials. The first analysis is determination of the non-volatile residue (NVR), which is obtained by the evaporation of the posttest fluids in a tared vessel using gentle warming under a gaseous nitrogen purge. The mass of the NVR is determined, then as applicable, the test scientist may use discretion in performing additional tests to determine the composition of the NVR. After the NVR has been obtained, 25 mL of purified water is added to the NVR vessel to extract ionic halides and metals. If necessary, heat is applied for 5 min to dissolve the NVR. Five (5) mL of the resultant solution is removed for halides analysis using ion chromatography. The remaining 20 mL is analyzed for metals, and is typically acidified using a high-purity grade nitric acid. Iron, nickel, and chromium are always analyzed, but depending on the constituent metals of the test material, other metals may also be analyzed. Results are reported in total μg if no other units are requested.

The following analytical techniques are available for posttest analysis of the sample material at the discretion of the chemist-in-charge: Differential Scanning Calorimetry (DSC), Thermomechanical Analysis (TMA), Fourier Transform Infrared Spectroscopy (FTIR), and Thermogravimetric Analysis-Fourier Transform Infrared Spectroscopy (TGA-FTIR).

Figure 11 shows the Immersion Test apparatus immersion tubes following a test with MMH and an incompatible O-ring material. The discoloration of the test fluid in the sample immersion tube (left) is evident. Additionally, swelling of the O-ring material was observed, although this cannot be discerned from this photograph.



Figure 11. Posttest O-Rings Immersed in MMH

(Note the Discoloration of the Test Fluid (left)
Relative to the Reference Fluid (right))

The ullage must be the same in the sample and the reference chambers because the gas evolution rate data are reported as standard $\text{cm}^3/(\text{cm}^2 \cdot \text{h})$. The fill line marked onto the sample and reference chambers ensures the ullage is constant in both chambers and the use of standard sample and reference surface areas ($25 \pm 5 \text{ cm}^2$) ensures that surface area is constant within the accepted limits of tolerance). Variations in the test fluid volumes are due to different sample and reference material volumes, but these do not enter into the gas evolution rate calculations. Variations in the test fluid volumes in the sample and the reference chambers are accounted for by calculating the masses of impurities rather than their concentrations.

Figure 12 depicts gas evolution rate plots of EPR AF-E-332 (an ethylene propylene terpolymer elastomeric propellant tank diaphragm material) versus PTFE in hydrazine. The similar, almost parallel gas evolution rates of hydrazine exposed to the EPR AF-E-332 (upper curve) relative to that of the reference (hydrazine exposed to PTFE) throughout the 48 h duration of test at 71°C is indicative that the sample and the reference materials are similarly not catalytically active with respect to hydrazine decomposition.

Hydrazine is catalytically decomposed to gases (primarily nitrogen, hydrogen, and lesser amounts of ammonia that are not decomposed) by a number of metals; surface area is also a factor. Stepwise, the catalytic decomposition of hydrazine may occur by the Equations 1 and 2:



The overall reaction for the catalytic decomposition of hydrazine may be written as (Equation 3):



Another reaction for the catalytic decomposition of hydrazine producing ammonia is (Equation 4):



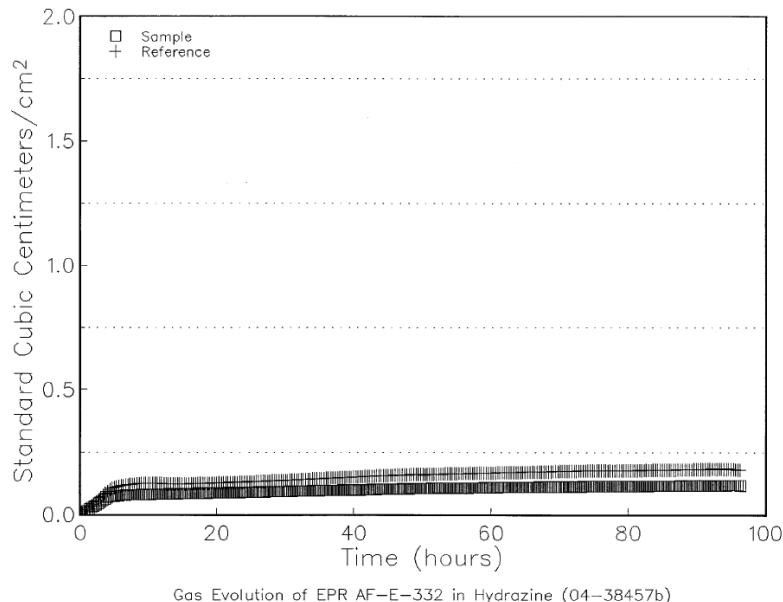


Figure 12. A Test 15 Pressure Plot for EPR AF-E-332 (an Ethylene Propylene Terpolymer) versus PTFE in Hydrazine.

Figure 13 depicts gas evolution rate plots of EPR E515-80 (another ethylene propylene rubber composition) and PTFE in hydrazine. The dramatically increased gas evolution rate of the EPR E515-80 (upper curve) versus PTFE (lower curve), is indicative of the catalytic decomposition of hydrazine. The test was terminated after approximately 40 h (8 h prior to completion of the standard 48 h duration at 71 °C) because the gas evolution rate would cause the pressure to exceed the system rating. This EPR formulation may have contained fillers or plasticizers that contained catalytically active materials.

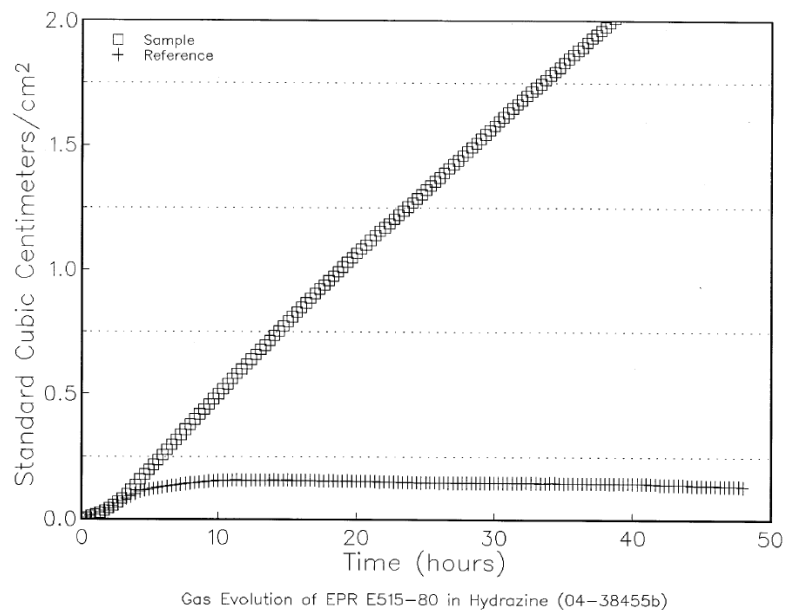


Figure 13. A Test 15 Pressure Plot for EPR E515-80 versus PTFE in Hydrazine

The NHB 8060.1C⁵ test report includes sample identification, configuration, fluid identity, test conditions, and observations from the test. In addition, any relevant analytical results for both the material and fluid should be included. Posttest photographs must be taken, as required, to document any abnormal occurrences. The test report (in an acceptable format) is submitted to MAPTIS. When there is a deviation from standard test parameters, such as nonstandard sample preparation, fluid composition, or test conditions, the test is identified as nonstandard.

For materials in systems containing reactive fluids, NHB 8060.1C⁵ required that if materials fail to meet the criteria of Test 15 for the fluid to which they are exposed (either directly or as a result of single barrier failures), a system evaluation must be conducted. This evaluation can be conducted by analysis or by testing. If the analytical approach is used, all possible sources of runaway exothermic reactions must be addressed, control methods developed, and the results documented. Possible initiation sources for runaway reaction include mechanical impact, rapid pressurization, sources of electrical energy, and other sources of heat. The rationale for use of materials that fail to meet the criteria of Test 15 must be documented and submitted to the responsible NASA Center materials organization for approval. If the material causes excessive fluid decomposition in Test 15 and potential initiation sources for runaway reactions are present, tests must be conducted to verify that no hazard exists in the use configuration at use conditions. Guidelines for configurational tests to evaluate runaway reactions in reactive fluid systems can be obtained from the responsible NASA Center materials organization.

NASA-STD-6001 Reactivity of Materials in Aerospace Fluids (Test 15)

Test 15, along with other NASA standard tests from NHB 8060.1C,⁵ transitioned verbatim to the NASA technical standard NASA-STD-6001, *Flammability, Odor, Offgassing, and Compatibility Requirements and Test Procedures for Materials in Environments that Support Combustion*, on February 9, 1998.⁶ NASA-STD-6001⁶ was previously published as NHB 8060.1C.⁵ With the exception of the cover and administrative information, NASA-STD-6001⁶ was essentially a verbatim copy of NHB 8060.1C.⁵ The paragraph numbering system, table numbers, and figure numbers remained unchanged. Consequently, refer to NHB 8060.1C⁵ for the relevant information for NASA-STD-6001⁶.

NASA-STD-(I)-6001.A and NASA-STD-(I)-6001.B Test 15 - Reactivity of Materials in Hydrazine, Monomethylhydrazine, Unsymmetrical Dimethylhydrazine, Aerozine 50, Nitrogen Tetroxide, and Ammonia

The next update to Test 15 after NHB 8060.1C⁵/NASA-STD-6001⁶ was NASA-STD-(I)-6001.A⁷ *Flammability, Offgassing, and Compatibility Requirements and Test Procedures*, an interim standard that was approved April 21, 2008 and remained unchanged with respect to Test 15 in the next interim standard update NASA-STD-(I)-6001.B,⁸ which was approved November 11, 2009 (though the cover page retained the April 21, 2008 approval date). An interim NASA standard is given an “-(I)-” designation and represents the technical consensus of the developing group but does not have final NASA approval. Interim NASA standards provide uniform engineering and technical requirements for processes, procedures, practices, and methods to meet urgent program and project technical needs, have the consensus of the developing group (Technical Working Group), but do not have the Agency-wide concurrence required for a NASA Technical Standard. The interim NASA-STD-(I)-6001.A and NASA-STD-(I)-6001.B^{7,8} standards were approved for use by NASA Headquarters and NASA Centers, including Component Facilities and Technical and Service Support Centers, and established requirements for evaluation, testing, and selection of materials that are intended for use in space vehicles, associated Ground Support Equipment (GSE), and facilities used during assembly, test, and flight operations. Included are requirements, criteria, and test methods for evaluating the flammability, offgassing, and compatibility of materials. The provisions of the standard, as with other NASA standards, will be included, as applicable, in all future contracts and programs involving space vehicles, payloads, and associated support equipment.

Interim standards NASA-STD-(I)-6001.A⁷ and NASA-STD-(I)-6001.B⁸, *Flammability, Offgassing, and Compatibility Requirements and Test Procedures*² were developed to provide the most recent standard test methods, including Test 15. NASA-STD-(I)-6001.A⁷ was approved April 21, 2008, expired April 20, 2009, and, after the correction of a typographical error in units in an unrelated test and some administrative updates, NASA-STD-(I)-6001.B⁸ was approved November 10, 2009, expired April 21, 2010, but was given the same April 21, 2008 approval date as NASA-STD-(I)-6001.A.⁷ Both NASA-STD-(I)-6001.A⁷ and NASA-STD-(I)-6001.B⁸ superseded NASA-STD-6001.⁶

As in NHB-8060.1C⁵/NASA-STD-6001,⁶ the interim NASA-STD-(I)-6001.A and NASA-STD-(I)-6001.B^{7,8} standards included Test 15, now titled “Reactivity of Materials in Hydrazine, Monomethylhydrazine, Unsymmetrical Dimethylhydrazine, Aerozine 50, Nitrogen Tetroxide, and Ammonia,” as the required test for material use in Reactive Fluids Environment. Test 15 acknowledged the handling of hazardous fluids has the potential to produce energetic events such as fire, thermal runaway, or explosion, that testing should be carried out with the appropriate engineering controls and protective equipment, and that the test systems should be in fume hoods approved for the handling of the test fluid.

NASA-STD-(I)-6001.A and NASA-STD-(I)-6001.B^{7,8} were developed with the joint cooperation of a technical working group consisting of members of several NASA Centers, most of which had direct experience with the tests. A substantial leap was made to update Test 15 to the current practice and many of the current capabilities. Significant clarifications and rewording to the test were made. As the title “Reactivity of Materials in Hydrazine, Monomethylhydrazine, Unsymmetrical Dimethylhydrazine, Aerozine 50, Nitrogen Tetroxide, and Ammonia (Test 15)” stated, the intended test fluids were specifically called out. As described, Test 15 was applicable to the hydrazine family of fuels, nitrogen tetroxide (and intended inclusion of mixed oxides of nitrogen), and ammonia. Previously, fluids such as unsymmetrical dimethylhydrazine and Aerozine 50 were tested at WSTF on a “non-standard” basis.

The interim NASA-STD-(I)-6001.A and NASA-STD-(I)-6001.B^{7,8} standards required the use of military performance specification grade fluids^{****} except for ammonia (which had a stated purity):

- MIL-PRF-25604 Performance Specification Propellant, *Uns*-Dimethylhydrazine¹⁸
- MIL-PRF-26536 Performance Specification Propellant, Hydrazine¹⁶
- MIL-PRF-26539 Performance Specification Propellants, Dinitrogen Tetroxide²⁰
- MIL-PRF-27402 Performance Specification Propellant, Hydrazine-*uns*-Dimethylhydrazine (50% N₂H₄– 50% UDMH)²¹
- MIL-PRF-27404 Performance Specification Propellant, Monomethylhydrazine¹⁷
- Ammonia is procured with a stated purity of 99.99 percent (liquid phase)

Prior experience with a high purity electronic grade liquid ammonia led to a failed test and contaminated system when the ammonia was withdrawn as a liquid rather than as a vapor then condensed to a liquid. The liquid ammonia obtained directly from the cylinder contained unacceptably gross heavy hydrocarbon and other contamination. Investigation later showed that even other sources of high purity liquid ammonia were contaminated with heavy hydrocarbons and other contaminants; consequently WSTF specifies ammonia with a low NVR specification in the liquid phase.

