704

FIRE HAZARDS OF MATERIALS 1980



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Standard System for the Identification of the Fire Hazards of Materials

NFPA 704 - 1980

1980 Edition of NFPA 704

This 1980 edition of NFPA 704, Standard System for the Identification of the Fire Hazards of Materials, was prepared by the Committee on Fire Hazards of Materials and was adopted by the National Fire Protection Association, Inc. on November 19, 1980, at its Fall Meeting in San Diego, California. It was released for publication by the Standards Council on December 10, 1980.

Origin and Development of NFPA 704

Work on this Recommended System 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 their 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, and 1975. This 1980 edition supersedes all previous editions.

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Standard System for the Identification of the Fire Hazards of Materials

NFPA 704 - 1980

Foreword

The Committee on Fire Hazards of Materials 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 and 1969.

As originally conceived, the purpose of the standard is to safeguard the lives of those individuals who may be concerned with fires occurring in an industrial plant or storage location where the fire hazards of materials may not be readily apparent.

Chapter 1 Scope and Application

- 1-1 This standard applies to facilities for the manufacturing, storage or use of hazardous materials. It is concerned with the health, fire, reactivity and other related hazards created by short term exposure as might be encountered under fire or related emergency conditions. This standard applies to industrial and institutional facilities. It does not apply to transportation or to use by the general public.
- 1-2 This standard provides a simple system of readily recognizable and easily understood markings, which will give at a glance a general idea of the inherent hazards of any material and the order of severity of these hazards as they relate to fire prevention, exposure and control. Its objectives are to provide an appropriate signal or alert and on-the-spot information to safeguard the lives of both public and private fire fighting personnel during fire emergencies. It will also assist in planning for effective fire fighting operations. This system should also find useful application by design engineers, and plant protection and safety personnel. It is recognized that local conditions will have a bearing in evaluating hazards; therefore, the discussions are kept in general terms.
- 1-3 This system identifies the hazards of a material in terms of three principal categories, namely, "health," "flammability," and "reactivity (instability)"; and indicates the order of severity numerically by five divisions ranging from "four (4)," indicating a severe hazard, to "zero (0)," indicating no special hazard. This information is presented by a spatial system of diagrams with "health" always being on the left; "flammability" at the top; and "reactivity (instability)" on the right. Examples of spatial arrangement are shown on page 15. For the sake of uniformity and understanding, the spatial arrangements shown in the examples shall be followed. Supplementing the spatial arrangement, color backgrounds or numbers are used for the three categories blue for "health" hazard, red for "flammability," and yellow for "reactivity (instability)."
- 1-4 The fourth space in the diagram (see Figure 1) shall be used to indicate unusual reactivity with water. The recommended signal to indicate this unusual reactivity with water and to alert the fire fighting personnel to the possible hazard of using water is the letter W with a line through the center (W). This space also may be used to indicate other additional information such as radioactivity (see Figure 1), proper fire extinguishing agent, or protective equipment required in case of fire or other emergency.

- 1-5 This system is intended to give basic information to fire fighting and emergency personnel enabling them to decide better whether to evacuate the area or to fight the fire and will guide them in the solution of fire fighting techniques and protective measures.
- 1-6 While this system is basically simple in application, the hazard evaluation which is required for the precise use of the signals in a specific location shall be performed by experienced, technically competent persons. Their judgment shall be based on factors encompassing a knowledge of the inherent hazards of different materials, including the extent of change in behavior to be anticipated under conditions of exposure to fire or to fire control procedures. For additional information see NFPA 49, Hazardous Chemicals Data; NFPA 57, Standard for Fumigation; and NFPA 325M, Fire Hazard Properties of Flammable Liquids, Gases and Volatile Solids.
- 1-7 The system for ranking degrees of hazard is based on relative rather than absolute values. Therefore, it is anticipated that conditions of storage and use may result in different degrees being assigned to the same material by different people of equal competence. Furthermore, the suggestions for criteria in the following chapters are limited. For example, flash point has been selected as the major guide in ranking degrees of flammability for flammable liquids, but there are many other guides that can be used when the degree to be assigned to a specific material is not immediately self-evident. These guides include, but are not limited to: ignition temperature, flammable range, and susceptibility of a container to rupture by an internal combustion explosion or to metal failure while under pressure, because of heat from external fire. In the case of ranking for reactivity, emphasis has been placed on the ease of initiation of energy producing reactions and the amount of energy released. Thus, true explosives capable of ready initiation of detonation would be in degree 4; substances requiring high temperatures or confinement or extremely large stimuli would be in degree 3; etc. Finally, under health hazard, there is consideration not only of the degree of hazard but also of the protective measures which may be taken to minimize the hazards of short term exposure.
- 1-8 In some situations, such as in a building, room or other localized area, a wide variety of materials may be stored having varying degrees of hazards. In such cases, the identifying symbol shall indicate the most severe degree of hazard in each category except when a high hazard rating would be misleading because of the presence of an insignificant quantity of the material requiring the rating.

