



**WORKING WITH MODERN
HYDROCARBON AND OXYGENATED SOLVENTS:
A GUIDE to FLAMMABILITY and STATIC ELECTRICITY**

**American Chemistry Council
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WORKING WITH MODERN HYDROCARBON AND OXYGENATED SOLVENTS: A GUIDE to FLAMMABILITY AND STATIC ELECTRICITY

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WORKING WITH MODERN HYDROCARBON AND OXYGENATED SOLVENTS: A GUIDE to FLAMMABILITY

Forward

Solvents have many beneficial uses, but they must be used safely. This Guide provides general information about the safe use of hydrocarbon and oxygenated solvents in industrial settings, with a particular emphasis on hazards of fire and explosion.

The Solvents Industry Group (SIG) of the American Chemistry Council (ACC) was established in 1995 to address health, safety, and environmental issues pertaining to modern hydrocarbon and oxygenated organic solvents. The SIG supports scientific research, participates in regulatory activities pertaining to solvents and works to ensure that solvents continue to be recognized as important components of a wide range of products that help make our lives safer and healthier while meeting the challenges of today's environmentally conscious world.

The Solvents Industry Group and its members promote the safe use of solvents with particular emphasis on hydrocarbon and oxygenated solvents. Statutory and regulatory requirements regarding flammability are important and SIG members work to help educate solvent users, distributors, and transporters so they can better understand these requirements. Some hydrocarbon and oxygenated solvents readily evaporate and are highly flammable. These solvents whether use occurs in the home or in an industrial setting, need to be managed carefully to minimize risks of a fire or explosion, particularly during loading and unloading, storing and when used in bulk. Safe handling consistent with both industry standards and information provided by the supplier should be carefully followed.

Section One of this Guide is a summary of key issues associated with the safe use and handling of hydrocarbon and oxygenated solvents in industrial settings. Section Two addresses the technical characteristics of the flammability of solvents and Section Three addresses the electrostatic discharge of solvents in more detail, and is intended for readers who want a more in-depth understanding of these characteristics. Topics include static electricity, flash point, autoignition temperature, solvent mists, minimum ignition energy, and sources of ignition. A glossary of some of the terms used in this guide is provided at the end of the document.

Many of the characteristics of hydrocarbon and oxygenated solvents can be understood from the general overview provided in this Guide. However, this Guide is not intended to cover specific solvents, nor specific applications of solvents. Solvent users should consult with the solvent supplier or solvent manufacturer, and view product information for instructions on how to handle specific solvents. For more information, see the Legal Notice for this Guide.

Scope of Guide

This Guide addresses oxygenated and hydrocarbon solvents in industrial settings. Oxygenated solvents are synthesized from other chemicals to form the desired solvent. Examples of classes of oxygenated solvents are alcohols, glycol ethers, esters, and glycol ether esters. Hydrocarbon solvents are complex mixtures derived from crude oil fractions and are sold on the basis of customer specifications. Typical specification properties include distillation range, flash point, density, aromatic content, and color. Aliphatic and aromatic hydrocarbons are examples of types of hydrocarbon solvents. This Guide does not address halogenated solvents, such as chlorinated hydrocarbons. At all times when this Guide refers to “solvents,” the reference applies to hydrocarbon and oxygenated solvents.

This Guide is intended for the United States (U.S.) and may not be applicable to other parts of the world. For a discussion of flammability from a European perspective, you may wish to visit the European Solvents Industry Group’s website (www.esig.org) to obtain, “Safe Working with Solvents; Flammability: A Safety Guide for Users.”

Legal Notice

This Guide was prepared by the Solvents Industry Group of the American Chemistry Council. It is intended to provide general information to persons who may use, handle, or store hydrocarbon or oxygenated solvents in an industrial setting. It is not intended to serve as a substitute for in-depth training or specific handling or storage requirements, nor is it designed or intended to define or create legal rights or obligations. It is not intended to be a “how-to” guide, nor is it a prescriptive guide. All persons involved in handling and storing solvents have an independent obligation to ascertain that their actions are in compliance with current federal, state, and local laws and regulations and should consult with legal counsel regarding such matters. This Guide is necessarily general in nature and individual solvent users may vary their approach with respect to particular practices based on specific factual circumstance. This Guide is not intended or designated to define or create legal rights or obligations.

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This document is posted on the Solvents Industry Group's new website, www.americanchemistry.com/solvents. Please consult the website to determine if a new version is available. For more information on material presented in this Guide, please contact your supplier.

Section 1: General Information

1.1 General Safety Considerations for Handling Solvents

There are many safety considerations when working with solvents. Some general principles and considerations that help to minimize flammability concerns are outlined below. These are by no means exhaustive, nor do they address specific solvents or specific handling situations. In some cases, one or more of these considerations may not be applicable at all due to site conditions, application requirements, or other exigent circumstances. They do, however, provide a helpful overview of some basic considerations, and provide a starting point for solvent users to develop their own practices and safe handling plans.

Understand the Solvent. Understanding the specific physical and chemical properties of the solvent being used is extremely important. The supplier's Material Safety Data Sheet (MSDS) should be consulted for basic information about the properties of a specific solvent, as well as volatility, vapor pressure, boiling point, flash point, basic handling, first aid and other associated information. Manufacturers or suppliers may also be consulted for additional information.

Follow Appropriate Regulations and/or Standards Applicable to Handling and Storage of Solvents.

For example, one or more of the following standards may be applicable:

- National Fire Protection Association (NFPA), "Flammable and Combustive Liquids Code," (NFPA 30).
- Occupational Safety and Health Standards-OSHA Part 1910, Subpart H, "Hazardous Materials," (1910.106).
- National Fire Protection Association (NFPA), "National Electric Code," (NFPA 70).

