GUIDELINES FOR

Safe Handling of Powders and Bulk Solids

CCPS
CENTER FOR
CHEMICAL PROCESS SAFETY
An AIChE Industry
Technology Alliance

CENTER FOR CHEMICAL PROCESS SAFETY
of the
American Institute of Chemical Engineers
Three Park Avenue, New York, New York 10016

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3 Park Avenue
New York, New York 10016-5991

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Library of Congress Cataloging-in-Publication Data:

CIP data applied for

ISBN 0-8169-0951-2

This book is available at a special discount when ordered in bulk quantities. For information, contact the Center for Chemical Process Safety at the address shown above.

CCPS Publication G-95

It is sincerely hoped that the information presented in this volume will lead to an even more impressive safety record for the entire industry; however, the American Institute of Chemical Engineers, its consultants, CCPS Subcommittee members, their employers, and their employers' officers and directors disclaim making or giving any warranties or representations, express or implied, including with respect to fitness, intended purpose, use or merchantability and/or correctness or accuracy of the content of the information presented in this document. As between (1) American Institute of Chemical Engineers, its consultants, CCPS Subcommittee members, their employers, their employers' officers and directors and (2) the user of this document, the user accepts any legal liability or responsibility whatsoever for the consequences of its use or misuse.

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ACKNOWLEDGMENTS

The American Institute of Chemical Engineers wishes to thank the Center for Chemical Process Safety (CCPS) and those involved in its operation, including its many sponsors whose funding made this project possible; the members of its Technical Steering Committee who conceived of and supported this Guidelines project, and the members of the Bulk Solids Handling subcommittee.

It is the subcommittee's belief that if the information contained in this book happens to prevent one bulk solids fire or dust explosion, the efforts of all those involved in preparing this work will be justified and rewarded.

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Finally, these individuals are thanked for their contributions to our principal authors:

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Prior to publication, all CCPS books are subjected to a thorough peer review process. For such effort, CCPS also gratefully acknowledges the thoughtful comments and suggestions of

John Alderman (RRS)
Sheila Beattie (Syngenta Crop Protection)
John V. Birtwistle
Larry Bowler
Reinhard E. Bruderer (PRED)
Wayne Cannell (Gowan Milling)
William Chandler (OSHA)
Don Connolley (Akzo)

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Samuel J. November (Rohm & Haas)
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Kenan Stevick (Dow)
Tony Thompson (Monsanto)
Alan Tyldesley (Health & Safety Executive, U.K)
Erdem A. Ural (Loss Prevention Science & Technologies, Inc.)

Chapter 1

INTRODUCTION AND OVERVIEW

1.1 PURPOSE OF BOOK

This book is intended to be a resource for process design and plant engineers who are responsible for designing and running processes handling powders and bulk solids in the chemical, pharmaceutical and related manufacturing industries. The book can also be an aid for process hazard analysis (PHA) teams and leaders, and for people operating small plants and toll operations. It may also be useful to insurance and regulatory personnel with assignments at industrial facilities that process, store, or transport large quantities of solid particulates.

The main focus of the book is on the instability, reactivity and combustibility hazards of particulate solids manufactured or handled in the chemical and pharmaceutical industries. Toxicity hazards are also discussed, but to a lesser extent than the other hazards. Much of the material presented may also apply to the food processing, grain handling and coal mining industries. The book does not cover the hazards of Explosives (UN-DOT Class 1 Materials) but does include UN-DOT Class 4 material (flammable solids, spontaneously combustible materials and materials that are dangerous when wet) Class 5 materials (oxidizers and organic peroxides), and Class 6.1 toxic materials, as well as the testing to distinguish explosives from the other UN-DOT categories.

