

Standard System for the Identification of the Hazards of Materials for Emergency Response

2017



IMPORTANT NOTICES AND DISCLAIMERS CONCERNING NFPA® DOCUMENTS

NOTICE AND DISCLAIMER OF LIABILITY CONCERNING THE USE OF NFPA DOCUMENTS

NFPA[®] codes, standards, recommended practices, and guides ("NFPA Standards"), of which the document contained herein is one, are developed through a consensus standards development process approved by the American National Standards Institute. This process brings together volunteers representing varied viewpoints and interests to achieve consensus on fire and other safety issues. While the NFPA administers the process and establishes rules to promote fairness in the development of consensus, it does not independently test, evaluate, or verify the accuracy of any information or the soundness of any judgments contained in NFPA Standards.

The NFPA disclaims liability for any personal injury, property or other damages of any nature whatsoever, whether special, indirect, consequential or compensatory, directly or indirectly resulting from the publication, use of, or reliance on NFPA Standards. The NFPA also makes no guaranty or warranty as to the accuracy or completeness of any information published herein.

In issuing and making NFPA Standards available, the NFPA is not undertaking to render professional or other services for or on behalf of any person or entity. Nor is the NFPA undertaking to perform any duty owed by any person or entity to someone else. Anyone using this document should rely on his or her own independent judgment or, as appropriate, seek the advice of a competent professional in determining the exercise of reasonable care in any given circumstances.

The NFPA has no power, nor does it undertake, to police or enforce compliance with the contents of NFPA Standards. Nor does the NFPA list, certify, test, or inspect products, designs, or installations for compliance with this document. Any certification or other statement of compliance with the requirements of this document shall not be attributable to the NFPA and is solely the responsibility of the certifier or maker of the statement.

REMINDER: UPDATING OF NFPA STANDARDS

Users of NFPA codes, standards, recommended practices, and guides ("NFPA Standards") should be aware that NFPA Standards may be amended from time to time through the issuance of Tentative Interim Amendments or corrected by Errata. An official NFPA Standard at any point in time consists of the current edition of the document together with any Tentative Interim Amendment and any Errata then in effect.

In order to determine whether an NFPA Standard has been amended through the issuance of Tentative Interim Amendments or corrected by Errata, visit the Document Information Pages on NFPA's website. The Document Information Pages provide up-to-date, document specific information including any issued Tentative Interim Amendments and Errata.

To access the Document Information Page for a specific NFPA Standard, go to http:// www.nfpa.org/docinfo to choose from the list of NFPA Standards or use the search feature on the right to select the NFPA Standard number (e.g., NFPA 101). The Document Information page includes postings of all existing Tentative Interim Amendments and Errata. It also includes the option to register for an "Alert" feature to receive an automatic email notification when new updates and other information are posted regarding the document.

ISBN: 978-145591419-7 (Print) ISBN: 978-145591420-3 (PDF)

IMPORTANT NOTICES AND DISCLAIMERS CONCERNING NFPA® STANDARDS

ADDITIONAL NOTICES AND DISCLAIMERS

Updating of NFPA Standards

Users of NFPA codes, standards, recommended practices, and guides ("NFPA Standards") should be aware that these documents may be superseded at any time by the issuance of new editions or may be amended from time to time through the issuance of Tentative Interim Amendments or corrected by Errata. An official NFPA Standard at any point in time consists of the current edition of the document together with any Tentative Interim Amendments and any Errata then in effect. In order to determine whether a given document is the current edition and whether it has been amended through the issuance of Tentative Interim Amendments or corrected through the issuance of Errata, consult appropriate NFPA publications such as the National Fire Codes® Subscription Service, visit the NFPA website at www.nfpa.org, or contact the NFPA at the address listed below.

Interpretations of NFPA Standards

A statement, written or oral, that is not processed in accordance with Section 6 of the Regulations Governing the Development of NFPA Standards shall not be considered the official position of NFPA or any of its Committees and shall not be considered to be, nor be relied upon as, a Formal Interpretation.

Patents

The NFPA does not take any position with respect to the validity of any patent rights referenced in, related to, or asserted in connection with an NFPA Standard. The users of NFPA Standards bear the sole responsibility for determining the validity of any such patent rights, as well as the risk of infringement of such rights, and the NFPA disclaims liability for the infringement of any patent resulting from the use of or reliance on NFPA Standards.

NFPA adheres to the policy of the American National Standards Institute (ANSI) regarding the inclusion of patents in American National Standards ("the ANSI Patent Policy"), and hereby gives the following notice pursuant to that policy:

NOTICE: The user's attention is called to the possibility that compliance with an NFPA Standard may require use of an invention covered by patent rights. NFPA takes no position as to the validity of any such patent rights or as to whether such patent rights constitute or include essential patent claims under the ANSI Patent Policy. If, in connection with the ANSI Patent Policy, a patent holder has filed a statement of willingness to grant licenses under these rights on reasonable and nondiscriminatory terms and conditions to applicants desiring to obtain such a license, copies of such filed statements can be obtained, on request, from NFPA. For further information, contact the NFPA at the address listed below.

Law and Regulations

Users of NFPA Standards should consult applicable federal, state, and local laws and regulations. NFPA does not, by the publication of its codes, standards, recommended practices, and guides, intend to urge action that is not in compliance with applicable laws, and these documents may not be construed as doing so.

Copyrights

NFPA Standards are copyrighted. They are made available for a wide variety of both public and private uses. These include both use, by reference, in laws and regulations, and use in private self-regulation, standardization, and the promotion of safe practices and methods. By making these documents available for use and adoption by public authorities and private users, the NFPA does not waive any rights in copyright to these documents.

Use of NFPA Standards for regulatory purposes should be accomplished through adoption by reference. The term "adoption by reference" means the citing of title, edition, and publishing information only. Any deletions, additions, and changes desired by the adopting authority should be noted separately in the adopting instrument. In order to assist NFPA in following the uses made of its documents, adopting authorities are requested to notify the NFPA (Attention: Secretary, Standards Council) in writing of such use. For technical assistance and questions concerning adoption of NFPA Standards, contact NFPA at the address below.

For Further Information

All questions or other communications relating to NFPA Standards and all requests for information on NFPA procedures governing its codes and standards development process, including information on the procedures for requesting Formal Interpretations, for proposing Tentative Interim Amendments, and for proposing revisions to NFPA standards during regular revision cycles, should be sent to NFPA headquarters, addressed to the attention of the Secretary, Standards Council, NFPA, 1 Batterymarch Park, P.O. Box 9101, Quincy, MA 02269-9101; email: stds_admin@nfpa.org

For more information about NFPA, visit the NFPA website at www.nfpa.org. All NFPA codes and standards can be viewed at no cost at www.nfpa.org/freeaccess.

Copyright © 2016 National Fire Protection Association®. All Rights Reserved.

NFPA®704

Standard System for the

Identification of the Hazards of Materials for Emergency Response

2017 Edition

This edition of NFPA 704, *Standard System for the Identification of the Hazards of Materials for Emergency Response*, was prepared by the Technical Committee on Classification and Properties of Hazardous Chemical Data. It was issued by the Standards Council on May 13, 2016, with an effective date of June 2, 2016, and supersedes all previous editions.

This edition of NFPA 704 was approved as an American National Standard on June 2, 2016.

Origin and Development of NFPA 704

Work on this standard originated in 1957. A great deal of the development work had been done by the NFPA Sectional Committee on Classification, Labeling, and Properties of Flammable Liquids starting in 1952. Background data were published by the Association in its quarterly magazine in 1954, 1956, and 1958. The material in its present form was first tentatively adopted in 1960. Official adoption was secured in 1961, and revisions were adopted in 1964, 1966, 1969, 1975, 1980, and 1985. In the 1987 and 1990 editions, the Committee on Fire Hazards of Materials introduced quantitative guidelines for assigning the Health Hazard and Reactivity Hazard Ratings. The 1996 edition introduced additional quantitative guidelines and an amended definition for *instability hazard rating*, formerly *reactivity hazard rating*.

The 2001 edition clarified numerous topics, including the following: rating of mixtures; three options of how to rate areas with multiple chemical storage and use; location of signs; more quantita ive criteria for flammability rat ngs for solids; and quantitative criteria for a flammability rating of zero, includ ng introduc ion of a new test method. Guidance material was added for quantifying the degree of water reactivity. An annex was added to cover water reactivity and identification criteria, as well as additional information on flash point test methods.

The 2007 edition clarified numerous topics, including the special hazards quadrant and placement and hierarchy of symbols. The new simple asphyxiant (SA) designation and other optional symbols, as well as requirements for the classification of flammability rating for dusts, were added.

The 2012 edition included reinstatement of the differential scanning calorimetry (DSC) hazard criterion to Table 7.2 as well as new guidance on the flammability hazard classification for aerosol products. The 2012 edition also included new text in Table 6.2 that emphasized the use of Annex D to classify the flammability hazard of a finely divided solid.

The 2016 edition has several key changes to text and added two explanatory annexes.

Information related to differential scanning calorimetry (DSC) exotherm onset temperature criteria was removed from Table 7.2.

Chapter 8 was modified to require the use of the SA symbol for liquefied carbon dioxide vapor withdrawal systems and where large quantities of dry ice are used in confined areas since there is currently no way of warning of this hazard in the existing NFPA 704.

A new Annex G explains key differences between the OSHA HazCom2012 and NFPA 704 and clarifies the reasons why the NFPA 704 rating system will remain unchanged by the implementation of HazCom2012.

A new Annex H provides sample placards that can be extracted into emergency response publications and training materials to ensure consistency.

The NFPA 704 Committee dedicates the 2017 edition to the memory of Dr. Arthur A. Krawetz, who had been a Committee member since 1979 and who died during active service to the Committee, in November 2015. He was founder and president of Phoenix Chemical Laboratory, Inc., in Chicago, engaged in analysis, research, and development, including characterizing chemical and physical properties, and quantifying performance expectancy of a wide variety of commercially important substances: fuels, lubricants, hydraulic fluids, greases, coatings, petrochemicals, additives, solvents, and rust preventatives. On learning of his passing, Arthur's colleagues on the committee expressed appreciation of his wisdom, expertise, leadership, humor, assertiveness, and general ability to contribute to the fun part of meeting in person for extended periods — hence this heartfelt tribute to a man who will be missed.

Technical Committee on Classification and Properties of Hazardous Chemical Data

Ron A. Kirsch, Chair OHS Associates, Inc., TN [SE]

Robert A. Michaels, *Secretary* RAM TRAC Corporation, NY [SE]

Christopher Allen, Montgomery County Government, MD [E]
Jason Beam, Casella Waste Systems, ME [U]
Laurence G. Britton, Process Safety Consultant, WV [SE]
Laura Draelos, Sandia National Laboratories, NM [U]
Richard Gowland, European Process Safety Centre, United Kingdom [U]
Walter Groden, AIG Property Casualty, NY [I]
David W. Hollinger, Drexel University, PA [U]
Arthur A. Krawetz, Phoenix Chemical Laboratory, Inc., IL [RT]
Kenneth D. Lewis, Evonik Degussa Corporation, AL [U]
Rep. NFPA Industrial Fire Protection Section

Caroline Miller, ChemADVISOR, Inc., NY [SE] Brian Primeau, MIT Lincoln Labs, MA [RT] Gary Robinson, Liberty Mutual Group, IL [I] Grayson Sack, Cashins and Associates, Inc., MA [SE] William J. Satterfield, III, Hydrogen Safety, LLC/Rode & Associates, LLC, RI [I] Stephen Sides, American Coatings Association, DC [M] James O. Vigerust, Jr., CB&I, NM [SE] David B. Wechsler, Consultant, TX [U] Rep. American Chemistry Council

Alternates

Karl Leipold, AIG Energy & Engineered Risk, MD [I] (Alt. to Walter Groden) Cynthia J. Wernet, The Boeing Company, CA [U] (Alt. to Kenneth D. Lewis)

Nonvoting

Jennifer H. Lawless, U.S. Department of Labor, DC [E]

Nancy Pearce, NFPA Staff Liaison

This list represents the membership at the time the Committee was balloted on the final text of this edition. Since that time, changes in the membership may have occurred. A key to classifications is found at the back of the document.

NOTE: Membership on a committee shall not in and of itself constitute an endorsement of the Association or any document developed by the committee on which the member serves

Committee Scope: This Committee shall have primary responsibility for documents on the classification of the relative hazards of all chemical solids, liquids and gases and to compile data on the hazard properties of these hazardous chemicals.

Contents

Chapter	1 Administration	704– 5
1.1	Scope	704– 5
1.2	Purpose	704– 5
1.3	Application	704– 5
1.4	Retroactivity.	704– 5
1.5	Equivalency	704– 5
Chapter	2 Referenced Publications	704– 6
2.1	General	704– 6
2.2	NFPA Publications.	704– 6
2.3	Other Publications.	704– 6
2.4	References for Extracts in Mandatory Sections.	
		704– 6
Chapter	3 Definitions	704– 6
3.1	General	704– 6
3.2	NFPA Official Definitions.	704– 6
3.3	General Definitions.	704– 6
Chapter	4 General	704– 7
$4.\hat{1}$	Description.	704– 7
4.2	Assignment of Ratings.	704– 7
4.3	Location of Signs.	704– 7
Chapter	5 Health Hazards	704– 7
5.1	General	704– 7
5.2	Degrees of Hazard.	704– 8
Chapter	6 Flammability Hazards	704– 9
6.1	General	704– 9
6.2	Degrees of Hazard	704– 9
6.3	Aerosols.	704– 11
Chapter		704– 11
7.1	General	704– 11

7.2	Degrees of Hazard		704– 11
Chapter	8	Special Hazards	704– 12
8.1		eral.	704– 12
8.2		bols	704– 12
	~)		
Chapter	9	Identification of Materials by Hazard	
		Rating System	704– 12
9.1	Sym	bol Arrangement	704– 12
Annex A		Explanatory Material	704– 14
Annex B		Health Hazard Rating	704– 16
Annex C		Flammability	704– 18
Annex D)	Combustible Dusts	704– 19
Annex E		Instability, Thermal Hazard Evaluation	
		Techniques	704– 19
Annex F		Water Reactivity Identification Criteria	704– 21
Annex G	r	Comparison of NFPA 704 Numerical	
		Hazard Rating with OSHA's Hazard	
		Classification System	704 – 23
Annex H	[Sample NFPA 704 Placard Information	
		for Use in Safety Publications	704– 23
Annex I		Informational References	704– 27
Index			704 – 29

NFPA 704

Standard System for the

Identification of the Hazards of Materials for Emergency Response

2017 Edition

IMPORTANT NOTE: This NFPA document is made available for use subject to important notices and legal disclaimers. These notices and disclaimers appear in all publications containing this document and may be found under the heading "Important Notices and Disclaimers Concerning NFPA Documents." They can also be obtained on request from NFPA or viewed at www.nfpa.org/disclaimers.