Address Potential Ignition Sources. Identifying potential ignition sources including static discharge and incorporating procedures for safe handling and storage into industrial operating practices, where appropriate, helps prevent ignition sources and solvent vapors from coming into contact. Many solvent vapors are heavier than air and steps should be taken to guard against the migration of the vapor to an ignition source. Examples of practices that can be appropriate in many situations are no-smoking signs and enforcement of no-smoking policies; setting and enforcing appropriate distance limits between the ignition source and solvent use areas; exercising careful equipment selection; taking steps to minimize static buildup by using suitable equipment and grounding arrangements; and creating and enforcing other safe systems of work practices. Specific practices will vary from site to site, depending on circumstances.

Understand Conditions for Autoignition. The autoignition temperature (AIT) is the temperature at which, in the presence of sufficient oxygen, a material will ignite on its own and burn¹. It is well documented that AITs are not absolute quantities, but vary with conditions such as pressure, movement of the vapor-air mixture relative to the hot surface within the volume of the container, and oxygen content.



Control Static Electricity. Appropriate storage and handling procedures should be established for: grounding of temporary and/or permanent equipment; bonding of tanks and vessels to reduce the likelihood of static discharge; dipping and sampling techniques; and switch loading. Typical grounding and bonding situations for many routine applications can be found in NFPA 77, “Recommended Practice on Static Electricity.”² Static electricity is discussed further in Section 3 of this Guide.

Maximize Ventilation as Appropriate to the Application. Good ventilation is an important tool in managing solvent use. Ventilation helps diffuse solvent vapors and maintain a supply of fresh air in the use area. While the degree of ventilation desirable varies depending on circumstances, methods for promoting ventilation may include working in an open atmosphere (e.g., keeping doors and windows open), working in laboratory hoods and using forced ventilation. Some key considerations regarding ventilation are the size of the area where solvents will be used, the circulation of air within that area, the amount of solvent used, the rate of solvent use, and the rate of solvent evaporation.

Maintain Appropriate Work Temperature. Working at lower ambient temperatures can slow the volatilization of solvents, decreasing the rate at which solvent vapors enter the atmosphere. Working with solvents when the air temperature is cooler can be a useful tool for managing solvent flammability.

Educate and Train. Appropriate education, information, instructions, and training should be provided to persons handling solvents.

Report Leaks and Spills in Accordance with Federal and State Regulations. Incidents such as solvent leaks or spills should be reported in accordance with the user’s company policies, Material Safety Data Sheet (MSDS) instructions, and any applicable statutory and regulatory requirements. Appropriate clean up and disposal facilities should be used.

Consider Providing Secondary Containment. Secondary containment, such as oversize drums, may be useful tools.

Develop Appropriate Loading and Unloading Procedures. Loading and unloading vehicles (e.g., tank trucks or rail cars) and containers such as drums may present special handling issues. Consider whether additional measures may be appropriate to reduce the likelihood of static charge buildup, or spills.

Consider Developing an Emergency Plan. An emergency plan for personnel should be considered at facilities where solvents are being used. It can be helpful to design a short, easy to understand plan that is readily available to personnel. If English is not the primary language of personnel, a multilingual emergency plan may be considered.

Consider Inert Storage Solutions. Where appropriate, consider use of inert storage practices such as nitrogen blankets to help remove oxygen from the system.

Some General Safety

Considerations for Handling Solvents

- Understand the Solvent
- Follow Appropriate Regulations and/or Standards Applicable to Handling and Storage of Solvents
- Address Potential Ignition Sources
- Understand Conditions for Autoignition
- Control Static Electricity
- Maximize Ventilation as Appropriate to the Application
- Maintain Appropriate Work Temperature
- Educate and Train
- Report Leaks and Spills in Accordance with Federal and State Regulations
- Consider Providing Secondary Containment
- Develop Appropriate Loading and Unloading Procedures
- Consider Developing an Emergency Plan
- Consider Inert Storage
- Consider Developing Standard Operating Procedures

Consider Developing Standard Operating Procedures. Some examples of areas for developing standard operating procedures could include handling solvents, minimizing leaks, and dissipating static charge.

1.2 Key Factors Relevant to Solvent Flammability

“Flash point” is defined by U.S. Occupational, Safety and Health Administration (OSHA) and the U.S. Department of Transportation (DOT) in the U.S. Code of Federal Regulations (CFR) as: “The minimum temperature at which a liquid gives off vapor within a test vessel in sufficient concentration to form an ignitable mixture with air near the surface of the liquid.”^{3,4} A low flash point (below room temperature) indicates a highly flammable material. Users may wish to consider special or additional handling practices (see Section 2.1.1 for additional discussion of flash points).

The limits of flammability are indicated by the LEL (Lower Explosion Limit) and the UEL (Upper Explosion Limit) for the material, which define the flammability range of the solvent. These limits are the minimum (LEL) and maximum (UEL) concentration of the material in air that will burn. The terms Lower Flammability Limit (LFL) and Upper Flammability Limit (UFL) are used interchangeably with LEL and UEL, respectively. Flammability range is discussed in greater detail in Section 2.1.

As discussed earlier, the autoignition temperature (AIT) is the temperature at which, in the presence of sufficient oxygen, a material will ignite on its own and burn.¹ The AIT can serve as a very rough guide to the maximum temperature that a mixture of a flammable solvent in air can reach before self-ignition. Note that the AITs of hydrocarbon and oxygenated solvents are well above their boiling points. There is no connection between the AIT of a substance and its flash point. Further discussion on AIT is contained in Section 2.1.2.

Droplet mists of solvents can be ignited at temperatures well below the flash point of the liquid. Additional information on mists is provided in Section 2.1.3.

Regardless of location, a wide range of sources are capable of igniting mixtures of flammable solvent vapors in the air. A few examples of ignition sources are flames, hot surfaces, and sparks from electrical equipment or metal tools falling.

Static electricity, discussed in more detail in Section 3 of this Guide, is also a possible source of ignition. It is important to note that due to their physical and chemical properties, hydrocarbon solvents and some oxygenated solvents can actually accumulate static electricity. In these solvents, discharge can occur in the form of sparks capable of igniting solvent vapors.