Test 15 was explicitly described as a screening test lasting 2 h, followed by a short-term immersion test lasting 48 h. It also stated that appropriate long-term tests would be conducted for materials with long-term exposure to fuels, oxidizers, and other hazardous fluids, and that the

^{****} Though the military specifications were stated in NASA-STD-(I)-6001 A and B, the type and grade of test fluids were not specified, as in NASA-STD-6001; rather, the selection of type and grade was left to the test requestor and the test organization.

responsible NASA Center's M&P organization should be consulted for guidance related to long-term exposure. Information on reactivity of materials with aerospace fluids may also be obtained using other tests such as accelerated rate calorimetry, isothermal microcalorimetry, or differential scanning calorimetry (DSC).

A supplemental test procedure for determining the effects of incidental exposure (minor amounts, such as a splash) of aerospace fluids on materials (incidental exposure time is considered to be ≤ 240 min) was described in Appendix A.7. Supplemental Test A.7 "Reactivity and Penetration of Materials due to Incidental Exposure to Hydrazine, Monomethylhydrazine, Unsymmetrical Dimethylhydrazine, Aerozine 50, Nitrogen Tetroxide, and Ammonia" is not part of Test 15, but as described, is supplemental. It was derived from Kennedy Space Center procedure KSC MTB 175-88, *Procedure for Casual Exposure of Materials to Hypergolic Fluids*.²²

The test criteria section described the use of Test 15 to determine and document the reactivity of a material and fluid in comparison to a reference material; therefore, test criteria are dependent on the intended use environment and configuration of the material. A section addressed specific failure criteria (material and fluid changes and degradation, burning, charring, fire, frothing, and pressure rise for dinitrogen tetroxide tests, nitration of polymers exposed to dinitrogen tetroxide, etc.), and included a discussion on the consideration of gas evolution rates for hydrazine fuels, non-volatile residue, and halide generation as related to evaluating suitability of a material for use without specific failure criteria.

The Screening Test ("Beaker Test") procedure details were elaborated considerably with respect to NHB 8060.1C/NASA-STD-6001.^{5,6} Notable changes included adding the test fluid to the specimen drop by drop, slowly at first, and observing for any evidence of gross reactivity. If no gross reactivity was observed, the remainder of the test fluid (typically 10 mL total; the test specimen mass remained ≤ 0.25 g) was added (the screening test may would be stopped at signs of gross reactivity). The specimen was observed for visible signs of reaction at the beginning and periodically during the test, and at the end of the 2-h exposure, the specimen was removed from the fluid, and observations were recorded. Post-exposure mass and dimensions^{††††} were taken when possible, and posttest visual observations were made using a set of defined standard terms (Table 2). If the material was determined to be reactive, it did not continue to the Immersion Test. If there was slight or no reactivity observed, the test lead may recommend the material be tested in the immersion test.

A material was considered to have failed the test if any of the following occurred in either the screening test or the immersion test:

- (1) Burning, charring, or fire.
- (2) Frothing.
- (3) The material dissolves in the test fluid.
- (4) The material crumbles, becomes friable, or generates particulate.
- (5) The material changes shape or physical dimensions by more than 20 percent.
- (6) The material suffers more than 20 percent degradation of the physical properties for which it was selected.
- (7) Visible changes in appearance of the test fluid (color and/or clarity).
- (8) For nitrogen tetroxide, a pressure rise >68.9 kPa (>10 psi).
- (9) For polymers exposed to nitrogen tetroxide, evidence of material nitration as indicated by DSC and/or FTIR.

^{††††} Posttest mass change was removed from the failure criteria. One criterion for failure was the material changes shape or physical dimensions by more than 20%, but the time between immersion and obtaining post-test sample dimensions and masses was still not specified nor was there a requirement to document the time.

The 2 percent mass change failure criterion from NHB 8060.1C/NASA-STD-6001^{5,6} was discontinued, and although it was still required to obtain a posttest sample mass, the time to obtain this measurement was not specified.

A non-standard screening test of a circuit board assembly in hydrazine is shown in Figure 14; the test is non-standard because the fluid volume is considerably greater than 10 mL (approximately 50 mL) and the test sample mass is approximately 40 g. Note the discoloration of the hydrazine (clear and colorless to blue-green and cloudy) near the bottom of the test vessel. Pre- and posttest photographs of the circuit board are shown in Figures 15 and 16, respectively; note the discoloration of the circuit board following exposure to hydrazine.



Figure 14. A Non-Standard Screening Test of a Circuit Board Assembly in Hydrazine

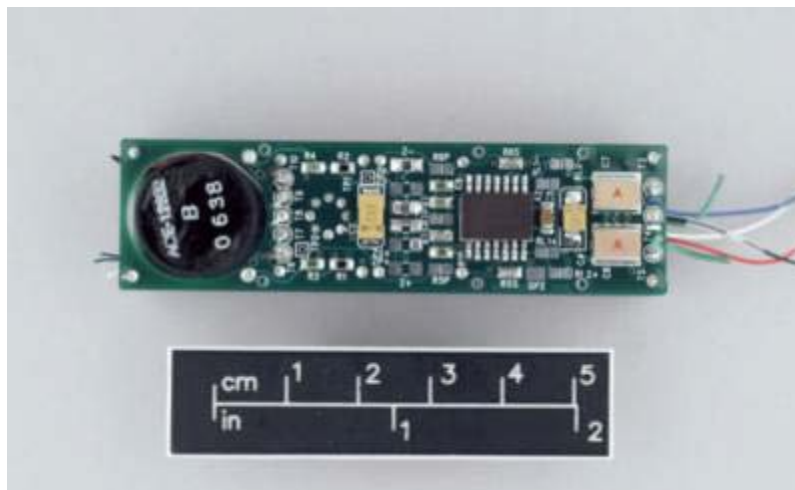
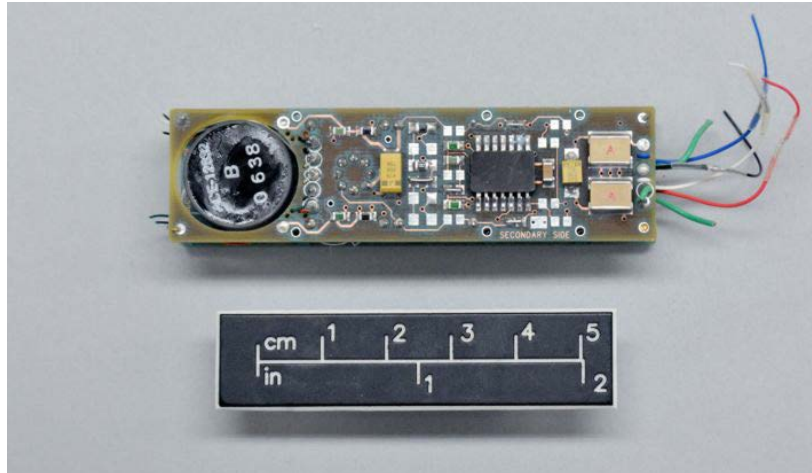


Figure 15. Pretest Photograph of a Circuit Board (Before a Screening Test in Hydrazine)



**Figure 16. Posttest Photograph of a Circuit Board
(After a Screening Test in Hydrazine)**

The Immersion Test standard conditions for hydrazine, MMH, unsymmetrical dimethylhydrazine (UDMH), Aerozine 50, nitrogen tetroxide, and the mixed oxides of nitrogen remained the same as in NHB 8060.1C/NASA-STD-6001^{5,6} (71 (±3) °C [160 (±5) °F] and the vapor pressure of the fluid at that temperature). The test temperature for ammonia was established to be 30 (±3) °C [86 (±5) °F] and the test pressure was the vapor pressure of ammonia at that temperature. The test duration remained the same as previous versions of Test 15, 48 h from the onset of heating, but allowed test termination earlier in the case of gross reactivity or of a pressure rise that may cause the immersion tube to relieve.

The preparation of samples (specimen preparation) elaborated from the requirements of NHB 8060.1C/NASA-STD-6001^{5,6} describing dimensions (4 x 1 x 0.15 cm (1.6 x 0.4 x 0.06 in)) of solid and foam materials to achieve the standard size (25 (±5) cm² [3.9 (±0.8) in²]) surface area requirement. Requirements were given for different test specimens:

- Greases, semisolids, and liquids applied to a stainless steel substrate.
- Wires and cables (electrical insulation stripped) to prepare the standard size specimen of the insulation.
- Inks, adhesives, coatings, and primers applied in the end-use thickness onto abraded standard size 304L stainless steel substrates; cured as requested; a default thickness of 0.013 cm (0.005 in) if the adhesive end-use thickness is not specified; and sufficient substrates coated to achieve the standard size specimen.
- Heat-shrinkable tubing pre-shrunk in accordance with manufacturer's instructions to simulate actual-use conditions and cut to achieve the standard size surface area.
- Pressure-sensitive tapes applied to both sides of three 4 x 1 x 0.15-cm (1.6 x 0.4 x 0.06-in) 304L stainless steel substrates to achieve the standard size surface area.
- O-rings and irregularly shaped items with segments cut or an appropriate number of O-rings or irregularly shaped items used to achieve the standard size surface area.
- Specimens cleaned and dried to end-use specifications.
- The specimen's mass determined, the approximate surface area reported, and any flaws or residual contamination inspected and reported.
- A reference specimen prepared for the immersion test.

The Immersion Test system (Figure 17) was described in a manner that reflected the current construction at WSTF:

- Consisting of one reference and one specimen immersion tube, each constructed of borosilicate glass and instrumented with a pressure transducer.
- Total ullage volume above the fill line (for each immersion tube) known and sufficient for accurate pressure measurement.
- The remainder of the system constructed of 304L stainless steel.
- Immersion tubes maintained in a temperature-controlled water bath instrumented with at least one thermocouple positioned in the bath near the immersion tubes.
- Test data (time, temperature, and pressure) recorded at appropriate intervals throughout the test.
- Provisions for inert atmosphere purging, filling operations, and cleaning.

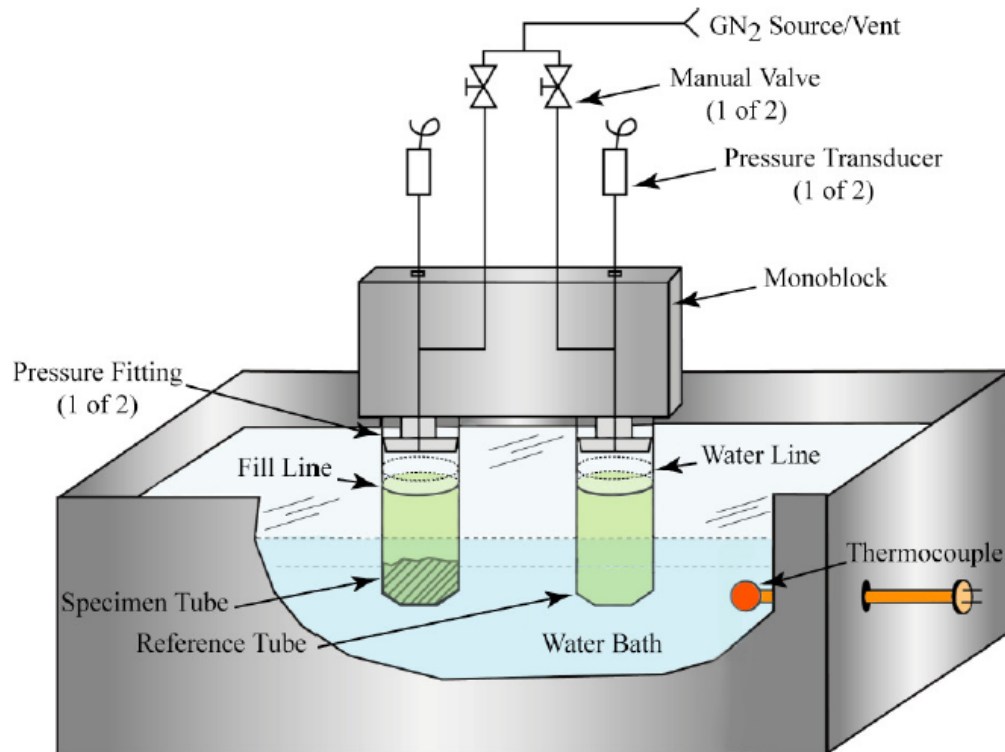


Figure 17. Immersion Test System for Test 15 (NASA-STD-I)-6001.A and B)^{7,8}

Figure 17 provided a clearer pictorial depiction of a Test 15 Immersion System than NHB 8060.1C/NASA-STD-6001^{5,6} (Figure 1).

The Immersion Test procedure details were elaborated considerably with respect to NHB 8060.1C/ NASA-STD-6001.^{5,6} The details of the procedure, which were largely based on the experience of WSTF test personnel, were now codified, as well as suitable explanatory information:

- Both the test specimen and the reference material specimen are exposed to the same fluid in their respective immersion tubes.
- Polytetrafluoroethylene is used as the reference material for nonmetallic specimens.
- 304L stainless steel is the reference material for metallic specimens.
- Specimen and the reference materials are placed in the appropriate immersion tubes and then purged with nitrogen to remove air.

