Avoiding Static Ignition Hazards in Chemical Operations

A CCPS CONCEPT BOOK

LAURENCE G. BRITTON

CENTER FOR CHEMICAL PROCESS SAFETY
of the
American Institute of Chemical Engineers
3 Park Avenue, New York, New York 10016-5901 USA
Avoiding Static Ignition Hazards in Chemical Operations
This is one in a series of CCPS Concept books. A complete list of publications available from CCPS appears at the end of this book.
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CONTENTS

Preface
Acknowledgments

1

INTRODUCTION
1-1. Purpose 1
1-2. Exclusions 4
1-3. Units 5
1-4. Organization of the Book 5

2

FUNDAMENTALS OF STATIC ELECTRICITY
2-1. What Is Static Electricity? 7
  2-1.1. Charge Separation 8
  2-1.2. Magnitude of Current and Potential 8
  2-1.3. Concentration of Charged Species 9
  2-1.4. Importance of Trace Contaminants 9
  2-1.5. Hazard Evaluation 10
  2-1.6. Statistics 10
2-2. Charge Generation 11
  2-2.1. Induction Charging 12
  2-2.2. Ionic Charging 13
### CONTENTS

#### 2-3. Charge Dissipation
- 2-3.1. Variability of Conductivity 15

#### 2-4. Charge Accumulation 16

#### 2-5. Ignition
- 2-5.1. Effective Energy 17

#### 2-6. Static Discharges 20
- 2-6.1. Corona Discharge 21
- 2-6.2. Brush Discharge 23
- 2-6.3. Bulking Brush Discharge 32
- 2-6.4. Spark Discharge 35
- 2-6.5. Propagating Brush Discharge (PBD) 38
- 2-6.6. Surface Streamer 43

#### 2-7. Personnel Spark and Shock Hazards 44
- 2-7.1. Body Capacitance and Resistance 44
- 2-7.2. Voltage (V) and Energy (W) Attained 45
- 2-7.3. Human Shock Response 46

### 3

#### EVALUATING THE HAZARD OF STATIC ELECTRICITY

#### 3-1. General 47

#### 3-2. Hazard Identification Methods 47
- 3-2.1. Decision Trees 48

#### 3-3. Charge Accumulation 48
- 3-3.1. Conductive Objects 48
- 3-3.2. Nonconductive Objects 49

#### 3-4. Energy Estimates 49
- 3-4.1. Charge Sharing 50

#### 3-5. Instrumentation 50
- 3-5.1. Charge 50
- 3-5.2. Electric Field 54
- 3-5.3. Potential 57
- 3-5.4. Ignition Energy 60
- 3-5.5. Conductivity of Liquids 63
CONTENTS

3-5.6. Resistivity of Solids 64
3-5.7. Resistance 65

3-6. Direct Observation of Discharges 66
3-7. Radio Frequency Detection of Discharges 66
3-8. Measuring the Effective Energy of Nonspark Discharges 66
3-8.1. Gas Composition 67

4

CONTROLLING ELECTROSTATIC HAZARDS

4-1. Bonding and Grounding 71
4-1.1. Definitions 71
4-1.2. Purpose of Bonding and Grounding 71
4-1.3. Resistance to Ground 72
4-1.4. Bonding and Grounding Systems 73
4-1.5. Ground Rods 73
4-1.6. Grounding and Cathodic Protection 74

4-2. Control of Charge Relaxation 75
4-2.1. Increase of Conductivity 75
4-2.2. Charge Neutralizers 76

4-3. Control of Personnel Charging 78
4-3.1. Personnel Grounding 78
4-3.2. Clothing 80
4-3.3. Gloves 80

4-4. Control of Flammable Atmospheres 81
4-4.1. Liquid Nitrogen/Liquid Air Hazards 81

5

FLAMMABLE LIQUIDS, VAPORS, AND GASES

5-1. Ignition Hazards of Liquid Vapor and Mist 83
5-1.1. Flammable Liquid 83
5-1.2. Flammable Limits 86
5-1.3. Liquid Mist 87
5-1.4. Minimum Ignition Energy (MIE) 89
CONTENTS

