

# Appendix A

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## HAZARDOUS MATERIALS CLASSIFICATION SYSTEMS

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## **NATIONAL FIRE PROTECTION ASSOCIATION, 704M SYSTEM**

The marking system designed by the National Fire Protection Association identifies hazard characteristics of materials at terminal and industrial sites. It uses a diamond divided into four quadrants, with each quadrant representing a different characteristic, as explained below.

The risk level ratings, ranging from four (highest risk) to zero (minimum risk), are based upon protective equipment normally used by firefighters.

### **Health (Blue)**

Health hazards in firefighting generally result from a single exposure, which may vary from a few seconds up to an hour. Only hazards arising out of an inherent property of the material are considered. It should be noted, however, that the physical exertion demanded in firefighting or other emergency conditions tends to intensify the effects of any exposure.

**Risk level 4:** Materials too dangerous to human health to expose firefighters. A few whiffs of the vapor could cause death or the vapor or liquid could be fatal on penetrating the firefighter'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.

**Risk level 3:** Materials extremely hazardous to health, but areas may be entered with extreme care. Full protective clothing including self-contained breathing apparatus, coat, pants, gloves, and boots, with bands around the legs, arms, and waist should be provided. No skin surface should be exposed.

**Risk level 2:** Materials hazardous to health, but areas may be entered freely with full facemask self-contained breathing apparatus that also provides eye protection.

**Risk level 1:** Materials only slightly hazardous to health. It may be desirable to wear self-contained breathing apparatus.

**Risk level 0:** Materials which on exposure under fire conditions would offer no hazard beyond that of ordinary combustible materials.

### **Flammability (Red)**

Susceptibility to burning is the basis for assigning risk levels within this category. The method of attacking the fire is influenced by the material's susceptibility factor.

**Risk level 4:** Very flammable gases or very volatile flammable liquids. Shut off flow and keep cooling water streams on exposed tanks or containers.

**Risk level 3:** Materials that can be ignited under almost all normal temperature conditions. Water may be ineffective because of the low flash point.

**Risk level 2:** Materials that 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.

**Risk level 1:** Materials that must be preheated before ignition will 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 that will extinguish the fire.

**Risk level 0:** Materials that will not burn.

### **Reactivity/Stability (Yellow)**

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 is one of the factors considered, along with conditions of shock and pressure.

**Risk level 4:** Materials that (in themselves) are readily capable of detonation or of explosive decomposition or reaction at normal temperatures and pressures. Includes materials that 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.

**Risk level 3:** Materials that (in themselves) are capable of detonation or of explosive decomposition or reaction that require a strong initiating source that must be heated under confinement before initiation. Includes materials that are sensitive to thermal or mechanical shock at elevated temperatures and pressures, or that react explosively with water without requiring heat or confinement. Firefighting should be done from an explosive-resistant location.

**Risk level 2:** Materials that (in themselves) are normally unstable and readily undergo violent chemical change, but do not detonate. Includes materials that can undergo chemical change with rapid release of energy at normal temperatures and pressures, or that can undergo violent chemical change at elevated temperatures and pressures. Also includes those materials that may react violently with water or that may form potentially explosive mixtures with water. In advanced or massive fires, firefighting should be done from a safe distance or from a protected location.

**Risk level 1:** Materials that (in themselves) are normally stable but that may become unstable at elevated temperatures and pressures or that may react with water with some release of energy, but not violently. Caution must be used in approaching the fire and applying water.

**Risk level 0:** Materials that (in themselves) are normally stable even under fire exposure conditions and that are not reactive with water. Normal firefighting procedures may be used.

