

Handling Flammable Liquids

JAMES C. MULLIGAN,
CHILWORTH TECHNOLOGY, INC.

Identify electrostatic hazards associated with liquid processing and understand the precautions available to control them.

MANY IGNITION SOURCES ARE RELATIVELY obvious, such as open flames; unpermitted hot work, including welding, cutting and grinding operations; electrical arcs from unrated electrical equipment; and even frictional and impact sparks from tramp metal or malfunctioning mechanical equipment. However, when the ignition source for an incident is not obvious, investigators sometimes point to static electricity by process of elimination or as the ignition source of last resort. This is often done without a true understanding of static electricity, which is frequently misperceived as a mysterious and arbitrary phenomenon.

Static electricity is, in fact, quantifiable, predictable, and thus, controllable. Electrostatic discharges have been confirmed by field measurement and laboratory simulation as the probable ignition source in numerous fire and explosion incidents that occur during the handling and processing of flammable and combustible liquids. These incidents range in scale from flash fires during the filling of small containers, to flash fires during the filling and sampling of tank trucks, to explosions resulting in the destruction of reactors and blend tanks.

While inerting is the most common and appropriate basis of safety during the handling and processing of flammable and combustible liquids, the purpose of this article is to help the reader understand and identify the electrostatic hazards associated with liquid processing so that control of these hazards can be effectively implemented as a secondary basis of safety, or as an alternative basis of safety in those limited situations where inerting is not possible.

ELECTROSTATIC CHARGE GENERATION

Electrostatic charge is generated on liquids when they flow through piping, hoses and filters and when they are stirred or agitated. Charge can accumulate on the liquid if it is: (1) insulating in electrostatic terms; or (2) isolated from electrical ground by piping or vessels that are made from: (a) an electrically insulating material, such as plastic;

or (b) electrically insulating linings in conductive piping or vessels, such as glass or polytetrafluoroethylene (PTFE). Accumulated charge can give rise to electrostatic discharges from the liquid surface sufficiently energetic to ignite a flammable atmosphere. This flammable atmosphere may be evolved from the liquid itself if the liquid is flammable or combustible and is at or above its flash point temperature, or in the form of a spray or mist.

Charged liquids also can cause ungrounded conductive vessels, piping and fittings to become electrostatically charged. Charge accumulated on such items can give rise

to spark-type electrostatic discharges sufficiently energetic to ignite flammable atmospheres. Electrostatically charged liquids can also cause propagating brush-type electrostatic discharges that can result in pinholing of glass-lined vessels and PTFE-lined piping, leading to leaks that can: pose a risk of fire, if the liquid is flammable; cause damage to the conductive shell of lined piping and vessels, if the liquid is corrosive; and result in personnel exposures.

In a more physical sense, electrostatic charge is generated when two dissimilar surfaces — such as the liquid and the walls of the vessel or piping — come into contact and then quickly separate. There is a transfer of electrons at the point of contact between the surfaces. One surface will have a propensity to donate electrons (and in doing so become positively charged), while the other surface will receive them (and become negatively charged). This mechanism is known as contact electrification or triboelectrification.

In cases involving two surfaces that are conductive in electrostatic terms, the charges recombine almost instantaneously as the surfaces are separated, and therefore, no net charge results. However, when one or both of the surfaces is insulating in electrostatic terms, the resistivity of the insulating surface limits recombination by inhibiting charge mobility. As a result, a net charge remains on insulating surfaces. The level of charge generated is principally a factor of the speed and force of the contact and the relative position of the contacting materials in the triboelectric series.

The triboelectric series is a ranking of materials based on their electron work function, which is a measure of the work required to remove an electron from a surface during contact electrification. Since it requires more work to remove an electron from a material having a higher electron work function, such materials will have a propensity to receive electrons and thus become negatively charged. Conversely, materials having a lower electron work function will have a propensity to donate electrons and thus become positively charged.

The electron work functions for selected materials are shown in Table 1, which represents a partial triboelectric series (1). The greater the difference in the electron work functions of the contacting surfaces, the greater the magnitude of electrostatic charge generated upon separation.

Double-layer charging

While contact electrification is believed to be the manner in which contacting solid surfaces become electrostatically charged and represents a useful general model of electrostatic charging, the actual mechanism by which liquids are believed to become electrostatically charged is known as double-layer charging (2). This can occur at liquid/solid and liquid/liquid interfaces, such as where a liquid makes contact with the wall of a pipe or vessel, or with a suspended particle, such as in a slurry. Ions of uniform (like) polarity are adsorbed at such interfaces. The adsorbed ions attract ions of opposite polarity within the liquid, thereby forming a layer. This layer is thin for conductive liquids and more diffuse in insulating liquids, due to reduced ion mobility (2).

As the liquid flows relative to the interface, the oppositely charged ions are moved apart, increasing the potential within the liquid. This effect, combined with the competing effect of ion recombination at the pipe or vessel wall, results in an unbalancing of charge within the liquid. While both conductive and insulating liquids can generate static charge during handling and processing, the principal difference between them is the rate at which ion recombination occurs.