5-7. Portable Tanks 149
   5-7.1. Metal Portable Tanks 149
   5-7.2. Plastic Portable Tanks 150

5-8. Portable Containers Less Than 60 Gallons Capacity 150
   5-8.1. All-Steel Drums 151
   5-8.2. Plastic Lined Drums 153
   5-8.3. Plastic Drums 154
   5-8.4. Hand-Held Containers 154
   5-8.5. Wet-Dry Vacuum Cleaners 157

5-9. Miscellaneous Flammable Atmospheres 157
   5-9.1. Clean Rooms 157
   5-9.2. Water and Steam Curtains 158
   5-9.3. Static Electrification in Gas Flow 158
   5-9.4. Ignition of Vented Gas 159
   5-9.5. Hazards of Plastic Sheet and Wrap 160
   5-9.6. Oxidant Enriched Atmospheres 161
   5-9.7. Elevated Temperature and Pressure 162
   5-9.8. Automotive and Marine 163
   5-9.9. Aerosol Spray Cans 164

5-10. Cathode Ray Tube Video Display Screens 165
   5-10.1. Cleaning 165
   5-10.2. Screens in Hazardous Locations 165
   5-10.3. Static Dissipating Screen Overlays 166

6

POWDER AND SOLIDS

6-1. Flammability of Dust Suspensions 167
   6-1.1. Flammable Limits 169
   6-1.2. Minimum Ignition Energy (MIE) of Dust Suspensions 170
   6-1.3. Hybrid Mixtures 172
   6-1.4. Unstable or Energetic Powders 175
   6-1.5. Effect of Temperature on Ignition Energy 176
   6-1.6. Effect of Moisture on Ignition Energy 177

6-2. Charging Mechanisms 177
   6-2.1. Charge Density 179
6-2.2. Classification of Powders Based on Conductivity

6-3. Pneumatic Conveying
   6-3.1. Charging in Pipeline Flow
   6-3.2. Special Grounding Cases

6-4. Types of Static Discharge in Powder Systems
   6-4.1. Sparks
   6-4.2. Bulking Brush Discharges
   6-4.3. Propagating Brush Discharge

6-5. General Operations
   6-5.1. Vacuum Trucks
   6-5.2. Bag Houses

6-6. Manual Transfers from Portable Containers

6-7. Flexible Intermediate Bulk Containers (FIBCs)
   6-7.1. Powder Transfers in Air Atmospheres
   6-7.2. Powder Transfers from FIBCs to Flammable Liquids
   6-7.3. Conductive and Antistatic FIBCs
   6-7.4. Vacuum FIBC Transfers

Appendix A. EXPLANATORY MATERIAL
   A-2-6.5. Propagating Brush Discharge
   A-4-1.3. Resistance to Ground
   A-5-1.4.4. MIE of Liquid Mists
   A-5-2.4.1. Hyperbolic Relaxation
   A-5-3.5. Filtration
   A-5-4.2.1. Effect of Road Tires
   A-5-6.1. Potentials during Water Washing of Tanks
   A-6-1.2. Effect of Particle Size on Dust MIE
   A-6-1.3.1. Ignition Energy of Hybrid Mixtures
   A-6-1.5. Effect of Temperature on Powder MIE

Appendix B. DATA TABLES
   Flammability Data for Gases and Vapors
CONTENTS

Typical Conductivities, Dielectric Constants and Relaxation (or Dissipation) Times of Liquids 227
Typical Resistivities, Dielectric Constants, and Breakdown Strengths of Solid Dielectrics 234

Appendix C. FORMULAS AND MATHEMATICAL RELATIONSHIPS (SI UNITS)

C-1. Principal Relationships 237
C-2. Analysis: Grounded Sphere above Charged Nonconductive Disc 238

References 249
Glossary 261
Index 273
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PREFACE

For nearly 40 years the American Institute of Chemical Engineers (AIChE) has been involved with process safety and loss control issues in the chemical, petrochemical, hydrocarbon process and related industries and facilities. AIChE publications are information resources for the chemical engineering and other professions on the causes of process incidents and the means of preventing their occurrence and mitigating their consequences.