- The system is checked for leaks, and sufficient test fluid (~25 mL) is added up to the fill line of the immersion tubes to cover the specimens completely and to produce the same ullage space in the specimen and the reference immersion tubes.
- The pressure and temperature recording system is activated.
- The immersion tubes are placed in the water bath.
- The water bath is heated at a rate of ~ 0.25 °C (~ 0.32 °F)/min.
- When not in use, the system is maintained under a dry nitrogen purge.
- The duration of a test is 48 hr; however, the test may be terminated early if excessive pressure generation is noted.
- The closed system is held at 71 (±3) °C [160 (±5) °F].
- Pressure is recorded as a function of time.
- At the end of the test, the immersion tubes are vented, removed from the water bath, and allowed to cool.
- The fluid is removed from the immersion tubes using inert atmosphere transfer and submitted for posttest analysis.
- The immersion tubes are removed from the system, inspected, rinsed with deionized water, and allowed to dry overnight.
- Posttest fluid analyses are determined by the fluid being tested.
- Posttest analyses for hydrazine fuels include assay or purity, carbon dioxide (CO₂), and NVR.
- Nitrogen tetroxide and ammonia posttest analyses include NVR. In each case, the NVR may be analyzed for the appropriate metals (metallic specimen) or anions (nonmetallic specimen).
- Posttest material analyses include photographic documentation, visual observations of the material using standard terms (Table 2), and determination of the mass and dimensions.
- Posttest material analyses for nitrogen tetroxide tests: DSC and FTIR are performed on the specimen after testing as a screen for the formation of potentially energetic materials produced by nitration.

Acknowledgement of the potential for energetic species formation by nitration in NASA-STD-(I)-6001.A and B^{7,8} is similar to the warning note in NHB 8060.1B⁴ and reflects the collective safety culture of the Test 15-developing group.

Analytical techniques were discussed for posttest analysis of the fluid and material, including NVR, gas chromatography, ion chromatography, DSC, and FTIR.

Table 2 provides standard descriptive terms and definitions for Test 15 posttest analysis (NASA-STD-(I)-6001A and B).^{7,8}

**Table 2. Standard Descriptive Terms and Definitions for Test 15 Posttest Analysis
(NASA-STD-(I)-6001A. and B)^{7,8}**

Descriptive Term	Definition
Adherent	Bonded or clinging to the surface of a material
Brittle	Easily fractured or broken, not malleable or ductile
Bubble	To form gaseous products
Char	To darken appreciably in color, as in oxidation
Decompose	To break down into component parts or disintegrate, either partially or completely
Degradation	An adverse physical or chemical change in a substance
Discolor	To alter the color
Dissolve	To pass into solution with little or no decomposition
Firm	Stiff and unyielding to pressure
Flexible	Capable of being bent; pliable
Friable	Property of a substance capable of being easily rubbed, crumbled, or reduced to powder
Frothing	A mass of bubbles adhering to the liquid surface; foam
Hard	Resistant to pressure, not readily penetrated, firm
Matte	Having a dull, nonreflective surface or finish
No Visible Reaction	No visual evidence of change
Opaque	Does not transmit light
Pitted	Marked by pits or small depressions, either regular or irregular
Powder	Ground, dispersed solid particles
Reaction	A chemical change in which a substance decomposes, combines with other substances, or interchanges constituents with other substances
Reactive Fluid	A fluid that readily responds to a stimulus through reaction
Rigid	Not bending; inflexible
Rough	A bumpy, uneven surface
Shape	The characteristic bulk configuration or form
Smooth	Having a surface free from irregularities, projections, roughness
Soft	Yielding readily to pressure or weight
Solid	Of definite shape and volume; a single piece
Swell	To increase in size or volume as a result of liquid absorption
Tacky	Adhesive or gummy to the touch
Translucent	Transmits light but does not permit the perception of images
Transparent	Transmits light to the extent that images can be perceived
Woven	Constructed from an interlacing of webs or strands
Wrinkled	Ridges or creases on surface

Requirements of the test report were to include specimen identification, method of preparation, configuration, fluid identity, test conditions, data, and observations from the test, including visual observations, photographs, gas evolution rate or system pressure with time, and results of posttest analyses. The test report (in the acceptable format) was required to be submitted to MAPTIS. If there was a deviation from standard test conditions (test duration, temperature, or specimen surface area), the test was identified as non-standard.

The Good Laboratory Practices section in NHB 8060.1C/NASA-STD-6001,^{5,6} which contained relatively primitive and some flawed data (due to carbon dioxide contamination), was replaced with a relatively short section imposing requirements on the pressure of the reference side of the system. Based on historical data, the pressure rise on the reference side of the system must be $< 0.4\text{kPa}$ ($< 0.06\text{ psia}$)/h for nitrogen tetroxide and ammonia; and $< 7.0 \times 10^{-3}$ standard $\text{cm}^3/(\text{cm}^2\text{ h})$ for the hydrazine fuels.

NASA-STD-6001.B Test 15 - Reactivity of Materials in Hydrazine, Monomethylhydrazine, Unsymmetrical Dimethylhydrazine, Aerozine 50, Nitrogen Tetroxide, and Ammonia

The next update to Test 15 after the interim NASA standards NASA-STD-(I)-6001.A and NASA-STD-(I)-6001.B^{7,8} was NASA-STD-6001.B, *Flammability, Offgassing, and Compatibility Requirements and Test Procedures*.² NASA-STD-6001.B², released August 26, 2011, had full NASA approval rather than just the technical consensus of the developing group as formerly indicated by the “-(I)-” designations in the interim versions. While there were a number of changes specific to other tests, relatively subtle but necessary changes were made to Test 15 - Reactivity of Materials in Hydrazine, Monomethylhydrazine, Unsymmetrical Dimethylhydrazine, Aerozine 50, Nitrogen Tetroxide, and Ammonia. Two of these changes were relevant to the type and grade of fluid; it was clearly stated that:

- Hydrazine shall meet the requirements of MIL-PRF-26536, *Propellant, Hydrazine*,¹⁶ high purity grade; and
- Nitrogen tetroxide and mixed oxides of nitrogen shall meet the requirements of MIL-PRF-26539, *Propellants, Dinitrogen Tetroxide*,²⁰ type MON-3.

These changes clearly stated that high purity hydrazine and MON-3 dinitrogen tetroxide were the standard fluids of interest. No clarification of other fluid type or grades was necessary because their respective military specifications refer only to one type or grade of fluid (with the exception of ammonia, which has a stated purity).

Another change of interest pertained to the time after which samples had been immersed and their posttest mass and dimensions were obtained. The NASA-STD-6001.B² requirement was that the determination of the material mass and dimensions was made after a documented drying time. No specific time was mandated, but documentation of the time the mass and dimensions were obtained was now required. This was in part due to acknowledgement that a high degree of variability/error could occur if the mass measurement is taken at a specified time while propellant is permeating from a sample and the measurement is taken on the steep portion of the mass-loss curve, such as that shown in Figure 18. Rather, it was left to the discretion of the test organization to record the time the measurements were taken. Figure 18 depicts a typical mass-loss curve of a MON-3 dinitrogen tetroxide-contaminated PTFE coupon. Note in this case the relatively steep portions of the mass-loss curve up to approximately 100 h.

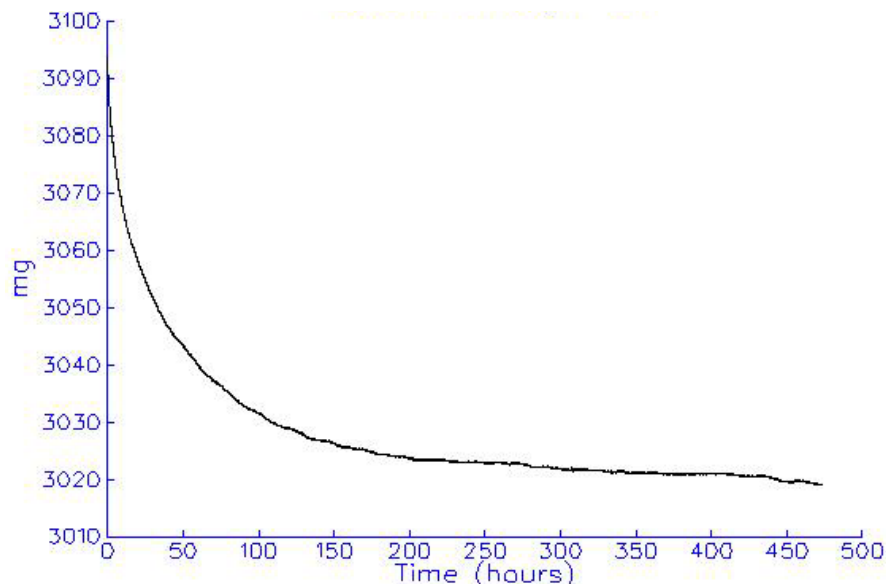


Figure 18. Mass Loss of a MON-3 Dinitrogen Tetroxide-Contaminated PTFE Coupon as a Function of Time²³

NASA-STD-6001.B Supplemental Test A.7 Reactivity and Penetration of Materials due to Incidental Exposure to Hydrazine, Monomethylhydrazine, Unsymmetrical Dimethylhydrazine, Aerozine 50, Nitrogen Tetroxide, and Ammonia

The supplementary test for materials usage in Reactive Fluids Environment in NASA-STD-(I)-6001.A, NASA-STD-(I)-6001.B, and NASA-STD-6001.B^{7,8,2} Test A.7, is titled *Reactivity and Penetration of Materials due to Incidental Exposure to Hydrazine, Monomethylhydrazine, Unsymmetrical Dimethylhydrazine, Aerozine 50, Nitrogen Tetroxide, and Ammonia*. It was adapted from Kennedy Space Center procedure KSC MTB 175-88, *Procedure for Casual Exposure of Materials to Hypergolic Fluids*.²² Test A.7 is a procedure for determining the effects of incidental exposure (minor amounts, such as a splash) of aerospace fluids on materials. Incidental exposure time is considered to be ≤ 240 min. This test is briefly discussed because it augments the Test 15 Screening Test, though it is not Test 15.

A material is exposed to hydrazine, UDMH, MMH, A-50, nitrogen tetroxide and mixed oxides of nitrogen, or ammonia (all meeting the stated requirements of NASA-STD-6001.B²) for ≤ 240 min. The test is applicable to films, fabrics, sheets, metals, composites, adhesives and coatings, tapes, greases and gels, and complex shapes (such as O-rings, cables, and pipes). The test is for the reactivity of the fluid or material and penetration of fluid into the material.

For determining the reactivity and penetration of films, fabrics, sheets, metals, and composites, the test specimen is placed over a beaker and the test fluid is added drop by drop, slowly at first, and observed for any evidence of gross reactivity. If no gross reactivity is observed, the remainder of the test fluid (typically 1 mL total) is added to the center of the specimen, without exposing the edges of the specimen to the fluid. The test fluid is allowed to stand on the specimen for the specified exposure time (additional test fluid should be added as required to maintain a liquid film on the test specimen during the exposure time); then the specimen is observed for visible signs of reaction such as burning, smoking, frothing, charring, solubility, swelling, fracture, or penetration of the specimen throughout the test. The test may be stopped at signs of gross reactivity. After testing, each component is subjected to functional tests and inspected for signs of degradation. The time of the first instance of penetration (first drop of liquid in the beaker) is recorded. For materials used in protective garments, the time of initial appearance of wetness on the underside of the test specimen is recorded. (Atmospheric condensation could form on the underside of the test specimen, giving a false indication of

penetration; verification of penetration should be made by applying a blotter that changes color in the presence of the test fluid).

For determining the reactivity and penetration of reactivity of all other materials, the specimen is placed on a watch glass or petri dish, test fluid is added drop by drop, slowly at first, and is observed for any evidence of gross reactivity. If no gross reactivity is observed, the remainder of the test fluid (typically 1 mL total) is added to the center of the specimen without exposing the edges of the specimen to the fluid. The test fluid is allowed to stand on the specimen for the specified exposure time (additional test fluid should be added as required to maintain a liquid film on the test specimen during the exposure time). The specimen is observed for visible signs of reaction such as burning, smoking, frothing, charring, solubility, swelling, fracture, or penetration of the specimen throughout the test. At the end of the specified exposure time, the test fluid is blotted from the specimen (the specimen should be rinsed with running water for 60 s), and allowed to air dry for 24 h before final evaluation. Greases or uncured materials are not rinsed or blotted; any excess test liquid is poured off and the test specimen is allowed to stand in air for 24 h before final evaluation.

Similar to NASA-STD-6001.B,² posttest material analysis includes photographic documentation, visual observations of the material using a set of defined standard terms, and determination of the mass and dimensions when possible.

The test report includes specimen identification, configuration, fluid identity, test conditions, and observations from the test, and any reactivity observed during the exposure, such as burning, smoking, frothing, charring, solubility, swelling, or fracture of the specimen, is recorded in the report. For penetration, the elapsed time at the first instance of penetration (or appearance of wetness for protective garments) is reported. Relevant posttest analysis results for the material are included, posttest photographs are included, as required, and the test report is submitted to MAPTIS.