Definitions and examples of these hazards and some key national and international standards covering them are presented in Section 1.2. All four generic hazards depend on particle size and various other particulate properties. Descriptions of these properties and their measurement are provided in Chapter 2 of this book. Accident scenarios and case histories are discussed briefly in Section 1.3, and in much more detail in Chapter 3. Particulate hazard assessment, via laboratory testing and other methods, is described in Chapter 4, with Appendix A being a listing of laboratories that conduct these tests. The types of particulate storage and handling equipment, are described in Appendix B. Chapter 5 is a discussion of the hazards and corresponding protection methods for the various equipment and operations in Appendix B. General protection measures applicable to particulate handling/processing equipment and facilities are described in Chapter 6. Chapter 7 discusses how plant operation and maintenance practices can influence particulate hazards. The final chapter, Chapter 8, describes occupational health and environmental concerns and regulations pertinent to potentially hazardous particulate material processing.

1.2 PARTICULATE HAZARDS

1.2.1 Combustibility Hazards

Combustibility hazards refer to the fire and explosion hazards of particulates in either bulk form, layer form, or in the form of a suspended dust cloud. NFPA 704 (2001) has a five-category flammability rating that provides an indication of the general combustibility hazard. The criteria for placing a particulate material in one of the five categories are shown in Table 1-1.

TABLE 1-1
NFPA 704 Flammability Categories for Particulates

NFPA 704 Flammability Hazard Category	Criteria for Particulate Materials
0	Materials will not burn in air when exposed to a temperature of 815.5°C (1500°F) for 5 minutes.
1	Combustible pellets with a representative diameter greater than 2 mm (# 10 mesh).
2	Solid materials in the form of powders or coarse dusts of representative diameter between 420 microns (# 40 mesh) and 2 mm (# 10 mesh) that burn rapidly but that generally do not form explosive mixtures with air; or Solid materials in a fibrous or shredded form that burn rapidly such as cotton and hemp.
3	Flammable or combustible dusts of representative diameter less than 420 microns (# 40 mesh); or Materials that burn with extreme rapidity, usually by reason of self-contained oxygen e.g., many organic peroxides; or Materials that on account of their physical form can form explosive mixtures with air.
4	Materials that ignite spontaneously in air.

One common particulate fire scenario that is applicable to many materials that are in flammability categories 1, 2, or 3 is the smoldering fire that develops in silos, bunkers, and hoppers. There have been numerous incidents of this type in grain silos, coal bunkers, and plastics manufacturing and processing facilities, and many of these fires have been very difficult to extinguish. Another common fire scenario is the overheating of particulates in various types of dryers. Both the drier fire scenario and the bulk storage smoldering are usually examples of particulate self-heating and spontaneous combustion. Many agricultural products are prone to self-heating due initially to microbiological activity, and later to oxidation during bulk storage. Examples include bagasse, compost, hay, pecans, soya beans, and walnuts. Activated carbon, hafnium and zirconium powder are examples of materials that can undergo oxidative self-heating when they are stored as fine particles.

A dust explosion hazard exists when flammability category 3 particulates are suspended in air at a concentration above the Minimum Explosible Concentration (MEC). As documented in Section 1.3.1, prevalent sites for particulate explosion scenarios include blenders, pulverizers, hoppers, conveyor/elevator transfer stations, and dust collectors. Important features of these locations are frequent dust clouds, moving mechanical parts representing potential ignition sources, and confinement to allow potentially damaging pressures to develop as a result of an accidental ignition. Descriptions of these and other particulate processing and transport equipment are provided in Chapter 5 along with a discussion of specific hazards associated with the equipment. Generic dust explosion hazard scenarios are described in Section 3.7.

Particulate fire and explosion prevention measures for general processing and handling facilities are described in NFPA 654. Preventive measures for electrical and electrostatic ignition sources are contained in additional standards such as NFPA 499, NFPA 77, and IEC 61241. Particulate explosion prevention systems and deflagration venting systems are presented in NFPA 69 and NFPA 68, respectively. There are also fire protection standards for specific particulate materials such as pesticides (NFPA 434) and organic coatings (NFPA 35).