UPDATES, ALERTS, AND FUTURE EDITIONS: New editions of NFPA codes, standards, recommended practices, and guides (i.e., NFPA Standards) are released on scheduled revision cycles. This edition may be superseded by a later one, or it may be amended outside of its scheduled revision cycle through the issuance of Tentative Interim Amendments (TIAs). An official NFPA Standard at any point in time consists of the current edition of the document, together with any TIAs and Errata in effect. To verify that this document is the current edition or to determine if it has been amended by any TIAs or Errata, please consult the National Fire Codes® Subscription Service or visit the Document Information (DocInfo) pages on the NFPA website at www.nfpa.org/docinfo. In addition to TIAs and Errata, the DocInfo pages also include the option to sign up for Alerts for each document and to be involved in the development of the next edition.

NOTICE: An asterisk (*) following the number or letter designating a paragraph indicates that explanatory material on the paragraph can be found in Annex A.

A reference in brackets [] following a section or paragraph indicates material that has been extracted from another NFPA document. As an aid to the user, the complete title and edition of the source documents for extracts in mandatory sections of the document are given in Chapter 2 and those for extracts in informational sections are given in Annex I. Extracted text may be edited for consistency and style and may include the revision of internal paragraph references and other references as appropriate. Requests for interpretations or revisions of extracted text shall be sent to the technical committee responsible for the source document.

Information on referenced publications can be found in Chapter 2 and Annex I.

Chapter 1 Administration

1.1 Scope. This standard shall address the health, flammability, instability, and related hazards that are presented by shortterm, acute exposure to a material under conditions of fire, spill, or similar emergencies.

1.2 Purpose.

1.2.1 This standard shall provide a simple, readily recognized, and easily understood system of markings that provides a general idea of the hazards of a material and the severity of these hazards as they relate to emergency response.

- **1.2.2** The objectives of the system shall be as follows:
- (1) To provide an appropriate signal or alert and on-the-spot information to safeguard the lives of both public and private emergency response personnel
- (2) To assist in planning for effective fire and emergency control operations, including cleanup
- (3) To assist all designated personnel, engineers, and plant and safety personnel in evaluating hazards

1.2.3 This system shall provide basic information to fire-fighting, emergency, and other personnel, enabling them to easily decide whether to evacuate the area or to commence emergency control procedures.

1.2.4 This system also shall provide those personnel with information to assist in selecting fire-fighting tactics and emergency procedures.

1.2.5 Local conditions can have a bearing on evaluation of hazards; therefore, discussion shall be kept in general terms.

1.3 Application.

1.3.1 This standard shall apply to industrial, commercial, and institutional facilities that manufacture, process, use, or store hazardous materials.

1.3.2* This standard shall not apply to transportation or use by the general public and is not intended to address the following:

- (1) Occupational exposure
- (2) Explosive and blasting agents, including commercial explosive material as defined in NFPA 495
- (3) Chemicals whose only hazard is one of chronic health hazards
- (4) Teratogens, mutagens, oncogens, etiologic agents, and other similar hazards

1.4 Retroactivity. The provisions of this standard reflect a consensus of what is necessary to provide an acceptable degree of protection from the hazards addressed in this standard at the time the standard was issued.

1.4.1 Unless otherwise specified, the provisions of this standard shall not apply to facilities, equipment, structures, or installations that existed or were approved for construction or installation prior to the effective date of the standard. Where specified, the provisions of this standard shall be retroactive.

1.4.2 In those cases where the authority having jurisdiction determines that the existing situation presents an unacceptable degree of risk, the authority having jurisdiction shall be permitted to apply retroactively any portions of this standard deemed appropriate.

1.4.3 The retroactive requirements of this standard shall be permitted to be modified if their application clearly would be impractical in the judgment of the authority having jurisdiction and only where it is clearly evident that a reasonable degree of safety is provided.

1.5 Equivalency. Nothing in this standard is intended to prevent the use of systems, methods, or devices of equivalent or superior quality, strength, fire resistance, effectiveness, durability, and safety over those prescribed by this standard.

1.5.1 Technical documentation shall be submitted to the authority having jurisdiction to demonstrate equivalency.

1.5.2 The system, method, or device shall be approved for the intended purpose by the authority having jurisdiction.

Chapter 2 Referenced Publications

2.1 General. The documents or portions thereof listed in this chapter are referenced within this standard and shall be considered part of the requirements of this document.

2.2 NFPA Publications. National Fire Protection Association, 1 Batterymarch Park, Quincy, MA 02169-7471.

NFPA 70[®], *National Electrical Code*[®], 2014 edition. NFPA 495, *Explosive Materials Code*, 2013 edition.

2.3 Other Publications.

2.3.1 ASTM Publications. ASTM International, 100 Barr Harbor Drive, P.O. Box C700, West Conshohocken, PA 19428-2959.

ASTM D92, Standard Test Method for Flash and Fire Points by Cleveland Open Cup, 2012b.

ASTM D3065, Standard Test Methods for Flammability of Aerosol Products, 2001 (2013).

ASTM D6668, Standard Test Method for the Discrimination Between Flammability Ratings of F = 0 and F = 1, 2001 (2010).

2.3.2 UN Publications. United Nations, UN Plaza, New York, NY 10017.

Manual of Tests and Criteria, 5th revised edition.

Recommendations on the Transport of Dangerous Goods, Model Regulations, 18th revised edition.

2.3.3 U.S. Government Publications. U.S. Government Printing Office, Washington, DC 20402.

Title 16, Code of Federal Regulations, "Method for Determining Flammable and Extremely Flammable Contents of Self-Pressurized Containers," Part 1500.45.

Title 49, Code of Federal Regulations, "Method of Testing for Sustained Combustibility," Part 173, Appendix H.

2.3.4 Other Publications.

Merriam-Webster's Collegiate Dictionary, 11th edition, Merriam-Webster, Inc., Springfield, MA, 2003.

2.4 References for Extracts in Mandatory Sections.

NFPA 1, Fire Code, 2015 edition.

NFPA 30, Flammable and Combustible Liquids Code, 2015 edition.

NFPA 55, Compressed Gases and Cryogenic Fluids Code, 2016 edition.

Chapter 3 Definitions

3.1 General. The definitions contained in this chapter shall apply to the terms used in this standard. Where terms are not defined in this chapter or within another chapter, they shall be defined using their ordinarily accepted meanings within the context in which they are used. *Merriam-Webster's Collegiate Dictionary*, 11th edition, shall be the source for the ordinarily accepted meaning.

3.2 NFPA Official Definitions.

3.2.1* Approved. Acceptable to the authority having jurisdiction.

3.2.2* Authority Having Jurisdiction (AHJ). An organization, office, or individual responsible for enforcing the requirements of a code or standard, or for approving equipment, materials, an installation, or a procedure.

3.2.3 Shall. Indicates a mandatory requirement.

3.2.4 Standard. An NFPA Standard, the main text of which contains only mandatory provisions using the word "shall" to indicate requirements and that is in a form generally suitable for mandatory reference by another standard or code or for adoption into law. Nonmandatory provisions are not to be considered a part of the requirements of a standard and shall be located in an appendix, annex, footnote, informational note, or other means as permitted in the NFPA Manuals of Style. When used in a generic sense, such as in the phrase "standards development process" or "standards development activities," the term "standards, Recommended Practices, and Guides.

3.3 General Definitions.

3.3.1* Boiling Point. The temperature at which the vapor pressure of a liquid equals the surrounding atmospheric pressure. [**30**, 2015]

3.3.2 Cryogenic Fluid. A fluid with a boiling point lower than -130° F (-90°C) at an absolute pressure of 14.7 psi (101.3 kPa). [55, 2016]

3.3.3 Fire Point. The lowest temperature at which a liquid will ignite and achieve sustained burning when exposed to a test flame in accordance with ASTM D92, *Standard Test Method for Flash and Fire Points by Cleveland Open Cup Tester.* [**30**, 2015]

3.3.4* Flash Point. The minimum temperature at which a liquid or a solid emits vapor sufficient to form an ignitible mixture with air near the surface of the liquid or the solid.

3.3.5* Frostbite. Frostbite is a localized condition that occurs when the layers of the skin and deeper tissue freeze.

3.3.6 Materials.

3.3.6.1 *Stable Materials.* Those materials that normally have the capacity to resist changes in their chemical composition, despite exposure to air, water, and heat as encountered in fire emergencies.

3.3.6.2 *Unstable Materials.* A material that, in the pure state or as commercially produced, will vigorously polymerize, decompose or condense, become self-reactive, or otherwise undergo a violent chemical change under conditions of shock, pressure, or temperature.

3.3.7 Simple Asphyxiant Gas. A gas that does not provide sufficient oxygen to support life and that has none of the other physical or health hazards. [1, 2015]

Chapter 4 General

4.1 Description.

4.1.1 This system of markings shall identify the hazards of a material in terms of the following three principal categories:

- (1) Health
- (2) Flammability
- (3) Instability

4.1.2 The system shall indicate the degree of severity by a numerical rating that ranges from 4, indicating severe hazard, to 0, indicating minimal hazard.

4.1.3 The information shall be presented by a spatial arrangement of numerical ratings, with the health rating always at the nine o'clock position, the flammability rating always at the twelve o'clock position, and the instability rating always at the three o'clock position.

4.1.4* Each rating shall be located in a square-on-point field (commonly referred to as a diamond), each of which is assigned a color as follows:

- (1) Blue for health hazard
- (2) Red for flammability hazard
- (3) Yellow for instability hazard

4.1.5 Alternatively, the square-on-point field shall be permitted to be any convenient contrasting color and the numbers themselves shall be permitted to be colored. (See Figure 9.1(a) through Figure 9.1(c) for examples of the spatial arrangements.)

4.1.6 The fourth quadrant, at the six o'clock position, shall be reserved for indicating special hazards and shall be in accordance with Chapter 8. No special color is associated with this quadrant.

4.2 Assignment of Ratings.

4.2.1 The hazard evaluation required to determine the correct hazard ratings for a specific material shall be performed by persons who are technically competent and experienced in the interpretation of the hazard criteria set forth in this standard.

4.2.2* Assignment of ratings shall be based on factors that encompass a knowledge of the inherent hazards of the material, including the extent of change in behavior to be anticipated under conditions of exposure to fire or fire control procedures.

4.2.3 The system shall be based on relative rather than absolute values, requiring that considerable judgment be exercised.

4.2.3.1 Based on professional judgment, the hazard rating shall be permitted to be either increased or decreased to more accurately assess the likely degree of hazard that will be encountered.

4.2.3.2* It shall be anticipated that different physical forms of the material or conditions of storage and use could result in different ratings being assigned to the same material.

4.2.3.3* Where more than one chemical is present in a building or specific area, professional judgment shall be exercised to indicate ratings using the following methods:

- (1) *Composite Method.* Where many chemicals are present, a single sign shall summarize the maximum ratings contributed by the material(s) in each category and the special hazard category for the building and/or the area.
- (2) *Individual Method.* Where only a few chemicals are present or where only a few chemicals are of concern to emergency responders (taking into account factors including physical form, hazard rating, and quantity), individual signs shall be displayed. The chemical name shall be displayed below each sign.
- (3) Composite-Individual Combined Method. A single sign shall be used to summarize the ratings via the Composite Method for buildings or other areas containing numerous chemicals. Signs based on the Individual Method shall be used for rooms or smaller areas within the building containing small numbers of chemicals.

4.2.3.4* When mixtures of chemicals are being rated, actual data on the mixture itself shall be used to obtain the ratings for health, flammability, and instability.

4.3* Location of Signs. Signs shall be in locations approved by the authority having jurisdiction and as a minimum shall be posted at the following locations:

- (1) Two exterior walls or enclosures containing a means of access to a building or facility
- (2) Each access to a room or area
- (3) Each principal means of access to an exterior storage area

Chapter 5 Health Hazards

5.1 General.

5.1.1* This chapter shall address the capability of a material to cause personal injury due to contact with or entry into the body via inhalation, skin contact, eye contact, or ingestion.

5.1.2 Injury resulting from the heat of a fire or from the force of an explosion shall not be considered.

5.1.3* Health hazards that can result from chronic or repeated long-term exposure to low concentrations of a hazardous material shall not be considered.

5.1.4* If the oral toxicity values indicate a health hazard rating that is significantly different from other, more likely routes of exposure or if the oral toxicity values would tend to either exaggerate or minimize the hazards likely to be encountered, then professional judgment shall be exercised in assigning the health hazard rating.

5.1.5* For purposes of assigning the health hazard rating, only the inherent physical and toxic properties of the material shall be considered. However, if the combustion or decomposition products are known, are generated in significant quantities, and present a significantly greater degree of risk, they shall be rated accordingly.

5.1.6 The degree of hazard shall indicate to fire-fighting and emergency response personnel one of the following:

- (1) They can work safely in the area only with specialized protective equipment. They can work safely in the area with suitable respiratory
- (2)protective equipment.

Table 5.2 Degrees of Health Hazards

(3) They can work safely in the area with ordinary clothing.

5.2* Degrees of Hazard. The degrees of health hazard shall be ranked according to the probable severity of the effects of exposure to emergency response personnel detailed in Table 5.2.

Degree of Hazard*	Criteria [†]
4 — Materials that, under emergency conditions, can be lethal	Gases whose LC_{50} for acute inhalation toxicity is less than or equal to 1000 parts per million (ppm)
	Any liquid whose saturated vapor concentration at 20°C (68°F) is equal to or greater than 10 times its LC_{50} for acute inhalation toxicity, if its LC_{50} is less than or equal to 1000 ppm
	Dusts and mists whose LC_{50} for acute inhalation toxicity is less than or equal to 0.5 milligram per liter (mg/L)
	Materials whose LD_{50} for acute dermal toxicity is less than or equal to 40 milligrams per kilogram (mg/kg)
	Materials whose LD_{50} for acute oral toxicity is less than or equal to 5 mg/kg
3 — Materials that, under emergency conditions, can cause serious or	Gases whose LC_{50} for acute inhalation toxicity is greater than 1000 ppm but less than or equal to 3000 ppm
permanent injury	Any liquid whose saturated vapor concentration at 20°C (68°F) is equal to or greater than its LC_{50} for acute inhalation toxicity, if its LC_{50} is less than or equal to 3000 ppm, and that does not meet the criteria for degree of hazard 4
	Dusts and mists whose LC_{50} for acute inhalation toxicity is greater than 0.5 mg/L but less than or equal to 2 mg/L
	Materials whose LD_{50} for acute dermal toxicity is greater than 40 mg/kg but less than or equal to 200 mg/kg
	Materials that are corrosive to the respiratory tract
	Materials that are corrosive to the eye or cause irreversible corneal opacity
	Materials that are corrosive to skin
	Cryogenic fluids that cause frostbite and irreversible tissue damage
	Compressed liquefied gases with boiling points at or below -55°C (-66.5°F) that cause frostbite and irreversible tissue damage
	Materials whose $\rm LD_{50}$ for acute oral toxicity is greater than 5 mg/kg but less than or equal to 50 mg/kg
2 — Materials that, under emergency conditions, can cause temporary	Gases whose LC_{50} for acute inhalation toxicity is greater than 3000 ppm but less than or equal to 5000 ppm
incapacitation or residual injury	Any liquid whose saturated vapor concentration at 20°C (68°F) is equal to or greater than one-fifth its LC_{50} for acute inhalation toxicity, if its LC_{50} is less than or equal to 5000 ppm, and that does not meet the criteria for either degree of hazard 3 or degree of hazard 4
	Dusts and mists whose LC_{50} for acute inhalation toxicity is greater than 2 mg/L but less than or equal to 10 mg/L
	Materials whose $\rm LD_{50}$ for acute dermal toxicity is greater than 200 mg/kg but less than or equal to 1000 mg/kg
	Compressed liquefied gases with boiling points between -30°C (-22°F) and -55°C (-66.5°F) that can cause severe tissue damage on contact, depending on duration of exposure
	(continues)

Table 5.2 Continued

Degree of Hazard*	$\mathbf{Criteria}^{\dagger}$		
	Materials that are respiratory irritants		
	Materials that cause severe but reversible irritation to the eyes or lacrimators		
	Materials that are primary skin irritants or sensitizers		
	Materials whose $\rm LD_{50}$ for acute oral toxicity is greater than 50 mg/kg but less than or equal to 500 mg/kg		
 Materials that, under emergency conditions, can cause significant irritation 	Gases and vapors whose LC_{50} for acute inhalation toxicity is greater than 5000 ppm but less than or equal to 10,000 ppm		
	Dusts and mists whose LC_{50} for acute inhalation toxicity is greater than 10 mg/L but less than or equal to 200 mg/L		
	Materials whose LD_{50} for acute dermal toxicity is greater than 1000 mg/kg but less than or equal to 2000 mg/kg		
	Materials that cause slight to moderate irritation to the respiratory tract, eyes, and skin		
	Materials whose $\rm LD_{50}$ for acute oral toxicity is greater than 500 mg/kg but less than or equal to 2000 mg/kg		
0 — Materials that, under emergency	Gases and vapors whose LC_{50} for acute inhalation toxicity is greater than 10,000 ppm		
conditions, would offer no hazard beyond that of ordinary combustible materials	Dusts and mists whose LC_{50} for acute inhalation toxicity is greater than 200 mg/L		
that of ortifiary combustible materials	Materials whose LD_{50} for acute dermal toxicity is greater than 2000 mg/kg		
	Materials whose LD_{50} for acute oral toxicity is greater than 2000 mg/kg		
	Materials that are essentially nonirritating to the respiratory tract, eyes, and skin		

*For each degree of hazard, the criteria are listed in a priority order based on the likelihood of exposure.

