

NFPA 704

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

2007 Edition



NFPA, 1 Batterymarch Park, Quincy, MA 02169-7471
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NFPA 704

Standard System for the

Identification of the Hazards of Materials for Emergency Response

2007 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 July 28, 2006, with an effective date of August 17, 2006, and supersedes all previous editions.

This edition of NFPA 704 was approved as an American National Standard on August 17, 2006.

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 the Instability Hazard Rating, formerly the 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 quantitative criteria for flammability ratings for solids; and quantitative criteria for a flammability rating of zero, including introduction 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.

This 2007 edition clarifies numerous topics, including the special hazards quadrant, placement and hierarchy of symbols, and the new Simple Asphyxiant (SA) designation and other optional symbols. Requirements have been added for the classification of flammability rating for dusts.

Technical Committee on Classification and Properties of Hazardous Chemical Data

Gary Robinson, *Chair*

Liberty Mutual Group, IL [I]
Rep. Property Casualty Insurers Association of America

Robert A. Michaels, *Secretary*

RAM TRAC Corporation, NY [SE]

Laurence G. Britton, Neolytica, WV [SE]

Lance Edwards, National Paint & Coatings Association,
DC [M]

Richard Gowland, European Process Safety Centre,
United Kingdom [U]

Ronald Keefer, Menlo Park Fire Protection District, CA [E]

Ron A. Kirsch, PureSafety, Incorporated, TN [SE]

Arthur A. Krawetz, Phoenix Chemical Laboratory
Incorporated, IL [RT]

F. Owen Kubias, Rocky River, OH [SE]

Roland J. Land, Risk Control Consultants, LLC, VA [SE]

Kenneth D. Lewis, Degussa Corporation, AL [U]

Rep. NFPA Industrial Fire Protection Section

David F. Peterson, Madison, Wisconsin, Fire
Department, WI [E]

William J. Satterfield, III, Hydrogen Safety, LLC/Rode
& Associates, LLC, RI [I]

David B. Wechsler, The Dow Chemical Company, TX [M]

Nonvoting

Ira Wainless, U.S. Department of Labor, DC [E]

Amy B. Spencer, 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.

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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 G. Editorial changes to extracted material consist of revising references to an appropriate division in this document or the inclusion of the document number with the division number when the reference is to the original document. 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 G.

Chapter 1 Administration

1.1 Scope. This standard shall address the health, flammability, instability, and related hazards that are presented by short-term, 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, *Explosive Materials Code*
- (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*®, 2005 edition.

NFPA 495, *Explosive Materials Code*, 2006 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 D 86, *Standard Test Method for Distillation of Petroleum Products at Atmospheric Pressure*, 2001.

ASTM D 92, *Standard Test Method for Flash and Fire Points by Cleveland Open Cup*, 1998.

ASTM D 6668, *Standard Test Method for the Discrimination Between Flammability Ratings of F = 0 and F = 1*, 2001.

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

Manual of Tests and Criteria, 3rd revised edition.

Recommendations on the Transport of Dangerous Goods, Model Regulations, 11th revised edition.

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

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, *Uniform Fire Code*TM, 2006 edition.

NFPA 30, *Flammable and Combustible Liquids Code*, 2003 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.

3.3 General Definitions.

3.3.1* Boiling Point. The temperature at which the vapor pressure of a liquid equals the surrounding atmospheric pressure. For purposes of defining the boiling point, atmospheric pressure shall be considered to be 14.7 psia (760 mm Hg). For mixtures that do not have a constant boiling point, the 20 percent evaporated point of a distillation performed in accordance with ASTM D 86, *Standard Test Method for Distillation of Petroleum Products at Atmospheric Pressure*, shall be considered to be the boiling point. [30, 2003]

3.3.2 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 D 92, *Standard Test Method for Flash and Fire Points by Cleveland Open Cup*.

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

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

3.3.5 Materials.

3.3.5.1 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.

3.3.5.2 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.

3.3.6 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, 2006]

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 four, indicating severe hazard, to zero, 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 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.
- (2) They can work safely in the area with suitable respiratory protective equipment.
- (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.

