

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



American Chemistry Council
Solvents Industry Group
January 2008

Table of Contents

Forward.....	1
Scope of Guide.....	1
Legal Notice.....	2
Section 1- General Information.....	3
1.1 Some General Safety Considerations for Handling Solvents.....	3
1.2 Key Factors Related to Solvent Flammability.....	5
Section 2- Technical Aspects of Flammability.....	6
2.1 Flammability Range.....	6
2.1.1 Flash Point.....	7
2.1.2 Autoignition Temperature.....	10
2.1.3 Mists of Flammable or Combustible Liquids.....	10
2.1.4 Minimum Ignition Energy.....	10
2.2 Sources of Ignition.....	11
2.2.1 Flames and Smoldering.....	11
2.2.2 Hot Surfaces.....	11
2.2.3 Friction and Impact.....	11
2.2.4 Electrical Discharges.....	11
2.2.4.1 Electrical Power.....	11
2.2.4.2 Electrical Discharges (Static Electricity).....	12
Glossary of Terms.....	13
References.....	13

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, 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, yet meet 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 need to be managed carefully to minimize risks of a fire or explosion, whether use occurs in the home or in an industrial setting — particularly during loading and unloading, storing and when used in bulk. Safe handling 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 in more detail, and is intended for readers who wish 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, the practicality and effectiveness of particular actions, and economic and technical feasibility.

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Section 1 General Information

1.1 Some 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 and incorporating procedures 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 the solvent use area; 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 burn.¹ 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;



Typical portable grounding cable for drums

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 Employees
- Report Leaks and Spills in Accordance with Federal and State Regulations
- Consider Providing Secondary Containment Solutions
- Develop Appropriate Loading and Unloading Procedures
- Consider Developing an Emergency Plan
- Consider Inert Storage Solutions
- Consider Developing Standard Operating Procedures

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 2 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 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 in which 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 to managing solvent flammability.

Educate and Train Employees. 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 regulatory requirements. Appropriate clean up and disposal facilities should be provided.

Consider Providing Secondary Containment Solutions. Secondary containment solutions, 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.

Consider Developing Standard Operating Procedures. Some examples of 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 OSHA (U.S. Occupational, Safety and Health Administration) and the DOT (U.S. Department of Transportation) 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.

In industrial facilities, a wide range of sources are capable of igniting mixtures of flammable solvent vapors in air. A few examples of ignition sources are flames; hot surfaces; and a spark from, for instance, electrical equipment or a metal tool falling on a floor.



Typical truck loading area with grounding connection, fire extinguisher, and fire alarm switch

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.⁵ 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).⁶ These values are different than the LEL, because the LEL only describes the minimum concentration of material in air that will burn.

Static electricity, discussed in more detail in Section 2.2.4.2 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.

Section 2 Technical Aspects of Flammability

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:

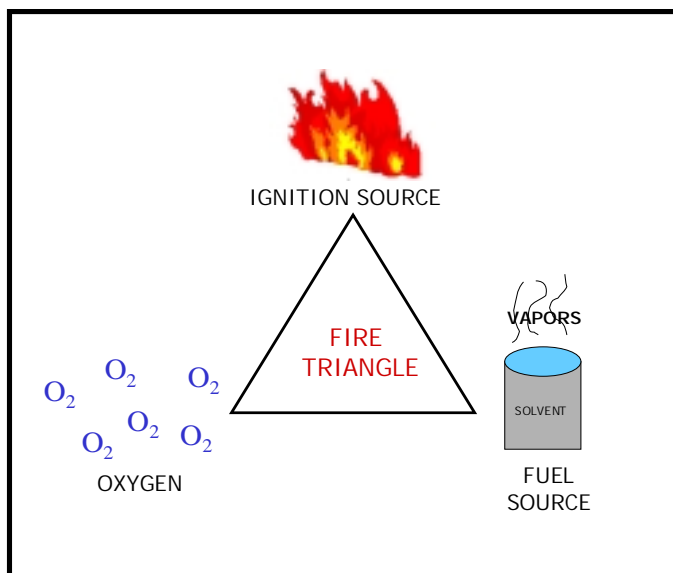
- Flammability Range
- Flash Point
- Autoignition Temperature
- Solvent Mists
- Minimum Ignition Energy
- Sources of Ignition

2.1 Flammability Range

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

Table 1- Examples of Typical Solvent 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	2.2	11.4	460
n-Heptane	-4	1.2	6.7	215
Dearomatized Hydrocarbon Solvent (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 Solvent (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 Solvent (200-230° C boiling range)	82	0.6	5	250
Dearomatized Hydrocarbon Solvent (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.

**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).

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 above.