[†]See Section B.3 for definitions of LC_{50} and LD_{50}

5.2.1 Data from all routes of exposure shall be considered when applying professional judgment to assign a health hazard rating.

Chapter 6 Flammability Hazards

6.1 General.

6.1.1 This chapter shall address the degree of susceptibility of materials to burning.Table 6.2 Degrees of Flammability Hazards

6.1.2* Because many materials will burn under one set of conditions but will not burn under others, the form or condition of the material shall be considered, along with its inherent properties.

6.2* Degrees of Hazard. The degrees of flammability hazard shall be ranked according to the susceptibility of materials to burning detailed in Table 6.2.

Degree of Hazard	Criteria
4 — Materials that rapidly or completely	Flammable gases
vaporize at atmospheric pressure and normal ambient temperature or that are readily	Flammable cryogenic materials
dispersed in air and burn readily	Any liquid or gaseous material that is liquid while under pressure and has a flash point below 22.8°C (73°F) and a boiling point below 37.8°C (100°F) (i.e., Class IA liquids)
	Materials that ignite spontaneously when exposed to air
	Solids containing greater than 0.5 percent by weight of a flammable or combustible solvent are rated by the closed cup flash point of the solvent.
	, i i (continu

(continues)

Table 6.2Continued

Degree of Hazard	Criteria
3 — Liquids and solids (including finely divided suspended solids) that can be ignited under almost all ambient temperature	Liquids having a flash point below 22.8°C (73°F) and a boiling point at or above 37.8°C (100°F) and those liquids having a flash point at or above 22.8°C (73°F) and below 37.8°C (100°F) (i.e., Class IB and Class IC liquids)
conditions. Materials in this degree produce hazardous atmospheres with air under almost all ambient temperatures or, though unaffected by ambient temperatures, are readily ignited under almost all conditions.	Finely divided solids, typically less than 75 micrometers (μ m) (200 mesh), that present an elevated risk of forming an ignitible dust cloud, such as finely divided sulfur, <i>National Electrical Code</i> Group E dusts (e.g., aluminum, zirconium, and titanium), and bis-phenol A
See Annex D for more information on ranking of combustible dusts.	Materials that burn with extreme rapidity, usually by reason of self-contained oxygen (e.g., dry nitrocellulose and many organic peroxides)
	Solids containing greater than 0.5 percent by weight of a flammable or combustible solvent are rated by the closed cup flash point of the solvent.
2 — Materials that must be moderately heated or exposed to relatively high ambient	Liquids having a flash point at or above 37.8°C (100°F) and below 93.4°C (200°F) (i.e., Class II and Class IIIA liquids)
temperatures before ignition can occur. Under normal conditions, these materials would not form hazardous atmospheres with	Finely divided solids less than 420 μm (40 mesh) that present an ordinary risk of forming an ignitible dust cloud
air, but under high ambient temperatures or under moderate heating they could release	Solid materials in a flake, fibrous, or shredded form that burn rapidly and create flash fire hazards, such as cotton, sisal, and hemp
vapor in sufficient quantities to produce	Solids and semisolids that readily give off flammable vapors
hazardous atmospheres with air. Materials in this degree also include finely divided suspended solids that do not require heating before ignition can occur. See Annex D for more information on ranking of combustible dusts.	Solids containing greater than 0.5 percent by weight of a flammable or combustible solvent are rated by the closed cup flash point of the solvent.
1 — Materials that must be preheated before ignition can occur Materials in this degree require considerable preheating, under all ambient temperature conditions, before ignition and combustion can occur. Materials in this degree also include finely divided	Materials that will burn in air when exposed to a temperature of 815 5°C (1500°F) for a per od of 5 minutes in accordance with ASTM D6668, <i>Standard Test Method for the Discrimination Between Flammability Ratings of</i> $F = 0$ and $F = 1$
	Liquids, solids, and semisolids having a flash point at or above 93.4°C (200°F) (i.e., Class IIIB liquids)
suspended solids that do not require heating before ignition can occur. See Annex D for more information on ranking of combustible dusts.	Liquids with a flash point greater than 35°C (95°F) that do not sustain combustion when tested using the "Method of Testing for Sustained Combustibility," per 49 CFR 173, Appendix H, or the UN publications <i>Recommendations on the Transport of Dangerous Goods, Model Regulations</i> and <i>Manual</i> of Tests and Criteria
	Liquids with a flash point greater than 35°C (95°F) in a water-miscible solution or dispersion with a water noncombustible liquid/solid content of more than 85 percent by weight
	Liquids that have no fire point when tested by ASTM D92, <i>Standard Test Method for Flash and Fire Points by Cleveland Open Cup</i> , up to the boiling point of the liquid or up to a temperature at which the sample being tested shows an obvious physical change
	Combustible pellets, powders, or granules greater than 420 μ m (40 mesh)
	Finely divided solids less than 420 μ m (40 mesh) that are nonexplosible in air at ambient conditions, such as low volatile carbon black and polyvinylchloride (PVC)
	Most ordinary combustible materials
	Solids containing greater than 0.5 percent by weight of a flammable or combustible solvent are rated by the closed cup flash point of the solvent.

Table 6.2 Continued

Degree of Hazard	Criteria
0 — Materials that will not burn under typical fire conditions, including intrinsically noncombustible materials such as concrete, stone, and sand.	Materials that will not burn in air when exposed to a temperature of 816° C (1500°F) for a period of 5 minutes in accordance with ASTM D6668, <i>Standard Test Method for the Discrimination Between Flammability Ratings of</i> $F = 0$ <i>and</i> $F = 1$

6.3 Aerosols. Aerosol products shall be rated based on the flash point or boiling point of the contents of the container or the results of the flame projection test as defined by ASTM D3065, *Standard Test Methods for Flammability of Aerosol Products*, or 16 CFR 1500.45, "Method for Determining Flammable and Extremely Flammable Contents of Self-Pressurized Containers," whichever is the higher degree of hazard.

6.3.1 An aerosol material having a flame projection of 457 mm (18 in.) or more when tested in accordance with ASTM D3065, *Standard Test Methods for Flammability of Aerosol Products*, or 16 CFR 1500.45, "Method for Determining Flammable and Extremely Flammable Contents of Self-Pressurized Containers," shall be ranked at a degree hazard of at least 3.

Chapter 7 Instability Hazards

7.1 General.

7.1.1* This chapter shall address the degree of hazard due to reaction with ambient air, light, or both, and the degree of intrinsic susceptibility of materials to release energy by self-reaction or polymerization.

7.1.2* Reaction with ambient air shall include the ability to form hazardous peroxides and the ability to generate sufficient release of energy to cause a hazard.

7.1.3 Water reactivity shall be assessed in accordance with Chapter 8.

7.1.4* Because of the wide variations of unintentional combinations possible in fire or other emergencies, these extraneous hazard factors (except for the effect of water) shall not be applied to a general numerical rating of hazards. Where large quantities of materials are stored together, inadvertent mixing shall be considered in order to establish appropriate separation or isolation.

7.1.5 The degree of instability hazard shall indicate to firefighting and emergency personnel whether the area shall be evacuated, whether a fire shall be fought from a protected location, whether caution shall be used in approaching a spill or fire to apply extinguishing agents, or whether a fire can be fought using normal procedures.

7.2 Degrees of Hazard. The degrees of hazard shall be ranked according to ease, rate, and quantity of energy release of the material in pure or commercial form detailed in Table 7.2.

Table 7.2 Degrees of Instability Hazards

Degree of Hazard	Criteria
4 — Materials that in themselves are readily capable of detonation or explosive	Materials that are sensitive to localized thermal or mechanical shock at normal temperatures and pressures
decomposition or explosive reaction at normal temperatures and pressures	Materials that have an instantaneous power density (product of heat of reaction and reaction rate) at 250°C (482°F) of 1000 W/mL or greater
3 — Materials that in themselves are capable of detonation or explosive decomposition or explosive reaction but that require a strong	Materials that have an instantaneous power density (product of heat of reaction and reaction rate) at 250°C (482°F) at or above 100 W/mL and below 1000 W/mL
initiating source or must be heated under confinement before initiation	Materials that are sensitive to thermal or mechanical shock at elevated temperatures and pressures
2 — Materials that readily undergo violent chemical change at elevated temperatures and pressures	Materials that have an instantaneous power density (product of heat of reaction and reaction rate) at 250°C (482°F) at or above 10 W/mL and below 100 W/mL
1 — Materials that in themselves are normally stable but that can become unstable at elevated temperatures and pressures	Materials that have an instantaneous power density (product of heat of reaction and reaction rate) at 250°C (482°F) at or above 0.01 W/mL and below 10 W/mL
0 — Materials that in themselves are normally stable, even under fire conditions	Materials that have an instantaneous power density (product of heat of reaction and reaction rate) at 250 $^\circ C$ (482 $^\circ F) below 0.01 W/mL$

Chapter 8 Special Hazards

8.1 General.

8.1.1* This chapter shall address water reactivity and oxidizing properties of the materials that cause special problems or require special fire-fighting techniques.

8.1.2 Special hazard symbols shall be shown in the fourth space of the sign or immediately above or below the entire sign.

8.2 Symbols. Special hazards shall be represented by a spatial arrangement denoted by symbols always at the six o'clock position.

8.2.1* Materials that react violently or explosively with water (i.e., water reactivity rating 2 or 3) shall be identified by the letter "W" with a horizontal line through the center ($\frac{W}{W}$).

8.2.2* Materials that possess oxidizing properties shall be identified by the letters "OX."

8.2.3* For chemicals requiring both "special hazard" symbols (i.e., Ψ and OX), the Ψ shall be displayed inside the special hazards quadrant, and the OX shall be displayed directly below or adjacent to the special hazards quadrant.

8.2.4* Materials that are simple asphyxiant gases shall be permitted to be identified with the letters "SA" and shall include the following gases: nitrogen, helium, neon, argon, krypton, and xenon.

8.2.4.1* The SA symbol shall also be used for liquefied carbon dioxide vapor withdrawal systems and where large quantities of dry ice are used in confined areas.

Chapter 9 Identification of Materials by Hazard Rating System

9.1 Symbol Arrangement. One of the systems delineated in Figure 9.1(a), Figure 9.1(b), or Figure 9.1(c) shall be used for the implementation of this standard.



FIGURE 9.1(a) Alternative Arrangements for Display of NFPA 704 Hazard Identification System.



Color of numerals 1, 2, 3, 4 should be as indicated.

Т Note: Style of numerals W Т W w shown is optional.



Size of hazard ratings					
Н	W		Т	A	В
25 (1) 51 (2) 76 (3) 102 (4) 152 (6)	18 (0.7) 36 (1.4) 53 (2.1) 71 (2.8) 107 (4.2)	4 8 12 16 24	(⁵ ⁄16) (¹⁵ ⁄32) (⁵ ⁄8)	64 (2½) 127 (5) 191 (7½) 254 (10) 381 (15)	32 (1¼) 64 (2½) 95 (3¾) 127 (5) 191 (7½)

All dimensions given in mm (in.)

Exception: For containers with a capacity of 3.78 L (1 gal) or less, symbols can be reduced in size, provided the following: (1) The reduction is proportionate. (2) The color coding is retained. (3) The vertical and horizontal dimensions of the diamond are not less than 25 mm (1 in.). (4) The individual numbers are no smaller than 3.2 mm (1/8 in.) tall.

FIGURE 9.1(b) Dimensions of NFPA 704 Placard and Numerals.

Arrangement and order of hazard ratings optional form of application

Distance at which hazard ratings are legible	Minimum size of hazard ratings required		
15.24 m (50 ft)	25 mm (1 in.)		
22.86 m (75 ft)	51 mm (2 in.)		
30.48 m (100 ft)	76 mm (3 in.)		
60.96 m (200 ft)	102 mm (4 in.)		
91.44 m (300 ft)	152 mm (6 in.)		

Note: This shows the correct spatial arrangement and order of hazard ratings used for identification of materials by hazard.



FIGURE 9.1(c) Minimum Size of Numerals for Legibility at Distance.

Annex A Explanatory Material

Annex A is not a part of the requirements of this NFPA document but is included for informational purposes only. This annex contains explanatory material, numbered to correspond with the applicable text paragraphs.

A.1.3.2 The Technical Committee on Classification and Properties of Hazardous Chemical Data recognizes that the potential exists for certain materials to cause a carcinogenic or teratogenic effect from acute exposure(s). However, sufficient data are not available to this committee to allow for the development of numerical ratings based on carcinogenic or teratogenic potential.

A.3.2.1 Approved. The National Fire Protection Association does not approve, inspect, or certify any installations, procedures, equipment, or materials; nor does it approve or evaluate testing laboratories. In determining the acceptability of installations, procedures, equipment, or materials, the authority having jurisdiction may base acceptance on compliance with NFPA or other appropriate standards. In the absence of such standards, said authority may require evidence of proper installation, procedure, or use. The authority having jurisdiction may also refer to the listings or labeling practices of an organization that is concerned with product evaluations and is thus in a position to determine compliance with appropriate standards for the current production of listed items.

