NFPA 704

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

1996 Edition

National Fire Protection Association, 1 Batterymarch Park, PO Box 9101, Quincy, MA 02269-9101
An International Codes and Standards Organization

IMPORTANT NOTICE ABOUT THIS DOCUMENT

NFPA codes, standards, recommended practices, and guides, 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 its codes and 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 this document. The NFPA also makes no guaranty or warranty as to the accuracy or completeness of any information published herein.

In issuing and making this document 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 this document. 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.

NOTICES

All questions or other communications relating to this document 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 documents during regular revision cycles, should be sent to NFPA headquarters, addressed to the attention of the Secretary, Standards Council, National Fire Protection Association, 1 Batterymarch Park, P.O. Box 9101, Quincy, MA 02269-9101.

Users of this document should be aware that this document may be amended from time to time through the issuance of Tentative Interim Amendments, and that an official NFPA document at any point in time consists of the current edition of the document together with any Tentative Interim Amendments then in effect. In order to determine whether this document is the current edition and whether it has been amended through the issuance of Tentative Interim Amendments, 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 above.

A statement, written or oral, that is not processed in accordance with Section 5 of the Regulations Governing Committee Projects 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.

The NFPA does not take any position with respect to the validity of any patent rights asserted in connection with any items which are mentioned in or are the subject of this document, and the NFPA disclaims liability for the infringement of any patent resulting from the use of or reliance on this document. Users of this document are expressly advised that determination of the validity of any such patent rights, and the risk of infringement of such rights, is entirely their own responsibility.

Users of this document should consult applicable federal, state, and local laws and regulations. NFPA does not, by the publication of this document, intend to urge action that is not in compliance with applicable laws, and this document may not be construed as doing so.

Licensing Policy

NFPA 704

Standard System for the

Identification of the Hazards of Materials for Emergency Response

1996 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 and acted on by the National Fire Protection Association, Inc., at its Annual Meeting held May 20–23, 1996, in Boston, MA. It was issued by the Standards Council on July 18, 1996, with an effective date of August 9, 1996, and supersedes all previous editions.

Changes other than editorial are indicated by a vertical rule in the margin of the pages on which they appear. These lines are included as an aid to the user in identifying changes from the previous edition.

This edition of NFPA 704 was approved as an American National Standard on July 26, 1996.

Origin and Development of NFPA 704

Work on this standard originated in 1957 with a great deal of the development work having been done by the NFPA Sectional Committee on Classification, Labeling and Properties of Flammable Liquids starting in 1952. Background data was published by the Association in its Quarterly magazine in July 1954, 1956, and 1958. The material in its present form was first Tentatively Adopted in 1960. Official Adoption was secured in 1961 and revisions 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. This 1996 edition contains additional quantitative guidelines and amended definitions for the Reactivity (Instability) Hazard Ratings.

Technical Committee on Classification and Properties of Hazardous Chemical Data

F. Owen Kubias, *Chair*
Rocky River, OH

Robert A. Michaels, *Secretary*
RAM TRAC Corp., NY

Jacqueline E. Alpert, Underwriters Laboratories Inc., IL
William J. Bradford, Brookfield, CT
Laurence G. Britton, Union Carbide Corp., WV
Paul L. Errico, Ogden Services, CT
Mark I. Grossman, Reliance Nat'l Risk Specialists, NY
Ron A. Kirsch, Occupational Health Services Inc., TN
Arthur A. Krawetz, Phoenix Chemical Laboratory Inc., IL
Roland J. Land, Jardine Insurance Brokers, NY
Whitney Fay Long, Nat'l Paint & Coatings Assn., DC
Jennifer L. Nelson, AT&T Co., NJ
Rep. NFPA Industrial Fire Protection Section
Curtis G. Payne, U.S. Coast Guard (G-MTH-1), DC
Gary Robinson, Liberty Mutual Insurance Co., IL
Rep. The Alliance of American Insurers
Norman E. Scheffler, The Dow Chemical Co., MI
Norman V. Steere, Norman V. Steere Assoc., Inc., MN

Alternates

Robert A. Kingsbury, Underwriters Laboratories Inc., IL
(Alt. to J. E. Alpert)

Nonvoting

Howard H. Fawcett, Wheaton, MD
(Member Emeritus)
Richard D. Tarr, U.S. Dept. of Transportation, DC
Jan van der Linde, Samsom Chemical Publishers, Netherlands
Ira Wainless, U.S. Dept. of Labor/OSHA, DC

Guy R. Colonna, NFPA Staff Liaison

This list represents the membership at the time the Committee was balloted on the text of this edition. Since that time, changes in the membership may have occurred.

