



## Project Summary

# Manual for Preventing Spills of Hazardous Substances at Fixed Facilities

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The purpose of this project was to prepare a manual that provides guidance on preventing spills of hazardous substances in fixed facilities that produce substances from raw or starter materials, store the substances, or transfer the substances to and from transportation terminals. The emphasis is on smaller-sized chemical manufacturing facilities.

The manual consists of seven sections and an Appendix: 1. Introduction; 2. Manual of Practice; 3. Hazardous Substances and Their Characteristics; 4. Fixed Facilities; 5. Facility Spill Prevention Practices; 6. Preventive Engineering Practices; and 7. Bibliography. The appendix contains descriptions of fixed facility chemical processing equipment components, from which a checklist of equipment items interacting with hazardous substances can be derived for use in preparing a Spill Prevention Plan.

*This Project Summary was developed by EPA's Hazardous Waste Engineering Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).*

### Introduction

The purpose of this project was to prepare a manual that provides guidance on preventing spills of hazardous substances from fixed facilities that produce hazardous substances from raw or starter materials as products, byproducts or waste products; store hazardous substances; or transport hazardous sub-

stances. The audience to be addressed includes managerial and supervisory personnel as well as "hands on" personnel associated with smaller-sized chemical manufacturing facilities. The hazardous substances in question number almost 700, excluding oil, and are those designated pursuant to Section 101 (14) of the Comprehensive Environmental Response, Compensation and Liability Act of 1980, otherwise known as CERCLA or Superfund (Public Law 96-510).

The earlier Clean Water Act (Public Law 92-500) in Section 311, required that the President issue regulations "establishing procedures, methods and equipment . . . to prevent discharges of oil and hazardous substances from vessels and from onshore and offshore facilities . . ." Under a 1973 executive order, the U.S. Environmental Protection Agency (EPA) was to promulgate regulations for preventing nontransportation-related spills.

In 1973, EPA issued oil pollution prevention regulations (40 CFR Part 112) that require certain fixed facilities to have on file a spill prevention, control and countermeasures plan (SPCC plan). These regulations have been largely accepted by industry and have proven to be effective in preventing oil spills.

In the case of hazardous substances, no similar federal regulations exist at this time. In its own interest, a large segment of the industry producing, storing, and handling hazardous substances has instituted internal spill prevention plans. However, many of the smaller affected facilities may not have generated spill prevention plans for various reasons. This manual is designed to assist them in preparing such plans.

Source material for this manual was derived from government, industry and commercial publications. Related oil spill prevention literature included: the Guide for Inspectors; a report on Prevention Practices at Small Petroleum Facilities; state contingency plans, such as the Oil Spill Contingency Plan of the State of California; and the extensive Oil Spill Prevention Control and Countermeasure Plan Review. Publications dealing with hazardous substances included cost analyses for hazardous substance pollution prevention, Best Management Practices (BMP) documents, an industrial spill prevention plan, and a treatise on Safety and Accident Prevention in Chemical Operations.

## Manual of Practice

Section 2 of the manual presents the procedure for developing a facility spill prevention master plan. The procedure is divided into 10 steps that are expanded in the remainder of the manual. The manager selected to oversee the plan, and constant support of upper level management, are essential for successful implementation of the project. Specialists, as required to perform the various tasks outlined below, and the involvement of people from different parts of the facility, will provide a wide base of support for the plan and increase its acceptance by plant personnel who will be its main beneficiaries. The 10 procedural steps are as follows:

1. Form a facility spill prevention organization supervised by a part-time or full-time manager and backed by the plant management.
2. Prepare a prevention policy statement approved by management.
3. Define facility boundaries and prepare flowsheets indicating generation and storage of all substances within these boundaries, as well as inflow and outflow of substances across the boundaries. Hazardous substances present in raw materials, products, byproducts, wastes, fuels, lubes, paints, pesticides, disinfectants, etc., should be identified. Normal and overload conditions should be noted.
4. List the substances that are hazardous by reference to Section 3 and the tables of hazardous substance characteristics contained therein. Note the environmental media into which the substances would be released, their physical behavior on release, and the hazards caused by the release.