A.3.2.2 Authority Having Jurisdiction (AHJ). The phrase "authority having jurisdiction," or its acronym AHJ, is used in NFPA documents in a broad manner, since jurisdictions and approval agencies vary, as do their responsibilities. Where public safety is primary, the authority having jurisdiction may be a federal, state, local, or other regional department or individual such as a fire chief; fire marshal; chief of a fire prevention bureau, labor department, or health department; building official; electrical inspector; or others having statutory authority. For insurance purposes, an insurance inspection department, rating bureau, or other insurance company representative may be the authority having jurisdiction. In many circumstances, the property owner or his or her designated agent assumes the role of the authority having jurisdiction; at government installations, the commanding officer or departmental official may be the authority having jurisdiction.

A.3.3.1 Boiling Point. For single-component liquids at the boiling point, the surrounding atmospheric pressure can no longer hold the liquid in the liquid state and the liquid boils. A low boiling point is indicative of a high vapor pressure and a high rate of evaporation.

Where an accurate boiling point is unavailable for the material in question or for mixtures that do not have a constant boiling point, for purposes of this standard the 20 percent point of a distillation performed in accordance with ASTM D86, *Standard Test Method for Distillation of Petroleum Products at Atmospheric Pressure*, can be used as the boiling point of the liquid. The user is warned that this definition of boiling point is inconsistent with that given in other flammability classification systems that generally use the initial boiling point of the distillation curve. Therefore, boiling points assigned for mixtures by these different classification systems are not interchangeable. For more information, see Britton, "Survey of Fire Hazard Classification Systems for Liquids." **A.3.3.4 Flash Point.** Flash point is a direct measure of a liquid's volatility, that is, its tendency to vaporize. The lower the flash point, the greater the volatility and the greater the risk of fire. Flash point is determined using one of several different test procedures and apparatus that are specified.

A.3.3.5 Frostbite. Frostbite causes the skin to have a pale waxy-white appearance, and the tissue becomes numb and hard. The blood vessels in the affected area constrict and decrease circulation. Ice crystals then form in the tissue and cause structural damage, with death of the affected cells.

In mild cases where ice crystal formation has not yet occurred or is very limited, recovery is usually complete, and circulation and tissue will revert to their normal state. Depending on the depth at which the tissue freezes, four degrees of severity can be distinguished. The first and second degrees of severity are limited to the top layers of skin where circulation is impaired. The second degree of severity results in blistering of the skin. Both the first- and second-degree levels do not extend beyond the top layers of the skin, and tissue death is limited. The third degree of severity involves tissue death below the skin layers. The fourth and most severe degree results in deep-tissue death that involves the muscle, tendon, and bone.

When exposure to cold is prolonged or extremely low temperatures are encountered as in the case of unprotected contact with cryogenic fluids, irreversible tissue damage generally occurs. In the more severe cases of frostbite, tissue viability is affected, resulting in tissue death. Depending on the severity of tissue damage and the location affected, surgical removal or amputation of affected tissue or extremity can be necessary.

A.4.1.4 No specific color shade is recommended, but the blue, red, and yellow used must provide adequate contrast so that the rating numbers are easily identified. Many environmental conditions can affect the stability of the colors.

A.4.2.2 The NFPA 704 ratings are applied to numerous chemicals in the NFPA *Fire Protection Guide to Hazardous Materials*, which contains the withdrawn standards NFPA 49 and NFPA 325. These were withdrawn as NFPA standards (and are therefore no longer published in the *National Fire Codes*[®]). However, they are maintained by NFPA staff in a database and in the NFPA *Fire Protection Guide to Hazardous Materials*. The Committee wishes to note that those documents were withdrawn solely for expediency in updating the data, which was not possible in a 3- to 5-year revision cycle.

A.4.2.3.2 Due to the large number of variables, the requirements and guidance presented in this standard are general in nature and are limited to the most important and common factors. For example, although flash point is the primary criterion for assigning the flammability rating, other criteria could be of equal importance. For example, autoignition temperature, flammability limits, and susceptibility of a container to failure due to fire exposure also should be considered. For instability, the emphasis is on the ease by which an energy-releasing reaction is triggered. These factors should all be considered when calling on one's judgment during the assignment of ratings.

A.4.2.3.3 The purpose of the Composite Method is to characterize the hazards as simply as possible where many chemicals are present. The sign reflects the rating for the area, not for individual chemicals. For example, say a building contains materials with individual chemical ratings of 1-2-1 OX,

1-2-2 \mathbf{W} , 3-1-2, and 2-3-4, and a specific area of the building contains individual chemicals with ratings of 1-2-1 OX and 2-3-4. This situation would result in the following:

- (1) The building would be placarded as 3-3-4 OX $\frac{1}{W}$.
- (2) This specific area would be placarded as 2-3-4 OX.

Using the Individual Method for the same building containing the same chemicals, there would be four signs with the following ratings: 1-2-1 OX, 1-2-2 Ψ , 3-1-2, and 2-3-4. Each sign would include the chemical name below the sign.

The specific area of the building would have two signs with the ratings of 1-2-1 OX and 2-3-4, each of which would include the chemical name below the sign. It should be recognized that the purpose of the standard is for recognition of hazards in an emergency; therefore, the number of signs displayed in a single place generally should not exceed five.

The Composite–Individual Combined Method allows users to utilize the best features of the other two methods. The outside of the building, enclosure, or area is posted with a single Composite sign for quick recognition of the overall hazards. Areas or rooms within the building are posted using either the Individual Method or the Composite Method, depending on the number of chemicals they contain.

A.4.2.3.4 In the absence of data on the specific mixture, the most conservative rating (numerically highest) for each component of the mixture for health and instability should be used, with adjustment for professional judgment in accordance with 4.2.3. The synergistic effects or reactions of the components of the mixture should also be considered when assigning the ratings.

When different materials are mixed together, the instability hazard of the m xture can be entirely different from those of the individual components. An example discussed by Stull, "Fundamentals of Fire and Explosion," is the unrecognized mixing of a reducing agent with an oxidizing agent. This compares directly to mixing a fuel with an oxidizer. In this example, a green pigment was manufactured by mixing the yellow pigment lead chromate with the blue pigment ferric ferrocyanide. During fine grinding in a hammer mill, the mixture ignited and deflagrated, resulting in a severe fire. Chemists recognize lead chromate as an oxidizing agent and ferric ferrocyanide as a reducing agent. In the NFPA rating system, although lead chromate should be labeled an oxidizer (OX) in the special hazards quadrant, there is no corresponding provision for labeling reducing agents, such as ferric ferrocyanide. While the individual components involved both have NFPA instability ratings of 0 or 1, the mixture could have a higher instability rating up to 3, depending on the ratio of the components and the intimacy of mixing.

Flammability ratings should be based on measured flash point rather than an estimated value, because the mixture's flash point and boiling point can be readily tested and quantified. In advance of testing, the flash point for a mixture can be predicted using the method described in Hanley, "A Model for the Calculation and the Verification of Closed Cup Flash Points for Multicomponent Mixtures." The flammability rating is determined per Annex C.

A.4.3 The quantity and location of NFPA 704 placards are based on factors such as fire department response and access; fire department operations; location, configuration, size, and arrangement of storage areas; location, configuration, and

construction of the buildings; and other factors. The authority having jurisdiction should be consulted regarding the placement of identification to assist in response to incidents at the location.

A.5.1.1 See Annex B for additional health hazard rating background information.

A.5.1.3 In general, the health hazard that results from a fire or other emergency condition is one of acute (single) short-term exposure to a concentration of a hazardous material. This exposure can vary from a few seconds to as long as 1 hour. The physical exertion demanded by fire fighting or other emergency activity can be expected to intensify the effects of any exposure. In addition, the hazard under ambient conditions will likely be exaggerated at elevated temperatures.

A.5.1.4 The oral route of exposure (i.e., ingestion) is highly unlikely under the conditions anticipated by this standard. In such cases, other routes of entry should be considered to be more appropriate in assessing the hazard. Similarly, inhalation of dusts and mists is unlikely under the conditions anticipated by this standard. In such cases, the health hazard ratings should also be based on data for the more likely routes of exposure.

A.5.1.5 Some materials have products of combustion or decomposition that present a significantly greater degree of hazard than the inherent physical and toxic properties of the original material. The degree of hazard is dependent on the conditions at the time of the incident. In limited cases, NFPA 49, provides information on the hazardous products of combustion or decomposition. (Note: Although NFPA 49, has been officially withdrawn from the *National Fire Codes*, the information is still available in the NFPA *Fire Protection Guide to Hazardous Materials.*)

In general, the Technical Committee on Classification and Properties of Hazardous Chemical Data does not consider elevating ratings based on decomposition or combustion products except for unusual circumstances. An example where the health rating could conceivably be increased is vinylidene chloride. Vinylidene chloride can emit a significant amount of phosgene under fire conditions, and under certain storage and use conditions, the rating of 2 could be increased to 4 for health. Another example is polyvinyl chloride, which emits hydrogen chloride and possibly chlorine under fire conditions. The rating of 0 or 1 could be increased to 3 or 4 for health. Conditions play a large part in any rating, as noted in Section 4.2, and professional judgment should be exercised.

A.5.2 Certain materials upon release can cause frostbite. Frostbite, as a health hazard, should be related to the skin/eye component of the health hazard rating criteria.

A.6.1.2 The definitions for liquid classifications are found in NFPA 30.

Solids should normally be rated as pellets unless the form and handling conditions of the solid require otherwise.

A.6.2 For water-miscible solutions and liquids that do not sustain combustion in accordance with the hazard rating 1 criteria, the individual performing the hazard evaluation should recognize that in large vapor spaces, evaporation of volatile components of the mixture can create a flammable mixture, which could increase the fire or explosion hazard. This could occur even though the bulk material meets the aforementioned criteria.

In the case of mixtures stored in noninerted tanks where the vapor space can contain ignitible vapor, the flammability rating should be based exclusively on a closed cup flash point test. In some cases, even solutions containing less than 1 percent volatile flammable materials could produce ignitible atmospheres (Britton).

A.7.1.1 The violence of a reaction or decomposition can be increased by heat or pressure. The violence of a reaction or decomposition can also be increased by mixing with other materials to form fuel–oxidizer combinations or by contact with incompatible substances, sensitizing contaminants, or catalysts.

A.7.1.2 Hazardous peroxides can form due to concentration of the original material via evaporation or by separation of the peroxide if it is insoluble in the original material. For additional information on peroxides, see NFPA 400.

A.7.1.4 The hazards of inadvertent mixing can be addressed by a chemical compatibility chart. Information to develop such a chart can be found in NFPA 491. (Note: Although NFPA 491 has been officially withdrawn from the *National Fire Codes*, the information is still available in NFPA's *Fire Protection Guide to Hazardous Materials.*) Information can also be found in Bretherick, *Handbook of Reactive Chemicals.*

A.8.1.1 Only two special hazard symbols (OX and W) are required by NFPA 704, and SA is an optional symbol inside the NFPA special hazards quadrant. Outside NFPA 704, limited, special situations might exist in which individual circumstances dictate use of a unique hazard symbol. Other user-defined symbols or markings must be placed outside the NFPA "diamond." Appropriate training and communication addressing these other markings are essential. Other special hazard symbo s (beyond OX and \mathbb{W}) should not be considered to be part of the NFPA 704 hazard rating system. In many cases, the hazards represented by these symbols are already considered in the health, flammability, or instability rating categories. For example, a polymerization hazard is covered by the numerical instability rating and does not require a separate symbol. Also, corrosive properties are considered in the health rating and, again, do not require a separate symbol. In addition, because these additional symbols are not defined by the standard, emergency responders might not recognize their significance.

A.8.2.1 Guidance on use of the $\frac{1}{W}$ symbol and other associated information are located in Annex F, Water Reactivity Identification Criteria.

A.8.2.2 For further information on oxidizers, including oxidizer classes, see NFPA 400.

The severity of the hazard posed by an oxidizer can be ranked according to the classification system presented in NFPA 400. This numerical class can be included in the special hazards quadrant of the NFPA 704 placard. For example, because ammonium permanganate is a Class 4 oxidizer (per NFPA 400), the special hazards quadrant would be marked OX 4 to better define the hazard.

The adding of the quantification of the oxidation helps to better define the hazard. For example, both manganese dioxide (NFPA 400, Class 1) and ammonium permanganate (NFPA 400, Class 4) would be listed under the current system as OX in the NFPA 704 system, with no information on the degree of hazard. **A.8.2.3** Both the \mathbf{W} and the OX are special hazards. However, the \mathbf{W} rating should be ranked as the primary special hazard by display of the \mathbf{W} symbol inside the special hazards quadrant, because it is deemed more important from a fire-fighting perspective. The Committee recognizes that water application is a common first approach to fire fighting. Responders need to be immediately alerted to the \mathbf{W} rating and should not apply water without understanding the consequences of that action. The OX is still important but is secondary and is displayed outside the quadrant, as shown in Figure 9.1(c).

A.8.2.4 See 3.3.7 for the definition of *simple asphysiant gas*. Gases that are simple asphysiants can displace the amount of oxygen in the air necessary to support life. Because these gases are colorless and odorless and offer no warning properties, the SA symbol added to the NFPA 704 diamond will alert responders to the potential hazard.

A.8.2.4.1 Even though carbon dioxide is technically not just a simple asphyxiant, the hazards created by the release of carbon dioxide are similar to those caused by a simple asphyxiant and the response for emergency responders should be similar to that for simple asphyxiants. Carbon dioxide poses additional health risks beyond being an asphyxiant.

Annex B Health Hazard Rating

This annex is not a part of the requirements of this NFPA document but is included for informational purposes only.

B.1 Development of Quantitative Guidelines for Health. In developing this edition of NFPA 704, the Technical Committee on Classification and Properties of Hazardous Chemical Data determined that the standard should provide quantitative guidelines for determining the numerical health hazard rating of a material (*see Table B.1*).

B.1.1 Inhalation Hazard Considerations Using DOT Criteria. In addition, the Committee agreed that a health hazard rating of 4 or 3 should be assigned to any material classified as a "Poison-Inhalation Hazard" by the U.S. Department of Transportation (DOT). The poison-inhalation hazard classification was adopted by DOT from the United Nations (UN) criteria detailed in the UN publication *Recommendations on the Transport* of Dangerous Goods — Model Regulations.

B.1.2 Inhalation Hazard Considerations Using UN Criteria. The UN criteria for inhalation toxicity are based on the LC_{50} and saturated vapor concentration of the material.

B.1.3 Oral and Dermal Hazard Considerations Using UN Criteria. Furthermore, in addition to inhalation toxicity, the UN has established criteria for oral and dermal toxicity, as well as corrosivity. Based on those criteria, the UN assigns materials to categories called Packing Groups. Packing Group I materials represent a severe hazard in transport, Group II materials represent a serious hazard, and Group III materials represent a low hazard.

The Committee decided to adopt the UN criteria for toxicity and corrosivity, and to correlate Packing Groups I, II, and III with the health hazard ratings 4, 3, and 2, respectively.