Note on LELs and TLVs

There is no link between Lower Explosion Limits (LELs), a flammability measurement, and Threshold Limit Values (TLVs) or Permissible Exposure Limits (PELs), which are values related to workplace exposure. A TLV is a time-weighted average concentration for a conventional 8-hour workday and a 40 hour work week for which it is believed that nearly all workers may be repeatedly exposed, day after day, without adverse effect. A PEL is defined by OSHA as the maximum concentration of a chemical to which a worker may be exposed without incurring adverse health effects. This value can be expressed as either a Ceiling Value (a value that cannot be exceeded at any time) or an 8-hour time-weighted average (average value of exposure for an 8-hour work shift of a 40 hour work week). These values are different than the LEL, because the LEL describes only the minimum concentration of material in air that will burn.

Section 2 :Technical Aspects of Flammability

2.1 Flammability Range

This section builds on the general information provided in the previous section and addresses technical characteristics of hydrocarbon and oxygenated solvents and how these characteristics affect the flammability of solvents. This section of the Guide provides a general introduction to the following topics:

- Flammability Range
- Flash Point
- Autoignition Temperature
- Solvent Mists
- Minimum Ignition Energy
- Sources of Ignition

Three components must be present for a fire or explosion to occur. They are combustible vapors (in the present context, solvent vapors), oxygen (which may be from the air, or another source) and a source of ignition. When the vapor of a flammable liquid solvent is mixed with air in certain concentrations, and in the presence of a source of ignition, a rapid combustion or an explosion can occur. The specific vapor/air concentration is called the “flammable range” and might also be referred to as the “explosive range.” In the flammable range, a flash will occur or a flame will spread if the mixture is ignited.

The borders of the flammable range are called Lower Explosion Limit (LEL) and Upper Explosion Limit (UEL). The LEL is the lowest concentration of vapor in air at which the vapor/air mixture will burn and the UEL is the highest concentration of vapor in air at which the vapor/air mixture will burn. LEL/UEL are usually expressed in terms of percentage by volume of vapor in air. Below the LEL, it is said that the mixture is “too lean” to burn and above the UEL, the mixture is “too rich” to burn.

Literature values for LEL and UEL are based upon normal atmospheric temperatures and pressures unless otherwise specified. These values are indicated in the supplier’s MSDS. Flammable limits can significantly vary with pressure or temperature. The general effect of increasing the pressure is to slightly lower the LEL and greatly raise the UEL.

It should be noted that many LELs and UELs are theoretical calculations and, accordingly, should be regarded as guide values only.

Another important parameter to keep in mind when characterizing the flammability properties of a solvent is the relative evaporation rate (RER). Flammable liquid solvents must evaporate into the air from the liquid before they can burn. The evaporation rate of a common solvent such as n-butyl acetate is typically used as a reference, and is assigned an RER equal to 1 (or 100). Solvents with larger RERs have faster evaporation rates and are therefore more volatile. The evaporation rate of a solvent is dependent on temperature and is directly proportional to the vapor pressure of the substance. The RER is inversely proportional to the boiling point and flash point of the solvent.

Typical solvent properties, under normal atmospheric conditions, are shown in Table 1 on page 11.



Table 1. Examples of Typical Solvent Flammability Properties Under Normal Atmospheric Conditions*

Substance	Closed Cup Flash Point (°C)	Lower Explosive Limit (% v/v)	Upper Explosive Limit (% v/v)	Autoignition Temperature (°C)**
Pentane	-49	1.5	7.8	285
n-Hexane	-22	1.2	7.5	233
Acetone	-18	2.6	12.8	485
Methyl Ethyl Ketone	-7	1.8	11.5	505
Ethyl Acetate	-4	2.1	1.4	460
n-Heptane	-4	1.2	6.7	215
Dearomatized Hydrocarbon Solvent s (100-140° C boiling range)	1	0.8	8	275
Toluene	4	1.3	7	535
Methanol	10	7.3	36	455
Isopropanol	12	2	12	425
Ethanol	13	3.3	19	365
n-Butyl Acetate	24	1.7	15	370
m-Xylene	25	1.1	7	525
n-Butanol	35	1.4	11.2	340
Mineral Spirits (150-200°C boiling range)	38-43	0.7	6.5	258
Dearomatized Hydrocarbon Solvents (150- 200°C boiling range)	39-43	0.6	6.5	260
Aromatic Solvent (160- 185°C boiling range)	47-50	1	7.5	496
Dearomatized Hydrocarbon Solvents (200- 230° C boiling range)	82	0.6	5	250
Dearomatized Hydrocarbon Solvents (250-270° C boiling range)	117	0.5	4.7	240

*Readers should contact their suppliers as values may vary slightly from one producer to the next. Flammability limits can significantly vary with pressure and temperature. Note that these are guide values only.

**Although the exact test method for the values cannot be determined, ASTM has developed a standard test method for Autoignition Temperature of liquid chemicals (ASTM E659).

Table 2. Summary of U.S. Criteria for Flammability Assignment ^{3,4}

Classification	DOT Classification Criteria	OSHA Classification Criteria
Flammable Liquid	Liquid having a flash point of not more than 60.5° C (141° F), or any material in a liquid phase with a flash point at or above 37.8° C (100° F) that is intentionally heated and offered for transportation or transported at or above its flash point in a bulk package, with the following exemptions: any liquid meeting one of the definitions specified in 49 CFR 173.115 (gases); and any mixture having one or more components with a flash point of 60.5° C (141° F) or higher, that make up as least 99% of the total volume of the mixture, if the mixture is not offered for transportation or transported at or above its flash point.	Any liquid having a flashpoint below 100° F (37.8° C), except any mixture having components with flashpoints of 100° F (37.8° C) or higher, the total of which make up 99% or more of the total volume of the mixture. Flammable liquids shall be known as Class liquids are divided into three classes as follows:
Class IA Liquids		Those liquids having flash points below 73°F (22.8° C) and having a boiling point below 100° F (37.8° C)
Class IB Liquids		Those liquids having flash points below 73°F (22.8° C) and having a boiling point at or above 100° F (37.8° C)
Class IC Liquids		Those liquids having flash points at or above 73° F (22.8° C) and having a boiling point below 100° F (37.8° C)

2.1.1 Flash Point

Flash point is the property commonly used to classify materials as flammable or combustible. Summaries of the criteria as defined by OSHA (U.S. Occupational, Safety, and Health Administration) and DOT (U.S. Department of Transportation) are shown in Tables 2 and 3. The flash point may increase with the boiling temperature of the product; however, this is not always true. For hydrocarbon solvents that are characterized by a boiling range instead of a boiling temperature, flash point is also determined by the breadth of the boiling range.