### **Special Information (White)**

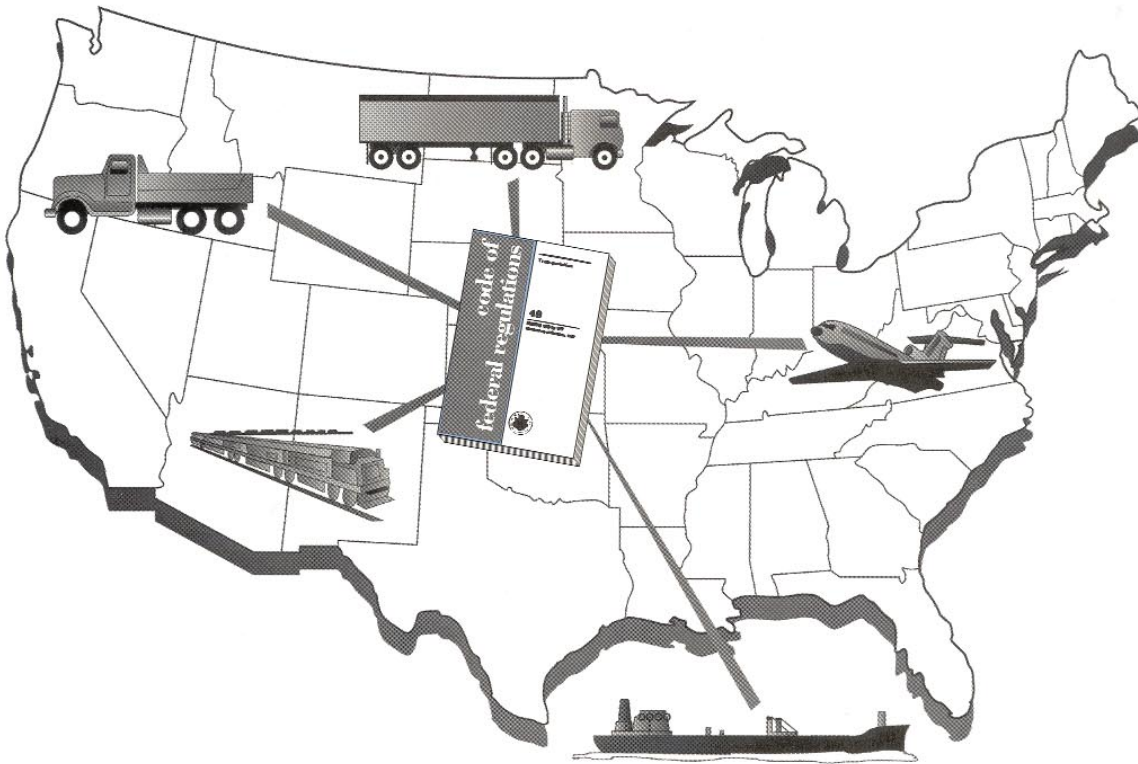
The quadrant includes information on specific characteristics of the material (e.g., reactivity with water, tendency to oxidize).



U.S. Department of  
Transportation  
Research and  
Special Programs  
Administration

# DOT CHART 11

## Hazardous Materials Marking, Labeling & Placarding Guide



Refer to 49 CFR, Part 172:

Marking - Subpart D

































Labeling - Subpart E

Placarding - Subpart F

Emergency Response - Subpart G

**NOTE:** This document is for general guidance only and must not be used to determine compliance with 49 CFR, Parts 100-185.