Chapter 2 Health Hazards

2-1 General.

- 2-1.1 This chapter deals with the capacity of a material to cause personal injury from contact with or absorption into the body. Only hazards arising out of an inherent property of the material will be considered. Injury resulting from the heat of a fire or force of an explosion is not included.
- 2-1.2 In general, health hazard in fire fighting or other emergency conditions is that of a single exposure which may vary from a few seconds up to an hour. The physical exertion demanded in fire fighting or other emergency conditions may be expected to intensify the effects of any exposure.
- 2-1.3 There are two sources of health hazards. One arises out of the inherent properties of the material. The other arises out of the toxic products of combustion or decomposition of the material. The hazard degree shall be assigned on the basis of the greater hazard that could exist under fire or other emergency conditions. The common hazards from the burning of ordinary combustible materials are not included.
- 2-1.4 The degree of hazard shall indicate to fire fighting 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 Definition.

2-2.1 A health hazard is any property of a material which either directly or indirectly can cause injury or incapacitation, either temporary or permanent, from exposure by contact, inhalation or ingestion.

2-3 Degrees of Hazard.

2-3.1 Degrees of hazard are ranked according to the probable severity of hazard to personnel as follows:



Materials which on very short exposure could cause death or major residual injury even though prompt medical treatment were given, including those which are too dangerous to be approached without specialized protective equipment. This degree should include:

Materials which can penetrate ordinary rubber

protective clothing;

Materials which under normal conditions or under fire conditions give off gases which are extremely hazardous (i.e., toxic or corrosive) through inhalation or through contact with or absorption through the skin.

Materials which on short exposure could cause serious temporary or residual injury even though prompt medical treatment were given, including those requiring protection from all bodily contact. This degree should include:

Materials giving off highly toxic combustion pro-

Materials corrosive to living tissue or toxic by skin absorption.

Materials which on intense or continued exposure could cause temporary incapacitation or possible residual injury unless prompt medical treatment is given, including those requiring use of respiratory protective equipment with independent air supply. This degree should include:

Materials giving off toxic combustion products;

Materials giving off highly irritating combustion products:

Materials which either under normal conditions or under fire conditions give off toxic vapors lacking warning properties.

Materials which on exposure would cause irritation but only minor residual injury even if no treatment is given, including those which require use of an approved canister type gas mask. This degree should include:

Materials which under fire conditions would give off irritating combustion products;

Materials which on the skin could cause irritation without destruction of tissue.

Materials which on exposure under fire conditions would offer no hazard beyond that of ordinary combustible material.

Chapter 3 Flammability Hazards

3-1 General.

3-1.1 This chapter deals with the degree of susceptibility of materials to burning. Many materials which will burn under one set of conditions will not burn under others. The form or condition of the material, as well as its inherent properties, affects the hazard.

3-2 Degrees of Hazard.

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



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

Gases;

Cryogenic materials;

Any liquid or gaseous material which is a liquid while under pressure and having a flash point below 73°F (22.8°C) and having a boiling point below 100°F (37.8°C). (Class IA flammable liquids.)