INTERNATIONAL STANDARDIZATION

The International Organization for Standardization (ISO) promulgated three international standards relevant to Test 15 in 2006. Products of Technical Committee 20 "Aircraft and Space Vehicles"/Subcommittee 14 "Space Systems and Operations" Working Group 1 "Design Engineering and Production" were as follows: ISO 14624-5:2006, *Space Systems — Safety and Compatibility of Materials — Part 5: Determination of Reactivity of System/Component Materials with Aerospace Propellants*²⁴ corresponded with NHB 8060.1C/NASA-STD-6001^{5,6} Test 15; and ISO 14624-6:2006, *Space systems — Safety and Compatibility of Materials — Part 6: Determination of Reactivity of Processing Materials with Aerospace Fluids*²⁵ and ISO 14624-7:2006, *Space systems — Safety and Compatibility of materials Part 7: Determination of Permeability and Penetration of Materials to Aerospace Fluids*²⁶ corresponded with KSC MTB-175-88, *Procedure for Casual Exposure of Materials to Hypergolic Fluids*²² (which was later adapted into Supplementary Test A.7, "Reactivity and Penetration of Materials due to Incidental Exposure to Hydrazine, Monomethylhydrazine, Unsymmetrical Dimethylhydrazine, Aerozine 50, Nitrogen Tetroxide, and Ammonia" in NASA-STD-(I)-6001.A, NASA-STD-(I)-6001.B, and NASA-STD-6001.B^{7,8,2}). The ISO standards provide less detail than the NASA documents from which they were derived, and, at this time, are outdated with respect to NASA-STD-6001.B.²

The British Standards Institution (BSI) adapted the ISO 14624-5, -6, and -7²⁴⁻²⁶ standards on May 31, 2006 as British Standards (BS) shortly after their issuance as ISO standards: BSI BS ISO 14624-5, *Space Systems — Safety and compatibility of materials — Part 5: Determination of Reactivity of System/Component Materials with Aerospace Propellants*,²⁷ BSI BS ISO 14624-6, *Space Systems — Safety and Compatibility of Materials — Part 6: Determination of Reactivity of Processing Materials with Aerospace Fluids*,²⁸ and BSI BS ISO 14624-7, *Space systems — Safety and compatibility of materials — Part 7: Determination of Permeability and Penetration of Materials to Aerospace Fluids*.²⁹ These BSI standards are identical to the corresponding ISO

standards and consequentially, provide less detail than the NASA documents from which they were derived and, at this time, are outdated with respect to NASA-STD-6001.B.²

It is not known whether any of the Test 15- or Supplementary Test A.7-derived ISO or BSI standards were ever used by any organization within or outside of the United States, or if they will be continued, discontinued, or updated as ISO or BSI standards during their next review cycle. These standards are, at the present, obsolete with respect to NASA-STD-6001.B.²

“ENHANCED” TEST 15

Test 15 identifies gross reactivity but only partially addresses the mechanical functionality of materials after exposure. An improved process for assessing the reactivity, mechanical functionality, and physical properties of nonmetals in aerospace fluids based on the Test 15 protocol was developed and tested with polychlorotrifluoroethylene (PCTFE) in MON-3 dinitrogen tetroxide,³⁰ and more recently Kalrez 1045[®],⁺⁺⁺ a perfluorinated elastomer with a mineral filler, in MON-3 dinitrogen tetroxide. The improved process uses a step-wise screening protocol to ensure it is safe to condition significantly larger sample sets for performing physical property testing including flexure, tensile/elongation, hardness, and compressive strength tests immediately after removal from the fluid. The step-wise screening protocol uses a 4-step process for hydrazine fuels and a 6-step process for dinitrogen tetroxide oxidizers:

- (1) Material Review (for both hydrazine fuels and dinitrogen tetroxide oxidizer tests)
- (2) Material verification (for both hydrazine fuels and dinitrogen tetroxide oxidizer tests)
- (3) NASA-STD-6001 2-h beaker test, ambient temperature and pressure (for both hydrazine fuels and dinitrogen tetroxide oxidizer tests)
- (4) 48-h immersion test at 71 °C (160 °F), ambient pressure (for both hydrazine fuels and dinitrogen tetroxide oxidizer tests)
- (5) Differential Scanning Calorimetry (DSC) (for dinitrogen tetroxide oxidizer tests only) and
- (6) Fourier Transform Infrared Spectroscopy (FTIR) (for dinitrogen tetroxide oxidizer tests only)

These sequential steps identify potential hazards, if any, with small quantities of material in the WSTF Chemistry & Materials Laboratory before the larger amounts required for mechanical functionality and physical property determinations are tested/conditioned in larger quantities in a concrete test cell in the WSTF Hazardous Fluids Test Area. After testing/conditioning in the WSTF Hazardous Fluids Test Area, the immersion chamber is taken to the WSTF Chemistry & Materials Laboratory where the materials are unloaded in a fume hood and subjected to various post-exposure testing.

Figure 19 shows polymeric samples prepared in a manner conforming to the appropriate ASTM method for enhanced Test 15 testing.

Figure 20 shows the enhanced Test 15 samples secured in a sample holder.

Figure 21 shows a sample holder containing enhanced Test 15 specimens in an immersion chamber prior to filling with test fluid.

Figure 22 shows the Hazardous Fluids Test Area (HFTA) at WSTF where the enhanced Test 15 immersion is performed.

Figure 23 shows a Universal Test Machine equipped with local exhaust ventilation where posttest propellant-exposed enhanced Test 15 samples are tested.

⁺⁺⁺ Kalrez[®] is a registered trademark of E.I. Du Pont de Nemours and Company, Wilmington, Delaware.

Figure 24 shows selected enhanced Test 15 posttest materials after tensile and compressive strength testing. Control samples (similarly prepared but not immersed in propellant) are also tested for comparison of changes.

Figure 25 shows enhanced Test 15 test data (ullage, liquid temperature, and chamber pressure) plotted as a function of time throughout the duration of a 48-h, 71 °C (160 °F) test of PTFE in MMH. These data remained in-specification throughout the duration of the test.

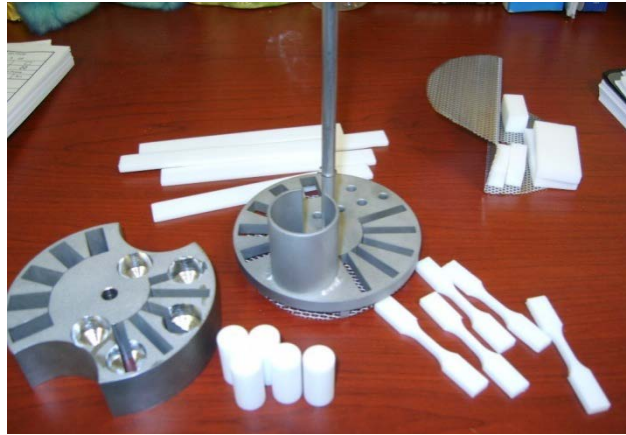


Figure 19. Enhanced Test 15 Samples



Figure 20. Enhanced Test 15 Samples Secured in a Sample Holder



Figure 21. Enhance Test 15 Samples and Sample Holder in an Immersion Chamber



Figure 22. An Enhanced Test 15 Immersion is performed in the WSTF Hazardous Fluids Test Area



Figure 23. A Universal Test Machine with Local Exhaust Ventilation



Figure 24. Enhanced Test 15 Posttest Samples following Tensile and Compressive Strength Testing

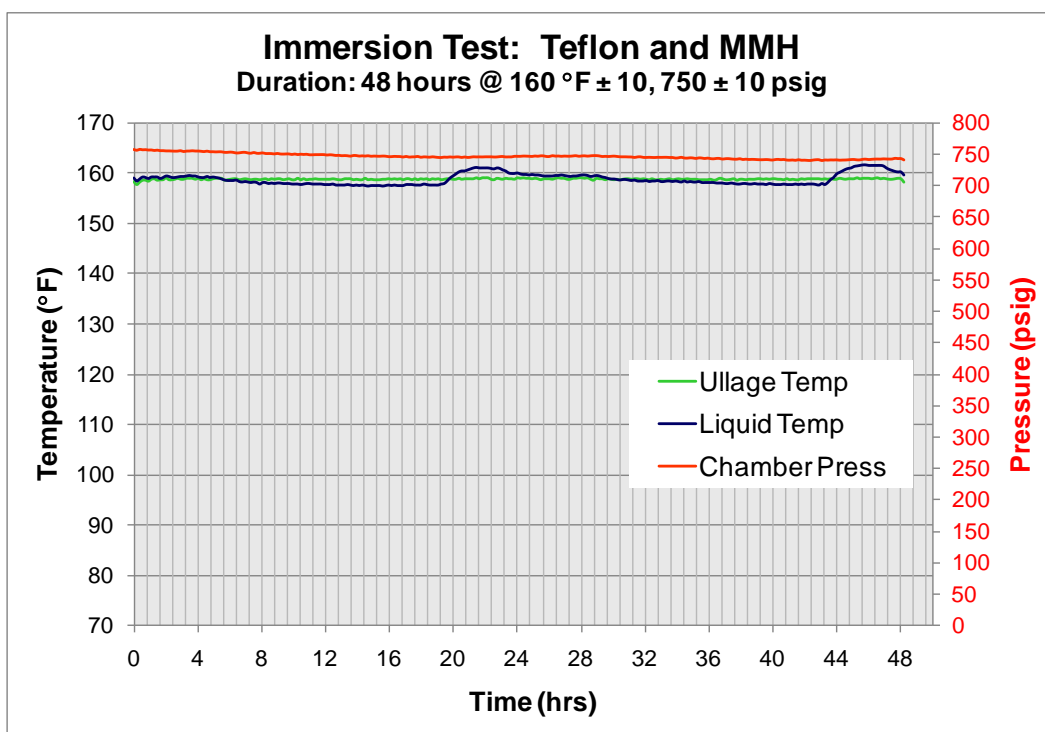


Figure 25. Example Enhanced Test 15 Pressure/Temperature Plots for PTFE in MMH

Mechanical and physical properties testing of enhanced Test 15 posttest propellant exposed samples (and unexposed controls) include: flexural testing (ASTM D790³¹), tensile testing (ASTM D638³²), hardness (ASTM D2240³³), compression testing (ASTM D695³⁴), changes in mass with time (i.e. with the use of a data-logging balance), and dimensional stability (swelling).

The screening process for the enhanced Test 15 utilizes an initial compatibility assessment based on possible chemical reactions between material and fluid.³⁵⁻³⁷ The screening process also relies on analytical tools, such as DSC and FTIR spectroscopy. Physical property testing (e.g., tensile, hardness, flexure, compressive strength) is performed without decontaminating specimens, to test the material as close to a wetted use condition as possible. Of interest, Barragan and McClure³⁸ presented results of polytetrafluoroethylene (PTFE) conditioned in monomethylhydrazine (MMH).

CONCLUSIONS

NASA standard test protocols originated with the Apollo program and progressed throughout the Space Shuttle Program and to the present, where they are still used for a variety of NASA programs, including the Space Station Program, NASA's Commercial Crew and Cargo Program, and for many other uses. Test 15 was not contained in the earlier NASA standard test protocols MSC-A-D-66-3, Rev. A, *Procedures and Requirements for the Evaluation of Spacecraft Nonmetallic Materials*,⁹ MSC-PA-D-67-13, *Apollo Spacecraft Nonmetallic Materials Requirements*,¹⁰ Addendum No. 1 to MSC-PA-D-67-13, *Apollo Spacecraft Nonmetallic Materials Requirements*,¹¹ and NHB 8060.1, *Flammability, Odor, Offgassing, and Compatibility Requirements and Test Procedures for Materials in Environments that Support Combustion*.¹³ Test 15 first appeared as a NASA standard test protocol in NHB 8060.1A, *Flammability, Odor, Offgassing, and Compatibility Requirements and Test Procedures for Materials in Environments that Support Combustion*.³ It progressed through NHB 8060.1B, *Flammability, Odor, Offgassing, and Compatibility Requirements and Test Procedures for Materials in Environments that Support Combustion*,⁴ NHB 8060.1C, *Flammability, Odor, Offgassing, and Compatibility Requirements and Test Procedures for Materials in Environments that Support Combustion*,⁵ and was republished verbatim to NHB 8060.1C⁵ as NASA-STD-6001, *Flammability, Odor, Offgassing and Compatibility Requirements and Test Procedures for Materials in Environments that Support Combustion*.⁶ NASA-STD-6001⁶ was rewritten to the interim standards NASA-STD-(I)-6001 A and B,^{7,8} and then issued as NASA-STD-6001.B, *Flammability, Odor, Offgassing and Compatibility Requirements and Test Procedures for Materials in Environments that Support Combustion*.² Test 15, along with all other standards tests in NASA-STD-6001, were brought to their current technical status.

International and British standards based on NASA-STD-6001⁶ were developed and published to gain international recognition (ISO 14624-5:2006, *Space systems — Safety and Compatibility of Materials — Part 5: Determination of Reactivity of System/Component Materials with Aerospace Propellants*,²⁴ ISO 14624-6:2006 *Space systems — Safety and Compatibility of Materials — Part 6: Determination of Reactivity of Processing Materials with Aerospace Fluids*,²⁵ ISO 14624-7 *Space Systems Safety and Compatibility of Materials Part 7: Determination of Permeability and Penetration of Materials to Aerospace Fluids*,²⁷ and BSI BS ISO 14624-5, *Space Systems — Safety and compatibility of materials — Part 5: Determination of Reactivity of System/Component Materials with Aerospace Propellants*,²⁷ and BSI BS ISO 14624-6, *Space Systems — Safety and Compatibility of Materials — Part 6: Determination of Reactivity of Processing Materials with Aerospace Fluids*,²⁸ and BSI BS ISO 14624-7: *Space systems — Safety and Compatibility of Materials — Part 7: Determination of Permeability and Penetration of Materials to Aerospace Fluids*.²⁹ However, it is not known if these procedures are used inside or outside of the United States, or whether they will be continued or updated. These international and British standards are, at the present, obsolete with respect to NASA-STD-6001.B.²

NASA-STD-6001.B² supplementary test Test A.7 *Reactivity and Penetration of Materials due to Incidental Exposure to Hydrazine, Monomethylhydrazine, Unsymmetrical Dimethylhydrazine, Aerozine 50, Nitrogen Tetroxide, and Ammonia* for materials usage in reactive fluids environment may be used in addition to Test 15. This supplementary test was adapted from Kennedy Space Center procedure KSC MTB 175-88, *Procedure for Casual Exposure of Materials to Hypergolic Fluids*.²² Test A.7 is a procedure for determining the effects of incidental exposure (minor amounts, such as a splash of aerospace fluids on materials. Incidental exposure time is considered to be ≤ 240 min. This test is briefly discussed because it augments the Test 15 Screening Test, though it is not Test 15. ISO and BSI standards based on KSC MTB 175-88²² were promulgated in 2006.

