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for the

IDENTIFICATION OF THE FIRE HAZARDS OF MATERIALS

May

1961

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National Fire Protection Association

International

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This is one of a large number of publications on fire safety issued by the Association. All NFPA standards and recommended practices, including this text, are prepared by the technical committees of the NFPA and adopted at an Annual Meeting of the Association. They are intended to prescribe reasonable measures for minimizing losses of life and property by fire.

This text and most other NFPA standards and recommended practices are published in the **National Fire Codes,** a compilation of NFPA's official technical material, issued in seven clothbound volumes. Full information on the availability of these Codes and other NFPA publications can be secured from the Association.

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SHALL is intended to indicate requirements.

SHOULD is intended to indicate recommendations, or that which is advised but not required.

APPROVED refers to approval by the authority having jurisdiction.

Units of measurements used here are U. S. standard. 1 U. S. gallon = 0.83 Imperial gallons = 3.785 liters. One foot = 0.3048 meters. One inch = 25.40 millimeters. One pound per square inch = 0.06805 atmospheres = 2.307 feet of water.

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IDENTIFICATION OF THE FIRE HAZARDS OF MATERIALS

NFPA No. 704M — 1961

This Recommended System for the Identification of the Fire Hazards of Materials was finally adopted by the NFPA at its Annual Meeting on May 18, 1961 on recommendation of the Committee on Fire Hazards of Materials. It was tentatively adopted in 1960.

A brief history of the development of the guide is given in the foreword on page 704M–2.

Recommended System

for the

IDENTIFICATION OF THE FIRE HAZARDS OF MATERIALS

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FOREWORD

The Committee on Fire Hazards of Materials has been working on this guide since early 1957 and a great deal of preliminary work was developed 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 guide was tentatively adopted in 1960, and finally adopted in 1961.

As provided in the Association procedures this guide is intended as an informative brochure to assist other committees of the Association in their scope assignments. This type of publication is not intended to be used as a standard.

As originally conceived, the purpose of the guide 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. It does not envision possible application to other situations, such as chemical laboratories, rail or truck transportation, lumber and coal storage yards and tobacco warehouses.

CHAPTER I. INTRODUCTION

10. This guide 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.

11. This system identifies the hazards of a material in terms of three principal categories, namely, "health," "flammability," and "reactivity (stability)"; 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 marking system of color diagrams, one color corresponding to each of the three hazard categories — blue for "health" hazard, red for "flammability," and yellow for "reactivity (stability)." Examples of spatial arrangement are shown on page 13. For the sake of uniformity, the spatial arrangements shown in the examples should be followed.

12. The fourth space in the diagram (see Figure 3, Page 13) may be used to indicate additional information such as: proper fire extinguishing agent, *unusual* reactivity with water, pressurized containers, radioactivity, or protective equipment required in case of fire or other emergency, etc.

13. This system is intended to give basic information to fire fighting 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.

14. 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 must be performed by experienced, technically competent persons. Their judgment must 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 fire exposure and control.

15. The system for ranking degrees of hazard is based on relative rather than absolute values. Therefore, it is anticipated that differing experiences resulting from differing 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 less on degree of reactivity (except that materials that are true explosives would be in degree 4) than on kind of reactivity — spontaneous, or with water, or stable only while containing additives or while refrigerated. 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 exposure.

CHAPTER II. HEALTH HAZARDS

20. General.

201. 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.

202. 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.

203. 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 should 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.

204. The degree of hazard should 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.

21. Definition.

211. 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.

22. Degrees of Hazard.

221. Degrees of hazard are ranked according to the probable severity of hazard to personnel as follows:

4 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.

3 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 products;

Materials corrosive to living tissue or toxic by skin absorption.

2 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.

1 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.

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

CHAPTER III. FLAMMABILITY HAZARDS

30. General.

301. 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.