# Hazardous Materials Warning Labels
























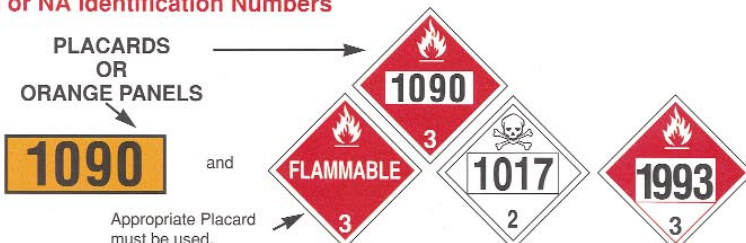
<p>CLASS 1 Explosive 1.1, 1.2, 1.3</p>  <p>*Include appropriate division number and compatibility group letter.</p>	<p>CLASS 1 Explosive 1.4</p>  <p>*Include appropriate compatibility group letter.</p>	<p>CLASS 1 Explosive 1.5</p>  <p>*Include appropriate compatibility group letter.</p>	<p>CLASS 1 Explosive 1.6</p>  <p>*Include appropriate compatibility group letter.</p>	<p>CLASS 2 Division 2.1</p>  <p>Flammable gas</p>	<p>CLASS 2 Division 2.2</p>  <p>Non-flammable gas</p>	<p>CLASS 2 Division 2.2</p>  <p>Oxygen</p>
<p>CLASS 2 Division 2.3</p>  <p>Poison gas</p>	<p>CLASS 3</p>  <p>Flammable liquid</p>	<p>CLASS 4 Division 4.1</p>  <p>Flammable solid</p>	<p>CLASS 4 Division 4.2</p>  <p>Spontaneously Combustible</p>	<p>CLASS 4 Division 4.3</p>  <p>Dangerous when wet</p>	<p>CLASS 5 Division 5.1</p>  <p>Oxidizer</p>	<p>CLASS 5 Division 5.2</p>  <p>Organic peroxide</p>
<p>CLASS 6 Division 6.1</p>  <p>Poison Inhalation Hazard only, Zone A or B.</p>	<p>CLASS 6 Division 6.1</p>  <p>POISON Placed 454 kg (1,000 lbs) or more of PG I or II, other than Zone A or B, Inhalation Hazard.</p>	<p>CLASS 6 Division 6.1</p>  <p>Poison-PG III</p>	<p>CLASS 6 Division 6.2</p>  <p>Infectious substance</p>	<p>CLASS 7</p>  <p>Radioactive WHITE-I</p>	<p>CLASS 7</p>  <p>Radioactive YELLOW-II</p>	
<p>CLASS 7</p>  <p>Radioactive YELLOW-III</p>	<p>CLASS 8</p>  <p>Corrosive</p>	<p>CLASS 9</p>  <p>Miscellaneous</p>	<p>SUBSIDIARY RISK LABELS</p>  <p>The class number may not be displayed on a subsidiary label (see Section 1.7.2.107)</p>		<p>EMPTY</p>  <p>Empty-Inhalation</p>	<p>FOR AIRCRAFT</p>  <p>Cargo Aircraft Only</p>
<p>TRANSITION-2001</p>  <p>EXPLOSIVE A</p>	<p>TRANSITION-2001</p>  <p>EXPLOSIVE B</p>	<p>TRANSITION-2001</p>  <p>EXPLOSIVE C</p>	<p>TRANSITION-2001</p>  <p>ELASTING AGENT</p>	<p>TRANSITION-2001</p>  <p>FLAMMABLE SOLID</p>	<p>TRANSITION-2001</p>  <p>IRRITANT</p>	

## HAZARDOUS MATERIALS MARKINGS

<p>INNER PACKAGES COMPLY WITH PRESCRIBED SPECIFICATIONS</p> <p>§1.1.1.2(b)(1)</p>  <p>§1.1.1.2(b)</p>	<p>MARINE POLLUTANT</p> <p>§1.72.302</p>  <p>HOT</p> <p>§1.72.305</p> 	<p><b>DANGER</b></p> <p>THIS CONTAINS A BIOHAZARD AGENT</p> <p><b>DO NOT ENTER</b></p> <p>§1.72.302(a) and §1.72.303</p> 	<p><b>INHALATION HAZARD</b></p> <p>§1.72.313(a)</p> 	<p>CONTAINER COMMODITY</p> <p>ORM-D</p> <p>§1.72.316(a)</p>  <p>CONTAINER COMMODITY</p> <p>ORM-D-AIR</p> <p>§1.72.316(a)(1)</p> 
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Keep a copy of the North American Emergency Response

