Arlington Fire District

Hazardous Materials Awareness Manual

Unit 1

Unit 1

Hazardous Materials: Laws, Regulations, and Standards

FIREFIGHTER'S HANDBOOK

Introduction

- Hazardous materials response is a specialty field within fire service
- Firefighters and EMS bombarded with exposures to hazardous materials
- Technology is changing to help monitor hazardous materials
- Even the most toxic chemicals are not dangerous if handled correctly

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- Introduction (cont'd.) • Hazardous material: any substance that when released is capable of creating harm to people, the environment, and property Agencies have more specific
 - definitions DOT hazardous material
 - EPA hazardous substances
 - OSHA hazardous chemicals

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Laws, Regulations, and Standards

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- Important for the first responder to have a basic understanding of legislative history of hazardous materials
- Many environmental and safety regulations affect how firefighters respond to emergencies
- Consult local environmental and OSHA offices

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Development Process

- Understand the differences among:
 - Laws - Regulations
 - Standards
- Important for firefighters to participate
- in development and review

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Emergency Planning

- Superfund Amendments and Reauthorization Act (SARA)
- Passed in 1986
 Protection of emergency responders and
- community
- Inform emergency responders of chemical hazards within community
- Emergency Planning and Community Right to Know Act (EPCRA) Plan for emergencies
 Provide a mechanism to get chemical storage information

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- State and Local Emergency Response Committees
- · Ensure the state has resources necessary to
- respond safely to chemical releases Local Emergency Planning Committees
 - (LEPCs): - Representatives of community
 - _ Emergency responders
 - Industry and hospitals
 - Media - Other government agencies





Local Emergency Response Plans

- Outline emergency contacts and procedures
- Important for personnel to have an understanding of this plan
- Important for emergency services to be an integral player in the LEPC
- Most federal HAZMAT grants are
- provided through LEPC

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- **Chemical Inventory Reporting**
- Facilities must report chemical information to the state
- To qualify as a reporting facility:
 Store more than 10,000 pounds of chemical
 Store one of 366 chemicals that the EPA considers an extremely hazardous substance (EHS)
- · Must submit Material Safety Data Sheets
- (MSDS) Purpose: to inform emergency responders

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OSHA HAZWOPER Regulation

Hazardous Waste Operations and Emergency Response (HAZWOPER)

- Far reaching effects:Requires that certain training must be provided
- Requires development of standard operating procedures
- Mandates certain requirements when handling chemical releases

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EPA also adopted HAZWOPER to cover volunteer firefighters as well

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Paragraph q

- · Majority covers employers' responsibilities at hazardous waste sites
- Paragraph q covers emergency response and applies to the fire service
- Established:
- Five levels of training Annual refresher training
- · Requires use of incident command system

Medical Monitoring

- A physical is needed if the person: Was exposed to a chemical above the permissible exposure limit Wears a respirator or is covered by OSHA respiratory regulation
 Was injured due to a chemical exposure
- Is a member of a hazardous materials team Physician determines extent of exam
- Medical records to be kept by the employer for 30 years past last date of employment

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Standards

- NFPA establishes most standards and a variety of committees
- Person can be held civilly liable for violating an NFPA standard
- NFPA standards have the weight of a regulation in hazardous materials arena
- OSHA has used general duty clause to cite employers for violating NFPA standard

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NFPA 472

- Listing of objectives required to meet training levels established by NFPA
- Expands requirements in order for employer to certify employees
- Added objectives related to terrorism response
- Mission-specific competencies reflect realities of real-world incidents

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NFPA 473

- Adds additional competencies above EMS issues
- Provides EMS Level I and Level II
- training levels Standard now relies on BLS and ALS providers

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Standard of Care

- Responders have to abide by a standard of care
- Personnel could face federal charges for violating the Clean Water Act
- Violations of this standard based on
 - three theories: - Liability
 - Negligence
 - Gross negligence
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Hazard Communication

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- Employers provide an MSDS for all chemicals located at a facility
- · Above "household quantities"
- Employer must provide training on these MSDS materials and hazard communication program
- · Firefighters are responsible for following this regulation

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Superfund Act

- Established for the cleanup of toxic waste
- When responding to a Superfund site, some additional concerns must be followed:
 - Site has existing emergency response
 - plan - Site should have its access limited