Enhancements to Test 15 include the performance of a variation of NHB 8060.1B⁴ with the intent of studying posttest propellant-exposed sample mechanical and physical properties, including flexural, tensile, hardness, and compression testing in accordance with ASTM methods, and determining changes in mass with time (i.e., with the use of a data-logging balance), and dimensional stability (swelling).

REFERENCES

1. NASA-STD-6016. **Standard Materials and Processes Requirements for Spacecraft**. NASA Technical Standard. National Aeronautics and Space Administration, Washington DC. July 7, 2008.
2. NASA-STD-6001.B. **Flammability, Odor, Offgassing and Compatibility Requirements and Test Procedures for Materials in Environments that Support Combustion**. NASA Technical Standard. National Aeronautics and Space Administration, Washington DC. August 26, 2011.
3. NHB 8060.1A. **Flammability, Odor, Offgassing, and Compatibility Requirements and Test Procedures for Materials in Environments that Support Combustion**. Office of Manned Space Flight. National Aeronautics and Space Administration, Washington DC. February 1974.
4. NHB 8060.1B. **Flammability, Odor, Offgassing, and Compatibility Requirements and Test Procedures for Materials in Environments that Support Combustion**. Office of Space Transportation Systems. National Aeronautics and Space Administration, Washington DC. September 1, 1981.
5. NHB 8060.1C. **Flammability, Odor, Offgassing, and Compatibility Requirements and Test Procedures for Materials in Environments that Support Combustion**. Office of Safety and Mission Quality. National Aeronautics and Space Administration, Washington DC. April 4, 1991.
6. NASA-STD-6001. **Flammability, Odor, Offgassing and Compatibility Requirements and Test Procedures for Materials in Environments that Support Combustion**. NASA Technical Standard. National Aeronautics and Space Administration, Washington DC. February 9, 1998.
7. NASA-STD-(I)-6001.A. **Flammability, Odor, Offgassing and Compatibility Requirements and Test Procedures for Materials in Environments that Support Combustion**. (NASA Interim Technical Standard). National Aeronautics and Space Administration, Washington DC. April 21, 2008.
8. NASA-STD-(I)-6001.B. **Flammability, Odor, Offgassing and Compatibility Requirements and Test Procedures for Materials in Environments that Support Combustion**. (NASA Interim Technical Standard). National Aeronautics and Space Administration, Washington DC. November 10, 2009.
9. MSC-A-D-66-3, Rev. A. Ringwood, A. F. **Procedures and Requirements for the Evaluation of Spacecraft Nonmetallic Materials**. NASA-TM-X-60754. National Aeronautics and Space Administration, Johnson Space Center, Houston, TX. June 5, 1967. URL accessed January 26, 2011:
http://ntrs.nasa.gov/archive/nasa/casi.ntrs.nasa.gov/19680003405_1968003405.pdf
10. MSC-PA-D-67-13. **Apollo Spacecraft Nonmetallic Materials Requirements**. NASA-TM-79368. National Aeronautics and Space Administration, Johnson Space Center, Houston TX, February 9, 1968. URL accessed January 26, 2011:
http://ntrs.nasa.gov/archive/nasa/casi.ntrs.nasa.gov/19780074255_1978074255.pdf
11. MSC-PA-D-67-13, Addendum No. 1 to MSC-PA-D-67-13 **Apollo Spacecraft Nonmetallic Materials Requirements**, February 9, 1968. NASA-TM-80417. National Aeronautics and Space Administration, Johnson Space Center. October 17, 1969. URL accessed January 26, 2011:
http://ntrs.nasa.gov/archive/nasa/casi.ntrs.nasa.gov/19790077398_1979077398.pdf
12. NASA-TM-79493 (draft copy). **Flammability, Odor, and Offgassing Requirements and Test Procedures for Materials in Environments which Support Combustion**. National Aeronautics and Space Administration, Kennedy Space Center, Cape Canaveral FL. December 1, 1970. URL accessed January 26, 2011:
http://ntrs.nasa.gov/archive/nasa/casi.ntrs.nasa.gov/19790073988_1979073988.pdf

13. NHB 8060.1. **Flammability, Odor, Offgassing, and Compatibility Requirements and Test Procedures for Materials in Environments that Support Combustion.** Office of Manned Space Flight. National Aeronautics and Space Administration, Washington DC. November 1971.
14. Liberto, Ralph R. **Titan II Storable Propellant Handbook** (Final Handbook Revision B). Prepared by Bell Aerosystems Company for the Air Force Ballistic Systems Division, Air Force Systems Command. Los Angeles, CA, March 1963.
15. Schmidt, E. W. **Hydrazine and Its Derivatives.** New York, NY: John Wiley & Sons, Inc., 2001.
16. MIL-PRF-26536. **Performance Specification Propellant, Hydrazine.** Defense Energy Support Center, Fort Belvoir, VA, April 1, 2011.
17. MIL-PRF-27404. **Performance Specification Propellant, Monomethylhydrazine.** Defense Energy Support Center, Fort Belvoir, VA, October 1, 1997.
18. MIL-PRF-25604, **Performance Specification Propellant, Uns-Dimethylhydrazine.** Defense Energy Support Center, Fort Belvoir, VA, October, 1997.
19. MSFC-HDBK-527 (JSC 09604) **Materials Selection List for Space Hardware Systems.** NASA Marshall Space Flight Center, Huntsville, AL (revision or date not specified).
20. MIL-PRF-26539. **Performance Specification Propellants, Dinitrogen Tetroxide.** Defense Energy Support Center, Fort Belvoir, VA, April 17, 2006.
21. MIL-PRF-27402. **Performance Specification Propellant, Hydrazine-uns-Dimethylhydrazine (50% N₂H₄– 50% UDMH).** Defense Energy Support Center, Fort Belvoir, VA, October 1, 1995.
22. KSC. **Procedure for Casual Exposure of Materials to Hypergolic Fluids.** Report Number MTB-175-88, Failure Analysis and Materials Evaluation Branch, Physical Testing Section, Kennedy Space Center, FL, September 12, 1994.
23. Greene, B., Mast D.J., and Maes, M. J. **Soft Goods Permeation, Offgassing, and Decontamination Studies with Monomethylhydrazine and MON-3 Nitrogen Tetroxide.** Joint Army Navy NASA Air Force (JANNAF) Propulsion and Subcommittee Meeting. Orlando, FL (December 2010).
24. ISO 14624-5: 2006, **Space systems — Safety and Compatibility of Materials — Part 5: Determination of Reactivity of System/Component Materials with Aerospace Propellants.** International Organization for Standardization. Geneva, Switzerland, 2006.
25. ISO 14624-6: 2006, **Space systems — Safety and Compatibility of Materials —Part 6: Determination of Reactivity of Processing Materials with Aerospace Fluids.** International Organization for Standardization. Geneva, Switzerland, 2006.
26. ISO 14624-7, **Space Systems Safety and Compatibility of Materials Part 7: Determination of Permeability and Penetration of Materials to Aerospace Fluids.** International Organization for Standardization. Geneva, Switzerland, 2006.
27. BSI BS ISO 14624-5: **Space Systems — Safety and Compatibility of Materials — Part 5: Determination of Reactivity of System/Component Materials with Aerospace Propellants.** BSI. London, UK, 2006.
28. BSI BS ISO 14624-6: **Space Systems — Safety and Compatibility of Materials — Part 6: Determination of Reactivity of Processing Materials with Aerospace Fluids.** BSI. London, UK, 2006.
29. BSI BS ISO 14624-7: **Space systems — Safety and Compatibility of Materials — Part 7: Determination of Permeability and Penetration of Materials to Aerospace Fluids.** BSI. London, UK, 2006.

30. Rathgeber, K. A.; Hornung, S. D.; Maes, M. J. ***An Improved Process for Assessing Reactivity of Nonmetals in Aerospace Fluids***. Reno, NV (August 2007).
31. ASTM D790. ***Standard Test Methods for Flexural Properties of Unreinforced and Reinforced Plastics and Electrical Insulating Materials***. ASTM International. West Conshohocken, PA, April 1, 2010.
32. ASTM D638. ***Standard Test Method for Tensile Properties of Plastics***. ASTM International. 100 Barr Harbor Drive, West Conshohocken, PA, May 15, 2010.
33. ASTM D2240. ***Standard Test Method for Rubber Property—Durometer Hardness***. ASTM International. West Conshohocken, PA, August 8, 2005.
34. ASTM D695. ***Standard Test Method for Compressive Properties of Rigid Plastics***. ASTM International. West Conshohocken, PA, April 1, 2010.
35. Greene, B., Mast, D.J., McClure, M.B., and Baker, D.L., ***Development of a Propellant and Material Reactivity Guide. Part I***. Joint Army Navy NASA Air Force (JANNAF) Propulsion and Subcommittee Meeting. Reno, NV (August 2007).
36. Greene, B., Mast, D.J., McClure, M.B., and Baker, D.L., ***Development of a Propellant and Material Reactivity Guide. Part II***. Joint Army Navy NASA Air Force (JANNAF) Propulsion and Subcommittee Meeting. Reno, NV (August 2007).
37. Greene, B., Mast, D.J., and Maes, M.J., ***Development of a Propellant and Material Reactivity Guide: Part III***. Joint Army Navy NASA Air Force (JANNAF) Propulsion and Subcommittee Meeting. Las Vegas, NV (April 2009).
38. Barragan, M. and McClure, M. B. ***Effects of Liquid Propellants on Mechanical Properties of Nonmetals (Invited Presentation)***. Joint Army Navy NASA Air Force (JANNAF) Propulsion and Subcommittee Meeting. Orlando, FL (December 2010).

Appendix A
Executive Summary of 1972 Incident
The Technician and the B-Nut

A series of tests at WSTF were being performed in support of a materials evaluation test program. The first phase of the program was to evaluate mechanical property degradation of materials exposed to dinitrogen tetroxide. Sample materials were loaded into test fixtures, which were sealed, leak checked, and then filled with dinitrogen tetroxide. The test fixture consisted of two 2-in. AN unions welded together, with $\frac{1}{4}$ in. fill and vent lines attached through the wall of the fittings, and the ends sealed with B-nuts. The test fixture had been filled with dinitrogen tetroxide and was lying in the bed of a pickup truck while another fixture was being filled. Figure A-1 depicts a test fixture and associated sample materials of EPR 50K42, an ethylene-propylene copolymer formulation. The technician, who had been performing the fill operation under the direction of the test conductor, sat on the tailgate of the pickup truck for a moment. This was approximately 15-20 min after the first test fixture had been filled with dinitrogen tetroxide. While he was seated on the tailgate, one of the test fixtures exploded. The technician moved a few steps away from the pickup truck and collapsed.

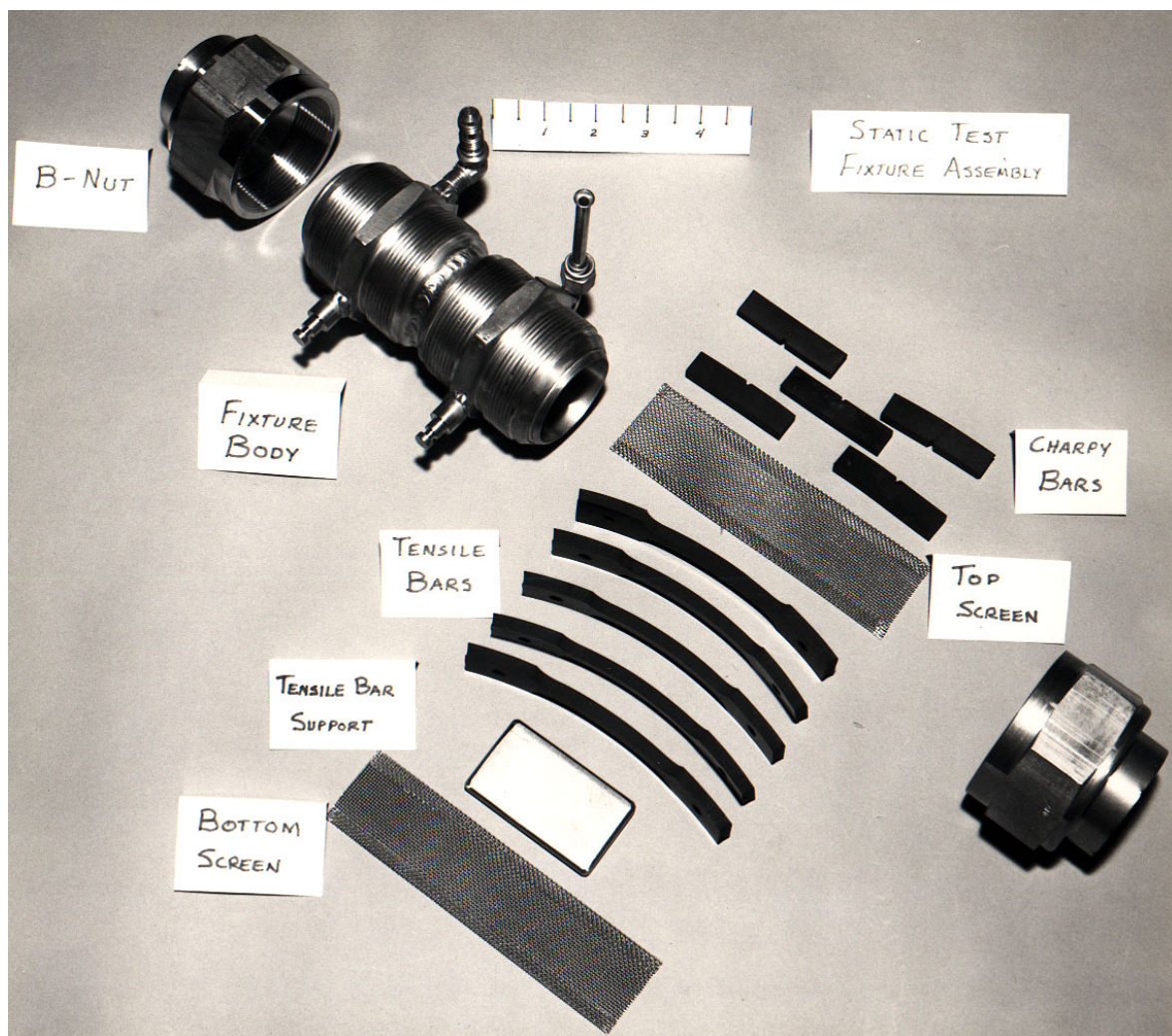


Figure A-1. A Test Fixture and Associated Sample Materials.