Flash point is defined by OSHA and DOT in the U.S. Code of Federal Regulations (CFR) as “The minimum temperature at which a liquid gives off vapor within a test vessel in sufficient concentration to form an ignitable mixture with air near the surface of the liquid.”^{3,4} The flash point is normally an indication of susceptibility to ignition. ASTM defines flash point as the “lowest temperature, corrected to a pressure of 760 mm Hg (1013 mbar), at which application of an ignition source causes the vapors of a specimen to ignite under specified conditions of test.” Continuous combustion will not occur at flash point temperature. This takes place at a higher temperature known as the fire point⁷.

DOT and OSHA classifications are based upon closed cup flash points determined by one of several methods:

- Standard Method of Test for Flash Point by Tag Closed Tester, (ASTM D 56)
- Standard Methods of Test for Flash Point of Liquids by Setaflash Closed Tester, (ASTM D 3278)
- Standard Test Methods for Flash Point by Small Scale Closed Tester, (ASTM D 3828)
- Standard Method of Test for Flash Point by Pensky—Martens Closed Tester, (ASTM D 93)

Table 3. Summary of U.S. Criteria for Combustibility Assignment^{3,4}

Classification	DOT Classification Criteria	OSHA Classification Criteria
Combustible Liquid	1). Any liquid that does not meet the definition of any other hazard class specified in 49 CFR subchapter C and has a flash point above 60.5° C (141° F) and below 93° C (200° F). 2). A flammable liquid with a flash point at or above 38° C (100° F) that does not meet the definition of any other hazard class may be reclassified as a combustible liquid.	Any liquid that has a closed cup flash point at or above 100° F (37.8° C). Combustible Liquids shall be divided as follows:
Class II Liquids		Any liquid having a flash point at or above 100° F (37.8° C) and below 140° F (60° C), except any mixture having components with flash points of 200° F (93.3° C) or higher, the volume of which make up 99% or more of the total volume mixture.
Class IIA Liquids		Any liquid having a flash point at or above 140° F (60° C) but below 200° F (93.3° C), except any mixture having components with flash points of 200° F (93.3° C) or higher, the volume of which make up 99% or more of the total volume mixture
Class IIB Liquids		Any liquid having a flash point at or above 200°F (93.3° C)

In addition to the closed cup flash point methods mentioned above, there are also open cup methods. Open cup flash point measurements are conducted in an open apparatus and generally result in flash points that are a few degrees above those obtained in one of the closed cup methods. The latter are intended for use with pure chemicals. The presence of non-flammable components (e.g., water) in a mixture can mask the flammable nature of the mixture. In these cases, the open cup method may be preferred.⁸

In practice, the temperature at which a flash point is recorded tends to be very close to the temperature where the vapor pressure and the resulting vapor concentration in air at one atmosphere corresponds to the LEL. Thus in many cases, flash point instead of LEL/UEL may be used as the main indication of flammability of a solvent. In very general terms, the lower the flash point, the more volatile the solvent, and hence, the more potentially flammable the solvent may be. For practical purposes flash point can be regarded as the lower temperature limit of flammability and is a function of pressure. Decreased pressure in vessels lowers the flash point of the contents.

Note that OSHA and DOT have somewhat different definitions for combustible and flammable liquids. It is important to check state and local regulations as well. Note that a material classified as combustible for transportation purposes may be classified as flammable for storage and handling.

2.1.2 Autoignition Temperature (AIT)

The autoignition temperature (AIT) is the temperature at which, in the presence of sufficient oxygen, a material will ignite on its own and burn¹. The AIT can serve as a very rough guide to the maximum temperature that a mixture of a flammable solvent in air can reach before self-ignition. It is used to evaluate the level of hazard that will be incurred by using a chemical in process equipment at elevated temperatures.

Note that the AITs of hydrocarbon and oxygenated solvents are well above their boiling points. There is no connection between the AIT of a substance and its flash point.

A common test method to measure AIT is described in ASTM E659.⁹ Because of the important potential variations between published AIT values and the real autoignition conditions of a process, it is important to note that AIT should not be regarded as a clear cut-off point between no ignition/self-ignition conditions. Instead, AITs are very rough indications of the maximum temperature to which flammable mixtures can be exposed without self-ignition. Working under the measured AIT helps avoid self ignition.

The autoignition temperature of industrial solvents is usually indicated in suppliers' MSDS.

2.1.3 Mists of Flammable or Combustible Liquids

Fine mists of solvents may be ignitable at temperatures substantially less than their flash points¹⁰. Mists of solvents can be generated in a number of ways, such as when used in spray finishing operations, when being ejected from a nozzle, or when being condensed. For example, mists are common in degreasing of metal parts by spraying techniques. Spray finishing using flammable and combustible materials is regulated by OSHA under 29 CFR 1910.107.⁴

Because they behave like vapors, droplets or mists may assist flame propagation. Mists are capable of propagating a flame if the quantity of solvent present is high enough and an explosion can occur in confined conditions.

The flammability range of mists also is characterized by LELs and UELs in the same way vapors are characterized; however, it is difficult to obtain reliable measures of LELs and UELs for mists due to the lack of uniformity of the droplets. Lower explosive limits are strongly affected by droplet size. Generally, the larger the droplet diameter, the higher the LEL.