5. List all facility areas and equipment items that interact with hazardous substances. Include storage vessels of all kinds (gas, liquid, solid), process vessels and columns, flow systems including valves and controls, receiving and shipping terminals of all kinds (road, rail, water, air), and waste treatment and disposal areas. Use Section 4, Fixed Facilities, to identify those areas and equipment that could interact with hazardous substances.
6. For each area and equipment item of interest, list possible failure modes; amount of hazardous substance involved; hazards caused by possible release of substance (from Step 4 above); and specific effects expected on the rest of the facility and surroundings, considering equipment and personnel at various times and varying weather conditions.
7. For each area and equipment item, look over Section 5, Facility Spill Prevention Practices (SPPs), and extract the applicable Preventive Engineering Practices.
8. For each area and equipment item, look over Section 6, Preventive Engineering Practices (PEPs), and extract the applicable PEPs.
9. Write a facility spill prevention master plan under direction of the manager by combining information from Steps 3 through 8. The plan should consider drainage to receiving waters and facility terrain, and should include a timetable for carrying out the SPPs and PEPs.
10. Have the plan approved by plant management and implemented under direction of the spill prevention organization, which also should be responsible for its periodic review and revision.

## Hazardous Substances and Their Characteristics

Section 3 of the manual contains tables of information on the almost 700 CERCLA-designated hazardous substances. Once all the substances within a plant have been identified, they should be checked against these tables to determine which are hazardous. Only those considered hazardous require further consideration.

Hazardous substances may be gases, liquids, or solids; and, they may be released to the air, water, or ground. The manual presents four tables: (1) liquids

and solids spilled on water, (2) liquids spilled on ground, (3) solids (particulates) released to air or ground, and (4) gases released to air (a sample page from each is provided here as Tables 1-4, respectively).

Table 1 contains (1) an alphabetical listing of substances, primarily chemical compounds; (2) chemical class, sometimes more than one; (3) Chemical Abstract Service (CAS) number, a standard in cases where substances are known by more than one name; (4) hazards in addition to toxicity; and (5) behavior in water — sink/float and soluble/insoluble. The fifth or last column, "Behavior in Water," is not included in Tables 2, 3, and 4.

The hazards listed in the fourth column of each table are defined in 49 CFR 173 (Department of Transportation (DOT) regulations), the Clean Water Act, and by the U.S. Department of Health and Human Services. In the following list, an asterisk designates definitions developed during this work.

- *Carcinogen* — substance identified as potentially cancer-producing in humans.
- *Combustible* — liquid or solid having a flash point at or above 100°F and below 300°F; the upper limit was changed from the DOT value of 200°F to 300°F to realistically include more substances as combustible.
- *Corrosive* — substance causing visible destruction or irreversible alterations in human skin tissue at the site of contact.
- *Explosive* — any chemical compound, mixture, or device providing substantial instantaneous release of gas and heat.
- *Flammable* — substance as defined in 49 CFR 173.300 (gas), 49 CFR 173.115 (liquid), and 49 CFR 173.150 (solid).
- *Oxidizer* — substance that yields oxygen readily to stimulate the combustion of organic matter.
- *Poison* — substance so classed or labelled in 49 CFR 172.101.
- *Polymerizable* — substance undergoing a rapid exothermic polymerization reaction initiated by exposure to heat, light, acids, caustics, or other sources.
- *Radioactive material* — substance spontaneously emitting ionizing radiation.
- *Reactive* — substance that readily undergoes violent change without