Materials which on account of their physical form or environmental conditions can form explosive mixtures with air and which are readily dispersed in air, such as dusts of combustible solids and mists of flammable or combustible liquid droplets.



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 degree should include:

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). (Class IB and Class IC flammable liquids);

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

Solid materials in a fibrous or shredded form which may burn rapidly and create flash fire

hazards, such as cotton, sisal and hemp;

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

Materials which ignite spontaneously when exposed to air.

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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 may release vapor in sufficient quantities to produce hazardous atmospheres with air. This degree should include:

Liquids having a flash point above 100°F (37.8°C), but not exceeding 200°F (93.4°C);

Solids and semisolids which readily give off flammable vapors.

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. This degree should include:

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

Liquids, solids and semisolids having a flash point above 200°F (93.4°C);

This degree includes most ordinary combustible materials.

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

Chapter 4 Reactivity (Instability) Hazards

4-1 General.

- 4-1.1 This chapter deals with the degree of susceptibility of materials to release energy. Some materials are capable of rapid release of energy by themselves, as by self-reaction or polymerization, or can undergo violent eruptive or explosive reaction if contacted with water or other extinguishing agents or with certain other materials.
- **4-1.2** The violence of reaction or decomposition of materials may be increased by heat or pressure, 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 in a general numerical scaling 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 hazard shall indicate to fire fighting and emergency personnel that the area should be evacuated, that the fire may be fought from a protected location, that caution must be used in approaching the fire and applying extinguishing agents, or that the fire may be fought using normal procedures.

4-2 Definitions.

- 4-2.1 Reactive materials are those which can enter into a chemical reaction with other stable or unstable materials. For purposes of this standard, the other material to be considered is water and only if its reaction releases energy. Reactions with common materials, other than water, may release energy violently. Such reactions shall be considered in individual cases, but are beyond the scope of this identification system.
- **4-2.2** Unstable materials are those which in the pure state or as commercially produced will vigorously polymerize, decompose or condense or become self-reactive and undergo other violent chemical changes.

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 are ranked according to ease, rate and quantity of energy release as follows:



Materials which in themselves are readily capable of detonation or of explosive decomposition or explosive reaction at normal temperatures and pressures. This degree should include materials which are sensitive to mechanical or localized thermal shock at normal temperatures and pressures.

- Materials which in themselves are capable of detonation or of explosive decomposition or explosive reaction but which require a strong initiating source or which must be heated under confinement before initiation. This degree should include materials which are sensitive to thermal or mechanical shock at elevated temperatures and pressures or which react explosively with water without requiring heat or confinement.
- Materials which in themselves are normally unstable and readily undergo violent chemical change but do not detonate. This degree should include materials which can undergo chemical change with rapid release of energy at normal temperatures and pressures or which can undergo violent chemical change at elevated temperatures and pressures. It should also include those materials which may react violently with water or which may form potentially explosive mixtures with water.
- Materials which in themselves are normally stable, but which can become unstable at elevated temperatures and pressures or which may react with water with some release of energy but not violently.
- Materials which in themselves are normally stable, even under fire exposure conditions, and which are not reactive with water.

Chapter 5 Special Hazards

5-1 General.

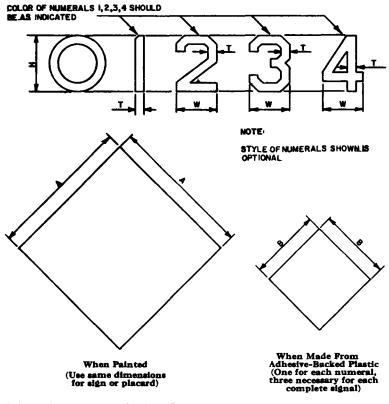
- 5-1.1 This chapter deals with other properties of the material which may cause special problems or require special fire fighting techniques.
- 5-1.2 Special hazards or similar problems shall be identified in the fourth space in the diagram.

5-2 Symbols.