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

Table 5.2 Degrees of Health Hazards

Degree of Hazard*	Criteria†
4 — Materials that, under emergency conditions, can be lethal	<p>Gases whose LC₅₀ for acute inhalation toxicity is less than or equal to 1000 parts per million (ppm)</p> <p>Any liquid whose saturated vapor concentration at 20°C (68°F) is equal to or greater than 10 times its LC₅₀ for acute inhalation toxicity, if its LC₅₀ is less than or equal to 1000 ppm</p> <p>Dusts and mists whose LC₅₀ for acute inhalation toxicity is less than or equal to 0.5 milligram per liter (mg/L)</p> <p>Materials whose LD₅₀ for acute dermal toxicity is less than or equal to 40 milligrams per kilogram (mg/kg)</p> <p>Materials whose LD₅₀ for acute oral toxicity is less than or equal to 5 mg/kg</p>

Table 5.2 *Continued*

Degree of Hazard*	Criteria†
3 — Materials that, under emergency conditions, can cause serious or permanent injury	<p>Gases whose LC₅₀ for acute inhalation toxicity is greater than 1000 ppm but less than or equal to 3000 ppm</p> <p>Any liquid whose saturated vapor concentration at 20°C (68°F) is equal to or greater than its LC₅₀ for acute inhalation toxicity, if its LC₅₀ is less than or equal to 3000 ppm, and that does not meet the criteria for degree of hazard 4</p> <p>Dusts and mists whose LC₅₀ for acute inhalation toxicity is greater than 0.5 mg/L but less than or equal to 2 mg/L</p> <p>Materials whose LD₅₀ for acute dermal toxicity is greater than 40 mg/kg but less than or equal to 200 mg/kg</p> <p>Materials that are corrosive to the respiratory tract</p> <p>Materials that are corrosive to the eye or cause irreversible corneal opacity</p> <p>Materials that are corrosive to skin</p> <p>Cryogenic gases that cause frostbite and irreversible tissue damage</p> <p>Compressed liquefied gases with boiling points at or below -55°C (-66.5°F) that cause frostbite and irreversible tissue damage</p> <p>Materials whose LD₅₀ for acute oral toxicity is greater than 5 mg/kg but less than or equal to 50 mg/kg</p>
2 — Materials that, under emergency conditions, can cause temporary incapacitation or residual injury	<p>Gases whose LC₅₀ for acute inhalation toxicity is greater than 3000 ppm but less than or equal to 5000 ppm</p> <p>Any liquid whose saturated vapor concentration at 20°C (68°F) is equal to or greater than one-fifth its LC₅₀ for acute inhalation toxicity, if its LC₅₀ 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</p> <p>Dusts and mists whose LC₅₀ for acute inhalation toxicity is greater than 2 mg/L but less than or equal to 10 mg/L</p> <p>Materials whose LD₅₀ for acute dermal toxicity is greater than 200 mg/kg but less than or equal to 1000 mg/kg</p> <p>Compressed liquefied gases with boiling points between -30°C (-22°F) and -55°C (-66.5°F) that can cause severe tissue damage, depending on duration of exposure</p> <p>Materials that are respiratory irritants</p> <p>Materials that cause severe but reversible irritation to the eyes or lacrimators</p> <p>Materials that are primary skin irritants or sensitizers</p> <p>Materials whose LD₅₀ for acute oral toxicity is greater than 50 mg/kg but less than or equal to 500 mg/kg</p>
1 — Materials that, under emergency conditions, can cause significant irritation	<p>Gases and vapors whose LC₅₀ for acute inhalation toxicity is greater than 5000 ppm but less than or equal to 10,000 ppm</p> <p>Dusts and mists whose LC₅₀ for acute inhalation toxicity is greater than 10 mg/L but less than or equal to 200 mg/L</p> <p>Materials whose LD₅₀ for acute dermal toxicity is greater than 1000 mg/kg but less than or equal to 2000 mg/kg</p> <p>Materials that cause slight to moderate irritation to the respiratory tract, eyes, and skin</p> <p>Materials whose LD₅₀ for acute oral toxicity is greater than 500 mg/kg but less than or equal to 2000 mg/kg</p>
0 — Materials that, under emergency conditions, would offer no hazard beyond that of ordinary combustible materials	<p>Gases and vapors whose LC₅₀ for acute inhalation toxicity is greater than 10,000 ppm</p> <p>Dusts and mists whose LC₅₀ for acute inhalation toxicity is greater than 200 mg/L</p> <p>Materials whose LD₅₀ for acute dermal toxicity is greater than 2000 mg/kg</p> <p>Materials whose LD₅₀ for acute oral toxicity is greater than 2000 mg/kg</p> <p>Materials that are essentially nonirritating to the respiratory tract, eyes, and skin</p>

*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 LC₅₀ and LD₅₀.