 - Local fire department should meet with site supervisor to learn hazards
 - Superfund sites vary greatly

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Clean Air Act

- Passed in 1990
- Requires certain facilities file additional planning documents
- LEPC and local fire service involved in
- training and exercises Facilities required to submit
- emergency plans

Respiratory Protection

- · Inclusion of two-in/two-out rule
- Required to fit test all firefighters and provide medical survey or a physical exam
- Specific records must be kept by fire department

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Firefighter Safety

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- Sometimes referred to when discussing hazardous materials issues
- "Broad-based" program
- · Focused on providing safe workplace for firefighters

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NFPA Chemical Protective Clothing

- NFPA Standards 1991 and 1992 for chemical protective clothing ensembles
- Establish design and use requirements NFPA 1994 has three levels of
- protective equipment
- Used in event of chemical or biological attack

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Lessons Learned

standards can be confusing - Most are not easy to read They are subject to interpretation and change frequently Emergency responders must keep abreast of those that affect their

everyday jobs

· Maze of laws, regulations, and

Unit 2

Unit 2

Hazardous Materials: Recognition and Identification

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Introduction

- Failure to recognize chemical hazards puts firefighters in severe danger
 Immediate effects from some materials

 Multiple exposures have far-reaching effects
- Hazardous materials incidents kill thousands
- Four basic clues to recognition and identification: Location and occupancy Placards, labels and markings
- Container types - Senses

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Location and Occupancy

- In general, the more industrialized a community is, the more hazardous materials it contains
- Buildings that store hazardous materials: - Hardware and auto parts stores
 - Hospitals
 - Dry cleaners Manufacturing facilities, print shops
 - Doctors' offices, photo labs, agricultural supply stores
 Etc.

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Placards, Labels, and Markings



Many systems are used to mark hazardous materials containers, buildings, and transport Result from laws, regulations, and standards

Building Officials Conference Association (BOCA) code

- Adopted as a regulation in local communities
 Require use of the NFPA 704M marking system for certain occupancies



Placards

- Department of Transportation (DOT) regulates movement of hazardous materials Rail, air, water, roadway, and pipeline
- Kail, air, water, roadway, and pipeline
 Shipper must placard a vehicle to warn of storage of chemicals
 Nine hazard classes that use more than 27 placards to identify a shipment
 Labels are smaller versions of placards

| ials that Require Placa Table 1) | arding at any Amount |
|---|--------------------------|
| HAZARD CLASS OR DIVISION | PLACARD TYPE |
| 1.1 | Explosives 1.1 |
| 12 | Explosives 1.2 |
| 1.3 | Explosives 1.3 |
| 23 | Poison gas |
| 4.3 | Dangerous when wet |
| 52 (Organic peroxide, type B, liquid or solid, temperature controlled) | Organic peroxide |
| 5.1 (Inhalation hazard Zone A or B) | Poison inhalation hazard |
| (radioactive label III only) | Radioactive |

| FIREFIG Materials ti (DOT Table 2 | HTING & EMERGENCY RESPONSE hat Require Placarding at 1,001 Pounds 2) |
|---|--|
| CLASS OR DIVISION | PLACARD TYPE |
| 1.4 | Explosives 1.4 |
| 1.5 | Explosives 1.5 |
| 1.6 | Explosives 1.6 |
| 2.1 | Flammable gas |
| 2.2 | Nonflammable gas |
| 3 Flammable liquid | Flammable |
| 3 Combustible liquid | Combustible |
| 4.1 | Flammable solid |
| 4.2 | Spontaneously combustible |
| 5.1 | Oxidizer |
| 5.2 (Other than organi | c peroxide) Organic peroxide |
| 6.1 (Other than inhala | tion) Poison |
| 6.1 (PG III) | Keep away from food |
| 8 | Corrosive |
| 9 | Class 9 |

| FIREFIGHTER'S HANDBOOK |
|--|
| Placards |
| DOT - 49 CFR 170-180 DOT system uses nine hazard classifications with more than 27 placards. DOT also requires United Nations/North America (UN/NA) identification number. |
| A 100 faite lange setting |











| FIREFIGHTER'S | HAN ENCY RESP | | ок |
|------------------------|------------------|------|-------|
| Type 6, Poisonou | s Mater | ials | |
| • Division 6.1 | | | |
| • Division 6.2 | | | |
| • Hazardous Zone A | | | |
| Hazardous Zone B | | | |
| a Mil Balan Supprising | | - | 25.15 |









Placards (cont'd.)