1.2.2 *Instability Hazards*

Particulate instability is the tendency of certain bulk solids to vigorously decompose, polymerize, become self-reactive, or oxidize at the temperatures and other conditions they are subjected to during physical processing, transport and storage. These exothermic reactions can generate potentially dangerous temperatures, pressures, or hazardous gases, or otherwise become violent.

NFPA 704 (2001) defines five hazard categories for unstable materials, with the lowest (zero) category for materials that do not have an exotherm at temperatures at or below 500°C. The four higher categories are defined qualitatively in terms of their instability initiation requirements, and quantitatively in terms of their instantaneous power density (heat of reaction multiplied by reaction rate) at 250°C. The instability category of a material is one of three factors that must be prominently displayed in industrial and commercial facilities manufacturing, processing, storing, or using hazardous materials. The U.S. Department of Transportation and the United Nations regulations for shipping of hazardous materials have generic classifications for self-reactive solids (UN 3224 and 3234), and specify packaging and testing requirements for these materials (49CFR Parts 172-173). One other source of instability hazard ratings is the Hazardous Materials Identification System promulgated by the National Paint and Coatings Association (NPCA).

Particulate materials that have either high NFPA 704 reactivity ratings, or are designated by criteria as U.N. self-reactives, or have been involved in noteworthy incidents include ammonium perchlorate, azodicarbonamide, methyl parathion, potassium nitrate, and sodium azide. The latter, which is designated as a U.N. Class 6.1 toxic material, has been involved in several explosion incidents at airbag propellant manufacturing facilities. Hydroxylamine is a self-reactive particulate material that is so prone to violent self-decomposition that it is always stored/transported in aqueous solutions, and has been involved in several explosions when the solution became too concentrated. Other decomposition incidents are described in Section 1.3.3.

Instability hazard scenarios involving external heating, self-heating, and other initiation modes are discussed in Section 3.1. Laboratory tests to assess particulate instability hazards are described in Section 4.3. In addition to the federal and U.N. standards mentioned above and various NFPA standards for different types of potentially unstable materials, there are general protection recommendations for unstable materials in the CCPS Guidelines (1995), and in VDI Guideline 2263 for powders and dusts.

1.2.3 Reactivity Hazards

Particulate reactivity is the tendency of certain bulk solids to react with other materials that they may contact during bulk storage, transport, or physical processing. These materials can be the container material itself, contamination from previous loads or batches, or, in the case of water-reactive materials, water leakage into the container or process vessel. NFPA 704 has a provision to designate water-reactive materials so that emergency responders will be aware of the reactivity hazard when they determine appropriate response measures. Four different NFPA 704 categories of water reactivity are defined in terms of the heat of reaction. Some examples of particulate materials with high water reactivity ratings are calcium carbide and calcium hypochlorite. The National Paint and Coatings Association's Hazardous Materials Identification System® has a similar provision for alerting plant personnel to the reactivity hazard of chemicals used in paint and coatings.

One well-known example of a reactive incident occurred when water inadvertently entered a blender containing water reactive materials, and caused the blender to explode because of an inadequately sized emergency vent (EPA/OSHA 1997). Another water reaction occurred in 1998 when steam was deliberately used in an attempt to clear an aluminum and aluminum chloride sludge blockage at the bottom of a linear alkylbenzene reactor. There has also been a series of fire incidents initiated from inadvertent wetting of the chlorinated swimming pool chemicals, calcium hypochlorite and trichloroisocyanuric acid, while stored in warehouses and building supply stores.

More complete descriptions of some of these water reactivity hazard incidents and scenarios are provided in Sections 3.3. Reactivity hazard scenarios involving contamination of particulates during transport and storage, and container/packaging reactivity are also presented in Section 3.3. Updated information on U.S. government activities on chemical reactivity hazards can be found in the OSHA Reactivity Web site, http://www.osha.gov/dep/reactivechemicals/index.html.