31. Degrees of Hazard.

311. 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. This degree should include:

Gaseous materials;

Cryogenic materials;

Any liquid or gaseous material which is a liquid while under pressure and having a vapor pressure greater than 14.7 psia at a temperature of 100° F;

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 of 100° F or below and having a vapor pressure not greater than 14.7 psia at 100° F;

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;

Solids which burn with extreme rapidity, usually by reason of self-contained oxygen (e.g., dry nitrocellulose);

Materials which ignite spontaneously when exposed to air.

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, but not exceeding 200° F;

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 for a period of 5 minutes or less;

Liquids, solids and semisolids having a flash point above 200° F;

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 for a period of 5 minutes.

CHAPTER IV. REACTIVITY (STABILITY) HAZARDS

40. General.

401. This chapter deals with the degree of susceptibility of materials to release energy either by themselves or in combination with other materials.

41. Definitions.

411. Stable materials are those having the relative capacity to resist changes in their chemical composition despite exposure to air, water and heat as encountered in fire emergencies.

412. Unstable materials are those which in the pure state or as commercially produced will vigorously polymerize, decompose, condense, or will become self-reactive or explode under conditions of shock, pressure, or temperature.

413. Reactive materials are those which can enter into a chemical reaction with other materials. For purposes of this guide the other materials primarily to be considered are water and other extinguishing agents. Only energy releasing reactions are considered.

42. Degrees of Hazard.

421. The degrees of hazard are ranked according to ease, rate and quantity of energy release as follows:

Materials which are readily capable of detonation or of explosive decomposition or reaction at normal temperatures and pressures. This degree should include:

Materials which are sensitive to thermal or mechanical shock;

Materials which are sensitive to a low order of temperature and pressure change.

Materials which readily undergo violent chemical change. This degree should include:

Materials which undergo rapid chemical change at normal temperatures and pressures or those which will undergo violent chemical change at elevated temperatures and pressures;

Materials which are capable of detonation under confinement;
Materials which will undergo violent chemical change if contaminated.

2 Materials which will react with water with release of significant quantities of energy. Water should not be used as an extinguishing agent without competent technical knowledge.

1 Materials which are normally unstable but have been rendered stable by the addition of inhibitors or by refrigeration.

0 Materials which are normally stable.

APPENDIX A

IDENTIFICATION OF MATERIALS BY HAZARD SIGNAL SYSTEM

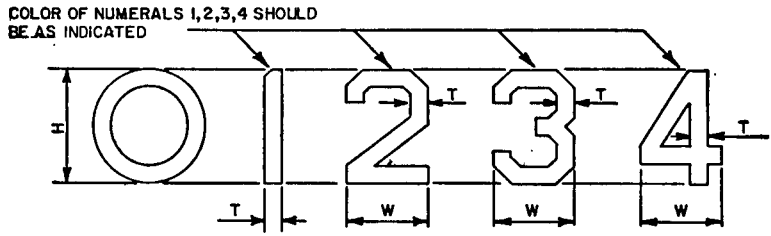
This is a system for the identification of hazards to life and property, as such hazards pertain to life and health of people and prevention and control of fires and explosions in the manufacture and storage of materials.

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.

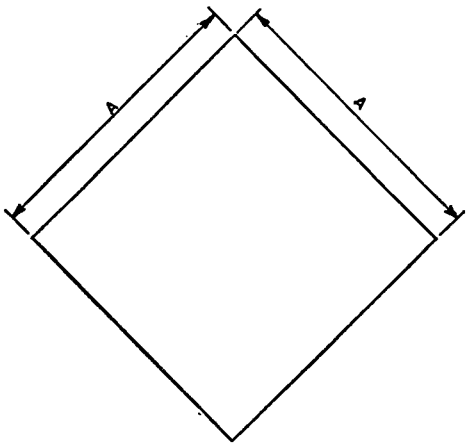
The system for identification of the type of hazard involved by a visual signal is outlined in the material on the following pages.