	Gas/	Vapor				
Degree of Hazard	Inhalation LC ₅₀ (ppm-v)	Saturated Vapor Concentration (× LC ₅₀ in ppm-v)	Dust/Mist Inhalation LC ₅₀ (mg/L)	Oral LD ₅₀ (mg/kg)	Dermal LD ₅₀ (mg/kg)	Skin/Eye Contact
4	0 to 1,000	10 to >10	0.00 to 0.5	0.00 to 5	0 to 40	
3	1,001 to 3,000	1 to <10	0.51 to 2	5.01 to 50	40.1 to 200	Corrosive, irreversible eye injury; corrosive if pH ≤2 or ≥11.5
2	3,001 to 5,000	0.2 to <1	2.01 to 10	50.1 to 500	201 to 1,000	Severe irritation, reversible injury; sensitizers, lacrimators; frostbite from compressed liquefied gases
1	5,001 to 10,000	0 to <0.2	10.1 to 200	501 to 2,000	1,001 to 2,000	Slight to moderate eye irritation; mild irritation is borderline 0/1
0	>10,000	0 to <0.2	>200	>2,000	>2,000	Essentially nonirritating

Table B.1 Health Hazard Rating Chart

Notes

(1)

[**B.**1a]

$$ppm = \frac{mg/m^3 \times 24.45}{molecular weight}$$

(2) Saturated vapor concentration (ppm) at 20°C and standard atmospheric pressure:

[B.1b]

SVC = $\frac{\text{Vapor pressure (mmHg)} \times 106}{760}$

(3) See Section B.3 for definitions of LC_{50} and LD_{50} .

B.1.4 Adoption of UN Criteria. Adoption of the UN system has several advantages.

B.1.4.1 First, it addresses hazards in transportation that are similar to the type of emergencies likely to be encountered by fire-fighting personnel and emergency responders. Most other hazard ranking systems have been developed for occupational exposures.

B.1.4.2 Second, the UN system is well established, and it is presumed that a large number of chemical manufacturers have already classified (or can easily classify) materials into the appropriate packing groups.

B.1.4.3 Finally, users of chemicals can assign a 4, 3, or 2 health hazard rating by establishing whether a chemical has been

assigned to a UN packing group due to toxicity or to corrosivity.

B.1.5 Hazard Considerations Using HMIS Criteria. To establish 1 and 0 health hazard rankings, the Committee utilized criteria for the 1 and 0 ratings contained in the Hazardous Materials Identification System (HMIS) developed by the American Coatings Association (ACA), formerly the National Paint & Coatings Association (NPCA) (*see Hazardous Materials Identification System Revised, Implementation Manual*). Although the ACA criteria were developed for occupational exposure, the 1 and 0 criteria are on the low end of the hazard spectrum and are fairly consistent with, and complementary to, the 4, 3, and 2 ratings based on the UN criteria. No UN criteria were established for eye irritation, and the Committee adopted ACA 3, 2, 1, and 0 criteria as health hazard ratings for eye irritation.

B.2 Additional Revisions to Health Hazard Rating. The Committee made a number of revisions to the proposed hazard rating system to provide conformity with existing industrial practice and to recognize the limitations and availability of corrosivity and eye irritation in a single "skin/eye contact" category and to utilize descriptive terms for the health hazard ratings. Minor changes were made to the 2, 1, and 0 criteria for oral toxicity and to the 1 and 0 criteria for dermal toxicity. Specifically, the distinction between solids and liquids in the oral toxicity criteria was eliminated, and the cutoff between 1 and 0 rankings for oral and dermal toxicity was lowered from 5000 to 2000 mg/kg.

In summary, the 4, 3, and 2 health hazard rankings for oral, dermal, and inhalation toxicity are based primarily on UN criteria. The 1 and 0 health hazard rankings for oral, dermal, inhalation toxicity, and all the "skin/eye contact" rankings are based primarily on ACA criteria.

B.3 UN Definitions. For the user's assistance in utilizing this standard, the following definitions are extracted from Section 6.5 of the UN publication *Recommendations on the Transport of Dangerous Goods — Model Regulations.* In the absence of data for the species defined as follows, the committee currently considers other mammalian species, including human data and professional judgment to assign health ratings. In addition, Table B.1 can be used for guidance.

B.3.1 LD_{50} (median lethal dose) for acute oral toxicity is the statistically derived single dose of a substance that can be expected to cause death within 14 days in 50% of young adult albino rats when administered by the oral route. The LD_{50} value is expressed in terms of mass of test substance per mass of test animal (mg/kg).

B.3.2 LD_{50} for acute dermal toxicity is that dose of the substance which, administered by continuous contact for 24 hours with the bare skin of albino rabbits, is most likely to cause death within 14 days in one half of the animals tested. The number of animals tested shall be sufficient to give a statistically significant result and be in conformity with good pharmacological practice. The result is expressed in milligrams per kg body mass.

B.3.3 LC_{50} for acute toxicity on inhalation is that concentration of vapor, mist, or dust which, administered by continuous inhalation to both male and female young adult albino rats for one hour, is most likely to cause death within 14 days in one half of the animals tested. A solid substance shall be tested if at least 10 percent (by mass) of its total mass is likely to be dust in the respirable range (e.g., the aerodynamic diameter of that particle-fraction is 10 microns or less). A liquid substance shall be tested if a mist is likely to be generated in a leakage of the transport containment. Both for solid and liquid substances more than 90 percent (by mass) of a specimen prepared for inhalation toxicity shall be in the respirable range as defined above. The result is expressed in milligrams per liter of air for dusts and mist, or in milliliters per cubic meter of air (part per million) for vapors.

B.4 The following information extracted from the UN publication, *Recommendations on the Transport of Dangerous Goods* — *Model Regulations*, also applies:

The criteria for inhalation toxicity of dusts and mists are based on LC50 data relating to 1 hour exposures and where such information is available it should be used. However, where only LC50 data relating to 4 hour exposures to dusts and mists are available, such figures can be multiplied by four and the product substituted in the above criteria, i.e., LC50 (4 hour) \times 4 is considered equivalent of LC50 (1 hour).

The criteria for inhalation toxicity of vapors are based on LC50 data relating to 1 hour exposures, and where such information is available it should be used. However, where only LC50 data relating to 4 hour exposures to dusts and mists are available, such figures can be multiplied by two and the product substituted in the above criteria, i.e., LC50 (4 hour) \times 2 is considered equivalent of LC50 (1 hour).

Annex C Flammability

This annex is not a part of the requirements of this NFPA document but is included for informational purposes only.

C.1 Development of Flammability Ratings. The selection of the flash point breaks for the assignment of ratings within the flammability category is based on the recommendations of the Technical Committee on Classification and Properties of Flammable Liquids of the NFPA Committee on Flammable Liquids. This Technical Committee initiated the study that led to the development of this standard. Close cooperation between the Technical Committee and the Committee on Fire Hazards of Materials has continued.

C.2 Significance of Flash Point. Flash point indicates several things:

- (1) If the liquid has no flash point, it is not a flammable liquid.
- (2) If the liquid has a flash point, it has to be considered flammable or combustible.
- (3) The flash point is normally an indication of susceptibility o ignition.

The flash point test can give results that would indicate if a liquid is nonflammable or if it should be rated 1 or 2 as a mixture containing, for example, carbon tetrachloride. As a specific example, sufficient carbon tetrachloride can be added to gasoline so that the mixture has no flash point. However, on standing in an open container, the carbon tetrachloride evaporates more rapidly than the gasoline. Over a period of time, the residual liquid first shows a high flash point, then a progressively lower one until the flash point of the final 10 percent of the original sample approximates that of the heavier fractions of the gasoline. To evaluate the fire hazard of such liquid mixtures, fractional evaporation tests can be conducted at room temperature in open vessels. After evaporation of appropriate fractions, such as 10, 20, 40, 60, and 90 percent of the original sample, flash point tests can be conducted on the residue. The results of such tests indicate the grouping into which the liquid should be placed if the conditions of use are such to make it likely that appreciable evaporation will take place. For open system conditions, such as in open dip tanks, the open cup test method gives a more reliable indication of the flammability hazard.

C.3 Flash Point Test Methods. In the interest of reproducible results, the following procedures are recommended for determining flash point:

(1) The flash point of liquids having a viscosity less than 5.5 mm²/s [5.5 centistokes (cSt)] at 40°C (104°F) or less than 9.5 mm²/s (9.5 cSt) at 25°C (77°F) and a flash point below 93.4°C (200°F) can be determined in accordance with ASTM D56, *Standard Method of Test for Flash Point by* *the Tag Closed Tester.* (In those countries that use the Abel or Abel-Pensky closed cup tests as an official standard, these tests will be equally acceptable to the Tag Closed Cup Method.)

- (2) For liquids having flash points in the range of 0°C (32°F) to 110°C (230°F), the determination can be made in accordance with ASTM D3278, Standard Test Methods for Flash Point of Liquids by Small Scale Closed-Cup Apparatus, or ASTM D3828, Standard Test Method for Flash Point by Small Scale Closed Tester.
- (3) For viscous and solid chemicals, the determination can be made in accordance with Test Method E 502, Standard Test Method for Selection and Use of ASTM Standards for the Determination of Flash Point of Chemicals by Closed Cup Methods.
- (4) The flash point of liquids having a viscosity of 5.5 mm²/s (5.5 cSt) or greater at 40°C (100°F) or 9.5 mm²/s (9.5 cSt) or greater at 25°C (77°F) can be determined in accordance with ASTM D93, *Test Methods for Flash Point by the Pensky-Martens Closed Tester.*

Annex D Combustible Dusts

This annex is not a part of the requirements of this NFPA document but is included for informational purposes only.

D.1 A combustible dust is considered to be a finely divided solid material that is 420 micrometers (μ m) or smaller in diameter (material passing a U.S. No. 40 Standard sieve) that presents an explosion hazard when dispersed and ignited in air.

When a dust becomes suspended in air, there is a risk of a dust cloud ignition leading to a flash fire. The minimum explosible concentration (MEC) is the minimum concentration of combustible dust suspended in a r, measured in mass per unit volume, that will support a deflagration as defined by the text procedure in ASTM E1515, *Standard Test Method for Minimum Explosible Concentration of Combustible Dusts.* Evaluation of the hazard of a combustible dust should be determined by the means of actual test data. Each situation should be evaluated and applicable tests selected. The following list represents the factors that are sometimes used in determining the deflagration hazard of a dust:

- (1) MEC
- (2) Minimum ignition energy (MIE)
- (3) Particle size distribution
- (4) Moisture content as received and as tested
- (5) Maximum explosion pressure at optimum concentration
- (6) Maximum rate of pressure rise at optimum concentration
- (7) K_{st} (normalized rate of pressure rise) as defined in ASTM E1226, Test Method for Pressure and Rate of Pressure Rise for Combustible Dusts
- (8) Layer ignition temperature
- (9) Dust cloud ignition temperature
- (10) Limiting oxidant concentration (LOC) to prevent ignition
- (11) Electrical volume resistivity
- (12) Charge relaxation time
- (13) Chargeability

See NFPA 68, NFPA 652, NFPA 654, and NFPA 664 for additional information about combustible dusts and combustible dust explosions. For purposes of better determining the flammability for a 2 or 3 rating, the most important aspects are particle size distribution, MIE, processing experience, housekeeping, and other related factors.

Additional information on combustible dust hazards can be found on the Occupational Safety and Health Administration (OSHA) website at www.osha.gov. The following publications are recommended for further reference:

Combustible dust explosions poster, available at https://www.osha.gov/Publications/combustibledustposter.pdf.

Combustible dust explosions fact sheet, available at https:// www.osha.gov/OshDoc/data_General_Facts/OSHAcombustibledust.html.

OSHA 3644, Combustible Dust: Firefighting Precautions at Facilities with Combustible Dust, 2013. https://www.osha.gov/OshDoc/ data_General_Facts/OSHAcombustibledust.html.

OSHA 3674, Combustible Dust: Precautions for Firefighters to Prevent Dust Explosions QuickCard, 2013. https://www.osha.gov/ Publications/OSHA_3674.pdf.

Annex E Instability, Thermal Hazard Evaluation Techniques

This annex is not a part of the requirements of this NFPA document but is included for informational purposes only.

E.1 Intrinsic Thermal Stability. Thermal stability for hazard evaluation purposes can be done by a number of methods. Frequently used techniques include differential scanning calorimetry (DSC) and accelerating rate calorimetry (ARC). These tests should be performed in a manner meeting or exceeding the requirements outlined in ASTM E537, *Standard Test Method for Assessing the Thermal Stability of Chemicals by Methods of Differential Thermal Analysis*, or ASTM E1981, *Guide for Assessing the Thermal Stability of Materials by Methods of Accelerating Rate Calorimetry*.

Obtaining the instability rating through testing and instantaneous power density (IPD) data is preferred. This method is discussed in Section E.2, and IPD takes precedence over other small-scale calorimetric methods. When data are unavailable to apply the IPD method, the following two alternatives are available: data from DSC or ARC (or their equivalent) can be used to determine the calculated adiabatic exotherm initiation temperature. This can be used to define ratings of 0, 1, or 2.

Materials that exhibit calculated adiabatic exotherm initiation temperatures below 200°C (392°F) should be rated at least 2; materials that polymerize vigorously with evolution of heat should also be rated at least 2.

Materials that exhibit calculated adiabatic exotherm initiation temperatures between 200°C (392°F) and 500°C (932°F) should be rated 1; materials that might polymerize when heated should also be rated 1.

Materials that do not exhibit an exotherm at temperatures less than or equal to 500°C (932°F) should be rated zero.

Professional judgment should be applied to a chemical being rated using this method that might have an instability rating of 2 or greater.

Reactive materials are far more likely to suffer catalytic or surface effects in small test containers, hence biasing the calculated adiabatic exotherm initiation temperature. This judgment should include comparisons with the qualitative criteria described in Table 7.2, analogy with chemicals of similar chemical structure and historical incidents, plus data obtained using the following methods.

Information to assist this professional judgment includes, but is not limited to, data obtained via DSC or ARC. ASTM D2879, *Standard Test Method for Vapor Pressure–Temperature Relationship and Initial Decomposition Temperature of Liquids by Isoteniscope*, can be used as an indication of thermal stability when data meeting the requirements of ASTM E537 are not available. Self-accelerating decomposition temperature (SADT) test results can also be used. Alternatively, calculations based on the ASTM computer program CHETAH[®] could be carried out. (*For further information on CHETAH, see E.3.*)

It should be noted that tests performed in small-volume analytical apparatus are not predictive of the explosive behavior of large masses of material and therefore cannot distinguish instability ratings of 3 and 4.

Appropriate testing should be conducted for mixtures because the mixtures might react differently than indicated by the individual components.

E.2 Instantaneous Power Density. IPD is calculated as the product of the enthalpy of decomposition/reaction and the initial rate of reaction, determined at 250°C (482°F). This quantity represents the amount of heat energy per unit time per unit volume (watts per milliliter) that a material will initially give at 250°C (482°F). The values that make up the power density can be obtained from thermodynamic tables, calculations, and experimental measurements. The values are obtained from appropriate measurements using DSC (see ASTM E698, Standard Test Method for Arrhenius Kinetic Constants for Thermally Unstable Materials), or ARC (see ASTM E1981, Guide for Assessing the Thermal Stability of Materials by Methods of Accelerating Rate Calorimetry). In a typical calculation, the rates of reaction as a function of temperature are obtained and expressed in terms of an Arrhenius expression and an overall, initial-rate expression (Laidler). This rate expression represents the initial rate of decomposition where the decrease in concentration of the material as a result of the decomposition/reaction has not progressed to a significant (<5 percent) level. This allows the initial concentration of the material to be used in the simplified rate expression. (See Table E.2.)