The test conductor was seated about 15 feet away recording data in the test log when he heard the explosion. He immediately went to the technician's aid. Seeing that he was injured he ran to the nearest phone and called for an ambulance from the WSTF Dispensary. He returned to the downed technician to see if he needed further immediate aid, and then turned to the test panels and vented them to allow the oxidizer to vent to a remote vent stack. He then turned on the fire hose to wash down the area and prevent any hazard from oxidizer contamination. When the ambulance arrived, the technician received first aid from the site nurse and was then transported to the site dispensary for additional first aid before being rushed to the local hospital. Figure A-2 depicts the scene of the explosion.

As a result of the explosion, one fragment of the test fixture penetrated the technician's left hip and lodged in his lower torso; other fragments inflicted wounds on his back and one arm. Fragments also pierced the bed and sides of the pickup truck in several places. The test conductor was not injured.

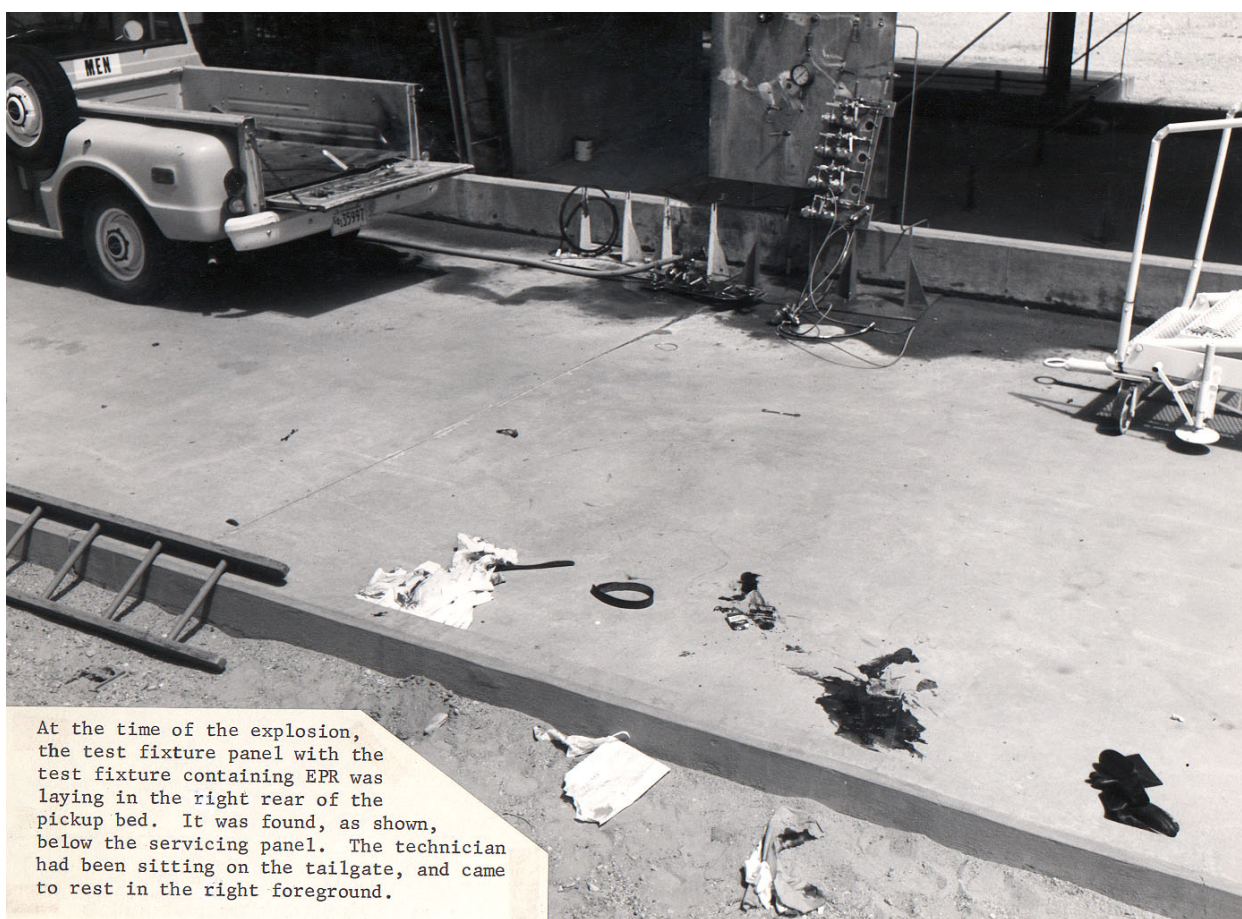


Figure A-2. The Scene of the Explosion.

The accident investigation determined that an EPR 50K42 formulation, which had been loaded into one of the test fixture, was grossly incompatible with dinitrogen tetroxide. One-gram samples of the material reacted with 10 mL of dinitrogen tetroxide within 30 min at room temperature. The material bubbled while reacting. The residue contained was analyzed and found to contain organic nitro and nitrate compounds. The resulting residue was tested for impact sensitivity and gave a positive reaction to pneumatic impact at approximately 2000 psig. Mechanical impact tests gave no indication of reaction.

Analysis of the base EPR 50K42 material showed it to contain, in addition to the ethylene-propylene copolymer units, various organic compounds (unsaturated (and/or aromatic) hydrocarbons, aromatic ester(s), and organic acid(s)), which are all susceptible to attack by dinitrogen tetroxide under various conditions and react extensively with dinitrogen tetroxide at room temperature. Whether the explosion was due to the formation of unstable organic nitro and nitrate compounds and their subsequent explosive decomposition or was due to a rapid oxidative attack of dinitrogen tetroxide on the organic materials was not known with certainty. The rates, mechanisms, and the extent of interacting variables including exposed surface area, total mass of material, temperature, pressure, reaction activation energies, and other variables were possibly involved in the explosion. Many competing exothermic reactions may have occurred simultaneously and were supplying heat to the system; the result of all these processes was an explosive rupture of the test fixture. A simulation of the accident was able to duplicate the explosive event with EPR loaded in the test fixture. The cause of the explosion was determined to be a chemical reaction between the dinitrogen tetroxide and EPR 50K42.

The test fixtures were designed with an operating pressure of 250 psig and a hydrostatic proof test of the sealed assembly to 375 psig had been performed. An actual hydrostatic proof test of 2000 psig was made. The test article fragmented into more than 20 pieces. Or put another way, only 20 pieces were recovered. The large fragment removed from the technician's torso was the only piece of the end cap B-nut (nearest the technician) that was recovered.



HISTORICAL EVOLUTION OF NASA STANDARD MATERIALS TESTING WITH HYPERGOLIC PROPELLANTS AND AMMONIA (NASA STANDARD 6001 TEST 15)

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Introduction

- White Sands Test Facility (WSTF) has performed testing of hazardous and reactive aerospace fluids with materials since the 1960's with the Apollo program
- Test 15 is a NASA standard test for evaluating reactivity of materials with aerospace fluids: hydrazine, MMH, UDMH, A-50, NTO and MON blends, and ammonia
- This presentation provides an overview of the history of Test 15 from prior to its development and first implementation as a NASA standard test in 1974 to its current refinement



What is Test 15?

- Test 1: Upward Flame Propagation
- Test 2: Heat and Visible Smoke Release Rates
- Test 3: Flash Point of Liquids
- Test 4: Electrical Wire Insulation Flammability
- Test 5: Electrical Connector Potting and Conformal Coating Flammability
- Test 6: Odor Assessment
- Test 7: Determination of Offgassed Products
- Test 8: Flammability Test for Materials in Vented or Sealed Containers
- Test 9: Electrical Overload for Sealed Containers
- Test 10: Configurational Flammability
- Test 11: Guidelines for Simulated Crew Bay Configuration Flammability Verification Test
- Test 12: Total Spacecraft Offgassing
- Test 13A: Mechanical Impact for Materials in Ambient Pressure LOX
- Test 13B: Mechanical Impact for Materials in Variable Pressure LOX and GOX
- Test 14: Pressurized Gaseous Oxygen Pneumatic Impact for Nonmetals
- **Test 15: Reactivity of Materials in Hydrazine, Monomethylhydrazine, Unsymmetrical Dimethylhydrazine, Aerozine 50, Nitrogen Tetroxide, and Ammonia**
- Test 16: Determination of Offgassed Products from Assembled Article
- Test 17: Upward Flammability of Materials in GOX
- Test 18: Arc Tracking (Dry Arc Propagation Resistance)



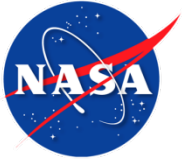
What is Test 15? (continued)

- Currently a two-step process
- Screening (beaker) test; ≤ 0.25 g material and 10 mL fluid; 2 hr exposure; observe for gross reactivity
- Immersion (25 cm^2 in ~ 25 mL fluid) in a test system (versus a reference) that monitors time, temperature and pressure in a known ullage for 48 hr at 160°F (71°C) (except for ammonia [86°F (30°C)] and calculates a gas evolution rate (standard $\text{cm}^3/(\text{cm}^2 \text{ hr})$)
- There are specific pass/fail criteria:
 - Burning, charring, or fire
 - Frothing
 - The material dissolves in the test fluid
 - The material crumbles, becomes friable, or generates particulate
 - The material changes shape or physical dimensions by more than 20 percent
 - The material suffers more than 20 percent degradation of the physical properties for which it was selected
 - Visible changes in appearance of the test fluid (color and/or clarity)
 - For nitrogen tetroxide, a pressure rise $>68.9 \text{ kPa}$ ($>10 \text{ psi}$)
 - For polymers exposed to nitrogen tetroxide, evidence of material nitration as indicated by DSC and/or FTIR



What is Test 15? (continued)

- Pressure rise in the system is indicative of a chemical reaction, which will vary depending on the fluid.
- Ammonia and nitrogen tetroxide do not degrade catalytically, and a pressure rise is an indication of a chemical reaction.
- For the hydrazine family of fuels (hydrazine in particular), the reaction is usually catalytic; the rate is dependent on the material and the surface area.
- No failure criteria for the gas evolution rate for the hydrazine fuels have been established because surface area of the use parts may be small, as in the case of O-rings or gaskets; however, the gas evolution data should be considered in material selection.



In the Beginning...1968-1969

- There were 12 standard tests and supplementary tests (Test 1, Test 2, Test 3...) for Apollo
 - MSC-A-D-66-3 *Procedures and Requirements for the Evaluation of Spacecraft Nonmetallic Materials*
 - MSC-PA-D-67-13, *Apollo Spacecraft Nonmetallic Materials Requirements*
 - Addendum No. 1 to MSC-PA-D-67-13, *Apollo Spacecraft Nonmetallic Materials Requirements*
- The focus was primarily on fire, flammability, ignition, combustion, offgassing, and odor testing
- Did not identify Test 15 or any form of equivalent testing of materials with hazardous fluids of other than oxygen



Still No Test 15...

- A draft *Flammability, Odor, and Offgassing Requirements and Test Procedures for Materials in Environments Which Support Combustion*, prepared by the Skylab Intercenter Working Group, was released as NASA-TM-79493 by the NASA Office of Manned Space Flight in 1970
- NASA Handbook (NHB) 8060.1, *Flammability, Odor, Offgassing, and Compatibility Requirements and Test Procedures for Materials in Environments that Support Combustion* released in November 1971
 - NHB 8060.1 was based on the materials technology developed during the Apollo and Skylab programs



Then there was Test 15...

- NHB 8060.1A (1974) Test 15 – Constant Temperature Immersion of Materials in Type J Fluids
- NHB 8060.1B (1981) Test 15 – Compatibility of Materials with Type “J” Fluids
- NHB 8060.1C (1991) Reactivity of Materials in Aerospace Fluids (Test 15)
- NASA-STD-6001 (1998) Reactivity of Materials in Aerospace Fluids (Test 15) (verbatim with NHB 8060.1C)
- NASA-STD-(I)-6001.A (2008) and .B (2009) Reactivity of Materials in Hydrazine, Monomethylhydrazine, Unsymmetrical Dimethylhydrazine, Aerozine 50, Nitrogen Tetroxide, and Ammonia (Test 15)
- NASA-STD-6001.B (2011) Reactivity of Materials in Hydrazine, Monomethylhydrazine, Unsymmetrical Dimethylhydrazine, Aerozine 50, Nitrogen Tetroxide, and Ammonia (Test 15)
- Supplemental Test A.7 Reactivity and Penetration of Materials due to Incidental Exposure to Hydrazine, Monomethylhydrazine, Unsymmetrical Dimethylhydrazine, Aerozine 50, Nitrogen Tetroxide, and Ammonia was incorporated into NASA-STD-(I)-6001.A and B, and NASA-STD-6001.B (2011)
- The “Enhanced Test 15” is not a standard test but is a natural extension of NASA-STD-6001.B which more closely resembles that described in NHB 8060.1A and .1B Test 15



NHB 8060.1A Test 15 (1974)

- *NHB 8060.1A Test 15 – Constant Temperature Immersion of Materials in Type J Fluids*
- Test 15 determined the gross compatibility of materials in Type J fluids
- The materials usage category “Type J” was introduced and defined as “Materials in Combustion-Supporting Environments Other than Oxygen”
- Included all materials exposed to fluids other than oxygen such as nitrogen tetroxide, hydrazine, and other oxidizers and fuels that were theoretically capable of undergoing reactions with the use environment



NHB 8060.1A Test 15

- Test was based on a 48 hr constant temperature immersion at 160 °F (71 °C) at maximum use pressure
- Test fixture constructed of 300 series SS or equivalent w/ rupture disk; penetrations for filling, pressurization (He), pressure and temperature measuring devices
- Minimum volume of 1.5L w/ a minimum of 2/3 this volume as ullage
- A minimum of 3 samples prepared in lengths of 2 in; normal sample size was 2 x ¼ x ¼ -in.
- Data reported included changes in temperature, condition of samples after testing, pertinent comments and observations
- A material was considered compatible if exposure did not result in chemical or physical changes such as tackiness, flaking, complete dissolution...
- Post-test mechanical impact, pneumatic impact, heating, or other configuration test applicable to the use conditions (or configuration analysis) was required
- Testing was performed in concrete test cells in the WSTF Hazardous Fluids Test Area. Test personnel wore full encapsulating protective suits with supplied breathing air.