Chapter 6 Flammability Hazards

6.1 General.

6.1.1 This chapter shall address the degree of susceptibility of materials to burning.

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.

Table 6.2 Degrees of Flammability Hazards

Degree of Hazard	Criteria
4 — Materials that rapidly or completely vaporize at atmospheric pressure and normal ambient temperature or that are readily dispersed in air and burn readily	<p>Flammable gases</p> <p>Flammable cryogenic materials</p> <p>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)</p> <p>Materials that ignite spontaneously when exposed to air</p> <p>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.</p>
3 — Liquids and solids that can be ignited under almost all ambient temperature 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.	<p>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)</p> <p>Finely divided solids, typically less than 75 micrometers (µm) (200 mesh), that present an elevated risk of forming an ignitable 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</p> <p>Materials that burn with extreme rapidity, usually by reason of self-contained oxygen (e.g., dry nitrocellulose and many organic peroxides)</p> <p>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.</p>
2 — Materials that must be moderately heated or exposed to relatively high ambient temperatures before ignition can occur. Materials in this degree would not under normal conditions form hazardous atmospheres with air, but under high ambient temperatures or under moderate heating could release vapor in sufficient quantities to produce hazardous atmospheres with air.	<p>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)</p> <p>Finely divided solids less than 420 µm (40 mesh) that present an ordinary risk of forming an ignitable dust cloud</p> <p>Solid materials in a flake, fibrous, or shredded form that burn rapidly and create flash fire hazards, such as cotton, sisal, and hemp</p> <p>Solids and semisolids that readily give off flammable vapors</p> <p>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.</p>

Table 6.2 Continued

Degree of Hazard	Criteria
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.	<p>Materials that will burn in air when exposed to a temperature of 815.5°C (1500°F) for a period of 5 minutes in accordance with ASTM D 6668, <i>Standard Test Method for the Discrimination Between Flammability Ratings of F = 0 and F = 1</i></p> <p>Liquids, solids, and semisolids having a flash point at or above 93.4°C (200°F) (i.e., Class IIIB liquids)</p> <p>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 of Tests and Criteria</i></p> <p>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</p> <p>Liquids that have no fire point when tested by ASTM D 92, <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</p> <p>Combustible pellets, powders, or granules greater than 420 µm (40 mesh)</p> <p>Finely divided solids less than 420 µm that are nonexplosible in air at ambient conditions, such as low volatile carbon black and polyvinylchloride (PVC)</p> <p>Most ordinary combustible materials</p> <p>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.</p>
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 D 6668, <i>Standard Test Method for the Discrimination Between Flammability Ratings of F = 0 and F = 1</i>

Chapter 7 Instability Hazards

7.1 General.

7.1.1* This chapter shall address the degree of intrinsic susceptibility of materials to release energy.

7.1.1.1 This chapter shall apply to those materials capable of rapidly releasing energy by themselves, through self-reaction or polymerization.

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

7.1.1.3* In the evaluation of the hazards of organic peroxides, additional factors shall be taken into account.

7.1.2* Because of the wide variations of unintentional combinations possible in fire or other emergencies, these extrane-

ous 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.

7.1.3 The degree of instability hazard shall indicate to fire-fighting 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 decomposition or explosive reaction at normal temperatures and pressures	Materials that are sensitive to localized thermal or mechanical shock 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 watts per milliliter (W/mL) or greater
3 — Materials that in themselves are capable of detonation or explosive decomposition or explosive reaction but that require a strong initiating source or must be heated under confinement before initiation	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 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°C (482°F) below 0.01 W/mL Materials that do not exhibit an exotherm at temperatures less than or equal to 500°C (932°F) when tested by differential scanning calorimetry

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 (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., W and OX), the W shall be displayed inside the special hazards quadrant, and the OX shall be displayed directly below or adjacent to the special hazards quadrant.