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

NFPA 704

Standard System for the

Identification of the Hazards of Materials for Emergency Response

1996 Edition

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

Information on referenced publications can be found in Appendix E.

FOREWORD

The Committee has been working on the material in this standard since early 1957. A great deal of preliminary work was developed as a manual by the Sectional Committee on Classification, Labeling and Properties of Flammable Liquids of the NFPA Committee on Flammable Liquids starting in 1952. Progress reports were given on this activity at NFPA Annual Meetings and reported in the NFPA *Quarterly* in July issues of 1954, 1956, and 1958. The material was tentatively adopted as a guide in 1960, adopted in 1961, and further amended in 1964, 1966, 1969, 1975, and 1980.

As originally conceived, the purpose of the standard is to safeguard the lives of those individuals who respond to emergencies occurring in an industrial plant or storage location where the hazards of materials are not readily apparent.

Chapter 1 General

1-1 Scope.

1-1.1 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.

1-1.2 This standard provides 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. The objectives of the system are:

(a) To provide an appropriate signal or alert and on-the-spot information to safeguard the lives of both public and private emergency response personnel;

(b) To assist in planning for effective fire and emergency control operations, including clean-up;

(c) To assist all designated personnel, engineers, plant and safety personnel in evaluating hazards.

1-1.3 It is recognized that local conditions will have a bearing on evaluation of hazards; therefore, discussion shall be kept in general terms.

1-2 Applicability.

1-2.1 This standard is applicable to industrial, commercial, and institutional facilities that manufacture, process, use, or store hazardous materials.

1-2.2 This standard is not applicable to transportation or use by the general public.

1-2.3* This standard is not intended to address:

(a) Occupational exposure;

(b) Explosive and blasting agents, including commercial explosive material as defined in NFPA 495, *Explosive Materials Code*;

(c) Chemicals whose only hazard is one of chronic health hazards;

(d) Teratogens, mutagens, oncogens, etiologic agents, and other similar hazards.

1-3 Purpose. This system is intended to 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. It is also intended to provide them with information to assist in selecting fire-fighting tactics and emergency procedures.

1-4 Description.

1-4.1 This system identifies the hazards of a material in terms of three principal categories: "health," "flammability," and "instability." The system indicates the degree of severity by a numerical rating that ranges from four (4), indicating severe hazard, to zero (0), indicating minimal hazard.

1-4.2 The information is 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. Each rating is located in a square-on-point field, each of which is assigned a color: blue for health hazard; red for flammability hazard; yellow for instability hazard. Alternately, 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 Figures 6-1 through 6-3 for examples of the spatial arrangements.

1-4.3 The fourth space, at the six o'clock position, is reserved for indicating any unusual reactivity with water. The standard symbol for indicating unusual reactivity with water is the letter "W" with a line through the center: W̶. No special color is associated with this symbol.

1-4.3.1 This space shall be permitted to be used to indicate other unusual hazards, but only if not needed to indicate reactivity with water. Approved symbols will be designated in Chapter 5 of this standard.

1-5 Assignment of Ratings.

1-5.1 While the system is basically simple in application, the hazard evaluation required to determine the correct numerical 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. 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. For additional information, see NFPA49, *Hazardous Chemicals Data*, and NFPA 325, *Guide to Fire Hazard Properties of Flammable Liquids, Gases, and Volatile Solids*.

1-5.2 The system is based on relative rather than absolute values. Therefore, it is anticipated that conditions of storage and use can result in different ratings being assigned to the same material by different persons. Furthermore, the guidance presented in the following chapters is necessarily limited. For example, flash point is the primary criterion for assigning the flammability rating, but other criteria might be of equal importance. For example, autoignition temperature, flammability limits, and susceptibility of a container to failure due to fire exposure also shall be considered. For instability, emphasis has been placed on the ease by which an energy-releasing reaction is triggered. For health, consideration shall be given not only to inherent hazards but also to protective measures that shall be taken to minimize effects of short-term exposure.

1-5.3 In some situations, such as warehouses, storage rooms or buildings, laboratory facilities, etc., a variety of materials can be present in one localized area. In such cases considerable judgment might be needed to properly assign ratings to the area.