- 5-2.1 Materials which demonstrate unusual reactivity with water shall be identified with the letter W with a horizontal line through the center (\(\formalfont{W}\)).
- 5-2.2 Materials which possess oxidizing properties shall be identified by the letters OX.
- 5-2.3 Materials possessing radioactivity hazards shall be identified by the standard radioactivity symbol.

Chapter 6 Identification of Materials by Hazard Signal System

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



Minimum Dimensions of White Background for Signals

(White Background is Optional)

| Size of Signals | | | | |
|-----------------------|---------------------------------|---------------------------------------|---------------------------|---------------------------|
| н | w | Т | _ A | В |
| 1 2 3 4 6 | 0.7 1.4 2.1 2.8 4.2 | 5 to 5 to 15 to 5 8 15 16 | 2½ 5 7½ 10 15 | 1½ 2½ 3¾ 5 7½ |

IDENTIFICATION OF MATERIALS BY HAZARD SIGNAL DIMENSIONS

All Dimensions Given in Inches

ADHESIVE-BACKED PLASTIC BACKGROUND PIECES - ONE NEEDED FOR EACH NUMERAL, THREE NEEDED FOR EACH COMPLETE SIGNAL.



Fig. 1. For Use Where Specified Color Background is Used with Numerals of Contrasting Colors.

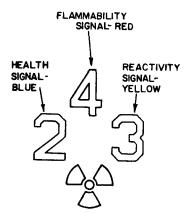


Fig. 2. For Use Where White Background is Necessary.

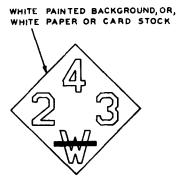


Fig. 3. For Use Where White Background is Used With Painted Numerals, or, For Use When Signal is in the Form of Sign or Placard

ARRANGEMENT AND ORDER OF SIGNALS - OPTIONAL FORM OF APPLICATION

| Distance at Which Signals Must be Legible | Minimum Size of Signals Required |
|---|---|
| 50 feet | 1" |
| 75 feet | 2" |
| 100 feet | 3′′ |
| 200 feet | 4" |
| 300 feet | 6'' |

NOTE:

This shows the correct spatial arrangement and order of signals used for identification of materials by hazard

IDENTIFICATION OF MATERIALS BY HAZARD SIGNAL ARRANGEMENT

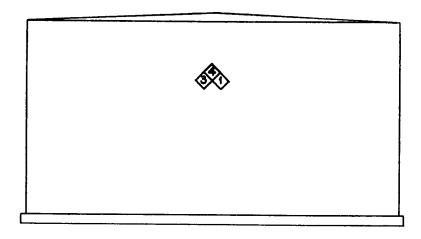


Fig. 4. Storage Tank

Appendix A

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

This is a system for the identification of hazards to life and health of people in the prevention and control of fires and explosions in the manufacture and storage of materials.

The bases for identification are the physical properties and characteristics of materials that are known or can be determined by standard methods. Technical terms, expressions, trade names, etc., are purposely avoided as this system is concerned only with the identification of the involved hazard from a standpoint of safety.

The explanatory material in this Appendix is to assist users of this guide, particularly the person who assigns the degree of hazard in each category.