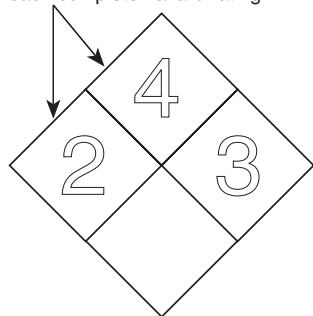
8.2.4* Materials that are simple asphyxiant gases shall be permitted to be identified with the letters "SA" and shall be limited to the following gases: nitrogen, helium, neon, argon, krypton, and xenon.

Chapter 9 Identification of Materials by Hazard Rating System

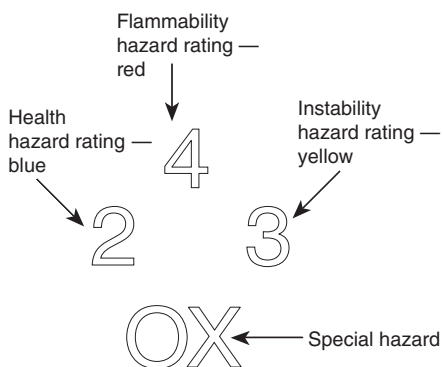
9.1 Symbol Arrangement. One of the systems delineated in Figure 9.1(a), Figure 9.1(b), or Figure 9.1(c) shall be used for the implementation of this standard.



Adhesive-backed plastic background pieces; one needed for each numeral, three needed for each complete hazard rating

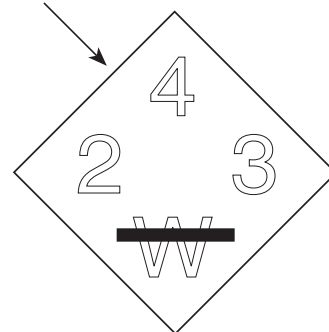


(a) For use where specified color background is used with numerals of contrasting colors



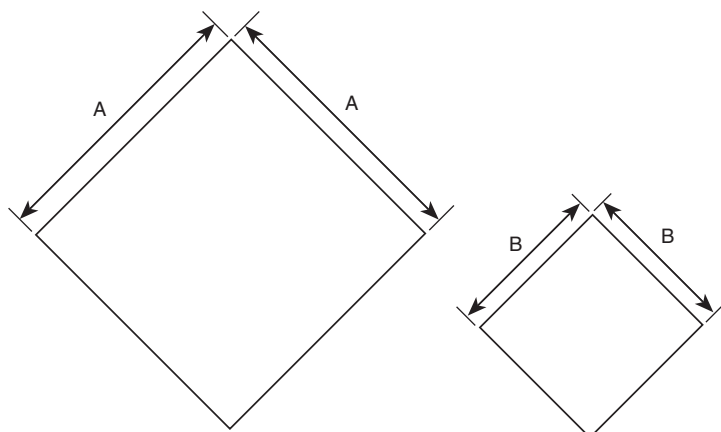
(b) For use where white background is necessary

White painted background or white paper or card stock



(c) For use where white background is used with painted numerals or for use when hazard rating is in the form of sign or placard

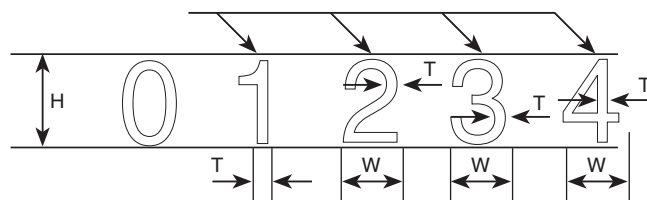
FIGURE 9.1(a) Alternative Arrangements for Display of NFPA 704 Hazard Identification System.



Where painted (use same dimensions for sign or placard)

Where made from adhesive-backed plastic (one for each numeral, three necessary for each complete hazard rating)

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



Note: Style of numerals shown is optional.