**Table 1. Releases in Water**

<i>Hazardous Substance</i>	<i>Chemical Class</i>	<i>CAS No.</i>	<i>Hazard(s), in Addition to Toxicity</i>	<i>Behavior in Water</i>
<i>Acenaphthene</i>	<i>Aromatics</i>	<i>83-32-9</i>	<i>Combustible</i>	<i>Insoluble Sinker</i>
<i>Acenaphthylene</i>	<i>Aromatics</i>	<i>208-96-8</i>	<i>Combustible</i>	<i>Insoluble Floater</i>
<i>Acetaldehyde</i>	<i>Aldehydes</i>	<i>75-07-0</i>	<i>Flammable Polymerizable</i>	<i>Soluble</i>
<i>Acetic acid</i>	<i>Acidic compounds, organic</i>	<i>64-19-7</i>	<i>Combustible Corrosive</i>	<i>Soluble</i>
<i>Acetic anhydride</i>	<i>Acidic compounds, organic</i>	<i>108-24-7</i>	<i>Combustible Corrosive</i>	<i>Soluble, decomposes</i>
<i>Acetone</i>	<i>Ketones</i>	<i>67-64-1</i>	<i>Flammable</i>	<i>Soluble</i>
<i>Acetone cyanohydrin</i>	<i>Cyanides and nitriles</i>	<i>75-86-5</i>	<i>Combustible w/toxic products Poison</i>	<i>Soluble</i>
<i>Acetonitrile</i>	<i>Cyanides and nitriles</i>	<i>75-05-8</i>	<i>Flammable w/toxic products</i>	<i>Soluble</i>
<i>Acetophenone</i>	<i>Ketones</i>	<i>98-86-2</i>	<i>Combustible</i>	<i>Insoluble Sinker</i>
<i>Acetyl bromide</i>	<i>Aliphatics, halogenated</i>	<i>506-96-7</i>	<i>Flammable w/toxic products Corrosive Reactive</i>	<i>Decomposes (Sinker)</i>
<i>Acetyl chloride</i>	<i>Aliphatics, halogenated</i>	<i>75-36-5</i>	<i>Flammable w/toxic products Corrosive Reactive</i>	<i>Decomposes (Sinker)</i>
<i>2-Acetylaminofluorene</i>	<i>Amines, aryl</i>	<i>53-96-3</i>	<i>Potential carcinogen</i>	<i>Insoluble Sinker</i>
<i>1-Acetyl-2-thiourea</i>	<i>Ureas</i>	<i>591-08-2</i>		<i>Soluble</i>
<i>Acrolein</i>	<i>Aldehydes, Olefins</i>	<i>107-02-8</i>	<i>Flammable Polymerizable Poison</i>	<i>Soluble</i>
<i>Acrylamide</i>	<i>Amides, anilides, and imides</i>	<i>79-06-1</i>	<i>Polymerizable</i>	<i>Soluble</i>

detonation in the presence of water or moist air, or even dry air or oxygen.

- **Toxic pollutant** — material which upon exposure, ingestion, inhalation, or assimilation into any organism, causes death, disease, behavioral abnormalities, cancer, genetic mutations, physiological malfunctions, or physical deformations.

A thorough understanding of the various hazards is essential for effective selection of preventive countermeasures. This section provides data in the form of four tables of Hazardous Substance Characteristics for identifying and listing those substances that are hazardous in accordance with Step 4 of the procedures for developing a facility spill prevention master plan. The first page of each of the following tables is presented as a sample.

**Table # Release Scenario**

<i>1</i>	<i>Releases in Water</i>
<i>2</i>	<i>Liquids Released on Land</i>
<i>3</i>	<i>Particulate Solids Released on Land</i>
<i>4</i>	<i>Compressed Gases Released Into Air</i>

### Fixed Facilities

The manual can be applied to any fixed facility. If one excludes the petroleum refining industry, which is covered by an existing Oil Pollution Prevention Regulation (40 CFR 112), there are 20 major industry categories defined in 40 CFR 124, Appendix D, as follows:

**No. Major Industry Category**

<i>1</i>	<i>Timber Products Processing</i>
<i>2</i>	<i>Steam Electric Power Plants</i>
<i>3</i>	<i>Leather and Leather Products</i>
<i>4</i>	<i>Iron and Steel Manufacturing</i>