The Center for Chemical Process Safety, a Directorate of the AIChE, was established in 1985 to develop and disseminate information for use in promoting the safe operation of chemical facilities and the prevention of chemical process incidents. With the support and direction of its Advisory and Management Boards, CCPS established a multifaceted program to address the need for process safety technology and management systems to reduce potential exposures to the public, the environment, personnel and facilities. This program entails the development, publication and dissemination of Guidelines relating to specific areas of process safety; organizing, convening and conducting seminars, symposia, training programs and meetings on process safety-related matters; and cooperating with other organizations and institutions, internationally and domestically, to promote process safety. Within the past several years, CCPS extended its publication program to include a “Concept Series” of books. These books are focused on more specific topics than books in the “Guideline Series” and are intended to complement them. With the issuance of this book, CCPS will have published over 40 books.

CCPS activities are supported by the funding and technical expertise of over 90 corporations. Several government agencies and nonprofit and academic institutions participate in CCPS endeavors.
In 1989, CCPS published the landmark *Guidelines for the Technical Management of Chemical Process Safety*. This book presented a model for Process Safety Management built on twelve distinct, essential and interrelated elements. The foreword to that book stated:

For the first time, all the essential elements and components of a model of a technical management program in chemical process safety have been assembled in one document. We believe the Guidelines provide the umbrella under which all other CCPS Technical Guidelines will be promulgated.

This "Concept Series" book supports several of the twelve elements of process safety enunciated in *Guidelines for the Technical Management of Chemical Process Safety*, including process knowledge and documentation, process risk management and enhancement of process safety knowledge. The purpose of the book is to assist designers and operators of chemical facilities to understand and reduce potential hazards associated with static electricity.
ACKNOWLEDGMENTS

The American Institute of Chemical Engineers and the Center for Chemical Process Safety (CCPS) express their gratitude to Union Carbide Corporation for their generous support in the preparation of this Concept Book. This book was written by Dr. Laurence G. Britton of Union Carbide Corporation (UCC). The author earned a BSc with 1st Class Honors and a PhD in Fuel and Combustion Science at the University of Leeds, England. In January 1978 he was appointed Research Fellow in Prof. A.W. "Bill" Bright's Applied Electrostatics Group at Southampton University where he worked primarily under military contract on various static ignition topics. In mid-1981 he joined Union Carbide's Safety Research Laboratory as Senior Combustion Scientist, later holding posts of Project Scientist and Research Scientist. He is currently a Principal Engineer in UCC's Process Safety Technology Group, involved in process fire and explosion hazards research. He is a Fellow of the Institute of Energy, a Member of AIChE and the Combustion Institute, and is a Chartered Engineer in the UK. He has served on NFPA's Technical Committees for "Static Electricity" (1983–), "Explosion Protection Systems" (1983–), and "Classification and Properties of Hazardous Chemicals" (1987–), the CCPS "Engineering Practices" Subcommittee (1988–) and more recently ASTM's "Hazard Potential of Chemicals" Committee plus several ad hoc committees such as CMA's "Flame Resistant Clothing Issues Group". He has authored numerous technical articles and book contributions and twice received AIChE's "Bill Doyle" Award for best loss prevention paper.

CCPS also acknowledges the contributions of other Engineering Practices Subcommittee members in recognizing the need for a Concept Book on this subject that would bridge the gap between various existing codes or standards and the general literature. The Chair of the Engineering Practices Subcommittee is Mr. Robert Walz of ABB Lummus Global Inc. Other members were: Messrs. Stephen Cloutier (UOP, retired), Glenn Davis (DuPont),
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DISCLAIMER
This work expresses only the opinions of the author and does not necessarily represent the opinions or practices either of Union Carbide Corporation or any other single company. Unpublished case histories used to illustrate the text were in most cases kindly supplied by peers from other companies and are used without either reference or identification of the company involved; this should not imply that the accounts are undocumented. The book should be used in conjunction with published guidelines and recommended practices such as NFPA 77 and references [1-7].
INTRODUCTION

1-1. Purpose

The purpose of this book is to assist the user in controlling the hazards associated with the generation, accumulation, and discharge of static electricity by presenting

- a basic understanding of the nature of static electricity,
- methods for identifying and assessing the hazards of static electricity,
- relevant practical aspects of ignition and combustion,
- techniques for controlling the hazards of static electricity,
- previously unpublished information and illustrative case histories,
- an extensive literature review, and
- appendix material including data tabulations and glossary of terms used in the text.