1-5.4 Based upon professional judgment it shall be permitted to either increase or decrease the hazard rating to more accurately assess the likely degree of hazard that will be encountered.

Chapter 2 Health Hazards

2-1 General.

2-1.1 This chapter shall address the capability of a material to cause personal injury due to contact with or entry into the body via inhalation, ingestion, skin contact, or eye contact. Only the hazards that arise from an inherent toxic property of the material or its products of decomposition or combustion shall be considered. Injury resulting from the heat of a fire or from the force of an explosion shall not be considered.

2-1.2 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 one 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. Health hazards that can result from chronic or repeated long-term exposure to low concentrations of a hazardous material shall not be considered.

2-1.3 The oral route of exposure, i.e., ingestion, is highly unlikely under the conditions anticipated by this standard. If situations are encountered, however, where the oral toxicity values indicate a significantly different health hazard rating than from other, more likely routes of exposure, or where 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. In such cases, other routes of entry shall 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 shall also be based on data for the more likely routes of exposure.

2-1.4* For purposes of assigning the health hazard rating, only the inherent physical and toxic properties of the material shall be considered, unless the combustion or decomposition products present a significantly greater degree of risk.

2-1.5 The degree of hazard shall indicate to fire fighting and emergency response personnel one of the following: that they can work safely only with specialized protective equipment; that they can work safely with suitable respiratory protective equipment; or that they can work safely in the area with ordinary clothing.

2-2 Definitions.

Health Hazard. The likelihood of a material to cause, either directly or indirectly, temporary or permanent injury or incapacitation due to an acute exposure by contact, inhalation, or ingestion.

2-3 Degrees of Hazard.

2-3.1* The degrees of health hazard shall be ranked according to the probable severity of the effects of exposure to emergency response personnel. For each degree of hazard the criteria are listed in a priority order based upon the likelihood of exposure. Data from all routes of exposure shall be considered when applying professional judgment to assign a health hazard rating.

4 Materials that, under emergency conditions, can be lethal. The following criteria shall be considered when rating materials:

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 68°F (20°C) is equal to or greater than ten times its LC_{50} for acute inhalation toxicity, if its LC_{50} is less than or equal to 1000 parts per million (ppm);

Dusts and mists whose LC_{50} for acute inhalation toxicity is less than or equal to 0.5 milligrams 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 milligrams per kilogram (mg/kg).

3 Materials that, under emergency conditions, can cause serious or permanent injury. The following criteria shall be considered when rating materials:

Gases whose LC_{50} for acute inhalation toxicity is greater than 1000 parts per million (ppm), but less than or equal to 3000 parts per million (ppm);

Any liquid whose saturated vapor concentration at 68°F (20°C) is equal to or greater than its LC_{50} for acute inhalation toxicity, if its LC_{50} is less than or equal to 3000 parts per million (ppm) and that does not meet the criteria for degree of hazard 4;

Dusts and mist whose LC_{50} for acute inhalation toxicity is greater than 0.5 milligrams per liter (mg/L), but less than or equal to 2 milligrams per liter (mg/L);

Materials whose LD_{50} for acute dermal toxicity is greater than 40 milligrams per kilogram (mg/kg), but less than or equal to 200 milligrams per kilogram (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 severely irritating and/or corrosive to skin;

Materials whose LD_{50} for acute oral toxicity is greater than 5 milligrams per kilogram (mg/kg), but less than or equal to 50 milligrams per kilogram (mg/kg).

2 Materials that, under emergency conditions, can causetemporary incapacitation or residual injury. The following criteria shall be considered when rating materials:

Gases whose LC_{50} for acute inhalation toxicity is greater than 3000 parts per million (ppm), but less than or equal to 5000 parts per million (ppm);

Any liquid whose saturated vapor concentration at 68°F (20°C) is equal to or greater than one-fifth ($^1/_5$) its LC_{50} for acute inhalation toxicity, if its $LC_{50}$is less than or equal to 5000 parts per million (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 milligrams per liter (mg/L), but less than or equal to 10 milligrams per liter (mg/L);

Materials whose LD_{50} for acute dermal toxicity is greater than 200 milligrams per kilogram (mg/kg), but less than or equal to 1000 milligrams per kilogram (mg/kg);

Materials that are respiratory irritants;

Materials that cause irritating but reversible injury to the eyes;

Materials that are primary skin irritants or sensitizers;

Materials whose LD_{50} for acute oral toxicity is greater than 50 milligrams per kilogram, but less than or equal to 500 milligrams per kilogram (mg/kg).