<i>5</i>	<i>Inorganic Chemicals Manufacturing</i>
<i>6</i>	<i>Textile Mills</i>
<i>7</i>	<i>Organic Chemicals Manufacturing</i>
<i>8</i>	<i>Nonferrous Metals Manufacturing</i>
<i>9</i>	<i>Paving and Roofing Materials</i>
<i>10</i>	<i>Paint and Ink Formulation and Printing</i>
<i>11</i>	<i>Soap and Detergent Manufacturing</i>
<i>12</i>	<i>Auto Wash and Other Laundries</i>
<i>13</i>	<i>Plastics and Synthetic Metals Manufacturing</i>
<i>14</i>	<i>Pulp, Paper and Board Mills, and Products Manufacturing</i>
<i>15</i>	<i>Rubber Processing</i>
<i>16</i>	<i>Miscellaneous Chemicals</i>
<i>17</i>	<i>Machinery and Mechanical Products Manufacturing</i>
<i>18</i>	<i>Electroplating</i>
<i>19</i>	<i>Ore Mining and Dressing</i>
<i>20</i>	<i>Coal Mining</i>

Several of these categories fall within the chemical manufacturing area. Others,

**Table 2. Liquids Released on Land**

Hazardous Substance	Chemical Class	CAS No.	Hazard(s), in Addition to Toxicity
Acetaldehyde	Aldehydes	75-07-0	Flammable Polymerizable
Acetic acid	Acidic compounds, organic	64-19-7	Combustible Corrosive
Acetic anhydride	Acidic compounds, organic	108-24-7	Combustible Corrosive
Acetone	Ketones	67-64-1	Flammable
Acetone cyanohydrin	Cyanides and nitriles	75-86-5	Combustible w/toxic products Poison
Acetonitrile	Cyanides and nitriles	75-05-8	Flammable w/toxic products
Acetophenone	Ketones	98-86-2	Combustible
Acetyl bromide	Aliphatics, halogenated	506-96-7	Flammable w/toxic products Corrosive Reactive
Acetyl chloride	Aliphatics, halogenated	75-36-5	Flammable w/toxic products Corrosive Reactive
Acrolein	Aldehydes, Olefins	107-02-8	Flammable Polymerizable Poison
Acrylic acid	Acidic compounds, organic, Olefins	79-10-7	Combustible Corrosive Polymerizable
Acrylonitrile	Cyanides and nitriles	107-13-1	Flammable w/toxic products Polymerizable Potential carcinogen Poison
Allyl alcohol	Alcohols and glycols, Olefins	107-18-6	Flammable Poison

such as mining (Nos. 19 and 20), metal processing in various forms (Nos. 4, 8, 18, and 19), and production of non-metals (Nos. 3, 6, 9, 13, 14, and 15), also deal with hazardous substances. Each industry has its own specialized equipment and facility areas. For the present purpose, this section lists and describes the equipment found in chemical manufacturing plants. For other industries, this section and the Appendix would have to be modified.

In accordance with Step 5 of the procedures for preparing a master plan, a list of plant component interactions with hazardous substances is required.

A check list of all facility areas and

components is useful for developing the final list. Reference to the Chemical Engineers' Handbook (1973, 5th edition) led to the identification of major facility area categories which cover processing, transportation, storage, waste treatment, and disposal. A detailed description of hazardous substance interactive systems and equipment (including further division of the major categories) is provided in the Appendix. A listing of the systems and equipment is provided here:

1. Transport and storage of fluids (pumps, pipes, valves, tanks, etc.)
2. Handling of bulk and packaged solids (conveyors, silos, etc.)

3. Size reduction and enlargement (mills, compactors, etc.)
4. Heat generation and transport (fired process equipment, incinerators, etc.)
5. Heat transfer equipment (heat exchangers, condensers, etc.)
6. Evaporative cooling and refrigeration (cooling towers, cryogenics, etc.)
7. Distillation columns
8. Gas absorption towers
9. Liquid extraction systems
10. Adsorption and ion exchange equipment
11. Miscellaneous separation processes (crystallization, membranes, etc.)
12. Liquid-gas systems (contacting, phase dispersion, phase separation)
13. Liquid-solid systems (contacting, phase dispersion, phase separation)
14. Gas-solid systems (contacting, phase dispersion, phase separation)
15. Liquid-liquid systems (contacting, phase dispersion, phase separation)
16. Solid-solid systems (contacting, phase dispersion, phase separation)
17. Waste treatment plants (equipment associated with primary, secondary, and tertiary treatment and disposal).