# Hazardous Materials Warning Placards

<p>CLASS 1</p>  <p>EXPLOSIVES *Enter Division Number 1.1, 1.2, or 1.3 and compatibility group letter, when required. Placard any quantity.</p>	<p>CLASS 1</p>  <p>EXPLOSIVES 1.4 *Enter compatibility group letter, when required. Placard 454 kg (1,001 lbs) or more.</p>	<p>CLASS 1</p>  <p>EXPLOSIVES 1.5 *Enter compatibility group letter, when required. Placard 454 kg (1,001 lbs) or more.</p>	<p>CLASS 1</p>  <p>EXPLOSIVES 1.6 *Enter compatibility group letter, when required. Placard 454 kg (1,001 lbs) or more.</p>	<p>CLASS 2</p>  <p>OXYGEN Placard 454 kg (1,001 lbs) or more gross weight of either compressed gas or refrigerated liquid.</p>
<p>CLASS 2</p>  <p>FLAMMABLE GAS Placard 454 kg (1,001 lbs) or more.</p>	<p>CLASS 2</p>  <p>NON-FLAMMABLE GAS Placard 454 kg (1,001 lbs) or more gross weight.</p>	<p>CLASS 2</p> <p style="text-align: right;">Division 2.3</p>  <p>POISON GAS Placard any quantity.</p>	<p>CLASS 3</p>  <p>FLAMMABLE Placard 454 kg (1,001 lbs) or more.</p>	<p>CLASS 3</p>  <p>GASOLINE May be used in the place of FLAMMABLE placard displayed on a cargo tank or a portable tank being used to transport gasoline by highway.</p>
<p>CLASS 3</p>  <p>COMBUSTIBLE Placard a combustible liquid when transported in bulk. See §172.504(f)(2) for use of FLAMMABLE placard in place of COMBUSTIBLE placard.</p>	<p>CLASS 3</p>  <p>FUEL OIL May be used in place of COMBUSTIBLE on a placard displayed on a cargo tank or portable tank being used to transport by highway fuel oil not classed as a flammable liquid.</p>	<p>CLASS 4</p>  <p>FLAMMABLE SOLID Placard 454 kg (1,001 lbs) or more.</p>	<p>CLASS 4</p>  <p>SPONTANEOUSLY COMBUSTIBLE Placard 454 kg (1,001 lbs) or more.</p>	<p>CLASS 4</p>  <p>DANGEROUS WHEN WET Placard any quantity of Division 4.3 material.</p>
<p>CLASS 5</p>  <p>OXIDIZER Placard 454 kg (1,001 lbs) or more.</p>	<p>CLASS 5</p>  <p>ORGANIC PEROXIDE Placard any quantity, TYPE B, temperature controlled. Placard 454 kg (1,001 lbs) or more other than TYPE B, temperature controlled.</p>	<p>CLASS 6</p>  <p>POISON-INHALATION HAZARD Placard any quantity of 6.1, Zone A or B inhalation hazard only.</p>	<p>CLASS 6</p>  <p>POISON Placard 454 kg (1,001 lbs) or more of PGI or II, other than Zone A or B inhalation hazard.</p>	<p>CLASS 7</p>  <p>RADIOACTIVE Placard any quantity - packages bearing RADIOACTIVE YELLOW-III labels only. Certain low specific activity radioactive materials in "exclusive use" will not bear the label, but the Radioactive placard is required for exclusive use shipments of low specific activity material and surface contaminated objects transported in accordance with §173.427 (b)(3) or (c).</p>
<p>CLASS 8</p>  <p>CORROSIVE Placard 454 kg (1,001 lbs) or more.</p>	<p>CLASS 9</p>  <p>MISCELLANEOUS Not required for domestic transportation. A bulk packaging containing a Class 9 material must be marked with the appropriate ID number displayed on a Class 9 placard, an orange panel or a white square-on-point display.</p>	<p>DANGEROUS</p> <p>A freight container, unit load device, transport vehicle, or rail car which contains non-bulk packagings with two or more categories of hazardous materials that require different placards specified in Table 2 may be placarded with DANGEROUS placards instead of the specific placards required for each of the materials in Table 2. However, when 1,000 kg (2,205 lbs) or more of one category of material is loaded at one loading facility, the placard specified in Table 2 must be applied.</p>	<p>SUBSIDIARY RISK PLACARD</p>  <p>Class numbers do not appear on a subsidiary risk placard.</p>	
<p>White square background required for placard for highway route controlled quantity radioactive material and for rail shipment of certain explosives and poisons, and for flammable gas in a DOT 113 tank car (see §§172.507 and 172.510).</p>	<p><b>UN or NA Identification Numbers</b></p> <p>PLACARDS OR ORANGE PANELS</p>  <p>Appropriate Placard must be used.</p>			<p>MUST BE DISPLAYED ON: (1) Tank Cars, Cargo Tanks, Portable Tanks, other Bulk Packaging, and (2) On vehicle or containers containing large quantities (8,820 lbs.) In non-bulk packages of only a single hazardous material, and certain quantities (2,205) of a material poisonous by inhalation in Hazard Zone A or B, having the same proper shipping name and identification number.</p>