Table 2- Summary of U.S. Criteria for Flammability Assignment (Ref. 3,4)

Classification	DOT Classification Criteria	OSHA Classification Criteria
Flammable Liquid	Any 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 49CFR 173.115 (gases); and any mixture having one or more components with a flash point of 60.5°C (141°F) or higher, that makes up at 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 percent or more of the total volume of the mixture. Flammable liquids shall be known as Class I liquids. Class I 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 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 the 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 point.⁷

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 (Ref. 3,4)

Classification	DOT Classification Criteria	OSHA Classification Criteria
Combustible Liquid	a) 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).	Any liquid that has a closed cup flash point at or above 100° F (37.8° C). Combustible Liquids shall be divided as follows:
	b) 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.	
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 percent or more of the total volume of the mixture.
Class IIIA 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 percent or more of the total volume of the mixture.
Class IIIB Liquids		Any liquid having a flash point at or above 200° F (93.3° C).

Which method to use is defined within the regulations.

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 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. 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 well below 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 points.¹⁰

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 falling on the floor 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 Electrical Discharges

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

2.2.4.1 Electrical Power

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 materials.

2.2.4.2 Electrostatic Discharges (Static Electricity)

Static electricity is a phenomenon of great importance when handling solvents, and in particular, hydrocarbon solvents.

One of the least understood and most difficult ignition sources to control is static electricity. Similar operations can produce different levels of static on different days, and often the first indication of static is a spark, which may ignite solvent vapors, if present.

Static electricity is produced by pumping of materials or by any other means of motion, such as agitation. The movement separates positive and negative charges, which then accumulate in the liquid and the containment system (for example, lines, tanks, drums). The charge on the containment system is dissipated quickly by grounding, but the charge in the liquid remains and is slowly dissipated, depending on the conductivity of the liquid. Typical grounding and bonding situations for many routine applications can be found in NFPA 77, "Recommended Practice on Static Electricity."

The conductivity of a liquid allows it to be classified as conductive ($>10^4$ Picosiemens/meter (pS/m)), semi-conductive (50 - 10^4 pS/m) or non-conductive (<50 pS/m). Of the solvents of interest here, alcohols and ketones tend to be conductive, acetate esters semi-conductive and hydrocarbons non-conductive. Conductivities obtained from published literature should be used with caution, as the values for a particular solvent vary depending on trace impurities such as water, sulfur, traces of acids or even trace quantities of metals present. For this reason, conductivity information obtained from the solvent supplier is an important reference tool, but should be considered in the context of the application.

Static charges can accumulate in non-conductive and semi-conductive liquids. In such liquids, high potential differences can be created that can discharge as sparks capable of causing ignition of solvent vapors. Discharges can occur from insulated conductors (plant items, drums), bulk liquids, mists and insulating plastic materials.

Once static charges have accumulated in a liquid, they will dissipate over time. The length of time for the charge to dissipate is called the relaxation time. This time is inversely related to the conductivity of the liquid, such that the lower the conductivity, the longer it will take to dissipate the accumulated charge. For example, a liquid with a conductivity of 0.5 pS/m (e.g. classical mineral spirits) has a relaxation time of about 36 seconds in a given container, while dearomatized mineral spirits and aromatic solvents in the same container have relaxation times of 4-5 minutes and a few seconds, respectively.

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.
- Movement or transport of powders, although not relevant in the case of solvents. There have been many incidents involving materials such as flour, where static accumulation has caused an explosion of flour dust.
- High velocity release of steam to atmosphere.

Glossary of Terms

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.¹

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.⁷

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

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.⁸

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.⁷

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.

Static Electricity: Static electricity is produced by pumping of materials or by any other means of motion, such as agitation. The movement separates positive and negative charges which can accumulate, creating high potential differences that 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.

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.

References

1. <http://www.uidaho.edu/safety/definitions.htm>.
2. National Fire Protection Association. 2000. Recommended Practice on Static Electricity (NFPA 77).
3. 49 CFR 173.120; Class 3- Definitions.
4. 29 CFR 1910.106; Flammable and Combustible Liquids.
5. TLVs and BEIs for Chemical Substances and Physical Agents. 2003. ACGIH Worldwide.
6. <http://www.osha.gov/SLTC/pel/>.
7. Britton, L. Avoiding Static Ignition Hazards in Chemical Operations. CCPS AIChE (1999).
8. Standard Test Method for Selection and Use of ASTM Standards for the Determination of Flash Point of Chemicals by Closed Cup Methods. E502-84. ASTM International, 2000.
9. Standard Test Method for Autoignition Temperature of Liquid Chemicals. E659-78, ASTM International (2000).
10. Mulligan, J. Handling Flammable Liquids. CEP Magazine, July 2003. p. 48.
11. Pratt, Thomas. Electrostatic Ignitions of Fires and Explosions. CCPS AIChE, (2000).

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