Another complexity caused by mists is the effect on electrostatic charges. The presence of mists, especially from spraying operations, may cause the concentration of static charges on electrically isolated surfaces. Discharge of such charges may be a source of ignition.¹¹

2.1.4 Minimum Ignition Energy (MIE)

Whatever the potential source of ignition, it must deliver a certain minimum amount of energy to initiate a flame front in the fuel/air mixture. However, very low energy levels can be sufficient to ignite solvent vapor/air mixtures (~0.01 – 2.0 milli joules).

A spark from a metal tool or a spark from an electrical switch may have sufficient energy to ignite a fire if the solvent vapors in air are within the flammable range. Static electricity generated by a person walking on a carpet has sufficient energy to ignite most solvent vapors under appropriate conditions.⁷

Many sources of ignition encountered in industrial activities can exceed the MIE of solvents. Careful control of these sources is important in handling solvents.

2.2 Sources of Ignition

Sources of ignition energy can be classified into 4 categories:

- Flames and Smoldering
- Hot Surfaces
- Friction and Impact
- Electrical Discharges (Electrical Power and Static Electricity)

2.2.1 Flames and Smoldering

This category of ignition sources includes all open flames such as welding torches, matches, and gas burners, as well as sporadic sources such as the exhaust of an engine. Smoldering covers all forms of incandescent materials such as cigarettes, and less obviously, catalysts.

2.2.2 Hot Surfaces

Hot surfaces may cause ignition of flammable solvent/air mixtures either directly or indirectly.

Direct ignition will occur if the surface is at a temperature above the autoignition temperature of the solvent/air mixture in the particular system considered.

Indirect ignition results from the burning or smoldering of material initiated by a hot surface. Hot surfaces are widespread in industrial areas; examples include walls of ovens and furnaces, electrical equipment, and heating pipes. Some operations can easily produce hot spots; examples are grinding, cutting, and welding operations.

2.2.3 Friction and Impact

Hot spots and incandescent sparks mainly arise from friction, and depend largely on the materials. For example, sparks produced during impacts involving metals (magnesium and their alloys, iron) with grit or rock generate high heat.

2.2.4 Electric Discharges

Electric discharge can be very widespread and may be hidden. They generally arise from two basic sources: electrical power and electrostatic discharge.

Main grid electricity as well as batteries are sources of sparks with sufficient energy to ignite solvent vapor/air blends. Routine operations of transformers, motors, circuit breakers, switches, and fuses—as well as electrical failures such as damaged cables—can be electrical ignition sources (there may be other sources as well).

Electromagnetic waves emitted by radio antennae may give rise to sparks in their vicinity or to a heat buildup of material. Electrostatic discharge is discussed further in Section 3 of this Guide.

Section 3: Understanding & Controlling Electrostatic Discharge

Static electricity can be produced under a number of different circumstances. It is most commonly produced by the abrasion or movement of one material against another. This movement separates positive and negative charges, thus creating a potential difference. The agitation of solids, liquids, and gases can all produce forms of static discharge. Activities that have the potential to produce static electricity or electrostatic discharge include, but are not limited to:

- Turbulent flow in pipelines, discharges, and tank mixing;
- Filtration or straining, especially with large surface area exposed to the flow;
- Splash filling of vessels or other practices that allow the falling of liquids through flammable vapors;
- Settling water droplets through liquid hydrocarbons;
- Bubbling gas or air through liquids;
- Mechanical movements (i.e., fans, belts, pulleys, people);
- High-velocity of non-conductive liquids through pipes; and,
- Introduction of dipping or sampling equipment into recently filled storage tanks.

3.1 Factors that contribute to electrostatic charging

Electrical Conductivity. Electrical Conductivity is a measure of the ability of a substance to conduct an electrical charge. Charge flows readily through substances with high values of conductivity and tends to build up on the surface of substances with low conductivities. If an adequate amount of surface charge is accumulated it is possible for the charge to migrate from the surface of the non-conductive substance to other more conductive materials in the form of an electrostatic discharge. It is important to note that resistivity is a function of conductivity (Conductivity = 1/Resistivity). Therefore as conductivity increases, resistivity decreases. Substances with low conductivities present more optimal conditions for static discharge to occur than those substances with high conductivities. Because of this, the ignition of flammable vapors is also more likely to occur when improperly handling very low conducting substances.

Below are the accepted values for classifying how conductive a substance is²:

Conductive	Greater than 10000 pS/m (picosiemens/meter)
Semi-conductive	$100 < x < 10000$ pS/m
Non-conductive	Typically less than 100 pS/m

It is important to note that conductivity varies greatly with temperature. Impurities such as water, acid, and metals can also greatly affect the electrostatic properties of materials. The effect impurities have on conductive and semi-conductive substances is negligible; however, it is not negligible when in the presence of non-conductive substances. It is important to realize that it is difficult to predict the precise effects that impurities will have on the conductivities of different substances. Individual care should be taken when handling solvents in different scenarios.

Dielectric Constant. The dielectric constant is an index of the ability of a substance to resist the transmission of an electrostatic force from one charged body to another. At 77°F, air has a dielectric constant of 1, while water, which will conduct or transfer electrostatic forces readily, has a dielectric constant of 81.¹² Dielectric constant values decrease as temperature increases. Substances with high dielectric constants are able to provide an atmosphere that is much more susceptible to electrostatic discharge than that of substances with low dielectric constants. Table 4 lists the dielectric constants of some commonly used solvents.

Minimum Ignition Energy (MIE). MIE is the amount of energy needed to be generated by an ignition source (such as an electrostatic discharge) to effect the ignition of a flammable vapor/air mixture. The MIE of a substance will vary depending on how much (% by volume) of the flammable vapor is present in the air. Ignition will occur only within the LEL and UEL of that particular substance. LELs and UELs can be obtained from a MSDS. Most forms of static discharges produce energy levels that exceed the MIEs for many flammable substances. Table 4 list the MIEs for a number of different solvents. Substances with very low MIEs present a greater ignition hazard due to electrostatic discharge than substances with high MIEs.