- · Problems with the placarding system
 - Relies on a human: To determine extent of load
 - To determine appropriate hazard classes
 - To interpret difficult regulations to determine if placard required
 Placard must be affixed to all four sides of a
 - vehicle
 - Only required for shipments that exceed 1,001 pounds
 Ten to twenty percent of trucks not placarded

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correctly

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 Shipping name of the material
 UN/NA identification number Shipping and receiving companies' names, addresses

Labels

- · Package markings must include:
 - Packages containing more than a Reportable Quantity (RQ) of material must be marked Packages listed as ORM-D materials should
 - be marked as such
 - · Labels identical to placards other than size 25.21

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Other Identification Systems

- Several other identification systems used in private industry to mark facilities and containers
- Military shipments and pipelines are also marked
- · Warnings are a clue to potential presence of hazardous materials

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NFPA 704 System

- Designed for buildings, not transportation Alerts first responders to potential hazards
- Triangular sign divided into four areas
 - Health hazard: blue - Fire hazard: red
 - Reactivity hazard: yellow
 - Special hazards: white
- · Ranking from zero to four Zero presents no risk



Hazardous Materials Information System

 HMIS designed to comply with federal hazard communication regulation

- HMIS can be developed by the facility or manufacturer of the labels
- One system may vary from another
 Colors and numbers usually same as NFPA Picture of required PPE for each substance may be provided

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Military Warning System

- Military uses DOT placarding system when possible
- Assume military is aware of incident involving extremely hazardous materials Higher hazards more likely to be shipment escort
- Driver of the truck may not be allowed to leave the cab of the truckNotify military if driver and escort crew killed
- or seriously injured

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Pipeline Markings

- · Pipeline owner is required to place sign if underground pipeline crosses mode of transportation
 - Sign must contain a warning, hazardous contents of pipe, owner's name and phone
 - Pipeline buried a minimum of three feet
 - Product can vary from liquefied gases and petroleum products to slurried material
 - Pipeline companies required to provide training and tours for emergency responders

Container Markings

- Most containers marked with contents
- Cylinders have name of product stenciled on side of the cylinder
- Bulk container has product stenciled
- on the side
- Trucks that are dedicated haulers also stencil product name on two

sides of vehicle

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Pesticide Container Markings

- Pesticides regulated by the EPA in terms of markings
- Label has manufacturer's name; no information about chemical make-up
- If label indicates "Danger," extreme caution should be taken
- "Warning" and "Caution" present lesser hazards

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- New warning label issued by the IAEA in 2007
- DOT still requires DOT labels and placards
- Responders should request assistance of radiation specialists



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Containers

- Hazardous materials come in containers of many shapes and sizes
- Type of material and end use for product determine packaging
- Household version usually different than industrial
 First responders should be alert for
- anything unusual
- Example: 55-gallon drum in a bedroom along with laboratory glassware



General

- · Most general containers for household use - Carried in large quantities when transported
- · Cardboard boxes ship hazardous materials Chemicals shipped in glass bottles usually insulated and packed in cardboard boxes - One-gallon glass bottles transported in carboys
- Glass bottles may be coated in plasticBags may carry anything from food items to poisons

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General (cont'd.)

- Drum construction gives clue as to contents Cylinders hazardous because of contents
- and pressure Relief valves mandated in the U.S.
- Totes and tanks have capacities between
- Hold flammable, combustible, toxic, and corrosive materials
- Transported on flatbed or box-type trailers
- Common incident during offloading

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Figure 25-42 The most common type of spill occurs when a valve is knocked off, releasing the extented

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Pipelines

- Sized between 1/2 inch and more than six feet - Commonly buried underground
- Some type of pipeline system is found in
- every state Larger pipelines along east coast and in Alaska Amount in pipeline varies; must have
- contact information for pipeline owner
- · If incident suspected, contact pipeline owner immediately