A number of introductory "static hazard" texts have been published [25, 33, 67, 72, 73]. Useful practical guidelines have also been published by ESCIS [4] and Walmsley [23], respectively based on the contemporary internal practices of Ciba-Geigy [196] and the Royal Dutch/Shell Group [189]. General reading, including electrostatic applications, can be found in the textbooks by Moore [109] and Cross [110].

In 1964, B. F. Skinner observed that "Education is what survives when what has been learnt has been forgotten" [219]. Another survivor is information appearing in such documents as company practices and published codes. Recommendations of uncertain origin are in some cases copied from previous editions or from other documents without thorough re-evaluation.
Since derivations and literature references are typically not given in detail (often not at all) it is difficult for users to recognize errors or assess the validity of some statements when applied to a particular situation. It would be helpful for the user to appreciate limitations of applicability and to consider risk tolerance when adopting a specific practice based on “minimum safe practices” given in codes.

The book is aimed at chemical engineers and other technically trained persons either curious about the origin of published recommended practices on static electricity or faced with one of the many situations not specifically covered. It is intended not as an introductory text but rather to help bridge the gap between recommended practices and the general literature on this subject. Owing to the wide variety of opinions expressed both in published recommended practices and in the general literature the author has carried out a critical review. In addition to material taken directly from the literature, the book contains a large amount of original information either derived from the critical review or taken from over 20 years of personal experience. The coverage should find particular application in safety analyses and accident investigations.

While only elementary electrostatic theory is typically used in this book, more advanced concepts are introduced where necessary. Examples include background discussions of tank filling and tank cleaning models. Electrostatic equations should look familiar to engineers with a background in heat transfer. This is because there is a close analogy between potential difference, governing the flow of charge, and temperature difference, governing the flow of heat. The reverse analogy has been widely used to help solve complex heat transfer problems with reference to analog resistive circuits in which temperature differences and heat flows are replaced by potential differences and currents. Table 1.1 lists some analogous quantities and equations.

In the simplest case of one-dimensional steady flow in the x direction, there is a parallel between Fourier's law for heat flow rate and Ohm's law for charge flow rate (i.e., electrical current). For three-dimensional steady-state, potential and temperature distributions are both governed by Laplace's equation. The right-hand terms in Poisson's equation are \( \frac{Q_V}{\varepsilon} \) = (volumetric charge density/permittivity) and \( \frac{Q_G}{k} \) = (volumetric heat generation rate/thermal conductivity). The respective units of these terms are \( \text{V m}^{-2} \) and \( \text{K m}^{-2} \). Representations of isopotential and isothermal surfaces are known respectively as potential or temperature fields. Lines of constant potential gradient (“electric field lines”) normal to isopotential surfaces are similar to lines of constant temperature gradient (“lines of flow”) normal to
isothermal surfaces. In electrostatic books, isopotentials are often described as "equipotentials."

To facilitate solution of the differential equations, analogous simplifying assumptions can be made. For example, owing to the high thermal conductivity of steel, the internal temperature of a hot steel billet upon being plunged into a large reservoir of cold water might be assumed spatially constant. The water reservoir might be considered as a "heat sink" at constant temperature into which heat is transferred across the boundary. Similarly, the potential of charged, electrically conductive liquid poured into a poorly conducting plastic jug might be assumed spatially constant. The large surrounding "charge sink" is the earth into which charge is transferred across the jug wall. The solution to the steel billet problem can be written in terms of temperature difference between the steel and the water as

\[ \Delta T = \Delta T_0 \exp(-B_i F_i) \]  

(1-1)

where \( \Delta T_0 \) is the initial temperature difference and \( B_i, F_i \) are respectively the Biot and Fourier dimensionless groups. If time is extracted from the Fourier number, Eq. (1-1) can be rewritten

\[ \Delta T = \Delta T_0 \exp(-t / \tau) \]  

(1-2)
where \( \tau \) is a time constant comprising the remaining terms of the dimensionless groups. Since heat or heat density is proportional to temperature difference, this result is analogous to Eq. (2-3.7) governing the rate of charge decay.