1 Materials that, under emergency conditions, can cause significant irritation. The following criteria shall be considered when rating materials:

Gases and vapors whose LC_{50} for acute inhalation toxicity is greater than 5000 parts per million (ppm), but less than or equal to 10,000 parts per million (ppm);

Dusts and mists whose LC_{50} for acute inhalation toxicity is greater than 10 milligrams per liter (mg/L), but less than or equal to 200 milligrams per liter (mg/L);

Materials whose LD_{50} for acute dermal toxicity is greater than 1000 milligrams per kilogram (mg/kg), but less than or equal to 2000 milligrams per kilogram (mg/kg);

Materials that are slightly irritating to the respiratory tract, eyes, and skin;

Materials whose LD_{50} for acute oral toxicity is greater than 500 milligrams per kilogram (mg/kg), but less than or equal to 2000 milligrams per kilogram (mg/kg).

0 Materials that, under emergency conditions, would offer no hazard beyond that of ordinary combustible materials. The following criteria shall be considered when rating materials:

Gases and vapors whose LC_{50} for acute inhalation toxicity is greater than 10,000 parts per million (ppm);

Dusts and mists whose LC_{50} for acute inhalation toxicity is greater than 200 milligrams per liter (mg/L);

Materials whose LD_{50} for acute dermal toxicity is greater than 2000 milligrams per kilogram (mg/kg);

Materials whose LD_{50} for acute oral toxicity is greater than 2000 milligrams per kilogram (mg/kg);

Essentially nonirritating to the respiratory tract, eyes, and skin.

Chapter 3 Flammability Hazards

3-1 General.

3-1.1 This chapter shall address the degree of susceptibility of materials to burning. Since 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. The definitions for liquid classification are found in NFPA 30, *Flammable and Combustible Liquids Code.*

3-2 Degrees of Hazard.

3-2.1* The degrees of hazard shall be ranked according to the susceptibility of materials to burning as follows:

4 Materials that will rapidly or completely vaporize at atmospheric pressure and normal ambient temperature or that are readily dispersed in air, and which will burn readily. This includes:

Flammable gases;

Flammable cryogenic materials;

Any liquid or gaseous material that is liquid while under pressure and has a flash point below 73°F (22.8°C) and a boiling point below 100°F (37.8°C) (i.e., Class IA liquids);

Materials that ignite spontaneously when exposed to air.

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. This includes:

Liquids having a flash point below 73°F (22.8°C) and having a boiling point at or above 100°F (37.8°C) and those liquids having a flash point at or above 73°F (22.8°C) and below 100°F (37.8°C) (i.e., Class IB and Class IC liquids);

Materials that on account of their physical form or environmental conditions can form explosive mixtures with air and that are readily dispersed in air;

Materials that burn with extreme rapidity, usually by reason of self-contained oxygen (e.g., dry nitrocellulose and many organic peroxides).

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 might release vapor in sufficient quantities to produce hazardous atmospheres with air. This includes:

Liquids having a flash point at or above 100°F (37.8°C) and below 200°F (93.4°C) (i.e., Class II and Class IIIA liquids);

Solid materials in the form of coarse dusts that burn rapidly but that generally do not form explosive atmospheres with air;

Solid materials in a fibrous or shredded form that burn rapidly and create flash fire hazards, such as cotton, sisal, and hemp;

Solids and semisolids that readily give off flammable vapors.

1 Materials that must be preheated before ignition canoccur. Materials in this degree require considerable preheating, under all ambient temperature conditions, before ignition and combustion can occur. This includes:

Materials that will burn in air when exposed to a temperature of 1500°F (815.5°C) for a period of 5 min or less;

Liquids, solids, and semisolids having a flash point at or above 200°F (93.4°C) (i.e., Class IIIB liquids);

Liquids with a flash point greater than 95°F (35°C) that do not sustain combustion when tested using the *Method of Testing for Sustained Combustibility*, per 49 CFR Part 173 Appendix H, or the UN *Recommendations on the Transport of Dangerous Goods*, 8th Revised Edition.

Liquids with a flash point greater than 95°F (35°C) 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 D 92, *Standard Test Method for Flash Point and Fire Point by Cleveland Open Cup*, up to the boiling point of the liquid or up to a temperature at which the sample being tested shows an obvious physical change;

Most ordinary combustible materials.