To clarify the calculation of IPD, a sample calculation is provided.

The initial rate of decomposition of the material at 250° C (482°F) can be calculated using the following Arrhenius expression, where R is the universal gas constant whose value is taken as 1.987 cal/(mol°C):

Rate =
$$\operatorname{conc}^{n} \times \operatorname{A}_{\operatorname{PRE}} \times \operatorname{e}^{-\operatorname{E}_{a/\operatorname{RT}}}$$

where:

conc = initial concentration of material or density of pure material = 0.80 g/mL

n = reaction order = 1

 A_{PRE} = Arrhenius pre-exponential = $1.60 \times 10^{15} \text{ s}^{-1}$

 E_a = Arrhenius activation energy = 36.4 kcal/mol

The units used are as follows:

$$\frac{g}{mL \times s} = \left(\frac{g}{mL}\right)^n \times \left(\frac{g}{mL \times s}\right)^{1-n} \times e^{-\frac{cal/mol}{cal/(mol \times K)^K}}$$

[E.2b]

Rate = $0.80^{+1} \times 1.60 \times 10^{+15} \times e^{-1.987 \times (273+250)}$

Rate =
$$0.79 \frac{g}{mL \times s}$$

Rate = $0.80^{+1} \times 1.60 \times 10^{+15} \times e^{-\frac{36400}{1039}}$

The power density is given as the product of this decomposition and the enthalpy of decomposition (the value of 4.184 W/cal/sec allows the use of units W/mL):

$$IPD = -\Delta H \times Rate$$

where:

[E.2a]

 Δ H = enthalpy of decomposition = -80.5 cal/g

The units used are as follows:

Units:
$$\frac{W}{mL} = \frac{cal}{g} \times \frac{g}{mL \times s} \times 4.184 \frac{W}{cal/s}$$

IPD = -(80.5) × 0.79 × 4.184 $\frac{W}{cal/s}$
IPD = $63 \frac{cal}{s \times mL} \times 4.184 \frac{W}{cal/s}$
IPD = $270 \frac{W}{mL}$

The IPD is used as a positive value: the greater the power density, the greater the rate of energy release per volume. Therefore, the exothermic enthalpy of reaction, thermodynamically taken with a negative sign to show release of heat to the surroundings, is taken as a negative so as to rectify the sign of IPD.

This material, having an IPD of 270 W/mL, would be rated a 3 per Table E.2.

Table E.2 Instability Rating as a Result of Thermal Instability

Instability Rating	Instantaneous Power Density at 250°C (482°F)
4	1000 W/mL or greater
3	At or above 100 W/mL and below 1000 W/mL
2	At or above 10 W/mL and below 100 W/mL
1	At or above 0.01 W/mL and below 10 W/mL
0	Below 0.01 W/mL

E.3 CHETAH. CHETAH is a computer program that is useful for several tasks, including the following:

- (1) Characterizing materials for their ability to decompose with violence
- (2) Estimating heats of reaction or combustion
- (3) Predicting lower flammability limits and certain other flammability parameters
- (4) Predicting thermochemical properties such as standard enthalpies of formation, heat capacities, and free energies of formation

An extensive database of common chemicals, primarily organics, is included in the program, along with a procedure to predict values for additional chemicals using the Benson group additivity method of describing molecules from molecular fragments.

For hazard evaluation, CHETAH is a conservative screening tool for use during the early stages of compound synthesis or process development. Its use should be integrated within an experimental program for testing reactive chemical hazards. CHETAH was not designed to replace the physical testing of materials. Rather, CHETAH's computational results should be used to complement experimental results to help identify the need for further testing in the areas of impact sensitivity and/or flammability.

The potential hazards associated with handling new chemicals will not, in general, be known a priori. Furthermore, experimentally determined thermochemical data for new chemicals used for process design and to predict hazards will often not be available. CHETAH exists largely to allow users to build compounds using group additivity methods, to predict thermochemical properties for compounds and reactions, and to use these predicted properties for hazard evaluation. Users can then use CHETAH's predictions with results from accelerating rate calorimetry (ARC), differential scanning calorimetry (DSC), drop-weight, or other tests to prepare, use, store, or dispose of new compounds safely. Personnel committed to ensuring the safe operations at sites where research, process development, or manufacturing occur could find CHETAH useful in reactive chemicals evaluation programs.

The user might wish to examine the following list of references for examples illustrating how CHETAH can be used to evaluate instability hazards. A more extensive list of references concerning CHETAH can be found at:

www.astm.org/BOOKSTORE/PUBS/DS51F.htm. CHETAH is distributed by ASTM International Inc.

References:

Britton, L. G.; Frurip, D. J. "Further Uses of the Heat of Oxidation in Chemical Hazard Assessment, Process Safety Progress," 22 (1), 1–19, 2003.

Frurip, D., et al., "The Role of ASTM E27 Methods in Hazard Assessment: Part I. Thermal Stability, Compatibility, and Energy Release Estimation Methods, Process Safety Progress," 23(4), 266–278, 2004.

Pasturenzi, C., et al., "Thermochemical stability: A comparison between experimental and predicted data, Journal of Loss Prevention in the Process Industries," 28, 79–91, 2014.

Annex F Water Reactivity Identification Criteria

This annex is not a part of the requirements of this NFPA document but is included for informational purposes only.

F.1 General. It is again noted that with the assignment of water reactivity ratings, a considerable degree of judgment can be needed, as noted in Section 4.2, combined with the guidance in this annex.

F.2 Numerical ratings indicating degrees of water reactivity hazards are detailed in Table F.2. The number, alongside the water reactivity symbol (e.g., W 2), can be used when the information is available to provide information about the degree of water reactivity for emergency responders.

It should be emphasized that the water reactivity rating is not shown in the instability hazard space in the sign, which refers specifically to the intrinsic instability of the material.

Materials that have a rating of 0 or 1 for water reactivity should not be given the ++ symbol in the special hazards space on the placard.

The special hazard \mathbf{W} rating of 3 is the highest rating for water reactivity; there is no special hazard rating of 4 for water reactivity. The purpose of water reactivity is to warn of cases where the use of water (in nonflooding quantities) during emergency response can increase the hazard or change the perceived hazard due to a chemical. Heat of mixing tests between a chemical and water can provide a measure of how vigorous the reaction with water will be in a fire-fighting scenario. The following two scenarios are to be considered: a material that rapidly releases heat on contact with water and a material that rapidly releases heat and gas on contact with water. These guidelines apply only to the first scenario, that is, a chemical that reacts exothermically to release heat on contact with water but does not produce gaseous or low boiling [<100°C (<212°F)] by-products, or azeotropes. The heat of mixing should be determined using a Two Drop Mixing Calorimeter (Hofelich et al.) or equivalent technique using a 1:1 wt/wt ratio of chemical to water. Alternatively, the heat of mixing data can be found in handbooks or calculated.

F.3 Water Reactivity Hazard Degree 0. The chemical is essentially nonreactive with water, therefore the \mathbf{W} symbol is not used. Using the Two Drop Mixing Calorimeter (Hofelich et al.) or equivalent technique, the heat of reaction is less than 30 calories per gram of total mixture (cal/g), using a 1:1 wt/wt ratio of chemical to water. Gas is not generated, although the evaporation rate of a volatile liquid chemical can be increased during water application. The heat of reaction can also be capable of generating sufficient water vapor pressure to damage some closed containers. An example of a water reactivity rating of 0 is diethanolamine with a -6.5 cal/g Two Drop Mixing Calorimeter test result, with no gas release.

F.4 Water Reactivity Hazard Degree 1. The heat of reaction is too small to preclude the use of water during emergency response. Because water is an acceptable agent for dilution of spills and for fire control, chemicals with this rating are not assigned the $\frac{1}{W}$ symbol. Using the Two Drop Mixing Calorimeter (Hofelich et al.) or equivalent technique, the heat of reaction is greater than or equal to 30 calories per gram of total mixture (cal/g) but less than 100 cal/g, using a 1:1 wt/wt ratio of chemical to water. The heat of reaction might be capable of causing the water to boil at atmospheric pressure.

Degree of Hazard	Criteria
4	Not applicable
3 — Requires a ₩ to be displayed in the special hazards quadrant	Materials that react explosively with water without requiring heat or confinement (qualitative description most applicable when assigning water reactivity ratings to solids because the heat of mixing is determined by physical characteristics and the degree to which the material has dissolved)
	Materials whose heat of mixing is greater or equal to 600 cal/g
2 — Requires a ₩ to be displayed in the special hazards quadrant	Materials that react violently with water, including the ability to boil water, or that evolve flammable or toxic gas at a sufficient rate to create hazards under emergency response conditions (qualitative description most applicable when assigning water reactivity ratings to solids because the heat of mixing is determined by physical characteristics and the degree to which the material has dissolved)
	Materials whose heat of mixing is at or above 100 cal/g and less than 600 cal/g
1 — Does NOT require a $\frac{1}{W}$ to be displayed in the special hazards	Materials that react vigorously with water, but not violently (criterion most applicable when assigning water reactivity rating to solids because the heat of mixing is determined by physical characteristics and the degree to which the material has dissolved)
	Materials whose heat of mixing is at or above 30 cal/g and less than 100 cal/g
	Materials that react with water, producing either heat or gas leading to pressurization or toxic or flammable gas hazards
0 — Does NOT require a ₩ to be displayed in the special hazards quadrant	Nonreactive below 30 cal/g

 Table F.2 Degrees of Water Reactivity Hazards

A chemical that on the basis of heat of reaction results alone would normally be assigned a water reactivity rating of 0 should be increased to a water reactivity rating of 1 if any gas is generated via reaction with water, even if the heat of reaction is below 30 cal/g.

The following are examples of chemicals whose release of gas raise them from a water reactivity rating of 0 to a water reactivity rating of 1.

- (1) 50 percent sodium hydroxide. The exothermic heat of solution measured using the Two Drop Mixing Calorimeter is -35.3 cal/g with no gas release; therefore, a water reactivity rating of 1 is assigned. It should be noted that the heat of solution of a solid material such as sodium hydroxide is not constant but decreases as the solid goes into solution. The first water that is added to sodium hydroxide could in fact boil, even though the Two Drop Mixing Calorimeter indicates a heat release of much less than 100 cal/g. Where large quantities of such solids are wetted by small quantities of water, the instability hazard might be better represented by a water reactivity rating of $\frac{W}{W}$ 2.
- (2) *Sodium hydrosulfite.* The exothermic reaction with water releases heat, which can lead to spontaneous combustion of a solid. The rating assigned to this chemical is a water reactivity rating of 1.
- (3) Acetic anhydride. The exothermic 1:1 molar reaction with water produces 2 moles of acetic acid and no gas release. Because the reactants are not completely miscible at ambient temperature, the reaction tends to be slow unless a solubilizing agent is present. The water reactivity rating assigned to this chemical is 1.

F.5 Water Reactivity Hazard Degree 2. The reaction with water is rapid and should be used only where it can be applied in flooding quantities (which can be imprac ical for large piles of solids). Using the Two Drop Mixing Calorimeter test, the heat of reaction is greater than or equal to 100 cal/g but less than 600 cal/g using a 1:1 wt/wt ratio of chemical to water. The heat of reaction is likely to boil the water at 1:1 wt/wt ratios and can be sufficient both to boil the water and to vaporize the chemical. Other than carbon dioxide or steam (or other nonhazardous gases), if flammable or toxic gases are generated in hazardous quantities via reaction with water, the water reactivity rating of 1 determined on the basis of heat of reaction would be raised to a water reactivity rating of 2 (Ψ 2). The following are examples of chemicals whose release of gas raise them from a water reactivity rating of 1 to a water reactivity rating of 2:

- (1) *Calcium carbide.* Although the dry solid does not burn, a nonviolent but vigorous exothermic reaction with water produces calcium hydroxide plus flammable acetylene gas. Trapped pockets of acetylene in a pile of solid can ignite and explode.
- (2) *Dichlorosilane*. In contact with water, exothermic hydrolysis is accompanied by evaporation of the volatile liquid phase. Toxic dichlorosilane plus hydrogen chloride gases are released and spontaneous ignition of the dichlorosilane can occur.
- (3) *Thionyl chloride.* The heat release using the Two Drop Mixing Calorimeter test is -61.1 cal/g with release of gas.

F.6 Water Reactivity Hazard Degree 3. Using the Two Drop Mixing Calorimeter test, the heat of reaction is greater than or equal to 600 cal/g. This is often sufficient to cause ignition of flammable components.

The Ψ 3 rating is not increased to a Ψ 4 rating if gas is generated, because "explosive reaction" already implies gas generation. An example of a Ψ 3 rating is triethyl aluminum. The heat release using the Two Drop Mixing Calorimeter test is -1008 cal/g with release of gas.

The Two Drop Mixing Calorimeter test data presented in this annex were published by Hofelich.

Annex G Comparison of NFPA 704 Numerical Hazard Rating with OSHA's Hazard Classification System

This annex is not a part of the requirements of this NFPA document but is included for informational purposes only.

G.1 NFPA and the Technical Committee on Classification are aware of the potential impact that the globally harmonized system (GHS) incorporation into OSHA's Hazard Communication Standard (HazCom) 2012 has on the NFPA 704 standard system and its users. Currently, NFPA 704 stands as written and there is no immediate plan to change the system. NFPA 704 is widely used and recognized by emergency responders and safety personnel for identifying the hazards of short-term/ acute exposure to materials under conditions of fire, spill, or similar emergencies. The Committee will carefully consider any impact before changing a consensus standard system that has been protecting emergency responders, employees, and the public for more than 50 years.

The NFPA 704 diamond remains as a warning sign for first responders. It provides information required for the first responders to assess hazards presented by materials within an occupancy or industrial location. It provides, in a concise format, a quick presentation of all hazardous materials present. This provides critical size-up information needed to evaluate potential short-term exposure to the hazardous materials within the facility against first responder training and personal protective equipment. From this initial information, informed decisions can be made about the next steps to take to protect responders and the community and what additional resources might be needed to mitigate the event.

OSHA and NFPA are in agreement that there are differences between HazCom 2012 and NFPA 704; the two systems were developed for different purposes. There are two distinct sets of numbers used for the two systems: HazCom 2012 uses a *hazard classification system* whereas NFPA 704 uses a *hazard rating system*. The NFPA 704 label was developed to provide information to emergency personnel responding to a spill or fire. In comparison, OSHA's hazard classification system provides information for workers exposed to materials primarily under normal conditions of use. The numbers that are part of the OSHA HazCom 2012 hazard classification for labels and safety data sheets in Appendixes A, B, and C of the OSHA standard. In contrast, the numbers in NFPA 704 are relative ratings of hazards developed for emergency response. HazCom 2012 numbers are included in Section 2 of the new safety data sheet (SDS) format. The concern is that these numbers could be mistakenly identified as NFPA 704 ratings and be transcribed to the NFPA 704 diamond. Because the two systems have inverse number systems (e.g., 4 is the most hazardous rating in NFPA 704 but the least hazardous in OSHA's classification), a transcription error could lead to incorrect identification of the hazard in an emergency response. It should be noted that the hazard classification numbers are *not* required on HazCom 2012 labels.