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Radioactive Material Containers

- Transport of radioactive materials regulated by DOT and Nuclear Regulatory Agency (NRC)
- Strong, tight container: for low-level radioactive material
- Excepted packaging: for materials that have low specific activity
- Type A container: for materials with higher radiation
- Type B container: must have ten inches of lead shielding 25.39

Highway Transportation Containers

- Tractor trailer can carry variety of hazardous materials and portable containers
- · Determining contents may be difficult
- Use extra care with refrigerated materials
- Specification plates list information about tank

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- Four basic types of tank trucks:
- DOT-406/MC-306 gasoline tank truck
 DOT-407/MC-307 chemical hauler
 DOT-412/MC-312 corrosive tanker
- MC-331 pressurized tanker

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Boiling Liquid Expanding Vapor Explosion (BLEVE)

- Heat inside container causes material to boil and vapors to expand
- Pressure inside container causes the
- tank to fail Withdraw immediately if rising sound from relief valve or discoloration of
- tank
- Fire must be fought from a distance with unmanned hose holders 25.41

| FIREFI | | | |
|--------|-----------|---|--------------------|
| | | No romana or canave let | |
| - | - | As had accessed intaks of saids the primare allocations in the load' of length to dok | Figure 25-60 |
| E I | - comming | At the pressure echange, the relief solar and costs, releases the set. The pressure, heavy reason than an ad pric | Diagram of a BLEVE |
| - | | The easier and feasits this field and spatial | |
| 2 | - | The relative set opens, and construct that is the relative for the final func- tion pressure will recrease in this tank | |
| 1 me | 1. | As the pressure in the spek a minimpro- tion saw may decisize and the state of the sew may decisize and the state of the sew advices are realise to state of the sew advices the state of the second as a \$2.72 | |

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Dangers Associated with BLEVE

- · Fireball can engulf responders and exposures
- Metal debris can fly considerable distances
- · Liquid propane can be released and ignite The shock wave, air blast, or flying metal created by the BLEVE can collapse
- buildings or move responders and equipment



Dangers Associated with BLEVE (cont'd.)

- Firefighters should withdraw immediately in the case of rising sound from a venting relief valve or discoloration of the tank ٠
- Fire must be fought from a distance with unmanned monitors or hoses that are cooling the tank with a minimum of 500 GPM
 - If water is vaporizing on contact, apply more water

Avoid icing around the relief valves

Dangers Associated with

BLEVE (cont'd.)

- Any tank that is exposed can fail at any time and in any direction
- If unmanned monitors are unavailable, firefighters should withdraw and let the fire burn

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Specialized Tank Trucks

- · Gases are liquefied and transported as with MC-331 tank trucks, refrigerated or compressed
- Dry bulk trucks carry variety of products Materials requiring high temperatures
- transported in special vehicles · Intermodal tanks similar to full size highway

tanks - Can be used on ships, railways, or highways

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Rail Transportation

- Rail incidents involve multiple cars, in rural areas and multiple agencies
- · Three basic types: non-pressurized,
- pressurized, specialized
- Dedicated railcars marked with the contents
- Non-pressurized cars have relief valve outside of expansion dome
- · Pressurized cars have valves, pipes
- under a protective housing 25.48

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Rail Transportation (cont'd.)

- Specialized railcars have same characteristics as highway vehicles – Highway box trailers often loaded onto railcars
- Railroads use same placarding
- system More extensive information, printed larger
- Some railcars may be painted in a
- configuration to identify hazardous loads 25.49



Bulk Storage Tanks

- Movement to remove underground storage tanks (UST) and replace with above ground storage tanks (AST)
- above ground storage tanks (AST)
 Inspection wells surround UST and detect
- leaks
- Two types of AST: upright and horizontal
 Vapors may accumulate in ordinary upright AST
- Floaters prevent vapor accumulation
- Specialized tanks have external cover appears to be a tank within a tank
- appears to be a tank within a tank 25.51

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Figure 25-80 This is an open floating root tank, in which the roof floats on good tank, which is the root starts on the rolease of vigors, at there is no vapor space, and reduces the fire potential.