0 Materials that will not burn. This includes any material that will not burn in air when exposed to a temperature of 1500°F (815.5°C) for a period of 5 min.

Chapter 4 Instability Hazards

4-1 General.

4-1.1 This chapter shall address the degree of susceptibility of materials to release energy. Some materials are capable of rapid release of energy by themselves, through self-reaction or polymerization, or can undergo violent explosive reaction through contact with water or other extinguishing agents or with certain other materials.

4-1.2 The violence of a reaction or decomposition of materials can be increased by heat or pressure, or by mixture with certain other materials to form fuel-oxidizer combinations, or by contact with incompatible substances, sensitizing contaminants, or catalysts.

4-1.3 Because of the wide variations of accidental combinations possible in fire or other emergencies, these extraneous hazard factors (except for the effect of water) cannot be applied to a general numerical rating of hazards. Such extraneous factors must be considered individually in order to establish appropriate safety factors, such as separation or segregation. Such individual consideration is particularly important where significant amounts of materials are to be stored or handled. Guidance for this consideration is provided in NFPA 49, *Hazardous Chemicals Data.*

4-1.4 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.

4-2 Definitions.

4-2.1 For the purposes of this standard, an unstable material is one that can enter into a violent chemical reaction with water. Guidelines for determination of water instability hazard ratings can be found in Appendix D. Reactions with other materials can also result in violent release of energy but are beyond the scope of this standard.

4-2.2 For the purposes of this standard, an unstable material is one 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. This calculation is not applicable for the evaluation/classification of organic peroxides. Refer to NFPA 43B, *Code for the Storage of Organic Peroxide Formulations*, for more specific information regarding the instability hazard rating of organic peroxides. Guidelines for determining thermal stability ratings can be found in Appendix D.

4-2.3 Stable materials are those that normally have the capacity to resist changes in their chemical composition, despite exposure to air, water, and heat as encountered in fire emergencies.

4-3 Degrees of Hazard.

4-3.1 The degrees of hazard shall be ranked according to ease, rate, and quantity of energy release as follows:

4 Materials that in themselves are readily capable of detonation or explosive decomposition or explosive reaction at normal temperatures and pressures. This includes 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 482°F (250°C) 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 initiating source or that must be heated under confinement before initiation. This includes:

Materials that have an instantaneous power density (product of heat of reaction and reaction rate) at 482°F (250°C) 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;

Materials that react explosively with water without requiring heat or confinement.

2 Materials that readily undergo violent chemical change at elevated temperatures and pressures. This includes:

Materials that have an instantaneous power density (product of heat of reaction and reaction rate) at 482°F (250°C) at or above 10 W/mL and below 100 W/mL;

Materials that react violently with water or form potentially explosive mixtures with water.

1 Materials that in themselves are normally stable, but that can become unstable at elevated temperatures and pressures. This includes:

Materials that have an instantaneous power density (product of heat of reaction and reaction rate) at 482°F (250°C) at or above 0.01 W/mL and below 10 W/mL;

Materials that react vigorously with water, but not violently;

Materials that change or decompose on exposure to air, light, or moisture.

0 Materials that in themselves are normally stable, even under fire conditions. This includes:

Materials that have an instantaneous power density (product of heat of reaction and reaction rate) at 482°F (250°C) below 0.01 W/mL;

Materials that do not react with water;

Materials that do not exhibit an exotherm at temperature less than or equal to 932°F (500°C) when tested by differential scanning calorimetry.

Chapter 5 Special Hazards

5-1 General.

5-1.1 This chapter shall address the other properties of the material that cause special problems or require special fire-fighting techniques.

5-1.2 Special hazards symbols shall be shown in the fourth space of the diagram or immediately above or below the entire symbol.

5-2 Symbols.

5-2.1 Materials that demonstrate unusual reactivity with water shall be identified by the letter W with a horizontal line through the center (W̶).

5-2.2 Materials that possess oxidizing properties shall be identified by the letters OX.

Chapter 6 Identification of Materials by Hazard Rating System

6-1 One of the systems delineated in the following illustrations shall be used for the implementation of this standard.