The commonest assumption when solving Poisson’s equation for potential distribution in charged liquids and powders is that the volumetric charge density is spatially constant. The assumption allows analytical solution in simple geometries such as spheres (Appendix C) and simplifies computer solution in more complex geometry via finite difference or element techniques. It is analogous to the heat transfer assumption that the volumetric heat generation rate is not only independent of time but also of position (for example, a dispersed radioisotope). Models based on the assumption of spatially constant charge density form the basis for setting flow rate limits during tank loading. The assumption implies that the filling pipe in a tank releases charge at a uniform rate throughout the liquid space and the tank is always completely full of liquid. As illustrated in the text by several case histories, such models can fail in practice owing to their simplifying assumptions. For example, poorly conducting froth layers might buoy up conductive solids such as chunks of ice or hydrates derived from the tank or inlet line, allowing static discharges to occur during transfer of relatively conductive liquids such as esters. Static discharges from nonconductive liquids are encouraged by inlet pipe orientations that allow convection of excessive charge to the free surface.

While it is important to appreciate mechanisms for production of static discharges it is often more important to recognize the factors influencing flammability and ease of ignition. As illustrated in the text by several case histories, static ignition can sometimes occur under conditions involving an unrecognized flammability hazard, such as a liquid at less than its flash point or a tank equipped with nitrogen padding. As discussed in Chapter 5, a side-effect of splash filling a tank is the associated dilution of vapor near the liquid surface via air entrainment. Since ignition via brush discharges typically occurs within 10 cm of the surface, air dilution might create an ignition hazard above liquids that would otherwise generate local vapor concentrations above their UFLs. The “ignition” component of “static ignition hazards” represents most of the problem suggested by the title of this book and consequently a large part of the text is concerned with flammability. In this respect the book differs significantly from other texts on static hazards.

1-2. Exclusions

This book is focused on static ignition hazards in chemical operations. The following are not specifically covered
1. INTRODUCTION

- **Intrinsic Safety.** Static electrical concepts such as minimum ignition energy do not directly apply when assessing the safety of electrical circuits such as radios, flashlights and instrumentation. Intrinsically safe electrical equipment is usually available which has been subjected to fault analysis and testing. The equipment must be certified for the flammable atmosphere in which it will be used (NFPA 497). Refer to texts on Intrinsic Safety such as [63].

- **Stray Electrical Currents and Induced Radio Frequency Currents.** For information on stray currents see API 2003 [3]. For information on both hazards see the author’s review “Sources of Ignition” in [157].

- **Electrostatic Discharge (ESD) Damage to Electronic Equipment.**
- **Marine Tankers and Barges** (see [5] “ISGOTT”).
- **Web and Printing Processes** (see NFPA 77).
- **Lightning Protection** (see NFPA 780).

1-3. Units

The SI system of units is normally used. For descriptions in the text, units were selected either to be most familiar to the user or most appropriate for the application. For example, because the scale is nonlinear, breakdown strength is expressed in length units of the order 1 cm or less, reflecting that measured values do not apply over one meter. Additionally, since the thickness of insulating layers is often measured in mils, the mil equivalent is given to avoid confusion between μm (micron), mil, and millimeter. For ease of reading, mixed SI and cgs units are sometimes used to avoid introducing exponents or small decimals; an example is the expression of dust concentration in g/m³ rather than kg/m³. Volumes and flow rates are expressed in terms of US gallons where this is helpful to the user. Where conversions are made between SI and other unit systems, values are often rounded off where lack of precision does not justify exact numbers.