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Senses

- · Never smell, taste, or touch to identify materials
- Use information from exposed individuals only after decontamination
- Can use hearing and vision Example: pitch of relief valve increases indicates pressure increasing
- Many chemicals are desensitizers
- Many severely toxic materials are
- colorless and odorless 25.55

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Chemical and Physical Properties

- As firefighter progresses through response levels, need for additional chemistry increases
- Firefighter should consult with hazardous materials team or other resources
- Basis of fire is a chemical reaction The better that firefighters understand chemical reactions, the better off they will be

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Containers and Properties

- When chemicals release, knowing how materials react is important
- Lower boiling point means more pressure in container in a fire Corrosives placed in wrong container
- cause container to fail - Good chance venting or rupture will be violent

 Lower flash point means greater fire risk

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Radiation

- · Atom comprised of electrons, neutrons, and protons - Protons and neutrons in the nucleus of the atom
- Electrons orbit the nucleus
- Protons have positive charge, determine element Neutrons are the same size as protons, but neutral
- Isotopes: forms of an element, determined by the number of neutrons

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Radiation (cont'd.)

- Radioisotopes: isotopes whose nuclei are unstable
- Emit radiation to become more stable If atom emits an alpha or beta particle, number of protons changes, becomes
- different element Uranium is base for radon, which decays into lead Half-life: amount of time for half of a
- radioactive source to decay
- Activity: number of decays per second





Types of Radiation

- Non-ionizing radiation: radio waves, microwaves, infrared, visible light
- Ionizing: alpha, beta, gamma and x-rays Energy and weight: particulates such as alpha, beta
 Just energy: gamma
- · Alpha: two neutrons, two protons
- Beta: electrons and positrons
- Moves farther in air and causes more damage

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Types of Radiation (cont'd.)

- Gamma: comes from energy changes in the nucleus of the atom
- Neutron: not common, but used in nuclear power
- Neutrons ejected from nucleus during fission
 Neutron radiation transfers its energy to water
 Human body 68 75 percent water
 Neutron radiation activates non-radioactive
 isotrone.
 - isotopes
 - Materials in nuclear reactor become radioactive
- X-rays comparable to gamma radiation
- 25.61



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- **Toxic Products of Combustion**
- · Firefighters suffer considerable chemical

Figure 25-92 Examples of risks for ionizing radiation.

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- exposures · Breathing smoke bombards body with toxic chemicals
- Many toxic chemicals produced in a fire House, car, and dumpster fires are worst
- type of chemical accident Brush fires may have pesticides, herbicides or other
- Wear all protective clothing, especially SCBA

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Lessons Learned

- · At any incident, there is always a factor that relates to identification of hazardous materials
- Know where to access hazardous materials information
- Materials with high vapor pressures present great risk
- Understanding the harms from radiation is an important safety consideration
- · Local hazardous materials responders a good source of information

Unit 3

Unit 3

Hazardous Materials: Information Resources

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Introduction

- Chemical information available through variety of sources
- Shipper and facility required to maintain certain documents
- Know what information is available • Understand how to interpret the
- information in common sources

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Emergency Response Guidebook

- Known as the "DOT Book" or the "Orange Book"
- Published every four
- years
- Covers Canada, Mexico, and the USA

http://hazmat.dot.gov/gyd ebook.htm

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Emergency Response Guidebook

- DOT makes one copy for every emergency response apparatus in the country
- Provides information regarding
- potential hazards
 - Intended as a guide for first responders during the initial phases of a hazardous materials incident



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Emergency Response Guidebook

- Consists of these major sections: Placard information
 - ADR/RID marking system information
 - Listing by DOT identification number - Alphabetical listing by shipping name
 - Response guides
 - Table of initial isolation and protective action distances

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- List of dangerous water-reactive materials

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Emergency Response Guidebook

• This Department of Transportation book provides a contact number for federal assistance, although responders should proceed initially by requesting local, state, and then federal assistance.

FIREFIGHTER'S HANDBOOK Emergency Response Guidebook • You must be familiar with guide prior to an incident • Abbreviations are used in the DOT ERG. • The guide provides a list of the hazard class system.