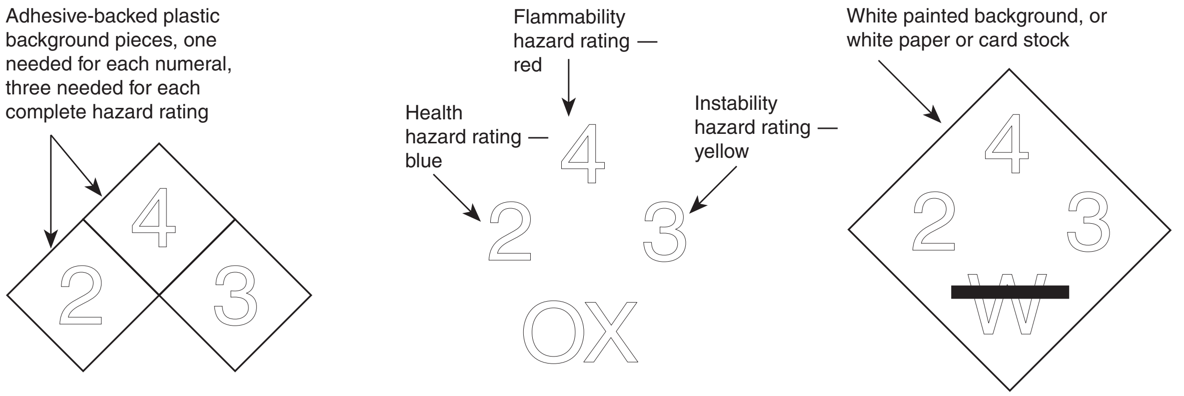
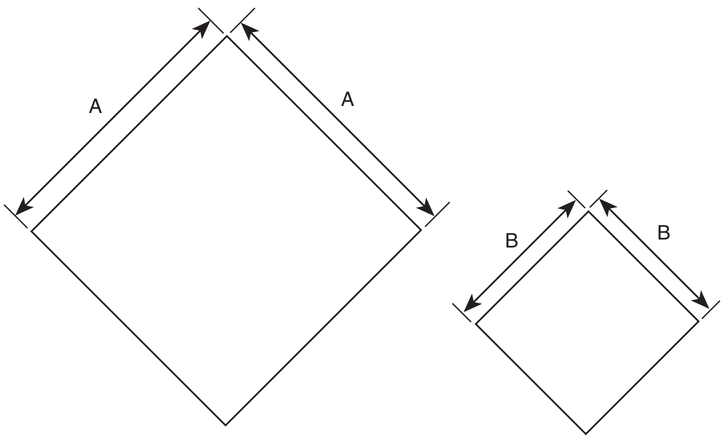


Figure 1 For use where specified color background is used with numerals of contrasting colors.

Figure 2 For use where white background is necessary.

Figure 3 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 6-1 Alternate arrangements for display of NFPA 704 Hazard Identification System.



When painted (use same dimensions for sign or placard)

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

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

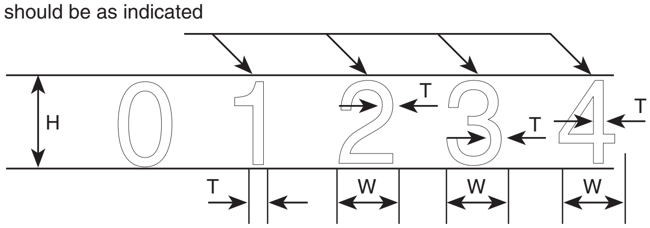
Size of hazard ratings H	W	T	A	B
1 (2.54)	0.7 (1.8)	5/32 (0.4)	2½ (6.35)	1¼ (3.18)
2 (5.08)	1.4 (3.6)	5/16 (0.79)	5 (12.7)	2½ (6.35)
3 (7.62)	2.1 (5.3)	15/32 (1.19)	7½ (19.05)	3¾ (9.53)
4 (10.16)	2.8 (7.1)	5/8 (1.59)	10 (25.4)	5 (12.7)
6 (15.24)	4.2 (10.7)	15/16 (2.38)	15 (38.1)	7½ (19.05)

All dimensions given in inches (cm)

Exception: For containers with a capacity of one gallon or less, symbols may be reduced in size, provided:

1. This reduction is proportionate.
2. The color coding is retained.
3. The vertical and horizontal dimensions of the diamond are not less than 1 in. (2.5 cm).
4. The individual numbers are no smaller than ⅛ in. (0.32 cm) tall.

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



Note: Style of numerals shown is optional.

Figure 6-2 Dimensions of NFPA 704 placard and numerals.