1.2.4 Toxicity Hazards

The most common toxicity hazard associated with particulates is the respirable hazard associated with particles in the size range 0.2 to 7 μm. Particles in this size range can flow through the bronchi and penetrate into the alveoli, where some particles can remain for decades (King, 1990). Submicron particles are more readily exhaled and therefore represent a lower hazard level than those in the 1–7 μm range. Once being lodged in the lungs, the chronic and acute effects of these particles depend on their biological activity and their solubility. Some examples of dust materials that are particularly hazardous in this regard are silica, coal dust, aluminum, and many heavy metals, such as beryllium, chromium, and plutonium (Kerfooot et al., 1995).

NFPA 704-2001 has five health hazard categories in its classification scheme for potentially hazardous materials. The criteria for placing a powder or dust in one of these categories are based in part on the LC_{50} concentration for acute inhalation toxicity. The specific criteria are given in Table 1-2.

Besides inhalation, the other pathways for small particles to enter the body include accidental ingestion, dermal contact, and eye entry. Toxicity hazards that can be manifested after entry into the body include systemic toxicity, allergic reaction, mutagenic effects, and carcinogenic reactions

TABLE 1-2
NFPA 704 Health Hazard Categories for Particulate Material Inhalation Toxicity

Health Hazard Category	LC_{50} (mg/L)
0	> 200
1	< 200 and > 10
2	< 10 and > 2
3	< 2 and > 0.5
4	< 0.5

(Kerfoot et al., 1995). The NFPA 704 health hazard categorization scheme includes criteria based on the LD50 values for acute dermal toxicity and for acute oral toxicity. Specific scenarios associated with both chronic exposures and acute exposures are discussed in Section 3.8. Asphyxia scenario examples are presented in Section 1.3.4.

1.3 ACCIDENT DATA AND CASE HISTORIES

As an introduction to the numerous case histories and other incident accounts described throughout this book, a statistical overview is presented here along with some representative examples of how the various particulate hazards have been manifested in accidents at industrial facilities.

1.3.1 Dust Explosion Data and Case Histories

Tabulations of materials and equipment involved in dust explosions have been compiled by various organizations. Representative data from organizations in the United States, Germany, and the United Kingdom are presented here. The data used to represent U.S. dust explosions are taken from insurance company loss history (Febo and Thornberg, 2001) because the losses were obtained from a broad cross-section of industrial facilities handling combustible particulates. The data from the U.K. were obtained from the Health and Safety Executive (HSE) and include particulate fires as well as explosions in U.K. facilities. The data for Germany were compiled by the German Institute for Safety at Work of the Trade Unions, as presented by Eckhoff (1997).

The data cited in Tables 1-3 and 1-4 represent only a small fraction of all the dust explosion incidents in the U.S., U.K., and Germany. In the U.S., there

TABLE 1-3
Particulate Materials Involved in Reported Dust Explosions

	U.S. (1985–1995) (FM Global, Febo, 2001)		U.K. (1979–1988)[a] (HSE)		Germany (1965-1980) (Eckhoff, 1997)	
Material	**Number Incidents**	**%**	**Number Incidents**	**%**	**Number Incidents**	**%**
Wood/Paper	56	37	69	23	120	34
Coal	27	18	24	8	33	9
Metals	19	13	55	18	47	13
Plastics	8	5	10	3	46	13
Food/Grain	?[b]	?[b]	94	31	88	25
Pharmaceuticals/Organic	?[b]	?[b]	27	9	?[b]	?[b]
Other/Unknown	4	27	24	8	23	6
Total	150	100	303	100	357	100

[a] The U.K. data include particulate fires as well as 140 reported explosions.