Guidebook handy!

Response begins with identification!

# General Guidelines on Use of Warning Labels and Placards

## LABELS

See 49 CFR, Part 172, Subpart E for complete labeling regulations.

- Until October 1, 1999, labels for materials poisonous by inhalation that conform to the requirements of the HMR in effect on September 30, 1997, may be used to satisfy the requirements of Subpart E.
- Those labels in boxes marked "TRANSITION 2001" on the chart are not authorized for use under Subpart E. (NOTE: these labels may be used if they were affixed to a package offered for transportation and transported prior to October 1, 2001, and the package was filled with hazardous materials prior to October 1, 1991.)
- For classes 1,2,3,4,5,6 and 8, text indicating a hazard (e.g., "CORROSIVE") IS NOT required on a label. The label must otherwise conform to Subpart E [Section 172.405].
- Any person who offers a hazardous material for transportation MUST label the package, if required [Section 172.400(a)].
- The Hazardous Materials Table [Section 172.101] identifies the proper label(s) for the hazardous material listed.
- When required, labels must be printed on or affixed to the surface of the package near the proper shipping name [Section 172.406(a)].
- When two or more labels are required, they must be displayed next to each other [Section 172.406(c)].
- Labels may be affixed to packages when not required by regulations, provided each label represents a hazard of the material contained in the package [Section 172.401].

## PLACARDS

See 49 CFR, Part 172, Subpart F for complete placarding regulations.

- Until October 1, 2001, placards for materials poisonous by inhalation, by all modes of transportation, may be used that conform to specifications for placards (1) in effect on September 30, 1991, (2) specified in the December 21, 1990 final rule, (HM-181) or (3) specified in the July 22, 1997 final rule (HM-205).
- All of the placards appearing on the Hazardous Materials Warning Placards chart may be used to satisfy the placarding requirements contained in Subpart F.
- Each person who offers for transportation or transports any hazardous material subject to the Hazardous Materials Regulations shall comply with all applicable requirements of Subpart F.
- Placards may be displayed for a hazardous material even when not required, if the placarding otherwise conforms to the requirements of Subpart F.
- For other than Class 7 or the OXYGEN placard, text indicating a hazard (e.g., "CORROSIVE") is not required on a placard [Section 172.519(b)].
- Any transport vehicle, freight container, or rail car containing any quantity of material listed in Table 1 must be placarded [Section 172.504].
- When the gross weight of all hazardous materials in non-bulk pkgs. covered in Table 2 is less than 454 kg (1,001 lbs), no placard is required on a transport vehicle or freight container [Section 172.504].

Effective October 1, 1994, and extending through October 1, 2001, these placards may be used for HIGHWAY TRANSPORTATION ONLY.



Illustration numbers in each square refer to Tables 1 and 2 below.

## Inhalation Hazard Materials



Materials which meet the inhalation toxicity criteria have additional "communication standards" prescribed by the HMR. First, the words "Poison-Inhalation Hazard" must be entered on the shipping paper, as required by Section 172.203(m)(3). Second, packaging must be marked "Inhalation Hazard" or, alternatively, when the words "Inhalation Hazard" appear on the label or placard, the "Inhalation Hazard" marking is not required on the package. Transport vehicles, freight containers, portable tanks and unit load devices that contain a poisonous material subject to the "Poison-Inhalation Hazard" shipping description, must be placarded with a POISON INHALATION HAZARD or POISON GAS placard, as appropriate. This shall be in addition to any other placard required for that material in Section 172.504.