Both systems have value for different purposes. The key to distinguishing the two systems is education. NFPA and OSHA developed a 'Quick Card' to explain the two systems and their differences. (*See Figure G.1.*) This card is available for download at www.nfpa.org/704 under Additional Information on the first tab, and on the OSHA website at: www.osha.gov/Publications/OSHA3678.pdf. You can also sign up for email alerts at the top of the document information page at www.nfpa.org/704 to receive an email alert when any additional NFPA 704 document-related information is posted to the page. NFPA will continue discussions with OSHA and with emergency responders to ensure that all concerns are addressed.

Annex H Sample NFPA 704 Placard Information for Use in Safety Publications

H.1 NFPA frequently receives requests for permission to use the NFPA 704 diamond in safety and emergency response publications and training materials. This annex is provided as an example of labels and text that can be used within publications and training documents that summarizes the NFPA 704 label system. [See Figure H.1(a) and Figure H 1(b).]

The following text should accompany the placard examples published in any document:

NFPA 704 provides a simple, readily recognizable, and easily understood system of markings that provides a general idea of the hazards of a material and the severity of these hazards as they relate to emergency response. The standard does not tell you when such labels are required but provides the criteria for labeling when such labels are required by another code, standard, regulation, or jurisdiction.

The ratings shown in Figure H.1(a) and Figure H.1(b) are in summary form only. The current edition of NFPA 704 should be consulted for the detailed criteria used to determine the correct numbers to be placed in the quadrants for a specific material.

Reprinted with permission from NFPA 704-2017, System for the Identification of the Hazards of Materials for Emergency Response, Copyright © 2016, National Fire Protection Association. This reprinted material is not the complete and official position of the NFPA on the referenced subject, which is represented solely by the standard in its entirety. The classification of any particular material within this system is the sole responsibility of the user and not the NFPA. NFPA bears no responsibility for any determinations of any values for any particular material classified or represented using this system.

OSHA®QUICK NFPA®OSHA®QUICK

Comparison of NFPA 704 and HazCom 2012 Labels

	22 W NFPA 704	HazCom 2012		
Purpose	Provides basic information for emergency personnel responding to a fire or spill and those planning for emergency response.	Informs workers about the hazards of chemicals in workplace under normal conditions of use and foreseeable emergencies.		
Number System: NFPA Rating and OSHA's Classification System	0–4 0–least hazardous 4–most hazardous	 1-4 1-most severe hazard 4-least severe hazard The Hazard category numbers are NOT required to be on labels but are required on SDSs in Section 2. Numbers are used to CLASSIFY hazards to determine what label information is required. 		
Information Provided on Label	 Health-Blue Flammability-Red Instability-Yellow Special Hazards*-White *OX Oxidizers W Water Reactives SA Simple Asphyxiants 	 Product Identifier Signal Word Hazard Statement(s) Pictogram(s) Precautionary statement(s); and Name, address, and phone number of responsible party. 		
Health Hazards on Label	Acute (short term) health hazards ONLY. Acute hazards are more typical for emergency response applications. Chronic health effects are not covered by NFPA 704.	Acute (short term) and chronic (long term) health hazards. Both acute and chronic health effects are relevant for employees working with chemicals day after day. Health hazards include acute hazards such as eye irritants, simple asphyxiants, and skin corrosives as well as chronic hazards such as carcinogens.		
Flammability/ Physical Hazards on Label	NFPA divides flammability and instability hazards into two separate numbers on the label. Flammability in red section. Instability in yellow section.	A broad range of physical hazard classes are listed on the label including explosives, flammables, oxidizers, reactives, pyrophorics, combustible dusts, and corrosives		
Where to get information to place on label	Rating system found in NFPA Fire Protection Guide to Hazardous Materials OR NFPA 704 Standard System for Identification of the Hazards of Materials for Emergency Response 2012 Edition. Tables 5.2, 6.2, 7.2 and Chapter 8 of NFPA 704.	OSHA Hazard Communication Standard 29 CFR 1910.1200 (2012). 1) Classify using Appendix A (Health Hazards) and Appendix B (Physical Hazards). 2) Label using Appendix C.		
Other	The hazard category numbers found in section 2 of the HC2012 compliant SDSs are NOT to be used to fill in the NFPA 704 diamond.	Supplemental information may also appear on the label such as any hazards not otherwise classified, and directions for use.		
website	www.nfpa.org/704	www.osha.gov OR www.osha.gov/dsg/hazcom/index.html		
For more information: National Fire Protection Association www.nfpa.org I 800.344.3555 National Fire Protection Association U.S. Department of Labor www.osha.gov I 800.321.0SHA (6742)				





The substance: "NOMIXUP 7042012"

To create an OSHA label per HazCom 2012:

<u>Step 1:</u> Perform the classification in accordance with Appendix A: Health Hazards & Appendix B Physical Hazards of 29 CFR 1910.1200 — this is where you find the criteria for each hazard class and hazard category.

Class: Flammable Gas, Category 1

Class: Carcinogen, Category 1B

Class: Specific Target Organ Toxicity (Single Exposure), Category 3

Class: Substances and Mixtures Which, in Contact with Water, Emit Flammable Gases, Category 3

<u>Step 2</u>: Gather labeling information (Pictograms, Signal Word, Hazard Statements) from Appendix C of 29 CFR 1910.1200 based on the chemical's hazard class and category.

Step 3: Create the Label

lenifier: NOMIXUP 7042	** 🚯 🚯 🕩	
azard Statements.	DANGER! Extremely Flammable Gas May Cause Cancer May Cause Reperancy Imitation	
ecautionary Statements	In Contact with Water Releases Flammable Gas Keep away from heat sparks open flames but surfaces. No Smoking Obtain special instructions before use. Do not hand/e umit all safer precausions have been rand and understood.	
	Los foit statule; tunn all safety precautions make exerting a numeroson. Avoid branthyre sagers and makes Movid branthyre sagers and make social statules and the safety If inhabet. Remove persons to fresh nat and keep confortable for breathing. Call proises exerting doesn't if you ded unwell. Leaking Gas Fare. Do not eximpash unless loak can be stopped safely. Eliminate all ignition sources if safe to do so.	
	Store in tightly closed container in a well-ventilated place, locked up. Use outdoors or use in a well-ventilated place. Dispose of contents in accordance with local regional national regulations. 3 Main SL Anveberg, NY, USA 1-800-000-1111	

To Create NFPA 704 label:

<u>Step 1</u>: Collect information on hazards from applicable sections of SDS. Some SDSs may provide the NFPA diamond symbol with hazard rating numbers filled in already. <u>Note: Do NOT</u> use the hazard category numbers given in section 2 of HazCom 2012 compliant SDS on 704 label!

If the diamond is not provided on the SDS you can obtain the information under the following sections of the SDS. Note that additional information may be provided in other sections of the SDS.

- · Health hazard information under Section 11
- Flammability information under Section 9
- Instability information under Section 10
- Special information under Section 9, 10, 11

<u>Step 2</u>: Obtain current edition copy of NFPA 704 or view on line at *www.nfpa.org/704*. Compare the criteria on the SDS sections as shown above with the criteria shown in Tables 5.2 (Health), 6.2 (Flammability), 7.2 (Instability) and 8.2 (Special Hazards).

<u>Step 3</u>: Place numbers for the degree of hazard associated with the criteria obtained in Step 2 in the correct guadrant of NFPA 704 placard.



FIGURE G.1 Continued

HAZARDOUS MATERIALS CLASSIFICATION

HEALTH RATING

- 4 Can be lethal
- 3 Serious or permanent injury
- 2 Temporary incapacitation or residual injury
- 1 Significant irritation
- 0 No hazard beyond ordinary combustibles

FLAMMABILITY RATING

- 4 Rapidly or completely vaporize and burn readily
- 3 Ignite readily in ambient conditions
- 2 Ignite when moderately heated
- 1 Require preheating for ignition
- 0 Will not burn under
 - normal fire conditions

SPECIAL HAZARDS

Oxidizers	OX
Water Reactives	₩
Simple Asphyxiants	SA

No other hazards should be listed in this quadrant. In cases where a unique hazard symbol exists it must be placed outside of the white special hazard quadrant.



INSTABILITY RATING

- 4 May detonate or have explosive reaction
- 3 Shock and heat may detonate or cause explosive reaction
- 2 Violent chemical change at elevated temperatures
- 1 Unstable if heated
- 0 Normally stable



FIGURE H.1(b) Hazardous Materials Classification.

Annex I Informational References

I.1 Referenced Publications. The documents or portions thereof listed in this annex are referenced within the informational sections of this standard and are not part of the requirements of this document unless also listed in Chapter 2 for other reasons

I.1.1 NFPA Publications. National Fire Protection Association, 1 Batterymarch Park, Quincy, MA 02169-7471.

NFPA 30, Flammable and Combustible Liquids Code, 2015 edition.

NFPA 68, Standard on Explosion Protection by Deflagration Venting, 2013 edition.

NFPA 400, Hazardous Materials Code, 2016 edition.

NFPA 652, Standard on the Fundamentals of Combustible Dust, 2016 edition.

NFPA 654, Standard for the Prevention of Fire and Dust Explosions from the Manufacturing, Processing, and Handling of Combustible Particulate Solids, 2017 edition.

NFPA 664, Standard for the Prevention of Fires and Explosions in Wood Processing and Woodworking Facilities, 2017 edition.

Fire Protection Guide to Hazardous Materials, 14th edition, 2010.

I.1.2 Other Publications.

I.1.2.1 ASTM Publications. ASTM International, 100 Barr Harbor Drive, P.O. Box C700, West Conshohocken, PA 19428-2959.

ASTM D56, Standard Method of Test for Flash Point by the Tag Closed Tester, 2005 (2010).

ASTM D86, Standard Test Method for Distillation of Petroleum Products at Atmospheric Pressure, 2012.

ASTM D93, Test Methods for Flash Point by the Pensky-Martens Closed Tester, 2013e1.

ASTM D2879, Standard Test Method for Vapor Pressure–Temperature Relationship and Initial Decomposition Temperature of Liquids by Isoteniscope, 2010.

ASTM D3278, Standard Test Methods for Flash Point of Liquids by Small Scale Closed-Cup Apparatus, 1996 (2011).

ASTM D3828, Standard Test Method for Flash Point by Small Scale Closed Tester, 2012a.

ASTM E537, Standard Test Method for Assessing the Thermal Stability of Chemicals by Methods of Differential Thermal Analysis, 2012.

ASTM E698, Standard Test Method for Arrhenius Kinetic Constants for Thermally Unstable Materials, 2011.

ASTM E1226, Test Method for Pressure and Rate of Pressure Rise for Combustible Dusts, 2012a.

ASTM E1515, Standard Test Method for Minimum Explosible Concentration of Combustible Dusts, 2007.

ASTM E1981, Guide for Assessing the Thermal Stability of Materials by Methods of Accelerating Rate Calorimetry, 1998 (2012)e2.

Test Method E502, Standard Test Method for Selection and Use of ASTM Standards for the Determination of Flash Point of Chemicals by Closed Cup Methods, 2007 (2013).

I.1.2.2 UN Publications. United Nations, UN Plaza, New York, NY 10017.

Recommendations on the Transport of Dangerous Goods, Model Regulations, 18th revised edition.

I.1.2 3 Other Publications.

American Coatings Association, *Hazardous Materials Identifica*tion System Revised, Implementation Manual, 1981.

Bretherick, L., *Handbook of Reactive Chemicals*, 7th edition, Boston: Butterworths, 2006.

Britton, L. G., "Survey of Fire Hazard Classification Systems for Liquids," *Process Safety Progress*, Vol. 18, No. 4, Winter, 1999.

Britton, L. G., Frurip, D. J. "Further Uses of the Heat of Oxidation in Chemical Hazard Assessment, Process Safety Progress," 22(1), 1–19, 2003.

Frurip, D., et al., "The Role of ASTM E27 Methods in Hazard Assessment: Part I. Thermal Stability, Compatibility, and Energy Release Estimation Methods, Process Safety Progress," 23(4), 266–278, 2004.

Hanley, B., "A Model for the Calculation and the Verification of Closed Cup Flash Points for Multicomponent Mixtures," *Process Safety Progress*, Summer 1998, pp. 86–97.

Hofelich, T. C., "A Quantitative Approach to Determination of NFPA Reactivity Hazard Rating Parameters," *Process Safety Progress*, Vol. 16, No. 3, p. 121, 1997.

Hofelich, T. C., D. J. Frurip, and J. B. Powers, "The Determination of Compatibility via Thermal Analysis and Mathematical Modeling," *Process Safety Progress*, Vol. 13, No 4. pp. 227–233, 1994. Hofelich, T. C. and LaBarge, M. S., "On the Use and Misuse of Detected Onset Temperature of Calorimetric Experiments for Hazardous Chemicals," *Journal of Loss Prevention in the Process Industries*, Vol. 15, pp. 163–8, 2002.

Laidler, K. L., *Chemical Kinetics*, Chapter 3, New York: McGraw-Hill, 1965.

Pasturenzi, C., et al., "Thermochemical stability: A comparison between experimental and predicted data," Journal of Loss Prevention in the Process Industries, 28, 79–91, 2014.

Stull, D. R., "Fundamentals of Fire and Explosion," AIChE Monograph Series, No. 10, Vol. 73, 1977.

I.2 Informational References. The following documents or portions thereof are listed here as informational resources only. They are not a part of the requirements of this document.

I.2.1 ASTM Publications. ASTM International, 100 Barr Harbor Drive, P.O. Box C700, West Conshohocken, PA 19428-2959.

ASTM D235, Standard Specification for Mineral Spirits (Petroleum Spirits) (Hydrocarbon Dry Cleaning Solvent), 2002 (2012).

ASTM D6668, Standard Test Method for the Discrimination Between Flammability Ratings of F = 0 and F = 1, 2001 (2010).

I.2.2 OSHA Publications. U.S. Department of Labor, Occupational Safety & Health Administration, 200 Constitution Ave., NW Washington, DC 20210.

Combustible dust explosions poster, available at https://www.osha.gov/Publications/combustibledustposter.pdf.

Combustible dust explosions fact sheet, available at https:// www.osha.gov/OshDoc/data_General_Facts/OSHAcombustibledust.html.

OSHA 3644, Combustible Dust: Firefighting Precautions at Facilities with Combustible Dust, 2013. https://www.osha.gov/Publications/OSHA_3644.pdf.

OSHA 3674, Combustible Dust: Precautions for Firefighters to Prevent Dust Explosions QuickCard, 2013. https://www.osha.gov/ Publications/OSHA_3674.pdf.

I.3 References for Extracts in Informational Sections. (Reserved)

Index

Copyright © 2016 National Fire Protection Association. All Rights Reserved.

The copyright in this index is separate and distinct from the copyright in the document that it indexes. The licensing provisions set forth for the document are not applicable to this index. This index may not be reproduced in whole or in part by any means without the express written permission of NFPA.