Minimum dimensions of white background for hazard ratings (white background is optional)

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

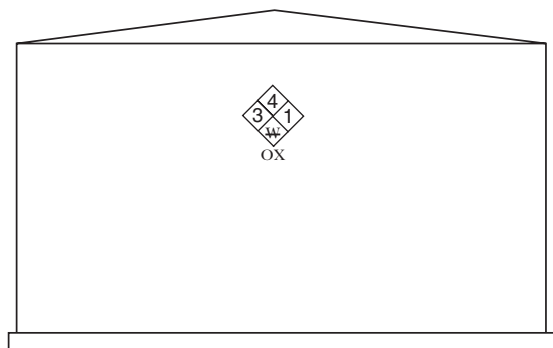


FIGURE 9.1(c) Minimum Size of Numerals for Legibility at Distance.

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 preven-

tion 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 D 86, *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.

A.3.3.3 Flash Point. Flash point is a direct measure of a liquid’s volatility, 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.3.3.4 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 liquefied cryogenic gases, 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 withdrawn standards NFPA 49, *Hazardous*

Chemicals Data, and NFPA 325, *Guide to Fire Hazard Properties of Flammable Liquids, Gases, and Volatile Solids*. 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 that will be available to the public electronically in the future and in updates of 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 \mathbf{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 \mathbf{W} , 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 mixture can be entirely different from those of the individual components. An example discussed by Stull 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. 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, *Hazardous Chemicals Data*, 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 NFPA's *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. Some materials have combustion or decomposition products 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.

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 classification are found in NFPA 30, *Flammable and Combustible Liquids Code*.

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 non-inerted tanks where the vapor space can contain ignitable 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 ignitable 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.7.1.1.3 Refer to NFPA 432, *Code for the Storage of Organic Peroxide Formulations*, for more specific information regarding the classification of organic peroxides.

A.7.1.2 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, *Guide to Hazardous Chemical Reactions*. (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.

A.8.1.1 Only 2 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 symbols (beyond OX and 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 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 430, *Code for the Storage of Liquid and Solid Oxidizers*.

The severity of the hazard posed by an oxidizer can be ranked according to the classification system presented in NFPA 430. 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 430), 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 430, Class 1) and ammonium permanganate (NFPA 430, 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 W and the OX are special hazards. However, the W rating should be ranked as the primary special hazard by display of the 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 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 defined term *simple asphyxiant gas*. Gases that are simple asphyxiants 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.

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*. (See also “Notice of Proposed Rulemaking,” *Federal Register*, and “Notice of Final Rule,” *Federal Register*.)



Table B.1 Health Hazard Rating Chart

Degree of Hazard	Gas/Vapor		Dust/Mist Inhalation LC ₅₀ (mg/L)	Oral LD ₅₀ (mg/kg)	Dermal LD ₅₀ (mg/kg)	Skin/Eye Contact
	Inhalation LC ₅₀ (ppm-v)	Saturated Vapor Concentration (× LC ₅₀ in ppm-v)				
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

Notes:

$$(1) \text{ ppm} = \frac{\text{mg/m}^3 \times 24.45}{\text{molecular weight}}$$

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

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

(3) See Section B.3 for definitions of LC₅₀ and LD₅₀.**B.1.2 Inhalation Hazard Considerations Using UN Criteria.**

The UN criteria for inhalation toxicity are based on the LC₅₀ 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.

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 National Paint & Coatings Association (NPCA) (*see Hazardous Materials Identification System Revised, Implementation Manual*). Although the NPCA 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 NPCA 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 NPCA criteria.

B.3 UN Definitions. For the user’s assistance in utilizing this standard, the following definitions are extracted from Section 6.5 of *Recommendations on the Transport of Dangerous Goods*. 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 LD₅₀ for acute oral toxicity: That dose of the substance administered which is most likely to cause death within 14 days in one half of both male and female young adult albino rats. 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 kilogram of body weight.

B.3.2 LD₅₀ for acute dermal toxicity: 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 kilogram of body weight.