Relaxation Time. Relaxation time refers to the length of time that it takes for charge to dissipate from a particular substance. It is a function of both dielectric constant and conductivity. Substances with very high relaxation times present a greater risk of static discharge than substances with low relaxation times. Generally, the introduction of dipping or sampling equipment into a tank should be done after 3 relaxation times have elapsed upon completion of filling. In the case of some very viscous non-conductive substances, relaxation times can be measured in minutes.² In these instances where there is an extremely high risk of electrostatic discharge, 30 minutes should be allowed to elapse between the completion of tank filling and a dipping or sampling event. Table 4 includes the relaxation times for a number of different solvents. It is important to note that because conductivity is greatly affected by both temperature and the presence of impurities, relaxation time can vary accordingly. For this reason, the values in Table 4 can serve as a reference tool, but additional information from the solvent manufacturer should be considered in the context of the application.



Table 4. Electrostatic Properties of Common Solvents^{7,17,18, 19}

Solvent	Conductivity (pS/m)	Dielectric Constant** (K)	Minimum Ignition Energy** (mj)	Relaxation Time (ms)
Isopropyl alcohol	350,000,000	19.9	0.65	0.0005
Methyl acetate	340,000,000	6.68	NA	0.00017
Propylene glycol methyl ether	45,000,000	NA	NA	NA
Methyl alcohol	44,000,000	32.7	0.14	0.0066
Ethylene glycol monobutyl ether	43,000,000	5.30	NA	NA
Octyl alcohol	13,900,000	10.3	NA	0.0069
Methyl ethyl ketone	10,000,000	18.5	0.53	0.016
Acetone	6,000,000	20.7	1.15	0.03
Pyridine	5,300,000	12.4	NA	0.021
Methyl isobutyl ketone	< 5,200,000	13.1	NA	> 0.022
t-Butyl alcohol	2,660,000	12.4	NA	0.042
Diethyl carbonate	1,700,000	2.82	NA	0.015
Isobutyl alcohol	912,000	17.5	NA	0.17
Ethyl alcohol	135,000	24.5	0.23	1.61
Ethyl acetate	46,000	6.02	0.46	1.20
n-Butyl acetate	4,300	NA	NA	NA
Gasoline*	10 to 3,000	~2.00	0.29	6.00 to 1,800
n-Butyl alcohol	910,000	18.2	NA	NA
Diesel	< 50	~2.00	NA	> 100,000
Diethyl ether	30	4.60	0.19	1,400
V M & P Naphtha†	~3	NA	0.20	NA
Cyclohexane	< 2	2.01	0.22	> 8,800
Toluene	1	2.38	0.24	21,000
n-Pentane	< 1	1.84	0.28	~100,000
Xylene (mixed isomers)	< 0.1	2.30	NA	> 100,000
n-Heptane	0.03	2.00	0.24	> 100,000
n-Hexane	0.01	1.91	0.24	> 100,000
Benzene	0.005	2.30	0.20	> 100,000
Cyclohexanone	0.0005	18.2	NA	NA
Dearomatized Hydrocarbon Solvents (25-40°C) & (40-100°C) boiling range	< 1	< 2.50	< .21	18,000
Mineral Spirits (150-200°C) boiling range	< 1	< 2.50	< 2.0	18,000
Aromatic Solvent (160-200°C) boiling range	< 10	< 2.50	< 2.0	18,000
Dearomatized Hydrocarbon Solvents (200-240°C) & (240-270°C) boiling range	< 1	< 2.50	< 2.0	18,000
Dearomatized Hydrocarbon Solvents (160-200°C) & (100-160°C) boiling range	< 1	< 2.50	< .21	18,000

NA= Not available, ~≈approximately. * = Wide range is due to the various grades of gasoline.

† U.S. Chemical Safety and Hazard Investigation Board. *Barton Solvents-Static Spark Ignites Explosion Inside Flammable Liquid Storage Tank. June 26, 2008.*

**Dielectric constant and minimum ignition energy both change with temperature and pressure

There are a number of other factors that may contribute to electrostatic charging and discharging (e.g., humidity, temperature, vapor concentration.) Each specific situation should be assessed with unique and individual care.

3.2 Understanding Static Discharge

As discussed in the above section, if atmospheric conditions are optimal and a substance accumulates enough charge, electrostatic discharge can occur. Under certain circumstances these discharges have the potential to produce enough energy to ignite flammable vapor/air mixtures. Because of this, it is important to understand the activities and processes that produce static electricity so that they can be assessed and dealt with accordingly. Although there are a number of types of electrostatic discharge, almost any type can generate sufficient energy to generate an ignition source. Different forms of electrostatic discharge could include:

Brush Discharges. Occurs between charged non-conductive surfaces and grounded conductors. Maximum effective energy produced varies from a few tenths of a millijoule to 4 to 5 millijoules.²

Bulking Brush Discharges. Occurs from partial surface discharge created during bulking of powder in containers. Maximum effective energy can reach up to 25 millijoules².

Propagating Brush Discharges. Discharge caused by electric breakdown of dielectric in capacitor. Maximum effective energy can reach up to 1000 millijoules.²

Corona Discharges. Electric discharge that results from an electric breakdown of gases by charges on surfaces with sharp edges. Maximum effective energy generally does not exceed 1 millijoule and in most cases is substantially lower than that².

3.2.1 Static Discharge Mitigation Measures

General Considerations. All electrical equipment used near or in the presence of solvents should be explosion proof. Cell phones, flashlights, and extension cords should not be utilized. Care should be taken to not inadvertently drop or introduce isolated conductors (e.g. metal cans, steel spectacles, pens) into tanks during filling, sampling, or discharge operations.