1-4. Organization of the Book

The practical content of this book is mostly contained in Chapter 5 (gases and liquids) and Chapter 6 (powders and hybrid mixtures) with other chapters providing supporting material. Chapter 2 contains a brief explanation of the nature of static electricity followed by a detailed discussion of the characteristics and effective energies of different static discharges. Since this
chapter is relatively technical the reader might wish to refer back to it as needed. Chapter 3 discusses techniques for evaluating static hazards including the instrumentation that is frequently used. Chapter 4 describes general bonding, grounding and other techniques used either to control static or prevent ignition. Following Chapter 6 are a series of appendices containing additional explanatory material, data tables, mathematical relationships, references, and glossary. The book is extensively cross-referenced by chapter and section. Complete text references are given in the “References” section, except for documents issued by ASTM or by the National Fire Protection Association (1, Batterymarch Park, Quincy, MA 02269-9101, USA) which are referred to in the text by their document numbers (e.g., ASTM E 502, NFPA 77).
2

FUNDAMENTALS OF STATIC ELECTRICITY

2-1. What Is Static Electricity?

As the name implies, the term originally referred to physical phenomena associated with charges at rest, such as on charged, isolated conductors. However, as used in this book, "static" charges may be either be at rest or moving. The elementary unit of negative charge is the electron, which carries \(-1.6 \times 10^{-19}\) Coulombs of charge. A positive charge is equivalent to the absence of electrons. In semiconductor theory a group of covalent bonds deficient of one electron is treated as a mobile positively charged entity, or "hole." This concept is used to describe the properties of semiconductive crystals used in transistors. However in the context of this book it is best to think of the flow of positive charge as a flow of positively charged particles or ions.

Static electricity hazards or nuisances arise when charge separation occurs leading to an accumulation of one sign of charge within some defined boundary, such as inside a container. The work performed in separating the charges results in differences of potential within or across the defined boundary and the accompanying generation of electric fields. If an electric field locally exceeds some threshold value, electrical breakdown of the intervening medium occurs in the form of a static discharge. This might come as a shock.

The "tingling" effects of static are caused by mutual repulsion between strands of hair carrying the same sign of charge, which tends to make them
stand up. The phenomena occur either as the result of polarization (2-2.1) or a net charge on the body. When the body is polarized by a strong electric field, the charged strands of hair are both repelled from one another and attracted in the direction of the electric field. This can be especially hair-raising.

2.1.1. Charge Separation

This occurs in a variety of ways. When solid surfaces are placed in contact, an electronic rearrangement occurs to minimize the energy at the interface. Since this process is generally not reversible, charge separation occurs when contact between the surfaces is lost. If the interface is disrupted at a rate faster than equilibrium conditions can be established, additional charge separation occurs. However, the maximum surface charge density is limited by electrical breakdown in the gap between the separating surfaces. During separation of nonconductive plastic sheets, one sheet gains a net positive charge and the other gains an equal quantity of negative charge. If this process occurs in air, corona discharges in the gap formed between the sheets limit the maximum surface charge density to \( \leq 2.65 \times 10^{-5} \text{ C/m}^2 \) (6-2.1.1). As a stream of water breaks up, ions associated with aligned water dipoles at the water-air interface separate into the fine mist created as the surface layer shears away, while ions of predominantly opposite sign separate into the coarser droplets formed from the body of the water stream. This results in a charged water mist after the coarser droplets settle out (5-6.1). Ionic charge-carrying species in liquids are adsorbed nonuniformly at the wall of a pipe such that one sign of charge predominates in a tightly held "fixed layer" while the countercharge is situated farther from the wall in a less tightly held "diffuse layer." When the liquid is pumped through the pipe the diffuse layer shears away and is convected downstream. The flow of charge is equivalent to a charging current or "streaming" current (5-2.1 and 5-3.1.1).