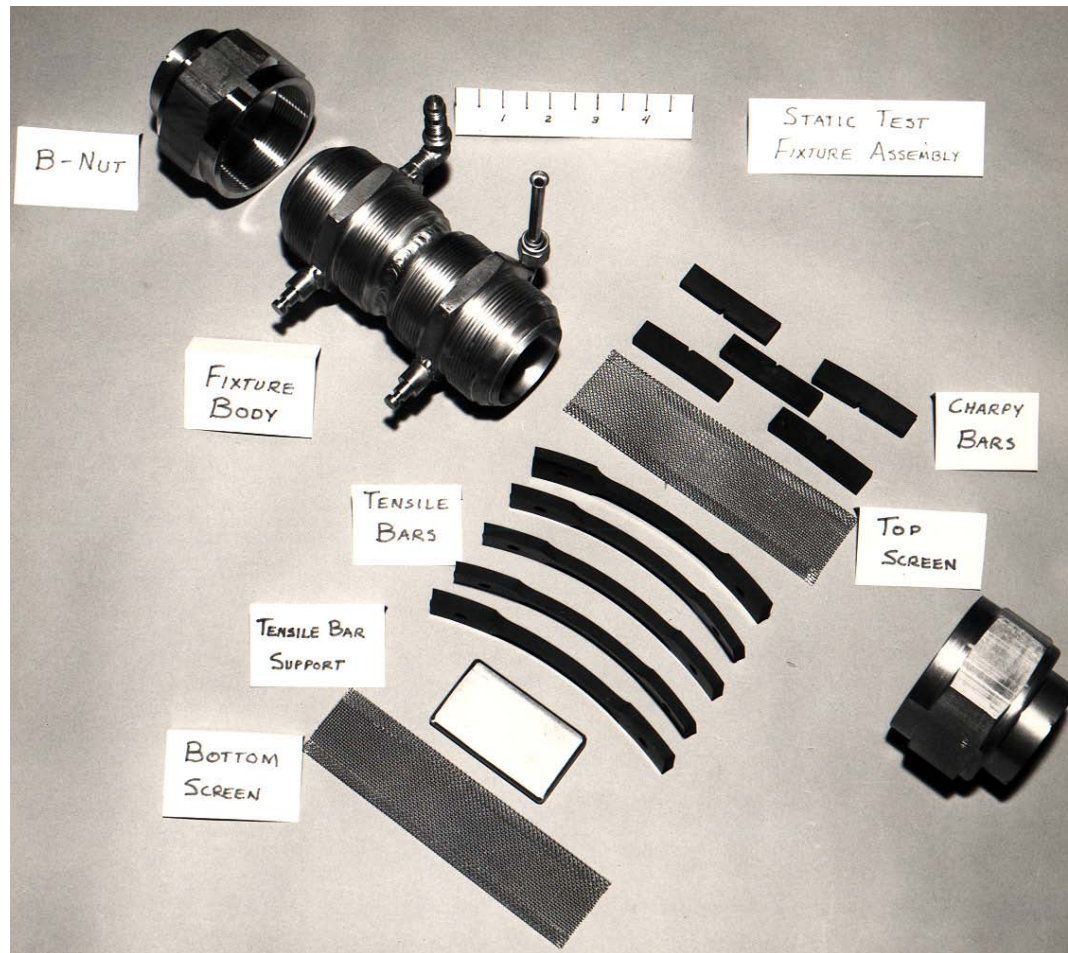


But Prior to NHB 8060.1A...

- WSTF was performing similar testing
- A very serious injury occurred at WSTF in 1972 when an incompatible material tested with a MON-oxidizer caused the test fixture to explode
- The material was EPR 50K42, an ethylene-propylene copolymer formulation
- Later shown to contain, in addition to the ethylene-propylene copolymer units, various organic compounds (unsaturated (and/or aromatic) hydrocarbons, aromatic ester(s), and organic acid(s), all which are susceptible to attack by dinitrogen tetroxide
- A simulation of the accident was able to duplicate the explosive event with EPR 50K42 loaded in the test fixture

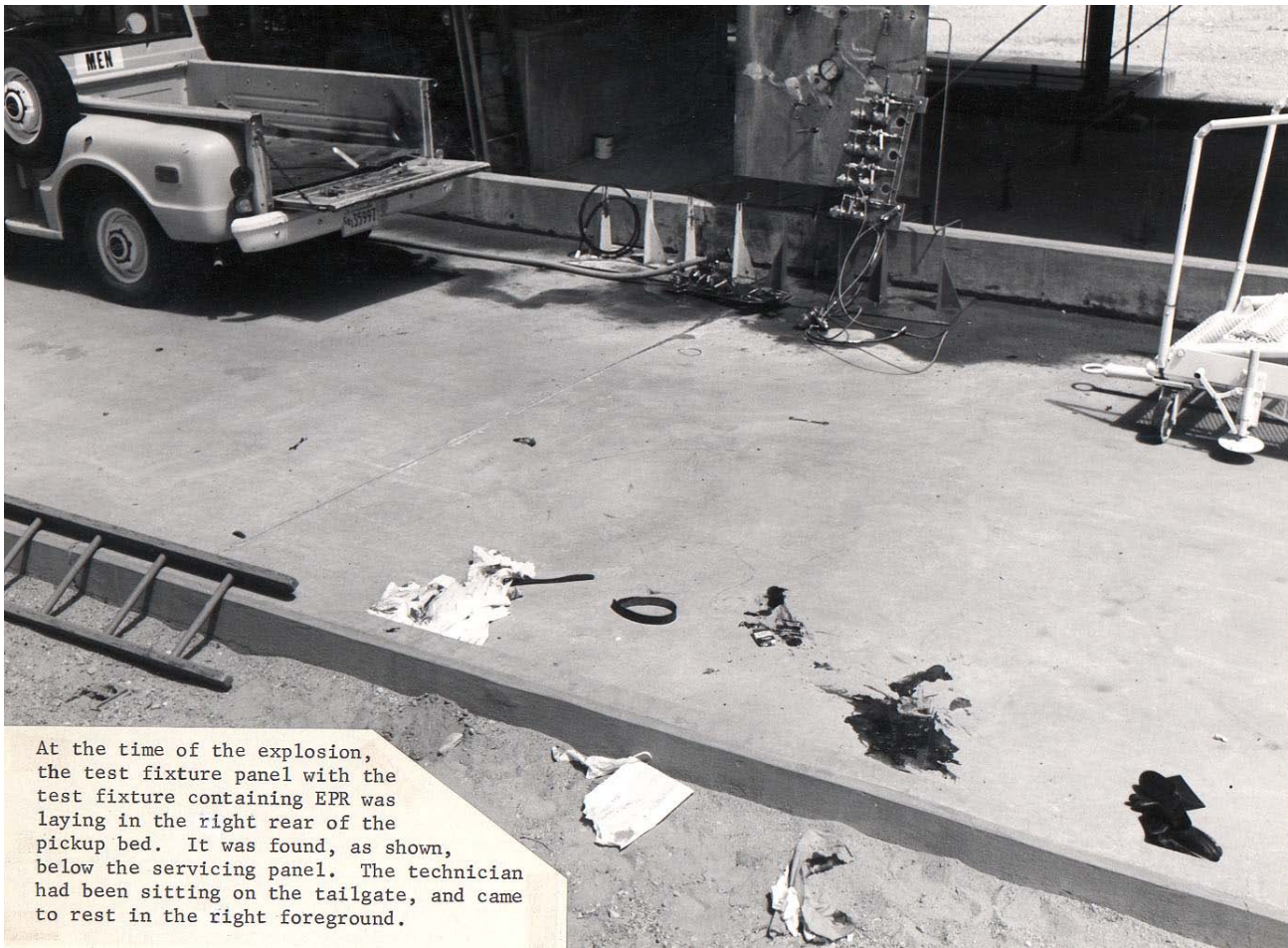


1972 Test Fixture





Scene of the Explosion



At the time of the explosion, the test fixture panel with the test fixture containing EPR was laying in the right rear of the pickup bed. It was found, as shown, below the servicing panel. The technician had been sitting on the tailgate, and came to rest in the right foreground.



NHB 8060.1B Test 15 (1981)

- *Test 15 – Compatibility of Materials with Type “J” Fluids*
- Remained 48 hr constant temperature immersion at 160 °F (71 °C) at maximum use pressure
- 2L SS test fixture with minimum of 1-liter volume as ullage permitted the option of testing in either liquid or vapor-phase, equipped w/ rupture disk suitable for protecting personnel and equipment
- Provided more detail than previous version, including elaboration on test materials as to being solids, semisolids, and/or liquids, and provided guidelines for preparation and cleaning prior to testing
- A warning note regarding potential hazards of materials exposed to Type J fluids stated:

“WARNING: Handling of materials exposed to Type J fluids may be extremely hazardous due to changes which may have occurred in the material due to exposure to the test fluid media. Procedures such as mechanical impact testing of small posttest samples should be established to evaluate the hazards associated with handling the material after test.”



NHB 8060.1B Test 15 (1981) (continued)

- Despite the warning, no requirements for pre-screening of materials, for testing that could lead to nitrated or other energetic, potentially shock sensitive materials
- The emphasis was on safe handling of posttest materials
- Testing was performed in concrete test cells in the WSTF Hazardous Fluids Test Area. Test personnel wore full encapsulating protective suits with supplied breathing air.
- However, local procedures were developed and implemented by WSTF requiring a screening test (beaker test) as part of the test protocol for nitrogen tetroxide oxidizers
- Known as the “beaker test”; it became part of test protocol in later revisions



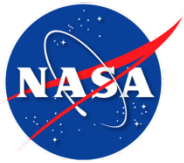
NHB 8060.1C (1991)

- *Reactivity of Materials in Aerospace Fluids (Test 15)*
- The Type J materials usage category was changed to “Reactive Fluid Environment”, where “reactive fluids” are fluids that are theoretically capable of reacting with materials in such a way as to create a hazard. Aerospace fuels such as hydrazine and oxidizers such as nitrogen tetroxide were examples of reactive aerospace fluids. Test 15 was identified as a required test for a Reactive Fluids Environment.
- A lab-scale test replaced the larger volume tests in the A and B revisions

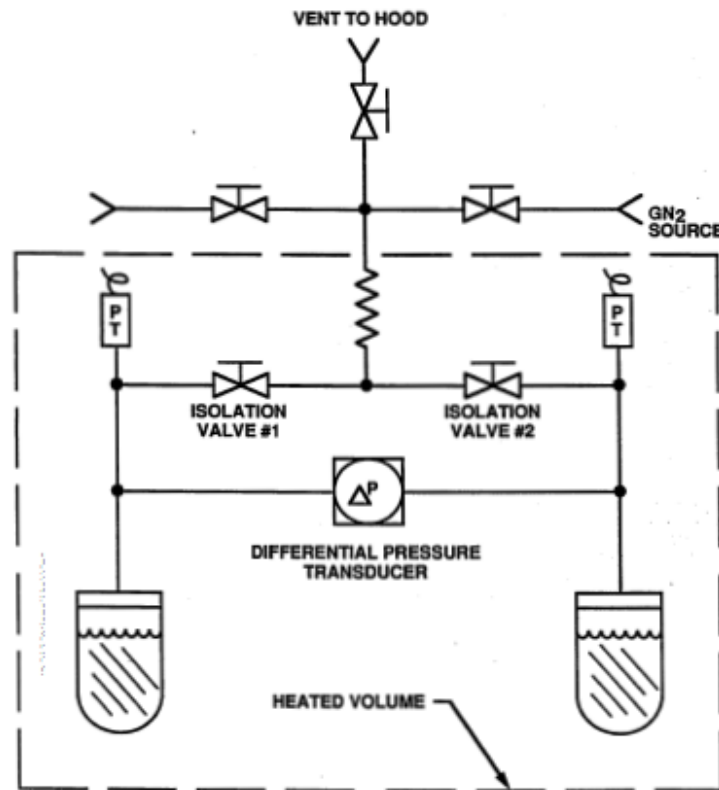


NHB 8060.1C (1991) (continued)

- Major changes to NHB 8060.1A and NHB 8060.1B Test 15 were made:
- The relatively large scale immersion tests as described in NHB 8060.1A and NHB 8060.1B were not included
- Definitions were added
- The “Screening Test” was introduced
- The “Immersion Test” was introduced along with a diagram of the test system
- Specific test criteria for compatibility were specified.
- Specific good laboratory practices were established
- Criteria for acceptability was established



NHB 8060.1C Immersion Apparatus





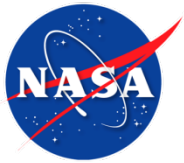
NHB 8060.1C (1991) (continued)

- The “Criteria for Acceptability” that was described in NHB 8060.1A and B Test 15 was replaced with “Test Criteria”:
 - Exposure of the material (Screening Test) to the fluid at ambient temperature for 2 h must not have visibly change the material or fluid
 - Exposure of the material (Immersion Test) to the fluid for 48 hours at the maximum system temperature or 160 °F (71 °C) must not cause a pressure rate increase 1.5 times the pressure rate increase caused by SS-304 exposed to the identical fluid at those conditions.
 - For fluids that do not decompose into gaseous products at the test temperature, a pressure increase greater than the vapor pressure of the fluid must not occur
 - After the sample had been decontaminated and dried, no visible change in color or texture of the material and test fluid could have occurred and the weight of the sample could not change by greater than 2%.
 - Changes in the fluid must also not have occurred:
 - The mass of impurities in the fluid after exposure to the material could not be greater than twice the mass of impurities in the identical fluid after exposure to PTFE (for nonmetals) or SS-304 (for metals)
 - Halide (F⁻, Cl⁻, and Br⁻) concentrations in the fluid after exposure to the material could not exceed the appropriate MIL specification for fluid purity.
 - The posttest mass was obtained after the sample has been decontaminated and dried, but the time from immersion to obtaining sample post-test masses was not specified nor was there a requirement to document the time. Consequently, the meaning of the 2% mass change subject to debate as time was a critical factor especially with respect to absorbed propellant evaporation.