Table 1 (Placard any quantity)

Placard class or division	Placard name
1.1	EXPLOSIVES 1.1
1.2	EXPLOSIVES 1.2
1.3	EXPLOSIVES 1.3
2.3	POISON GAS
4.3	DANGEROUS WHEN WET
5.2 (Organic peroxide, Type B, liquid or solid, temperature controlled)	ORGANIC PEROXIDE
6.1 (Inhalation Hazard, Zone A or B)	POISON INHALATION HAZARD
7 (Radioactive Yellow III label only)	RADIOACTIVE

Table 2 (Placard 1,001 pounds or more)

1.4	EXPLOSIVES 1.4
1.5	EXPLOSIVES 1.5
1.6	EXPLOSIVES 1.6
2.1	FLAMMABLE GAS
2.2	NON-FLAMMABLE GAS
3	FLAMMABLE
Combustible Liquid	COMBUSTIBLE
4.1	FLAMMABLE LIQUID
4.2	SPONTANEOUSLY COMBUSTIBLE
5.1	OXIDIZER
5.2 (Other than organic peroxide, Type B, liquid or solid, temperature controlled)	ORGANIC PEROXIDE
6.1 (PG I or II, other than Zone A or B, Inhalation Hazard)	POISON
6.1 (PG III)	KEEP AWAY FROM FOOD
8.2	NONE
8	CORROSIVE
9	CLASS 9
ORM-D	NONE

For complete details, refer to one or more of the following:

- Code of Federal Regulations, Title 49, Transportation, Parts 100-185. [All Modes]
- International Civil Aviation Organization (ICAO) Technical Instructions for Safe Transport of Dangerous Goods by Air [Air]
- International Maritime Organization (IMO) Dangerous Goods Code [Water]
- Transportation of Dangerous Goods Regulations of Transport Canada. [All Modes]



U.S. Department of Transportation  
Research and Special Programs Administration

Copies of this Chart can be obtained by writing

OHMIT/DHM-51,  
Washington, D.C. 20590

or

Phone: 202-366-4900

E-mail: [training@rspa.dot.gov](mailto:training@rspa.dot.gov)

Web site: <http://hazmat.dot.gov>

CHART 11  
REV. JULY 1998



## **MATERIAL SAFETY DATA SHEETS**

The Material Safety Data Sheet (MSDS) has become a major source of chemical information. It is the key document used to provide hazard information to employees and can become an invaluable tool for emergency response personnel when used in a chemical emergency.

The Occupational Safety and Health Administration's (OSHA) Hazard Communication Standard (29 CFR 1910.1200) requires all manufacturers of pure chemicals and/or mixtures to evaluate their products and relate, via MSDSs, any hazards that may be encountered while handling these materials. This standard is intended for all workplaces, manufacturing and nonmanufacturing alike. The Environmental Protection Agency's (EPA) Emergency Response and Community Right-to-Know Act of 1986 ensures the availability of MSDSs to emergency response personnel, such as fire departments, first aid crews, and hospital emergency room staff.

The MSDS contains a wealth of information that may be understood with a minimum of training. Below is a brief explanation of the format and information found in a properly prepared MSDS.

### **Section 1**

This section identifies the material by product or trade name and chemical name. It is the product or trade name that is usually found on the container labels, although the chemical name is also required by some states. Section I also contains the manufacturer's name, address, and telephone number.

### **Section 2**

Section 2 provides physical data about the product that can be utilized for proper identification. Included are specifics such as color, odor, specific gravity (weight), vapor pressure, and boiling point.

### **Section 3**

This section lists the chemical ingredients of the material, if they are known or suspected to be hazardous. Hazardous materials that are not carcinogens must be reported if they represent 1 percent or more of the product. Carcinogens must be reported and identified as such if their levels are 0.1 percent or higher. Also included in Section 3 are Threshold Limit Values (TLVs) and the OSHA Permissible Exposure Limit (PEL).