Arrangement and order of hazard ratings—optional form of application

Distance at which hazard ratings must be legible	Minimum size of hazard ratings required
50 ft (15.24 m)	1 in. (2.54 cm)
75 ft (22.86 m)	2 in. (5.08 cm)
100 ft (30.48 m)	3 in. (7.62 cm)
200 ft (60.96 m)	4 in. (10.16 cm)
300 ft (91.44 m)	6 in. (15.24 cm)

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

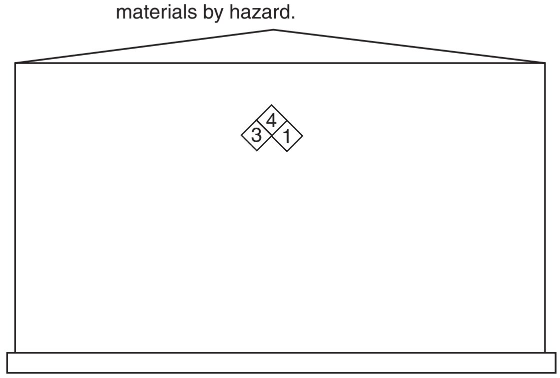


Figure 6-3 Minimum size of numerals for legibility at distance.

Appendix A Explanatory Material

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

A-1-2.3 The Committee recognizes that the potential exists for certain materials to cause a carcinogenic or teratogenic effect from acute exposure(s). However, there is not sufficient data available to this Committee to allow for the development of numerical ratings based upon carcinogenic or teratogenic potential.

A-2-1.4 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. NFPA 49, *Hazardous Chemicals Data*, provides information on products of combustion when available.

A-2-3.1 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-3-2.1 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 in the vapor space which could increase the fire or explosion hazard. This could occur even though the bulk material meets the aforementioned criteria.

Appendix B Health Hazard Rating

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

In developing this edition of NFPA 704, the Committee on Classification and Properties of Hazardous Chemicals Data determined that the standard should provide quantitative guidelines for determining the numerical health hazard rating of a material. In addition, the Committee agreed that a “4” or a “3” health hazard rating should be assigned to any material classified as a “Poison-Inhalation Hazard” by the U.S. Department of Transportation (DOT). This classification, “Poison-Inhalation Hazard,” was adopted by DOT from the United Nations (UN) criteria detailed in the UN publication, *Recommendations on the Transport of Dangerous Goods*, 4th Edition - Revised, 1986. (See also “Notice of Proposed Rulemaking,” Federal Register, Vol. 50, p. 5270 et seq., February 7, 1985, and “Notice of Final Rule,” Federal Register, Vol. 50, p. 41092 et seq., October 8, 1985.)

The UN criteria for inhalation toxicity are based upon the LC_{50} and saturated vapor concentration of the material. Furthermore, in addition to inhalation toxicity, the UN has established criteria for oral and dermal toxicity, as well as corrosivity. Based upon these criteria, the UN assigns a given material to categories called Packing Groups I, II, or III. Packing Group I materials represent a severe hazard in transport, Group II materials a serious hazard, and Group III materials a low hazard.

The Committee decided to adopt the UN criteria for toxicity and corrosivity, and correlate Packing Groups I, II, and III with the health hazard ratings "4," "3," and "2," respectively. Adoption of the UN system has several advantages. First, it addresses hazards in transportation, which 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.

Secondly, 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. Finally, users of chemicals can assign "4," "3," or "2" health hazard ratings by establishing whether chemicals have been assigned to UN Packing Groups due to toxicity or corrosivity.

In order 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) (*Hazardous Materials Identification System Revised, Implementation Manual*, 1981). 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 upon the UN criteria. No UN criteria were established for eye irritation, and the Committee adopted NPCA "3," "2," and "1," and "0" criteria as health hazard ratings for eye irritation.

The Committee made a number of revisions to the proposed hazard rating system to provide conformity with existing industrial practice and to recognize limitations and availability of corrosivity and eye irritation into a single "skin/eye contact" category and 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 of the "skin/eye contact" rankings are based primarily on NPCA criteria.

For the assistance of the user of this standard, the following definitions are quoted from Section 6.5 of *Recommendations on the Transport of Dangerous Goods*, 4th Revised Edition, 1986, published by the United Nations, New York, NY.

LD_{50} 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.

LD_{50} 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.

LC_{50} 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."