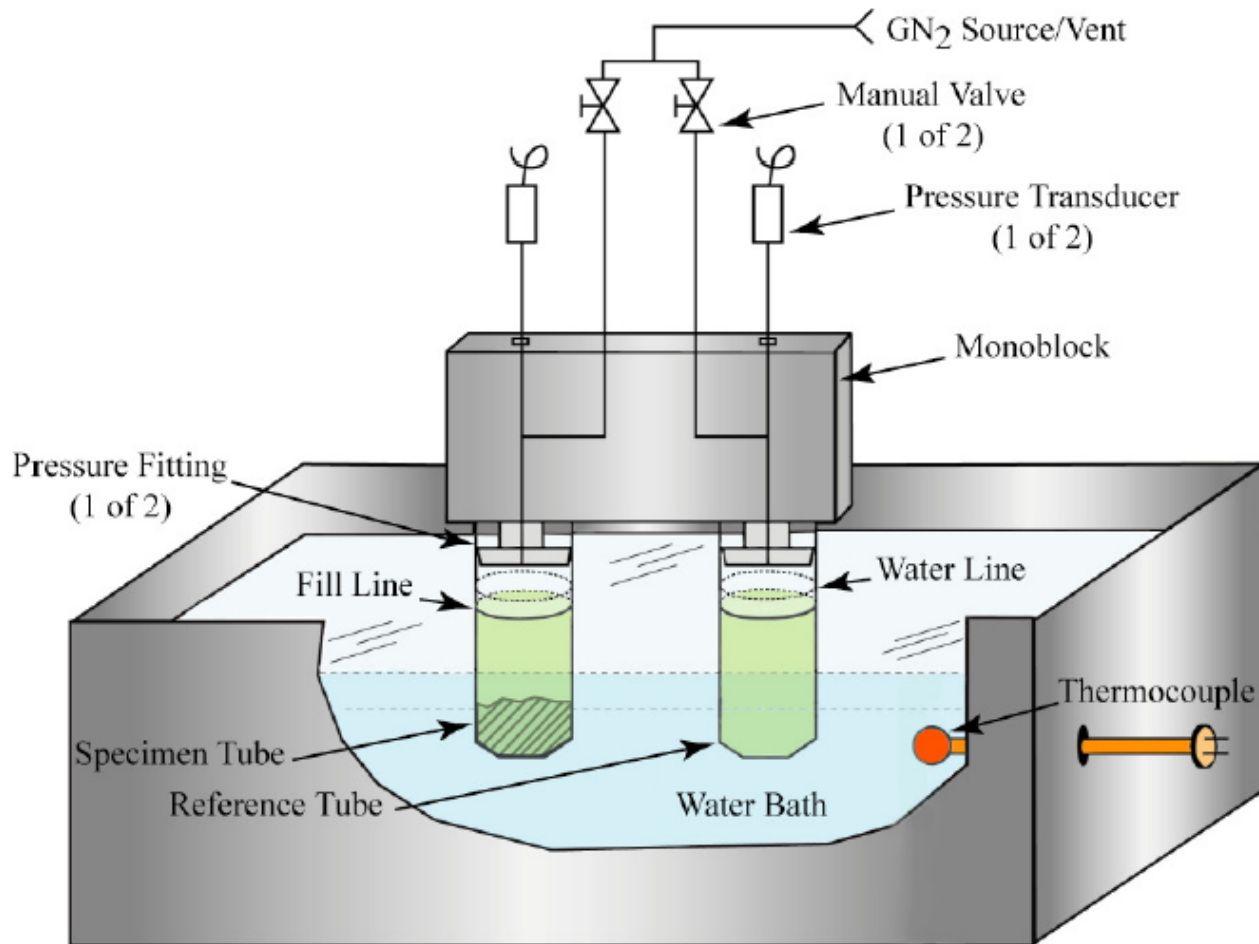


Next...

- *NASA-STD-6001 (1998) Reactivity of Materials in Aerospace Fluids (Test 15)*– transitioned verbatim from NHB 8060.1C
- *NASA-STD-(I)-6001.A (2008) Reactivity of Materials in Hydrazine, Monomethylhydrazine, Unsymmetrical Dimethylhydrazine, Aerozine 50, Nitrogen Tetroxide, and Ammonia (Test 15)* - NASA interim
- *NASA-STD-(I)-6001.B (2009) Reactivity of Materials in Hydrazine, Monomethylhydrazine, Unsymmetrical Dimethylhydrazine, Aerozine 50, Nitrogen Tetroxide, and Ammonia (Test 15)* - NASA interim
- *NASA-STD-6001.B (2010) Reactivity of Materials in Hydrazine, Monomethylhydrazine, Unsymmetrical Dimethylhydrazine, Aerozine 50, Nitrogen Tetroxide, and Ammonia (Test 15)*
- The latest NASA Standard revisions brought Test 15 to the current procedure
 - Eliminated non-value steps and ambiguity
 - Incorporated best practices and reporting criteria
 - Defined fluids and specifications
 - Expanded/clarified failure criteria



NASA-STD-6001B Test 15 Apparatus



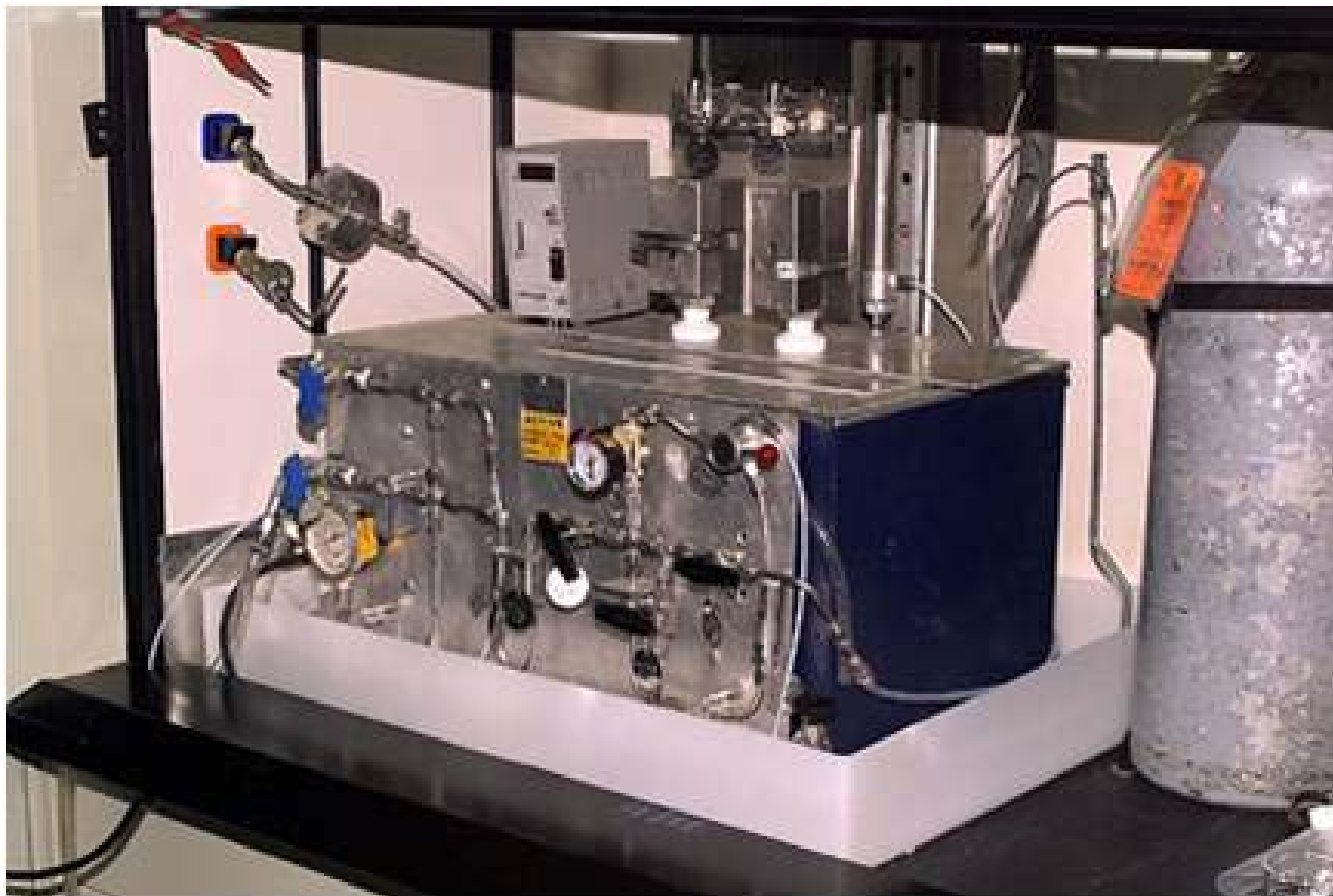


Examples





Examples



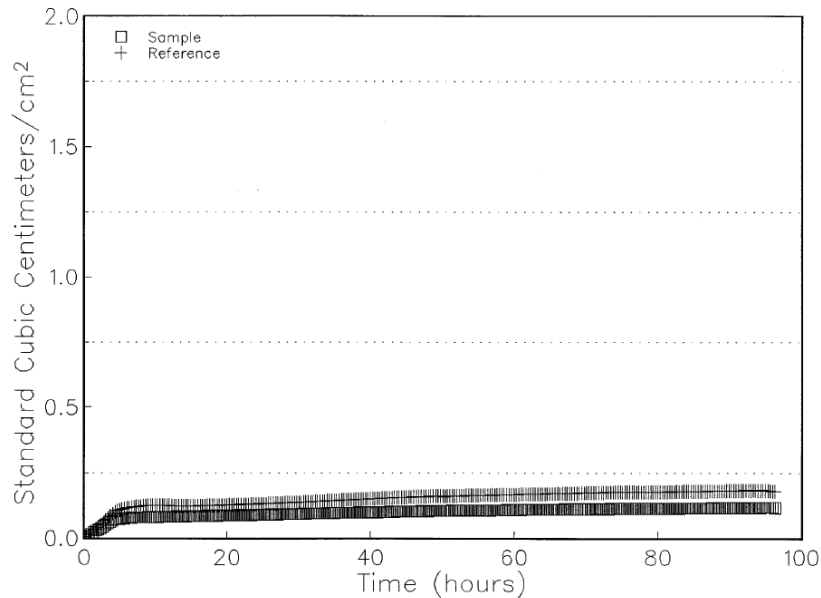


Examples



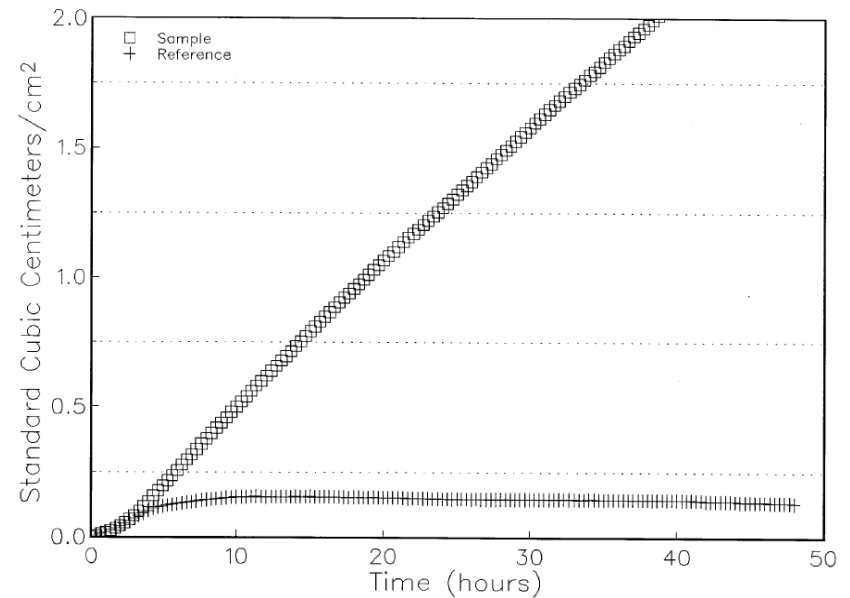


Examples



Gas Evolution of EPR AF-E-332 in Hydrazine (04-38457b)

AF-E-332 vs. PTFE in
Hydrazine 😊



Gas Evolution of EPR E515-80 in Hydrazine (04-38455b)

EPR E515-80 vs. PTFE
in Hydrazine 😞



Conclusions

- Test 15 is the NASA standard test for reactivity of materials in hydrazine, MMH, UDMH, A-50, NTO, and ammonia
- It was first published in 1971 and its latest update was 2011
- 40 years of experience and data have resulted in a wealth of data and improved testing while maintaining standardization
- Repeatable results can be obtained by any version as long as it is specified
- Integral to NASA spacecraft/fluid systems/GSE materials and processes materials selections