[b] This material category was not explicitly identified in the cited reference.

is no centralized national database and no requirement to report all explosion incidents. In the U.K., the HSE maintains a centralized national database, but receives reports on only a small fraction of all the incidents. The British Materials Handling Board (BMHB) conducted a voluntary survey in 1984 to assess the frequency of dust fires and explosions (Abbott, 1988). For the years 1979–1984, 84 incidents were reported in the BMHB survey, but only 3 of these were reported to the HSE. Furthermore, the data sources do not necessarily contain proportionate representation from the various industries and facilities handling combustible particulates. Therefore, the following tabulations are merely indicative of the types of materials and equipment that have been involved in dust explosions, and are not a reflection of the relative risks of specific materials and equipment.

Both the U.S. (FM) data and the German data in Table 1-3 indicate that the material most frequently involved in reported dust explosions is some form of wood or paper dust. In the U.K., food/grain particulate matter has the highest frequency of reported explosions. Food/grain is the second most frequently involved material in German dust explosions, and is also involved in a large percentage of U.S. dust explosions despite its absence

TABLE 1-4
Equipment Involved in Dust Explosions

Material	U.S. (1985–1995) (FM Global, Febo, 2001)		U.K. (1979–1988) (HSE)		Germany (1965–1980) (Eckhoff, 1997)	
	Number Incidents	%	Number Incidents	%	Number Incidents	%
Dust Collectors	156	42	55	18	73	17
Grinders/Pulverizers	35	9	51	17	56	13
Silos/Bunkers	27	7	19	6	86	20
Conveying System[a]	32	9	33	11	43	10
Dryer/Oven	22	6	43	14	34	8
Mixers/Blenders	>12	>3	7	2	20	5
Other or Unknown	84	23	95	31	114	27
Total	372	100	303	100	426	100

[a] Conveying systems include conveyors, ducts, and elevators.

from the FM tabulation in Table 1-3. A tabulation reported by Schoeff (2001) indicates that there have been 122 U.S. grain dust explosions in the 10-year period 1991 to 2000.

Metal powders/dusts have been involved in 13–18% of reported dust explosions in the three compilations shown in Table 1-3. The combined category of plastics and pharmaceuticals has been responsible for 37 U.K. explosions (12%) in the 10-year reporting period, and at least 46 explosions (13%) in Germany. Similar percentages of plastic and pharmaceutical dust explosions are contained in the 222 dust explosion losses reported by Industrial Risk Insurers (IRI) for the years 1975–2001 (Thornberg, 2001).

Process equipment frequently involved in dust explosions can be ascertained from the compilations in Table 1-4. In both the U.S. and the U.K., dust collectors have been most frequently involved. Three possible reasons for the high occurrence of dust collector explosions are (1) they are almost omnipresent in particulate handling facilities, (2) they inherently concentrate the smaller particles which are easier to ignite than the mostly larger particles in other equipment, and (3) dust collectors are often structurally weaker than other process equipment, and therefore more prone to explosion damage. In Germany, silos and bunkers have been most frequently involved, whereas they have only been involved in 6% to 7% of the reported dust explosions in the U.S. and the U.K. In all three compilations, grinders/mills and pulverizers have been involved in between 9% and 17% of all the reported

TABLE 1-5

Fires Following Dust Explosions (Thornberg, 2001)

Fires after dust explosions?	Number	%
Yes	156	70.3
No	56	25.2
Unknown	10	4.5

incidents. Particulate conveying systems have been involved to 9 to 11% of the reported explosions, and dryers/ovens have been involved in 6 to 14% of the tabulations in Table 1-4. Many of the larger explosions involved multiple types of equipment, with conveying systems and dust collectors often receiving damage from explosions initiated in other process equipment.

Most dust explosions are followed by fires as evidenced by the statistics in Table 1-5 from the IRI database (Thornberg, 2001). The fires are presumably caused by burning particles landing on nearby combustible materials.