### **Section 4**

Section 4 includes fire and explosion hazard data. This information is especially useful when devising both in-house and community contingency plans. Plant first responders, local fire departments, and hazmat teams need unlimited access to this information.

## **Section 5**

Section 5 contains health hazard data. It describes any acute (short-term exposure) and/or chronic (long-term exposure) effects on the body. These include routes of exposure (inhalation, dermal contact, ingestion) and the bodily organs affected, as well as the signs and symptoms of overexposure. First aid procedures are also be found in this section. (NOTE: First aid measures recommended in MSDSs are not always correct and should be confirmed.)

## **Section 6**

This section contains information on the reactivity of the product. It lists other chemicals that, when mixed with the product, will result in a chemical reaction. If a product is water reactive, it will be noted.

Also included in Section 6 is information on hazardous decomposition products, such as carbon monoxide and other hazardous gases, that are formed and emitted during chemical reactions or fires. It is imperative that this section be carefully noted by both in-house and local firefighters.

## **Section 7**

Section 7 lists the procedures that should be used if the product spills or leaks, including waste disposal methods.

## **Section 8**

Section 8 contains information regarding the proper personal protective equipment (PPE) necessary to handle the product in a manner that will minimize exposure. Ventilation practices are also listed in this section.

## **Summary**

A Material Safety Data Sheet can aid in making the right decisions on health and safety issues in a plant or in a community. It must be noted, however, that it is but one of many references that should be used to make final determinations. MSDSs are offered by manufacturers for identification and verification and are not the last word on safety and health practices.

## 1. MATERIAL SAFETY DATA SHEET

PRODUCT NAME:	CAS #
CHEMICAL NATURE:	
% ACTIVITY:	

## 2. PHYSICAL DATA

BOILING POINT, 760 MM HG	FREEZE POINT
SPECIFIC GRAVITY	VAPOR PRESSURE AT 20 C
VAPOR DENSITY	SOLUBILITY IN H2O
PER CENT VOLATILES BY WEIGHT	IONIC NATURE
APPEARANCE AND ODOR	

## 3. CHEMICAL INGREDIENTS

MATERIAL	%	TLV (Units)

## 4. FIRE AND EXPLOSION HAZARD DATA

FLASH POINT (test methods)	AUTOIGNITION TEMPERATURE			
FLAMMABLE LIMITS IN AIR, % by volume	<table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 33%;">Lower</td> <td style="width: 33%;"></td> <td style="width: 33%;">Upper</td> </tr> </table>	Lower		Upper
Lower		Upper		
EXTINGUISHING MEDIA				
SPECIAL FIRE FIGHTING PROCEDURES				
UNUSUAL FIRE AND EXPLOSION HAZARDS				

SAMPLE MATERIAL SAFETY DATA SHEET

## 5. HEALTH HAZARD DATA

TRESHOLD LIMIT VALUE

EFFECTS OF EXPOSURE

EMERGENCY AND FIRST AID  
PROCEDURES

## 6. REACTIVE DATA

STABILITY

UNSTABLE

STABLE

CONDITIONS  
TO AVOID

COMPATIBILITY

HAZARDOUS RECOMPOSITION  
PRODUCTS

HAZARDOUS POLYMERIZATION

CONDITIONS  
TO AVOID

## 7. SPILL OR LEAK PROCEDURES

STEPS TO BE TAKEN OR  
MATERIAL IS RELEASED OR  
SPILLED

WASTE DISPOSAL METHOD

## 8. SPECIAL PROTECTION INFORMATION

RESPIRATORY PROTECTION

VENTILATION

LOCAL EXHAUST

MECHANICAL

SPECIAL

OTHER

PROTECTIVE GLOVES

EYE PROTECTION

OTHER PROTECTIVE  
EQUIPMENT

## 9. SPECIAL PRECAUTIONS

PRECAUTIONARY LABELING

OTHER HANDLING AND STORAGE  
CONDITIONS

SAMPLE MATERIAL SAFETY DATA SHEET