B.3.3 LC₅₀ for acute toxicity on inhalation: 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. If the substance is administered to the animals as dust or mist, more than 90 percent of the particles available for inhalation in the test must have a diameter of 10 microns or less, provided that it is reasonably foreseeable that such concentrations could be encountered by man during transport. The result is expressed in milligrams per liter of air for dusts and mists or in milliliters per cubic meter of air (parts per million) for vapors.

B.4 The following information extracted from Section 6.4 of *Recommendations on the Transport of Dangerous Goods* 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) × 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) × 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 to 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 D 56, *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 D 3278, *Flash Point of Liquids by Set-Flash Closed Tester*, or ASTM D 3828, *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 $5.5 \text{ mm}^2/\text{s}$ (5.5 cSt) or greater at 40°C (100°F) or $9.5 \text{ mm}^2/\text{s}$ (9.5 cSt) or greater at 25°C (77°F) can be determined in accordance with ASTM D 93, *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 (μm) 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 air, measured in mass per unit volume, that will support a deflagration as defined by the text procedure in ASTM E 1515, *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 E 1226, *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 654, *Standard for the Prevention of Fire and Dust Explosions from the Manufacturing, Processing, and Handling of Combustible Particulate Solids*; NFPA 664, *Standard for the Prevention of Fires and Explosions in Wood Processing and Woodworking Facilities*; and NFPA 68, *Guide for Venting of Deflagrations*, 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.

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 E 537, *Standard Test Method for Assessing the Thermal Stability of Chemicals by Methods of Differential Thermal Analysis*, or ASTM E 1981, *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 adiabatic exotherm initiation temperature. This can be used to define ratings of 0, 1, or 2.

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

Materials that exhibit adiabatic exotherm initiation temperatures between 200°C and 500°C 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 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 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 D 2879, *Standard Test Method for Vapor Pressure-Temperature Relationship and Initial Decomposition Temperature of Liquids by Isotenscope*, can be used as an indication of thermal stability when data meeting the requirements of ASTM E 537 are not available. Self-Accelerating Decomposition Temperature (SADT) test results can also be used. Alternatively, calculations based on the CHETAH program could be carried out.

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 E 698, *Standard Test Method for Arrhenius Kinetic Constants for Thermally Unstable Materials*), or ARC (see ASTM E 1981, *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%) level. This allows the initial concentration of the material to be used in the simplified rate expression. (See Table E.2.)

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

Instability Rating	Instantaneous Power Density at 250°C
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

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

DSC was carried out, and the following parameters were obtained for a material of interest:

Enthalpy of decomposition (ΔH):	-80.5 cal/g
Arrhenius activation energy (E_a):	36.4 kcal/mol
Arrhenius pre-exponential (A_{PRE}):	$1.60 \times 10^{15} \text{ s}^{-1}$
Reaction order (n):	1
Initial concentration of material or density of pure material (conc.):	0.80 g/mL

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):

$$\text{Rate} = \text{conc}^{\text{order}} \times A_{PRE} \times e^{-E_a/RT}$$

The units used are as follows:

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

$$\text{Rate} = 0.80^{+1} \times 1.60 \times 10^{+15} \times e^{-\frac{36400}{1.987 \times (273+250)}}$$

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

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

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):

$$\text{IPD} = -\Delta H \times \text{Rate}$$

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

$$\text{IPD} = -(80.5) \times 0.79 \times 4.184 \frac{\text{W}}{\text{cal/s}}$$

$$\text{IPD} = 63 \frac{\text{cal}}{\text{s} \times \text{mL}} \times 4.184 \frac{\text{W}}{\text{cal/s}}$$

$$\text{IPD} = 270 \frac{\text{W}}{\text{mL}}$$

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 positive 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.

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 ~~W~~ symbol in the special hazards space on the placard.

The special hazard ~~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 shall 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.



Table F.2 Degrees of Water Reactivity Hazards

Degree of Hazard	Criteria
4	Not applicable
3 — Requires a W 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 W 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 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 W to be displayed in the special hazards quadrant.	Nonreactive below 30 cal/g

F.3 Water Reactivity Hazard Degree 0. The chemical is essentially nonreactive with water, therefore the ~~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 ~~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.

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 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 ~~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 impractical 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 non-hazardous 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 (~~W~~ 2). The following are examples of chemicals whose release of gas raise