### Facility Spill Prevention Practices

In general, spill prevention practices (SPPs) are independent of the exact nature of the facility, its processes and products. While most SPPs are based on common sense and experience and provide few new revelations, it is useful to have this compilation of procedures when preparing a spill prevention master plan.

SPPs have been drawn from government and industry reports and publications. Some, listed here, overlap into related areas such as response to a spill, maintenance, and training. If the facility already has plans and procedures in these areas, they can be adapted to the present purpose. A short discussion for each SPP listed below is given in the manual.

- SPILL PREVENTION ORGANIZATION
- RISK IDENTIFICATION AND ASSESSMENT
- MATERIALS COMPATIBILITY
- REPORTING AND RECORDKEEPING
- GOOD HOUSEKEEPING
- PREVENTIVE MAINTENANCE
- INSPECTION SYSTEMS
- SECURITY
- EMPLOYEE TRAINING

**Table 3. Particulate Solids Released on Land**

<i>Hazardous Substance</i>	<i>Chemical Class</i>	<i>CAS No.</i>	<i>Hazard(s), in Addition to Toxicity</i>
<i>Acenaphthene</i>	<i>Aromatics</i>	<i>83-32-9</i>	<i>Combustible</i>
<i>Acenaphthylene</i>	<i>Aromatics</i>	<i>208-96-8</i>	<i>Combustible</i>
<i>2-Acetylaminofluorene</i>	<i>Amines, aryl</i>	<i>53-96-3</i>	<i>Potential carcinogen</i>
<i>1-Acetyl-2-thiourea</i>	<i>Ureas</i>	<i>591-08-2</i>	
<i>Acrylamide</i>	<i>Amides, anilides and imides</i>	<i>79-06-1</i>	<i>Polymerizable</i>
<i>Adipic acid</i>	<i>Acidic compounds, organic</i>	<i>124-04-9</i>	
<i>Aldicarb</i>	<i>Esters</i>	<i>116-06-3</i>	
<i>Aldrin</i>	<i>Aromatics, halogenated</i>	<i>309-00-2</i>	<i>Combustible w/ toxic products Potential carcinogen Poison</i>
<i>Aluminum phosphide</i>	<i>Phosphorous and compounds</i>	<i>20859-73-8</i>	<i>Flammable w/ toxic products Reactive</i>
<i>Aluminum sulfate</i>	<i>Sulfates</i>	<i>10043-01-3</i>	
<i>5-(Aminomethyl)-3-isoxazolol</i>	<i>Amine, alkyl</i>	<i>2763-96-4</i>	
<i>Amitrole</i>	<i>Azo compounds</i>	<i>61-82-5</i>	<i>Potential carcinogen</i>
<i>Ammonium acetate</i>	<i>Organic ammonium compounds</i>	<i>631-61-8</i>	
<i>Ammonium benzoate</i>	<i>Organic ammonium compounds</i>	<i>1863-63-4</i>	<i>Combustible w/ toxic products</i>
<i>Ammonium bicarbonate</i>	<i>Organic ammonium compounds</i>	<i>1066-33-7</i>	
<i>Ammonium bichromate</i>	<i>Chromates</i>	<i>7789-09-5</i>	<i>Corrosive Oxidizer Flammable</i>

## Preventive Engineering Practices

Preventive engineering practices (PEPs) may be thought of as SPPs that are oriented toward equipment rather than procedures. They are specific to groups of toxic and hazardous substances and to the potential sources of spill, that is: storage areas; loading/unloading areas; inplant transfer, process and materials-handling areas; drainage from plant site and secondary containment structures; and waste storage, treatment and disposal facilities.

PEPs are divided into pre-release and post-release groups, both designed to

confine release within the facility boundaries. The difference between the two is that pre-release PEPs are of a general precautionary nature, whereas post-release PEPs are activated as spill control devices by a release. Typical pre-release PEPs include monitoring and alarm systems, non-destructive testing, labeling all storage, process and flow equipment, and proper storage procedures. Typical post-release PEPs include secondary containment of liquids and solids by dikes and berms, flow diversion, vapor control, and dust control.

The manual discusses the following subsections (grouped by equipment cate-

gories, emphasizing components found in chemical manufacturing facilities).