The dust explosions reported to the various national safety authorities have caused numerous injuries and fatalities. For example, there were 103 fatalities and 492 injuries in the 357 dust explosions reported to the German Institute for Safety at Work of the Trade Unions, as presented by Eckhoff (1997). There were 100 injuries and 5 fatalities in the 140 dust explosions reported to the HSE for the period 1979-1988. More recent (1988–1993) HSE data reported by Owens and Hazeldean (1995) reveal that there were 827 injuries and 30 deaths in the 1273 dust explosions. There were 16 fatalities and 147 injuries in the 122 U.S. grain dust explosion reports compiled by Schoeff (2001) and the U.S. Department of Agriculture. The ratio of injuries per reported dust explosion in these data compilations ranges from 0.65 to 1.38, and the ratio of deaths per dust explosion ranges from 0.024 to 0.289.

A few brief case studies can best illustrate how and why some dust explosions are relatively inconsequential, while others involve tragic losses of life, numerous injuries, and major facility destruction.

Yowell (1968) described three minor dust explosions that occurred in a polycarbonate manufacturing plant in 1966-1967. The first two explosions occurred during loading of a phenolic intermediate called bisphenol-A into a storage silo. In both silo explosions, the bisphenol-A was being transferred from hopper trucks via positive pressure blowers in the trucks. The most probable ignition source in both incidents was reported to be an electrostatic discharge in the silo. Apparently, electrostatic charging of the powder occurred at it was transferred at a relatively high flow rate through an unbonded rubber hose connection from the truck to the transfer piping, and then directly into the silos. The transfer system was subsequently changed to a vacuum transfer from the hopper car by means of a vacuum blower downstream of the filters on top of the silos. The powder enters the silos by first passing through a rotary air lock valve below the filter.

Both silo explosions caused the explosion venting silo covers to lift and relieve the deflagration pressure as intended. There was some minor damage to the covers and piping on top of the silo, but no damage to the silo itself, and no personnel injuries. After the phenolic transfer system was changed, Yowell reports there were no further silo explosions but there was one minor explosion caused by an employee trying to free a plugged transfer line with a compressed air hose. Compressed air pressure caused the transfer line to separate and a cloud of bisphenol-A formed and was ignited, perhaps again by an electrostatic discharge. Although the employee was injured, he managed to extinguish the fire before seeking first aid. Fortunately, the explosion did not propagate away from the vicinity of the site where the transfer line was blown off.

On February 25, 1999, a devastating dust explosion occurred involving a phenol-formaldehyde resin being used along with sand to make foundry casting molds. After blending, the sand–resin mixture was conveyed to eight shell mold fabrication booths. A central dust collection system served all eight booths, and over a period of time resin dust accumulated in the ducting and on the various equipment and structural surfaces in and around the mold fabrication booths. Each booth had gas-fired ovens for curing the molds. On the day of the explosion, the oven burner flame ignited either a gas-air mixture formed following a temporary flameout, or a dust cloud formed from the shaking/striking of a flexible hose dust collection line (often called an elephant trunk). The initiating event caused flame and a pressure wave to enter the main dust collection ducting network and propagate the explosion to all the other mold booths in the building. The secondary dust explosion that occurred in the building caused extensive burn injuries to twelve employees, three of whom subsequently died. One entire masonry wall and portions of two other walls collapsed from the deflagration pressure (Joint Foundry Explosion Investigation Team Report, 2000). This was one of two similar multifatality secondary dust explosions that occurred that month (Zalosh, 2000).

The primary difference between the phenolic intermediate dust explosions at the foundry and the phenolic intermediate explosions described by Yowell (1968) was the propagation of the dust explosion away from the initiating site, and the eventual involvement of dust/powder that had accumulated in the ducting and on structural surfaces. The occurrence of secondary dust explosions is due in large part to the extended accumulation of dust layers throughout a large portion of either interconnected process equipment or building surfaces. These secondary explosions can be prevented by (1) designing and maintaining equipment to prevent particulate accumulations, (2) frequent and thorough cleaning of ducting and surfaces on which accumulated dust layers have developed, and (3) installing explosion isola-