Emergency Response

Guidebook

Blue section

- Alphabetical listing by chemical shipping name
- For reference with shipping papers
- High lightened numbers turn to orange and green sections

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and green sections



| FIRE | FIGHTER'S HANDBOOK |
|---------------------------|-------------------------------------|
| | FIREFIGHTING & EMERGENCY RESPONSE |
| | Emergency Response |
| | Guidebook |
| | |
| Two p | pages per guide, divided into three |
| sectio | ons |
| - | Potential hazards |
| V.L | Public safety |
| - Chan- | Emergency response |
| | |

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Using the DOT Emergency Response Guidebook

- Look up the three digit guide number of the material in either:
 – ID number index
- Name of the material index
- Turn to the numbered guide







• WMD cross reference is now available. • PPE levels of protection are listed. • It is available for online reference and download.

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Using the DOT Emergency Response Guidebook



- Approach incidents from an uphill/upwind direction
- Identify the material by finding one of the following:
- Four digit ID on placard/ID panel
 Four digit ID number on shipping document or
- package Name of material on shipping document, placard, or package

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Material Safety Data Sheets

- Result of the hazard communication standard
- Employers with larger than "household quantities" must create MSDS
- Required to have a variety of information
- Intent is to protect employees working at the facility

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Material Safety Data Sheets

- · Quality of information varies from MSDS to MSDS
- Typical MSDS provides a worst-case scenario
- Firefighter should rely more on technical information on MSDS
- MSDS has remained the same since inception 26.21

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Using the MSDS Wisely

- · Always use more than one source of information
- Determine action plan using MSDS - Determine chemical threat
 - Don appropriate level PPE
 - If material has released, follow
 - evacuation procedure and secure building
 - Determine which extinguishing agents
 - are required

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Accidents and How the **MSDS** Relates

- Chemical information on MSDS usually presents hazards associated with particular product
- Once product is placed in a process some factors may change
- Increase, decrease, or elimination of hazards
- Factors include:

- Reactions with other chemicals - Changes in temperature, pressure, or physical characteristics

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MSDS in the Workplace

- Employers to provide employees with an MSDS for every hazardous chemical
- An MSDS provides information on physical/chemical characteristics and first-aid procedures

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MSDS in the Workplace

- Can be insufficient depending on provider
 - Vagueness

 - Technical jargon
 Understandability
 - Product versus process
 - Missing information

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Shipping Papers

- Shipping papers generally provide the following information:
 Shipping company
 - Shipping company
 Destination of packages
 - Emergency contact information
 Number and weight of packages
 - Proper shipping name of materials
 - Hazard class of materials
 - Special notation for hazardous materials

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Mode of Transportation

- Shipping papers are also called a bill of lading
- · Papers should be close to the driver
- On tank trucks a duplicate set is located in a tube attached near landing gear
 Hazardous materials are sometimes color
- coded
- For rail, shipping papers are called consist or waybill and placed in control of the engineer

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Mode of Transportation

- Most railcars are identified well
 Standard Transportation Commodity Code
 (STCC)
 (STCC)
- Seven-digit number
 Number beginning with "49" are hazardous
 On a ship, papers are called dangerous
 cargo manifest (DCM) and placed in
- control of the captain
- In air, shipping paper are called Air Bills and placed in control of the captain

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Facility Documents

- Those with an MSDS requirement: - Tier 2 form
- Site plan
- Those with extremely hazardous substances (EHS)
- Emergency plan
 Many facilities leave MSDS binder at gate with security guard
- SARA reports updated annually and should be reviewed by responders

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Chemtrec

- Chemical Transportation Emergency Center
 - Information service provided by American Chemistry Council
 Chemtrec service
- Chemtrec is well connected
- Chemtrec does not make regulatory notifications

Chemtrec

Responder should have the following information when calling Cherntrec:
 Caller's name and phone number
 Name of the shipper or manufacturer
 Shipping paper information

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Industrial Technical Assistance

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- Each community usually has a technical specialist in a given field
- Many areas of the country have industrial mutual aid groups designed to assist each other
- Each industrial facility usually has a person responsible for safety and health
- Many facilities have industrial hygienists 26.32

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Lessons Learned

- Obtain as much information as possible
- Information combined with reference sources can provide useful data
- Obtain as much information as possible prior to arriving on scene
- Responders should not take risks attempting to get this information