The following information quoted from Section 6.4 of the above-cited *Recommendations* also applies:

"The criteria for inhalation toxicity of dusts and mists are based on LC_{50} data relating to 1 hour exposures and where such information is available it should be used. However, where only LC_{50} 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., LC_{50} (4 hour) × 4 is considered equivalent of LC_{50} (1 hour).

The criteria for inhalation toxicity of vapors are based on LC_{50} data relating to 1 hour exposures, and where such information is available it should be used. However, where only LC_{50} 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., LC_{50} (4 hour) × 2 is considered equivalent of LC_{50} (1 hour)."

Appendix C Flammability

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

The selection of the flash point breaks for the assigning of ratings within the Flammability category has been based upon 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.

Flash point indicates several things. One, if the liquid has no flash point, it is not a flammable liquid. Two, if the liquid has a flash point, it must be considered flammable or combustible. Three, 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 will evaporate more rapidly than the gasoline. Over a period of time, the residual liquid will first show a high flash point, then a progressively lower one until the flash point of the final 10 percent of the original sample will approximate that of the heavier fractions of the gasoline. In order 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 as 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 will give a more reliable indication of the flammability hazard.

In the interest of reproducible results, it is recommended that:

The flash point of liquids having a viscosity less than 45 SUS (Saybolt Universal Seconds) at 100°F (37.8°C) and a flash point below 200°F (93.4°C) 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.)

The flash point of aviation turbine fuels can be determined in accordance with ASTM D 3828, *Test Method for Flash Point by Setaflash ClosedTester.*

For liquids having flash points in the range of 32°F (0°C) to 230°F (110°C) the determination may be made in accordance with ASTM D 3278, *Flash Point of Liquids by Setaflash Closed Tester.*

For viscous and solid chemicals the determination may be made in accordance with ASTM E 502, *Flash Point of Chemicals by Closed Cup Methods.*

The flash point of liquids having a viscosity of 45 SUS (Saybolt Universal Seconds) or more at 100°F (37.8°C) or a flash point of 200°F (93.4°C) or higher may be determined in accordance with ASTM D 93, *Test Methods for Flash Point by the Pensky-Martens Closed Tester.*

Appendix D Instability, Thermal Hazard Evaluation Techniques

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

D-1 Water Reactivity.

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. There are two scenarios 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, i.e., a chemical that reacts exothermically to release heat on contact with water but does not produce gaseous or low boiling [< 212°F (< 100°C)] by-products or azeotropes.

The heat of mixing should be determined using a Two Drop Mixing Calorimeter (Hofelich, 1994) or equivalent technique using a 1:1 ratio of chemical to water.

INSTABILITY RATING	HEAT OF MIXING	DESCRIPTOR
4		Reactivity with water not considered for rating of 4
3	600 cal/gm or greater	Explosive
2	At or above 100 cal/gm and below 600 cal/gm	Violent
1	At or above 30 cal/gm and below 100 cal/gm	Vigorous
0	Below 30 cal/gm	Nonreactive

D-2 Thermal Stability.

Thermal stability for hazard evaluation purposes can be done by a number of methods. Frequently used techniques include DTA (Differential Thermal Analysis), DSC (Differential Scanning Calorimetry), and ARC (Accelerating Rate Calorimetry). 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* (for DTA or DSC) or ASTM E XXX, *Standard Test Method for Assessing the Thermal Stability of Chemicals by Methods of Accelerating Rate Calorimetry* (in development for ARC).

D-3 Instantaneous Power Density.

Instantaneous power density (IPD) is calculated as the product of the enthalpy of decomposition/reaction and the initial rate of reaction, determined at 482°F (250°C). This quantity represents the amount of heat energy per unit time per unit volume (W/mL) that a material will initially give at 482°F (250°C). The values that make up the power density can be obtained from thermodynamic tables, calculations and experimental measurements. The values are most easily obtained from appropriate measurements using differential scanning calorimetry (ASTM E 698, *Standard Test Method for Arrhenius Kinetic Constants for Thermally Unstable Materials*) or adiabatic runaway calorimetry (Townsend, 1980). 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, 1965). 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 one to use the initial concentration of the material in the simplified rate expression. (*See Appendix E for the references.*)

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

In order to clarify the calculation of instantaneous power density, a sample calculation is provided.

Differential scanning calorimetry 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 ($^A PRE$):	$1.60 \times 10^{+15}\ s^{-1}$
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 482°F (250°C) can be calculated using the following Arrhenius expression, where R is the universal gas whose value is taken as 1.987 cal/(mol°C):