-A-Administration, Chap. 1 Application, 1.3 Equivalency, 1.5 Purpose, 1.2 Retroactivity, 1.4 Scope, 1.1 Approved Definition, 3.2.1, A.3.2.1

Authority Having Jurisdiction (AHJ) Definition, 3.2.2, A.3.2.2

-B-

Boiling Point Definition, 3.3.1, A.3.3.1

-C-

Combustible Dusts, Annex D Comparison of NFPA 704 Numerical Hazard Rating with OSHA's Hazard Classification System, Annex G Cryogenic Fluid

Definition, 3.3.2

Definit ons, Chap. 3

Fire Point

-E-

-D-

Explanatory Material, Annex A

-F-

Definition, 3.3.3 Flammability, Annex C Development of Flammability Ratings, C.1 Flash Point Test Methods, C.3 Significance of Flash Point, C.2 Flammability Hazards, Chap. 6 Aerosols, 6.3 Degrees of Hazard, 6.2, A.6.2 General, 6.1 Flash Point Definition, 3.3.4, A.3.3.4 Frostbite Definition, 3.3.5, A.3.3.5

-G-

General, Chap. 4 Assignment of Ratings, 4.2 Description, 4.1 Location of Signs, 4.3, A.4.3

-H-

Health Hazard Rating, Annex B
Additional Revisions to Health Hazard Rating, B.2
Development of Quantitative Guidelines for Health, B.1
Adoption of UN Criteria, B.1.4
Hazard Considerations Using HMIS Criteria, B.1.5
Inhalation Hazard Considerations Using DOT Criteria, B.1.1
Inhalation Hazard Considerations Using UN Criteria, B.1.2
Oral and Dermal Hazard Considerations Using UN Criteria, B.1.3
UN Definitions, B.3
Health Hazards, Chap. 5
Degrees of Hazard, 5.2, A.5.2

-I-

Identification of Materials by Hazard Rating System, Chap. 9 Symbol Arrangement, 9.1
Informational References, Annex I
Instability Hazards, Chap. 7 Degrees of Hazard, 7.2 General, 7.1
Instability, Thermal Hazard Evaluation Techniques, Annex E CHETAH, E.3 Instantaneous Power Densi y, E 2 Intrinsic Thermal Stability, E.1

-M-

Materials Definition, 3.3.6 Stable Materials Definition, 3.3.6.1 Unstable Materials Definition, 3.3.6.2

General, 5.1

-R-

Referenced Publications, Chap. 2

-S-

Sample NFPA 704 Placard Information for Use in Safety Publications, Annex H Shall Definition, 3.2.3 Simple Asphyxiant Gas Definition, 3.3.7 Special Hazards, Chap. 8 General, 8.1 Symbols, 8.2 Standard Definition, 3.2.4 -W-Water Reactivity Identification Criteria, Annex F General, F.1 Water Reactivity Hazard Degree 0, F.3 Water Reactivity Hazard Degree 1, F.4 Water Reactivity Hazard Degree 2, F.5 Water Reactivity Hazard Degree 3, F.6

Sequence of Events for the Standards Development Process

Once the current edition is published, a Standard is opened for Public Input.

Step 1 – Input Stage

- Input accepted from the public or other committees for consideration to develop the First Draft
- Technical Committee holds First Draft Meeting to revise Standard (23 weeks); Technical Committee(s) with Correlating Committee (10 weeks)
- Technical Committee ballots on First Draft (12 weeks); Technical Committee(s) with Correlating Committee (11 weeks)
- Correlating Committee First Draft Meeting (9 weeks)
- Correlating Committee ballots on First Draft (5 weeks)
- First Draft Report posted on the Doc Info Page

Step 2 – Comment Stage

- Public Comments accepted on First Draft (10 weeks) following posting of First Draft Report
- If Standard does not receive Public Comments and the Technical Committee chooses not to hold a Second Draft meeting, the Standard becomes a Consent Standard and is sent directly to the Standards Council for issuance (see Step 4) or
- Technical Committee holds Second Draft Meeting (21 weeks); Technical Committee(s) with Correlating Committee (7 weeks)
- Technical Committee ballots on Second Draft (11 weeks); Technical Committee(s) with Correlating Committee (10 weeks)
- Correlating Committee Second Draft Meeting (9 weeks)
- Correlating Committee ballots on Second Draft (8 weeks)
- Second Draft Report posted on the Doc Info Page

Step 3 – NFPA Technical Meeting

- Notice of Intent to Make a Motion (NITMAM) accepted (5 weeks) following the posting of Second Draft Report
- NITMAMs are reviewed and valid motions are certified by the Motions Committee for presentation at the NFPA Technical Meeting
- NFPA membership meets each June at the NFPA Technical Meeting to act on Standards with "Certified Amending Motions" (certified NITMAMs)
- Committee(s) vote on any successful amendments to the Technical Committee Reports made by the NFPA membership at the NFPA Technical Meeting

Step 4 - Council Appeals and Issuance of Standard

- Notification of intent to file an appeal to the Standards Council on Technical Meeting action must be filed within 20 days of the NFPA Technical Meeting
- Standards Council decides, based on all evidence, whether to issue the standard or to take other action

Notes:

- 1. Time periods are approximate; refer to published schedules for actual dates.
- 2. Annual revision cycle documents receiving certified amending motions take approximately 101 weeks to complete.
- 3. Fall revision cycle documents receiving certified motions take approximately 141 weeks to complete.

Committee Membership Classifications^{1,2,3,4}

The following classifications apply to Committee members and represent their principal interest in the activity of the Committee.

- 1. M *Manufacturer:* A representative of a maker or marketer of a product, assembly, or system, or portion thereof, that is affected by the standard.
- 2. U *User:* A representative of an entity that is subject to the provisions of the standard or that voluntarily uses the standard.
- 3. IM *Installer/Maintainer*: A representative of an entity that is in the business of installing or maintaining a product, assembly, or system affected by the standard.
- 4. L *Labor:* A labor representative or employee concerned with safety in the workplace.
- 5. RT *Applied Research/Testing Laboratory:* A representative of an independent testing laboratory or independent applied research organization that promulgates and/or enforces standards.
- 6. E *Enforcing Authority:* A representative of an agency or an organization that promulgates and/or enforces standards.
- 7. I *Insurance:* A representative of an insurance company, broker, agent, bureau, or inspection agency.
- 8. C *Consumer:* A person who is or represents the ultimate purchaser of a product, system, or service affected by the standard, but who is not included in (2).
- 9. SE *Special Expert:* A person not representing (1) through (8) and who has special expertise in the scope of the standard or portion thereof.

NOTE 1: "Standard" connotes code, standard, recommended practice, or guide.

NOTE 2: A representative includes an employee.

NOTE 3: While these classifications will be used by the Standards Council to achieve a balance for Technical Committees, the Standards Council may determine that new classifications of member or unique interests need representation in order to foster the best possible Committee deliberations on any project. In this connection, the Standards Council may make such appointments as it deems appropriate in the public interest, such as the classification of "Utilities" in the National Electrical Code Committee.

NOTE 4: Representatives of subsidiaries of any group are generally considered to have the same classification as the parent organization.

Submitting Public Input / Public Comment Through the Online Submission System:

Soon after the current edition is published, a Standard is open for Public Input.

Before accessing the Online Submission System, you must first sign in at www.NFPA.org. Note: You will be asked to sign-in or create a free online account with NFPA before using this system:

- a. Click on Sign In at the upper right side of the page.
- b. Under the Codes and Standards heading, click on the List of NFPA Codes & Standards, and then select your document from the list or use one of the search features.

OR

a. Go directly to your specific document page by typing the convenient shortcut link of www.nfpa.org/ document# (Example: NFPA 921 would be www.nfpa.org/921). Sign in at the upper right side of the page.

To begin your Public Input, select the link "The next edition of this standard is now open for Public Input" located on the About tab, Current & Prior Editions tab, and the Next Edition tab. Alternatively, the Next Edition tab includes a link to Submit Public Input online.

At this point, the NFPA Standards Development Site will open showing details for the document you have selected. This "Document Home" page site includes an explanatory introduction, information on the current document phase and closing date, a left-hand navigation panel that includes useful links, a document Table of Contents, and icons at the top you can click for Help when using the site. The Help icons and navigation panel will be visible except when you are actually in the process of creating a Public Input.

Once the First Draft Report becomes available there is a Public Comment period during which anyone may submit a Public Comment on the First Draft. Any objections or further related changes to the content of the First Draft must be submitted at the Comment stage.

To submit a Public Comment you may access the Online Subm ssion System utilizing the same steps as previously explained for the submission of Public Input.

For further information on submitting public input and public comments, go to: http://www.nfpa.org/publicinput.

Other Resources Available on the Document Pages

About tab: View general document and subject-related information.

Current & Prior Editions tab: Research current and previous edition information on a Standard.

Next Edition tab: Follow the committee's progress in the processing of a Standard in its next revision cycle.

Technical Committee tab: View current committee member rosters or apply to a committee.

Technical Questions tab: For members and Public Sector Officials/AHJs to submit questions about codes and standards to NFPA staff. Our Technical Questions Service provides a convenient way to receive timely and consistent technical assistance when you need to know more about NFPA codes and standards relevant to your work. Responses are provided by NFPA staff on an informal basis.

Products & Training tab: List of NFPA's publications and training available for purchase.

Information on the NFPA Standards Development Process

I. Applicable Regulations. The primary rules governing the processing of NFPA standards (codes, standards, recommended practices, and guides) are the NFPA *Regulations Governing the Development of NFPA Standards (Regs)*. Other applicable rules include NFPA *Bylaws*, NFPA *Technical Meeting Convention Rules*, NFPA *Guide for the Conduct of Participants in the NFPA Standards Development Process*, and the NFPA *Regulations Governing Petitions to the Board of Directors from Decisions of the Standards Council.* Most of these rules and regulations are contained in the *NFPA Standards Directory*. For copies of the *Directory*, contact Codes and Standards Administration at NFPA Headquarters; all these documents are also available on the NFPA website at "www.nfpa.org."

The following is general information on the NFPA process. All participants, however, should refer to the actual rules and regulations for a full understanding of this process and for the criteria that govern participation.

II. Technical Committee Report. The Technical Committee Report is defined as "the Report of the responsible Committee(s), in accordance with the Regulations, in preparation of a new or revised NFPA Standard." The Technical Committee Report is in two parts and consists of the First Draft Report and the Second Draft Report. (See *Regs* at Section 1.4.)

III. Step 1: First Draft Report. The First Draft Report is defined as "Part one of the Technical Committee Report, which documents the Input Stage." The First Draft Report consists of the First Draft, Public Input, Committee Input, Committee and Correlating Committee Statements, Correlating Input, Correlating Notes, and Ballot Statements. (See *Regs* at 4.2.5.2 and Section 4.3.) Any objection to an action in the First Draft Report must be raised through the filing of an appropriate Comment for consideration in the Second Draft Report or the objection will be considered resolved. [See *Regs* at 4.3.1(b).]

IV. Step 2: Second Draft Report. The Second Draft Report is defined as "Part two of the Technical Committee Report, which documents the Comment Stage." The Second Draft Report consists of the Second Draft, Public Comments with corresponding Committee Actions and Committee Statements, Correlating Notes and their respective Committee Statements, Correlating Revisions, and Ballot Statements. (See *Regs* at 4.2.5.2 and Section 4.4.) The First Draft Report and the Second Draft Report together constitute the Technical Committee Report. Any outstanding objection following the Second Draft Report must be raised through an appropriate Amending Motion at the Association Technical Meeting or the objection will be considered resolved. [See *Regs* at 4.4.1 (b).]

V. Step 3a: Action at Association Technical Meeting. Following the publication of the Second Draft Report, there is a period during which those wishing to make proper Amending Motions on the Technical Committee Reports must signal their intention by submitting a Notice of Intent to Make a Motion (NITMAM). (See *Regs* at 4.5.2.) Standards that receive notice of proper Amending Motions (Certified Amending Motions) will be presented for action at the annual June Association Technical Meeting. At the meeting, the NFPA membership can consider and act on these Certified Amending Motions as well as Follow-up Amending Motions, that is, motions that become necessary as a result of a previous successful Amending Motion. (See 4.5 3.2 through 4 5.3 6 and Table 1, Columns 1-3 of *Regs* for a summary of the available Amending Motions and who may make them.) Any outstanding objection following action at an Association Technical Meeting (and any further Technical Committee consideration following successful Amending Motions, see *Regs* at 4.5.3.7 through 4.6.5.3) must be raised through an appeal to the Standards Council or it will be considered to be resolved.

VI. Step 3b: Documents Forwarded Directly to the Council. Where no NITMAM is received and certified in accordance with the Technical Meeting Convention Rules, the standard is forwarded directly to the Standards Council for action on issuance. Objections are deemed to be resolved for these documents. (See *Regs* at 4.5.2.5.)

VII. Step 4a: Council Appeals. Anyone can appeal to the Standards Council concerning procedural or substantive matters related to the development, content, or issuance of any document of the Association or on matters within the purview of the authority of the Council, as established by the Bylaws and as determined by the Board of Directors. Such appeals must be in written form and filed with the Secretary of the Standards Council (see *Regs* at Section 1.6). Time constraints for filing an appeal must be in accordance with 1.6.2 of the *Regs*. Objections are deemed to be resolved if not pursued at this level.

VIII. Step 4b: Document Issuance. The Standards Council is the issuer of all documents (see Article 8 of *Bylaws*). The Council acts on the issuance of a document presented for action at an Association Technical Meeting within 75 days from the date of the recommendation from the Association Technical Meeting, unless this period is extended by the Council (see *Regs* at 4.7.2). For documents forwarded directly to the Standards Council, the Council acts on the issuance of the document at its next scheduled meeting, or at such other meeting as the Council may determine (see *Regs* at 4.5.2.5 and 4.7.4).

IX. Petitions to the Board of Directors. The Standards Council has been delegated the responsibility for the administration of the codes and standards development process and the issuance of documents. However, where extraordinary circumstances requiring the intervention of the Board of Directors exist, the Board of Directors may take any action necessary to fulfill its obligations to preserve the integrity of the codes and standards development process and to protect the interests of the Association. The rules for petitioning the Board of Directors can be found in the *Regulations Governing Petitions to the Board of Directors from Decisions of the Standards Council* and in Section 1.7 of the *Regs.*

X. For More Information. The program for the Association Technical Meeting (as well as the NFPA website as information becomes available) should be consulted for the date on which each report scheduled for consideration at the meeting will be presented. For copies of the First Draft Report and Second Draft Report as well as more information on NFPA rules and for up-to-date information on schedules and deadlines for processing NFPA documents, check the NFPA website (www.nfpa.org/aboutthecodes) or contact NFPA Codes & Standards Administration at (617) 984-7246.



Our online community lets you connect with NFPA® technical staff, network with professionals worldwide, and explore content on everything from fire protection systems, electrical, building and life safety, emergency response, and more. Plus, you can:

SHARE ideas ASK questions POST discussions

Have a question about the code or standard you're reading right now? NFPA Members enjoy exclusive access to the 'Members Only' section on NFPA Xchange, where you can submit technical standards questions,* as well as search questions submitted by others and view the answers!

JOIN NFPA Xchange TODAY—IT'S FREE AND EASY!







INformation. INtelligence. Get INvolved.

*For the full terms of use, please visit nfpa.org/standard_items/terms-of-use#xchange. NFPA® is a registered trademark of the National Fire Protection Association, Quincy, MA 02169