Personnel handling solvents or performing activities in the presence of solvents should wear electrostatic dissipative (EDS) footwear (antistatic footwear) and gloves. Removal of clothing in any areas where a flammable vapor may be present may create static discharges. The operator's total resistance to the earth via footwear should not exceed 10^6 ohms¹³. The National Fire Protection Association 99, *Standard for Health Care Facilities*, provides information on test methods for evaluating the antistatic performance of apparel.²

Bonding and Grounding. Grounding (earthing) is the process of connecting one or more objects to the ground by means of a conductor so that all objects are at zero electrical potential. *Bonding* is the process of connecting two or more objects to each other by means of a conductor so that they are at the same electric potential (not zero) but not necessarily the same potential as the ground. In situations where electrostatic discharge may be possible, both bonding and grounding should be exercised. Sufficient inspection and testing of bonding and grounding applications should be practiced as well. In systems that are covered by insulated surface coatings or are prone to corrosion or movement, self-testing bonding clamps and systems can be used to test the resistance to ground. The accepted value of resistance in grounding and bonding applications is 10 ohms or less.² Connections can be made by using clamps or bolts. If clamps are utilized there must be adequate pressure to penetrate any protective coatings or rust to ensure sufficient contact with the base metal. Adequate grounding and bonding practices for many routine applications can be found in National Fire Protection Association 77, "Recommended Practice on Static Electricity".

Use of Antistatic Additives. Antistatic additives are used to alter the electrostatic properties of materials. They are generally added to highly resistive substances in order to increase conductivity and reduce the risk of charge accumulation. They also can be used to coat highly resistive surfaces such as floors or clothing. It is important to note when using antistatic film or sheeting in a very low humidity environment (typically less than 30 %) that antistatic coatings can become much less effective thus increasing the possibility of accumulating electrostatic charge².

Most antistatic additives are primarily used with non-conductive aromatic solvents such as xylene. Some antistatic additives have low flash points and the addition to non-conductive substances can substantially increase the flammability of the entire mixture. It is necessary to evaluate the application of antistatic additives to ensure that conductivity remains adequately high during operation and that there is no impact on product quality¹⁴. It is also very important to regularly monitor the conductivity of a substance when utilizing antistatic additives. Measurements should be taken after antistatic dosing in order to ensure that the overall conductivity of the mix has been adequately increased for use.

Petroleum fuels such as gasoline and diesel are examples of where antistatic additives are directly added to a substance to decrease resistivity. It is important when utilizing these additives that they have the ability to increase the conductivity of substances over an extended period of time to allow for transportation and storage. Additives should not be resistant to removal from the fuel in the presence of water or impurities and they should not affect the ability of the fuel to separate from the water. Some antistatic additives contain traces of sulfur, their use can increase the overall sulfur content in solvents thus affecting the quality of product as well as introducing the possibility of becoming non-compliant with EPA emission regulations¹³. Concentrations of these additives vary depending on the application¹⁴. It is important to contact manufacturers and suppliers of antistatic additives to ensure that they are properly utilized.

Nitrogen Blanketing. Nitrogen blanketing or tank blanketing is the process by which nitrogen is pumped into the empty headspace in storage tanks in order to replace oxygen and create an atmosphere that is less-ignitable. Nitrogen is most commonly used due to its inert properties, availability, low cost, and utility on any scale of tank. When performing blanketing, care must be taken to ensure that personnel in the area are not subjected to high concentrations of the inert gas. The use of blanketing in commercial and industrial applications is subject to OSHA regulations.¹⁵ It is important to check with state and local regulations as well.

Though the proper use of the methods described above can substantially decrease the risk of electrostatic discharge occurring, they do not completely eliminate the possibility of it taking place. Each specific situation is unique and must be assessed with individual care.

3.3 Handling and Storage of Solvents

Tank/Tank Transfers. The procedure to transfer solvents from one tank to another should be well-documented. Bonding and grounding should both be considered. Splash-filling can be avoided by the use of a main inlet line at low level or a fill pipe at the tank bottom.

Typically, linear velocity of solvents with conductivities below 50 pS/m (e.g., hydrocarbons) should be kept below 1 m/s until the inlet pipe is covered to twice its diameter or 0.6 meters, whichever is applicable.¹³ At that time, the pumping rate can be increased to a maximum of 7 m/s, however the linear velocity should be kept as low as practical, typically 2-3 m/s. In the presence of a second phase (i.e. water) the pumping rate should be kept at 1 m/s or lower.

Dipping & Sampling. Following tank transfer, it may be necessary to dip or sample the solvent. Dipping or sampling should not occur during transfer or filling operations. It is also important to not dip or sample solvents in adverse weather conditions (lightning, snow or hail storms).

Static charge may have built up in the tank during transfer or agitation, thus sufficient time must be allowed for the charge to dissipate (relaxation time). For conductive and semi-conductive substances, a period of time no less than three (3) relaxation times should be allowed to elapse before dipping or sampling. Because most hydrocarbon solvents contain a small amount of second phase (i.e. water), the recommended relaxation time before dipping or sampling of non-conductive substances is 30 minutes unless a fixed sampling or sounding tube is used¹³.

Dipping equipment is recommended to be metal or natural fiber and grounded. Sampling cords should also be made of natural fibers that are unlikely to accumulate static charge.

3.3.1 Loading & Filling Operations Bulk

Bulk. The discharging liquid should not be allowed to fall through the vapor space during any filling operation (splash-filling). Splash-filling can cause the liquid to take on a static charge relative to the tank shell if the tank is grounded. Splash-filling can be avoided by using bottom entry or by using a fill pipe terminating close to the bottom of the tank. As is the case with tank to tank transfers, the linear velocity of solvents with conductivities below 50 pS/m (i.e. hydrocarbons) should be kept below 1 m/s until the inlet pipe is covered to twice its diameter or 0.6 meters, whichever is applicable. At that time, the pumping rate could be increased up to 7 m/s. Provisions should be made to reduce the resistance to earth between any vessel to no more than 10 ohms and all hoses should be electrically conductive.

A formula relating linear velocity and pipe diameter can be used to calculate optimal pumping rates:¹³

$$(\text{Linear Velocity}) \times (\text{Pipe Diameter}) < 0.5 \text{ m}^2/\text{s}$$

For a 0.1 meter diameter pipe, the maximum linear flow should not exceed 5 m/s during filling or loading; however in practice the pumping rate would normally be substantially less than this¹³.

These filling rates do not apply to switch loadings (see below).