Identification of Health Hazard Color Code: BLUE		Identification of Flammability Color Code: RED		Identification of Reactivity (Stability) Color Code: YELLOW	
Signal	Type of Possible Injury	Signal	Susceptibility of Materials to Burning	Signal	Susceptibility to Release of Energy
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.	4	Materials which 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 conditions.	3	Materials which readily undergo violent chemical change.
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 will react with water with release of significant quantities of energy.
1	Materials which on exposure would cause irritation but only minor residual injury even if no treatment is given.	1	Materials that must be preheated before ignition can occur.	1	Materials which are normally unstable but have been rendered stable by the addition of inhibitors or by refrigeration.
0	Materials which on exposure under fire conditions would offer no hazard beyond that of ordinary combustible material.	0	Materials that will not burn.	0	Materials which are normally stable.

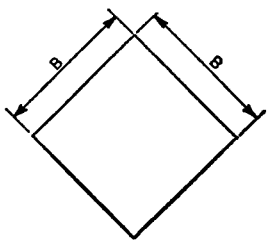


NOTE:

STYLE OF NUMERALS SHOWN IS OPTIONAL



When Painted
(Use same dimensions for sign or placard)



When Made From Adhesive-Backed Plastic (One for each numeral, three necessary for each complete signal)

Dimensions of White Background for Signals

(White Background is Optional)

Size of Signals H	W	T	A	B
1	0.7	5/32	2 1/2	1 1/4
2	1.4	5/16	5	2 1/2
3	2.1	15/32	7 1/2	3 3/4
4	2.8	5/8	10	5
6	4.2	15/16	15	7 1/2

All Dimensions Given in Inches

IDENTIFICATION OF MATERIALS BY HAZARD SIGNAL DIMENSIONS

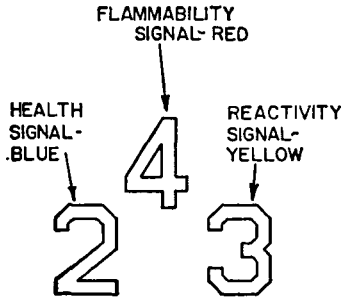


Fig. 1. For Use Where White Background Is Not Necessary.

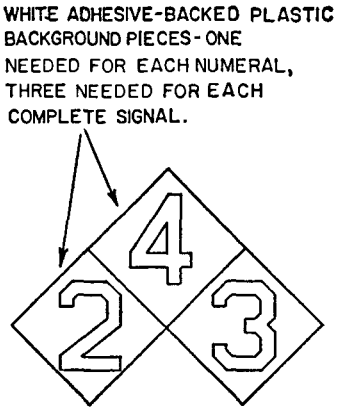


Fig. 2. For Use Where White Background is Used With Numerals Made From Adhesive-Backed Plastic

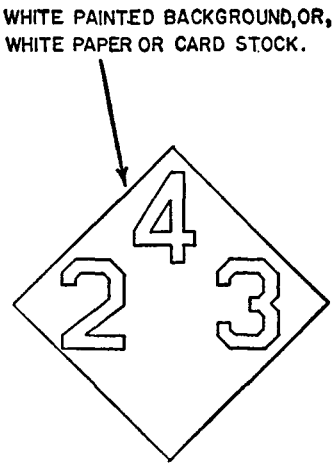


Fig. 3. For Use Where White Background is Used With Painted Numerals, or, For Use When Signal is in the Form of Sign or Placard

ARRANGEMENT AND ORDER OF SIGNALS — OPTIONAL FORM OF APPLICATION

Distance at Which Signals Must be Legible	Size of Signals Required
50 feet	1″
75 feet	2″
100 feet	3″
200 feet	4″
300 feet	6″

NOTE:

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

IDENTIFICATION OF MATERIALS BY HAZARD SIGNAL ARRANGEMENT

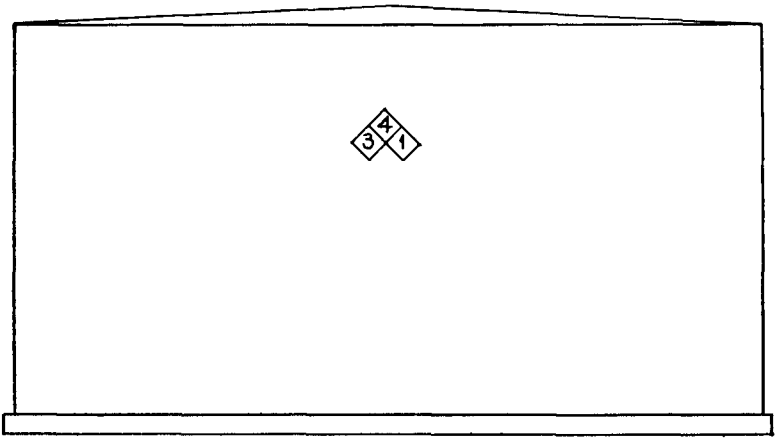


Fig. 4. Storage Tank

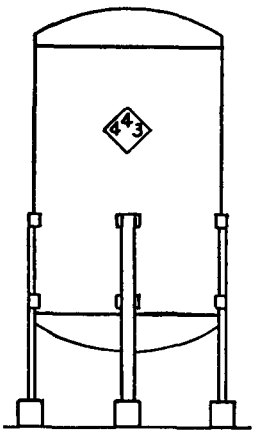


Fig. 5. Processing Tank

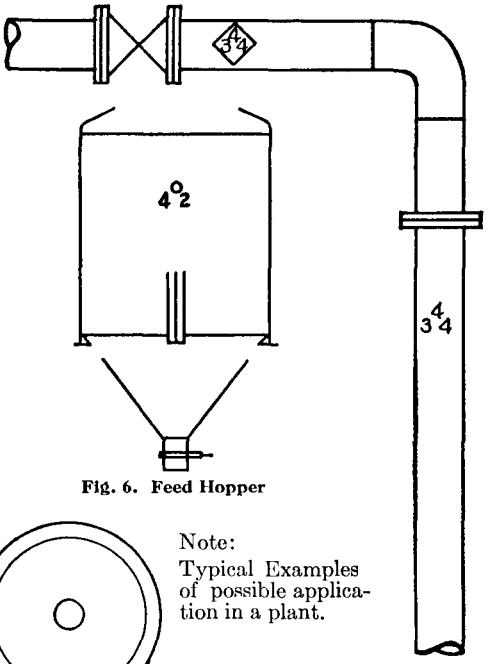


Fig. 6. Feed Hopper

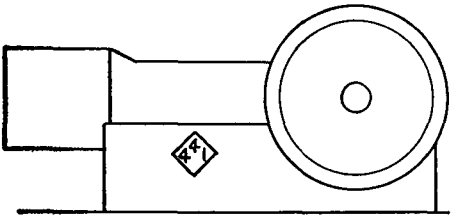


Fig. 7. Compressor

Note:
Typical Examples of possible application in a plant.

Fig. 8 Large Pipeline

APPENDIX B. FLAMMABILITY

The selection of the flash point breaks for the assigning of degrees within the Flammability category has been based upon the recommendations of the Sectional Committee on Classification, Labeling and Properties of Flammable Liquids of the NFPA Committee on Flammable Liquids. This Sectional Committee initiated the study which led to the development of this guide. Close cooperation between the Sectional Committee and the Committee on Fire Hazards of Materials has continued during the developmental stages of this guide.

The following discussion on flash point and methods of testing were the recommendations of the Sectional Committee in 1956 as modified by subsequent meetings they have held.

Flash point tells several things. One, if the liquid has no flash point, it is not a flammable liquid. Two, if it has a flash point, it must be considered flammable or combustible. Three, the flash point is normally an indication of susceptibility to ignition. Because of the greater volatility of some liquids it was agreed that a break point would be at the absolute vapor pressure of 14.7 pounds per square inch at 100° F. Vapor pressure as a break point is particularly desirable for liquids which are mixtures of two or more components of which at least one boils above 100° F and and at least one below 100° F. The vapor pressure determination should be made by the "Standard Method of Test for Vapor Pressure of Petroleum Products (Reid Method)" of the American Society for Testing Materials (ASTM D-323).