| Identification of Health Hazard Color Code: BLUE | | Identification of Flammability Color Code: RED | | Identification of Reactivity (Stability) Color Code: YELLOW | | |
|---|---|--|--|---|---|--|
| Type of Possible Injury | | Susceptibility of Materials to Burning | | Susceptibility to Release of Energy | | |
| Signal | | Signal | | Signal | | |
| 4 | Materials which on very short exposure could cause death or major residual injury even though prompt medical treatment were given. | 4 | Materials which will rapidly or completely vaporize at atmospheric pressure and normal ambient temperature, or which are readily dispersed in air and which will burn readily. | 4 | Materials which in themselves are readily capable of detonation or of explosive decomposition or reaction at normal temperatures and pressures. | |
| 3 | Materials which on short exposure could cause serious temporary or residual injury even though prompt medical treatment were given. | 3 | Liquids and solids that can be ignited under almost all ambient temperature condi- tions. | 3 | Materials which in themselves are capable of detonation or explosive reaction but require a strong initiating source or which must be heated under confinement before initiation or which react explosively with water. | |
| 2 | Materials which on intense or continued exposure could cause temporary incapacitation or possible residual injury unless prompt medical treatment is given. | 2 | Materials that must be moderately heated or exposed to relatively high ambient temperatures before ignition can occur. | 2 | Materials which in themselves are normally unstable and readily undergo violent chemical change but do not detonate. Also materials which may react violently with water or which may form potentially explosive mixtures with water. | |
| 1 | Materials which on exposure would cause irritation but only minor residual injury even if no treatment is given. | 1 | Materials that must be pre- heated before ignition can occur. | 1 | Materials which in themselves ar normally stable, but which can be come unstable at elevated tempera tures and pressures or which may re act with water with some release of energy but not violently. | |
| 0 | Materials which on exposure under fire conditions would offer no hazard beyond that of ordinary combustible ma- terial. | 0 | Materials that will not burn. | 0 | Materials which in themselves are normally stable, even under fire exposure conditions, and which are not reactive with water. | |

Appendix B

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

The information contained within Appendix B is derived from introductory explanatory material on the 704M system contained within NFPA 49, Hazardous Chemicals Data; NFPA 57, Standard for Fumigation; and NFPA 325M, Fire Hazard Properties of Flammable Liquids, Gases and Volatile Solids. The following paragraphs summarize the meanings of the numbers in each hazard category and explain what a number should tell fire fighting personnel about protecting themselves and how to fight fires where the hazard exists.

Health.

In general, health hazard in fire fighting is that of a single exposure which may vary from a few seconds up to an hour. The physical exertion demanded in fire fighting or other emergency conditions may be expected to intensify the effects of any exposure. Only hazards arising out of an inherent property of the material are considered. The following explanation is based upon protective equipment normally used by fire fighters.

- Materials too dangerous to health to expose fire fighters. A few whiffs of the vapor could cause death or the vapor or liquid could be fatal on penetrating the fire fighter's normal full protective clothing. The normal full protective clothing and breathing apparatus available to the average fire department will not provide adequate protection against inhalation or skin contact with these materials.
- Materials extremely hazardous to health but areas may be entered with extreme care. Full protective clothing, including self-contained breathing apparatus, coat, pants, gloves, boots, and bands around legs, arms and waist should be provided. No skin surface should be exposed.
- Materials hazardous to health, but areas may be entered freely with full-faced mask self-contained breathing apparatus which provides eye protection.
- Materials only slightly hazardous to health. It may be desirable to wear self-contained breathing apparatus.
- Materials which on exposure under fire conditions would offer no hazard beyond that of ordinary combustible material.

Flammability.

Susceptibility to burning is the basis for assigning degrees within this category. The method of attacking the fire is influenced by this susceptibility factor.

- Very flammable gases or very volatile flammable liquids. Shut off flow and keep cooling water streams on exposed tanks or containers.
- Materials which can be ignited under almost all normal temperature conditions. Water may be ineffective because of the low flash point.
- Materials which must be moderately heated before ignition will occur. Water spray may be used to extinguish the fire because the material can be cooled below its flash point.
 - Materials that must be preheated before ignition can occur. Water may cause frothing if it gets below the surface of the liquid and turns to steam. However, water fog gently applied to the surface will cause a frothing which will extinguish the fire.
- Materials that will not burn.

Reactivity (Stability).

The assignment of degrees in the reactivity category is based upon the susceptibility of materials to release energy either by themselves or in combination with water. Fire exposure was one of the factors considered along with conditions of shock and pressure.



Materials which (in themselves) are readily capable of detonation or of explosive decomposition or explosive reaction at normal temperatures and pressures. Includes materials which are sensitive to mechanical or localized thermal shock. If a chemical with this hazard rating is in an advanced or massive fire, the area should be evacuated.