Because isotainers are normally one large compartment, they will tend to accumulate greater static charge and bonding directly to the loading system is recommended. The static charge build-up is reduced where there are baffles to help dissipate the static.

The use of compressed air or water for clearing or flushing lines containing low flash point solvents should be avoided.

Use of Plastic Buckets. Charge accumulation can occur even with conductive fluids when the container being filled is made of a non-conductive material such as plastic. It can also occur with conductive containers (i.e. metal) when proper bonding and grounding methods are not practiced¹³. The use of plastic buckets during filling operations should be avoided if compatible with processes involved. When using metal buckets or containers, proper bonding or grounding techniques discussed previously in this manual should be utilized.

Use of Filters or Strainers. Filters or strainers with pore sizes below 1 micrometer can generate very large currents with non-conductive substances.² To prevent charge from entering receiving vessels, placing filters far enough upstream helps ensure that sufficient time has passed for the charge to dissipate. If the conductivity of the liquid is not known, 30 second period of time for the substance to remain in the pipe downstream from the filter generally provides adequate *residence time*. In cases where the conductivity is known, elapse of 3 relaxation times from the time the substance exits the filter or strainer to the time it enters the receiving vessel is usually adequate.

Switch Loading. This is a potentially dangerous practice that is known to have led to explosions and fires. It is a practice whereby vessels are not sufficiently cleaned between deliveries. New product is loaded into compartments where vapors may exist from previous loads. This practice is hazardous with non-conductive substances especially when the prior load was flammable and the new load is highly viscous. In cases where switch loading cannot be avoided, consider the following important precautions:

- Organize loading schedules to eliminate switch loading.
- Purge the vapors from all compartments previously containing flammable liquids before loading the next product.
- Ensure that all dip tubes, filling arms, and pipes are adequately grounded.
- Keep maximum loading rates at half the level of the pumping rates calculated according to the equation on page 21.

When two or more of the following conditions during loading or switch loading are present, preventative measures such as further reduction of pipe velocity, increase in residence time or avoidance of switch loading all together should be considered:¹³

- Fluid conductivity is very low (less than 5 pS/m).
- Flow velocity is approaching maximum allowable levels.
- Residence time after filtration or screening is at or below minimum time.
- Turbulence generator is present (i.e. partially open valves, irregularities in pipe).

Intermediate Bulk Containers (IBCs). Splash-filling should be avoided. Grounding and bonding should be practiced. Filling at the bottom of the container and at a linear velocity no more than 1 m/s should be considered. Metered filling should be metered to avoid an over-flow or spill when the container volume is exceeded.

Drums & Cans. Splash-filling should be avoided. Bonding and grounding should be practiced. Filling should take place at the bottom of the container and at a linear velocity not exceeding 1 m/s. Metered filling helps avoid an over-flow or spill when the container volume is exceeded. Drums and cans can be grounded with a grounding clip to penetrate any protective coating and ensure that the earth resistance does not exceed 10 ohms.

Examples of operations that can generate static charges:

- High velocity and turbulent conditions, for example in pipelines, or the discharge of jets from nozzles and tank mixing.
- Filtration, particularly through micropore elements.
- Liquid droplets or foam falling through a vapor. For example, a spray or mist formation in vapor spaces, splash filling of tanks, tankers, drums or intermediate bulk containers.
- Settling water droplets through liquid hydrocarbon. For example, after a line has been pigged off into a tank with water.
- Bubbling of gas or air through liquids.
- Mechanical movements such as belts or pulleys used as air blast coolers.
- The movement of vehicles, fans or even people.

Glossary of Terms

Antistatic Additive: A compound that is either directly added to or coated on to a substance or material in order to increase conductivity and reduce or eliminate charge accumulation, thus lowering the chance of a electrostatic discharge. Also referred to as static dissipative additives (SDA) or conductivity improver.

Autoignition Temperature: The autoignition temperature (AIT) is the temperature at which, in the presence of sufficient oxygen, a material will ignite on its own and burn.

Bonding: The process of connecting two or more conductive objects together by means of a conductor so that they are at the same potential as each other but not necessarily at the same potential as the earth.

Boiling Point: Temperature at which the compound converts from a liquid to a gas; the boiling point of water, for example, is 212° F.

Electrical Conductivity: An intrinsic property of a substance that governs the substances ability to conduct electricity.

Flash Point: The minimum temperature at which a liquid gives off vapor within a test vessel in sufficient concentration to form an ignitable mixture with air near the surface of the liquid.^{3,4} Also, the lowest temperature, corrected to a pressure of 760 mm Hg (1013 mbar), at which application of an ignition source causes the vapors of a specimen to ignite under specified conditions of test.

Grounding: A specific form of bonding in which one or more bonded, conductive objects is also connected to the ground so that each is at the same potential as the earth.

Lower Explosion Limit (LEL): Lowest concentration of vapor in air at which the vapor/air mixture will burn. Also referred to as “Lower Flammability Limit” or LFL.

MIE (Minimum Ignition Energy): The minimum energy (usually expressed in millijoules) that is sufficient to effect the ignition of a flammable vapor/air mixture.

Static Electricity: Static electricity is generated by the movement of one material against another, such as pumping or agitation. The movement separates positive and negative charges that can accumulate if a high resistance to charge flow is encountered. The accumulation charge differences can discharge as sparks capable of igniting solvent vapors.

Switch Loading: A transfer of organic liquids with a vapor pressure of less than 1.5 psia (77.5 mm Hg) under actual loading condition into any tank truck, trailer or railroad tank car that was loaded with an organic liquid with a vapor pressure of 1.5 psia (77.5 mm Hg) or greater immediately preceding the transfer.

Relaxation Time: The amount of time that it takes charge to dissipate from a particular substance.

Tank Blanketing: The process of filling the empty headspace in a tank or container with an inert gas, such as nitrogen, in order to create an atmosphere that is virtually un-ignitable.

Upper Explosion Limit (UEL): Highest concentration of vapor in air at which the vapor/air mixture will burn. Also referred to as “Upper Flammability Limit” or UFL.

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