2.1.2. Magnitude of Current and Potential

Static electricity hazards and nuisances are typified by the generation of large potentials (0.1–100 kV) by small charging currents (0.01–100 \( \mu \text{A} \)) flowing in high resistance circuits (10\(^8\)–10\(^{15}\) \( \Omega \)). This in part differentiates static electricity from other electrical phenomena. For example, stray currents in low resistance circuits are typically of the order 1 A for potential differences of the order 1 volt (A-4-1.3). The electric field at any point in relation to a conductor is proportional to its potential, while magnetic field is proportional to
the current flowing through the conductor. Since static electricity involves high potentials and very low currents, it can be differentiated from "current electricity" phenomena by its associated electric field but the absence of any significant magnetic field.

2.1.3. Concentration of Charged Species

The occurrence of static electricity is highly dependent on the presence of charged chemical species at extremely small concentrations. This is because only a minuscule fraction of an electrostatically charged substance carries a net charge. One Coulomb represents the same charge as $6.25 \times 10^{18}$ electrons, or an equal number of ionic species each carrying one elementary unit of charge. A mole of substance contains the Avogadro number, $6.023 \times 10^{23}$ molecules. Hence a charge density of one Coulomb per mole is equivalent to 1 molecule in 96,400 (~10 ppm) carrying an elementary charge. One Coulomb per mole is an extremely large charge density. The volumetric charge densities found in charged liquids typically range from 1 to 5000 $\mu C/m^3$. For a typical maximum charge density of 1000 $\mu C/m^3$, assuming a liquid with specific gravity 1.0 and molecular weight 100, the involvement of molecules in the net charge carrying process is one part per trillion.

Similarly, 1 m$^3$ of this substance contains $6.023 \times 10^{27}$ molecules. The maximum surface charge density of $\leq 2.65 \times 10^{-5} \text{ C/m}^2$ (2.1.1) corresponds to $1.6 \times 10^{14}$ electrons. If the surface charge is assumed to reside in a slice of the substance 10 Angstroms thick, containing $6.023 \times 10^{18}$ molecules, approximately 27 ppm of these molecules carry an elementary charge. A similar concentration (about 7 ppm) is found for the more realistic case of a plastic with molecular weight 20,000 and specific gravity 0.8, where the charge is trapped in a surface layer ~1 $\mu m$ thick.

2.1.4. Importance of Trace Contaminants

The electrostatic behavior of intrinsically nonconductive substances, such as most pure thermoplastics and saturated hydrocarbons, is generally governed by chemical species regarded as "trace contaminants." These are components that are not deliberately added and which may be present at less than detectable concentrations. Since charge separation occurs at interfaces, both the magnitude and polarity of charge transfer can be determined by contaminants that are surface active. This is particularly important for nonconductive liquids, where the electrostatic behavior can be governed by contaminants present at much less than 1 ppm (2.1.3).
An unpredictable charge density increase or polarity reversal caused by a "pro-static agent" (5-3.1.2) may lead to static ignition after years of uneventful operation under ostensibly identical conditions. For example, a change from positive to negative charging of a liquid may lead to formation of an incendive "positive brush" discharge (2-6.2). Such situations may be exacerbated by a coincidental decrease of ignition energy. An example is a temperature change that affects both charging of the condensed phase and flammability of the surrounding space. Many surface active trace contaminants increase the magnitude of charging in liquids. However, at higher concentrations they can have a beneficial effect by increasing the liquid conductivity to the extent that significant charge no longer accumulates in grounded containers. Special formulations are known as "antistatic additives" (5-2.6).

Trace contaminants are also significant at charged solid surfaces, affecting both the charging process and the surface conductivity. In ambient air atmospheres their effect is often determined by interaction with adsorbed water vapor, whose dominant concentration may be sufficiently large to form a monolayer. Topical antistatic agents for solids typically rely on interaction with adsorbed water and can lose effectiveness at low relative humidity (4-2.1).