- Bulk Storage
  - Tank Construction
  - Tank Support
  - Tank Placement
  - Tank Monitoring
  - Material Storage
  - Alarms
  - Fire Protection Systems
  - Secondary Containment
- Loading and Unloading Areas
  - Tank Truck Loading/Unloading
  - Railroad Tank Car Loading/Unloading
  - Marine Loading/Unloading
- In-Plant Process and Transfer
  - Process Materials/Equipment
  - Instrumentation
  - Piping
  - Valving
  - Venting
  - Color Coding/Labeling
- Drainage Control
  - Facility Diking
  - Road Drainage
  - Plant Drainage
  - Drainage Valving
  - Secondary Containment
- Waste Storage, Treatment and/or Disposal.

## Appendices

The manual includes the following appendices:

- Fixed Facility Chemical Process Equipment Components
  - Transport and Storage of Fluids
  - Handling of Bulk and Packaged Solids
  - Size Reduction/Enlargement
  - Heat Generation and Transport
  - Heat Transfer Equipment
  - Evaporative Cooling and Refrigeration
  - Distillation Columns
  - Gas Absorptive Towers
  - Liquid Extractive Systems
  - Adsorption and Ion Exchange Equipment
  - Miscellaneous Separation Processes
  - Liquid-Gas Systems
  - Liquid-Solid Systems
  - Gas-Solid Systems
  - Liquid-Liquid Systems
  - Solid-Solid Systems
  - Waste Treatment Plants

**Table 4. Compressed Gases Released Into Air**

<i>Hazardous Substance</i>	<i>Chemical Class</i>	<i>CAS No.</i>	<i>Hazard(s), in Addition to Toxicity</i>
<i>Ammonia</i>	<i>Ammonia</i>	<i>7664-41-7</i>	<i>Corrosive</i>
<i>Carbon oxyfluoride</i>	<i>Halides, alkyl</i>	<i>353-50-4</i>	<i>Reactive</i>
<i>Chlorine</i>	<i>Halogens</i>	<i>7782-50-5</i>	<i>Oxidizer Poison</i>
<i>Cyanogen</i>	<i>Cyanides and nitriles</i>	<i>460-19-5</i>	<i>Flammable w/toxic products Poison</i>
<i>Dichlorodifluoromethane</i>	<i>Halides, alkyl</i>	<i>75-71-8</i>	
<i>Dimethylamine</i>	<i>Amines, alkyl</i>	<i>124-40-3</i>	<i>Flammable w/toxic products Corrosive</i>
<i>Fluorine</i>	<i>Halogens</i>	<i>7782-41-4</i>	<i>Corrosive Reactive Oxidizer Poison</i>
<i>Formaldehyde</i>	<i>Aldehydes</i>	<i>50-00-0</i>	<i>Flammable</i>
<i>Hydrogen sulfide</i>	<i>Sulfides and mercaptans</i>	<i>7783-06-4</i>	<i>Flammable w/toxic products Poison</i>
<i>Methyl bromide</i>	<i>Halides, alkyl</i>	<i>74-83-9</i>	<i>Combustible w/toxic products Poison</i>
<i>Methyl chloride</i>	<i>Halides, alkyl</i>	<i>74-87-3</i>	<i>Flammable w/toxic products</i>
<i>Methyl mercaptan</i>	<i>Sulfides and mercaptans</i>	<i>74-93-1</i>	<i>Flammable w/toxic products Corrosive</i>
<i>Monomethylamine</i>	<i>Amines, alkyl</i>	<i>74-89-5</i>	<i>Flammable w/toxic products Corrosive</i>
<i>Nitric oxide</i>	<i>Oxides</i>	<i>10102-43-9</i>	<i>Poison Oxidizer</i>
<i>Phosgene</i>	<i>Halides, organic</i>	<i>75-44-5</i>	<i>Combustible w/toxic products Poison</i>

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*The complete report, entitled "Manual for Preventing Spills of Hazardous Substances at Fixed Facilities," (Order No. PB 87-232 815/AS; Cost: \$18.95, subject to change) will be available only from:*

*National Technical Information Service  
5285 Port Royal Road  
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Telephone: 703-487-4650*

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