In the case of liquids consisting of a single commercially pure chemical compound, a boiling point break of 100° F is acceptable in lieu of the 14.7 psia at 100° F vapor pressure break.

The flash point test may give results which would indicate that the liquid is nonflammable or that it comes under degree 1 or 2 when it is 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 opened container, the carbon tetrachloride will evaporate more rapidly than the gasoline. Over a period of time, therefore, the residual liquid will first show a high flash point, then a progressively lower one until the flash point of the final 10 per cent 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 per cent 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.

In the interest of reproducibility of results, it was recommended that:

Except for fuel oils, the flash point of flammable liquids having a flash point below 175° F (79° C) should be determined in accordance with the standard method of test for flash point by means of the Tag. Closed Tester (ASTM D-56). (In those countries which use the Abel or Abel-Pensky closed cup tests as an official standard, they will be equally acceptable to the Tag. closed cup method.)

The flash point of fuel oils should be determined by the standard method of test for flash point by means of the Pensky-Martens Closed Tester (ASTM D-93).

The flash point of flammable liquids having a flash point above 175° F should be determined in accordance with the standard method of test for flash point by means of the Cleveland Open Cup Tester (ASTM D-92).

APPENDIX C. REFERENCES

The determination of the fire hazards of materials pertaining to health, flammability and reactivity may require the search of technical literature in order to find an important physical and chemical characteristic. However, normally all the necessary information is available in published form or can be obtained by a direct request to the manufacturer. The following references may be of assistance.

The Analytical Chemistry of Industrial Poisons, Hazards and Solvents — 1944
Morris B. Jacobs, Interscience Publishers, Inc., New York, N. Y.

Chemical Engineers' Handbook
John H. Perry — Editor, McGraw-Hill Book Company, Inc., 330 West 42nd Street, New York 36, N. Y.

Chemistry in Relation to Fire Risk and Fire Extinction
A. M. Cameron, Sir Isaac Pitman & Sons, Ltd., London, England

The Classification of Fire Hazards and Extinction Methods — 1954
James D. Birchall, Ernest Benn, Ltd., London, England

Code of Federal Regulations — Title 46 — Shipping, Parts 146 to 149 — Revised January 1, 1958 and Title 49 — Transportation, Parts 71–78.
Los Angeles Fire Prevention Code — Divisions 70–76 inclusive. Bureau of Fire Prevention, City of Los Angeles Fire Dept., Los Angeles, Calif. Federal Register Division, National Archives & Records Service, General Services Administration, U. S. Government Printing Office, Washington 25, D. C.

Concise Chemical and Technical Dictionary — 1947
H. Bennett, Chemical Publishing Company, Inc., Brooklyn, N. Y.

Condensed Chemical Dictionary
Arthur and Elizabeth Rose, Reinhold Publishing Company, 430 Park Avenue, New York 22, N. Y.

Compilation of Labeling Laws and Regulations for Hazardous Substances
Chemical Specialties Manufacturers Association, Inc., 50 East 41st Street, New York 17, N. Y.

(The text includes a compilation of laws and regulations regarding the labeling of hazardous substances pertaining primarily to poisons and household chemicals. However, it does give information on industrial chemicals. The table of contents indicates the various state labeling laws and regulations for household chemicals. This reference material will be helpful in determining hazards of materials.)

Dangerous Goods — Third Edition plus one supplement — 1950
Jules Acby, Editions Lloyd Anversois, Antwerp, Belgium

Dangerous Properties of Industrial Materials — 2nd Edition
N. Irving Sax, Reinhold Publishing Company, 430 Park Avenue, New York 22, N. Y.