2-1.5. Hazard Evaluation

The ignition hazard analysis in 2-5 begins with evaluating whether static electricity can accumulate, with the assumption that flammability has already been addressed. However, as reflected in Chapters 3, 5, and 6, a practical safety analysis should begin by evaluating whether a flammable mixture may be present, since this determines whether or not any ignition hazard exists in the first place. The usefulness of a hazard evaluation is determined largely by the evaluation of flammability, since this governs the ignition hazard with respect to any ignition source. Order-of-magnitude estimates may in some cases be sufficient to rule out ignition via static discharges. Conversely, if a large risk exists, or in the aftermath of an explosion, order-of-magnitude estimates may be inadequate. In such situations the coverage given in this book should be especially helpful.

2-1.6. Statistics

Static ignition statistics must be used with prudence not only because of possible misdiagnosis of the cause of ignition but also because of the way the losses are often grouped together. As discussed in Chapters 5 and 6 the likeli-
hood of ignition is related most strongly to the ignition energy of the flammable atmosphere involved. In road tanker operations, although switch loading is sometimes considered separately, accident statistics usually fail to identify fires involving pure liquids which can represent the most hazardous case (5-1.4.1). The sheer bulk of some operations having a small likelihood of ignition, such as gasoline trucking, can lead to misinterpretation of incident rate by incorporating and hiding those products with a much greater likelihood of ignition, such as toluene. Other grouping errors may involve the use of antistatic additives in certain products (5-2.6). Powder ignition is similarly much more likely for certain products, especially where a substantial mass fraction comprises fine powder or the process by its nature tends to accumulate easily ignitable dust. The methods outlined in this book should help identify those products and operations most at risk.

2-2. Charge Generation

The principal mechanisms are

a. contact and separation of solids (including frictional charging or tribocharging),
b. fragmentation of solids having nonuniform surface charge densities,
c. shear at liquid–solid, liquid–gas and two-phase liquid interfaces,
d. gravitational separation of suspended material having nonuniform size and charge,
e. induction charging, and
f. ionic charging.

Mechanisms (a) through (d) are process-specific as discussed in Chapters 5 and 6. The latter mechanisms require the presence of large electric fields and represent processes whereby charge can be transferred between systems that are electrically isolated from each other. Charge generation may be a discrete process, in which case it is associated with a transferred charge (Coulombs) resulting in a net charge density (Coulombs per unit area, volume or mass), or can continue indefinitely, in which case the rate of production of charge (Coulombs/second) is equivalent to a charging current (Amperes). An example of a discrete charging process is the electrophorus induction charging apparatus (see “Glossary”) while examples of continuous charging processes include flow of liquid or powder through pipelines.
2-2.1. Induction Charging

This is the process of momentarily grounding a conductor which has been polarized by an electric field, then removing the conductor from the electric field so that it gains a net charge. Polarization is the movement of charges to new locations by the action of an electric field acting on an ungrounded conductor, or the movement of an ungrounded conductor into an existing electric field. The electric field causes electron redistribution in the conductor and the performance of work, which raises its potential. An important feature of induction charging is that an ungrounded conductive object in an electric field can achieve a high potential and become a spark hazard without any contact or charge exchange with other objects. Once a spark occurs, the conductor gains a net charge and has become “inductively charged.”

2-2.1.1. Production of Two Sparks via Induction

Consider an ungrounded conductive object whose potential has been raised by an external electric field to the extent that it sparks to a neighboring grounded object. When this process occurs the potential of the ungrounded conductor is reduced approximately to ground potential by the spark, which can be considered as a conductive channel. When the spark occurs, a net charge flows to ground so as to minimize the potential energy of the ungrounded conductor in the electric field. Should the electric field be removed, the net charge now existing on the ungrounded conductor results in an elevated potential relative to ground and a second spark may occur to a grounded object.

2-2.1.2. Practical Examples

1. An uncharged person wearing nonconductive shoes is influenced by the electric field from a plastic tote bin containing charged resin. Since human bodies are conductive, charges move in the electric field leading to polarization and an increase in body potential even though no charge is transferred. If the person touches the grounded metal frame of the tote bin, a spark (static shock) occurs owing to the potential difference between the person and ground. The spark causes a net transfer of charge to the person, who may carry this net “induced charge” out of the influence of the electric field and suffer a second shock when again touching grounded metal, since once out of the influence of the electric field the charged body gains a potential difference with respect to ground.