Nomenclature

C = capacitance, F
 d = pipe inside diameter, m
 E = energy, J
 I_c = streaming or charging current, mA or A
 L = pipe length, m
 R = resistance, Ω
 v = flow velocity, m/s
 V = voltage, V
 V_b = breakdown voltage, kV

Greek letters

γ = electrical conductivity, pS/m or S/m
 τ = liquid charge-relaxation time, s
 ρ_v = volume resistivity, Ωm

The amount of charge generated during the handling and processing of a liquid is dependent primarily on the distribution and mobility of the ions and on the flow characteristics of the liquid, including turbulence and flow velocity. Various models have been proposed to describe the rate of charge generation during the pipeline flow of an insulating (low conductivity) liquid (3–7). Britton has proposed the following general equation for estimating the streaming or charging current (I_c) generated by the turbulent flow of an insulating liquid through a pipe (8):

$$I_c \approx 10v^2d^2(1 - e^{-L/\tau}) \quad (1)$$

where, I_c is the streaming current in mA, v is the flow velocity in m/s, d is the pipe inside diameter in m; L is pipe

Table 1. Triboelectric series of selected materials (1).

Material	Electron Work Function, eV
Polytetrafluoroethylene (PTFE)	5.75
Polystyrene (PS)	4.9
Polyethylene (PE)	4.9
Polycarbonate	4.8
Polymethylmethacrylate (PMMA)	4.68
Polyvinylacetate (PVA)	4.38
Poly-2-vinylpyridine-styrene	4.27
Polyethylene oxide	3.95–4.50

length in m, and τ is the liquid charge-relaxation time in s.

Streaming current is the amount of charge generated over time. Eq. 1 shows that I_c increases as v and d increase. Thus, for a given pipe diameter, it is possible to reduce electrostatic charge generation in liquids by limiting flow velocity. The equation is conservative because it is based on turbulent flow, which occurs at higher flow velocities than laminar flow. Further, the equation is useful for estimating the rate of charge generation in larger-scale processes because flow in such processes is mostly turbulent.

The streaming current generated during the flow of a liquid reaches a steady-state value as the length of the pipeline through which it flows increases. The pipeline may be considered to be infinitely long if (9):

$$L > 3v\tau \quad (2)$$

This is true because the exponential term in Eq. 1 is close to zero for values of L exceeding $3v\tau$. The steady-state streaming current is typically on the order of 0.1 mA for pure and single-phase insulating liquids, and may reach as high as 1,000 mA if an insulating liquid flows through a fine-particle filter or if it contains solid or liquid immiscibles (9). Filters and immiscibles aggravate electrostatic charging of liquids by providing additional surface area for double-layer charging.

Electrical conductivity

In addition to flow velocity, the amount of charge generated during the handling and processing of a liquid is a factor of the mobility of liquid ions. The principal indicator of ion mobility in liquids is the electrical conductivity, γ , which is typically reported in units of siemens per meter (S/m) or picosiemens per meter (pS/m). The conductivities of selected liquids are shown in Table 2 (10).

According to NFPA 77, the U.S. consensus practice on static electricity, liquids having conductivities less than 100 pS/m are classified as insulating in electrostatic terms, while liquids having conductivities greater than 10,000 pS/m are classified as conductive (11). Liquids having conductivities between these values are classified as semiconductive. As suggested by the data in Table 2, electrical conductivity is a factor of temperature, which affects ion mobility. In this regard, the conductivity of liquids generally decreases as temperature decreases. Liquids with conductivities as high as 1,000 pS/m are capable of generating and accumulating a haz-

Table 2. Electrical conductivities of selected liquids.

Liquid	Electrical Conductivity, γ , pS/m
Conductive liquids ($\gamma > 10^4$ pS/m)	
Acetaldehyde (15°C)	1.7×10^8
Acetonitrile (20°C)	7×10^8
Ethyl acetate (25°C)	4.6×10^4
Ethyl alcohol (25°C)	1.35×10^5
Ethylene glycol	1.16×10^8
Methyl alcohol (18°C)	4.4×10^7
Methyl ethyl ketone (25°C)	1×10^7
Methyl isobutyl ketone	$< 5.2 \times 10^6$
Phenol	1×10^6
Isopropyl alcohol (25°C)	3.5×10^8
Water, distilled	$\sim 1 \times 10^9$
Semi-conductive liquids ($\gamma = 100\text{--}10^4$ pS/m)	
Methylene chloride	4,300
Trichloroethylene	800
Non-conductive liquids ($\gamma < 100$ pS/m)	
Benzene, purified	5×10^{-3}
Carbon tetrachloride	4×10^{-4}
Heptane, purified	3×10^{-2}
Hexane, purified	1×10^{-5}
Styrene monomer	10
Toluene	< 1
Xylene	0.1

ardous level of static charge under certain conditions, such as when they: contain immiscible solids and liquids, *e.g.*, in slurries, dispersions, suspensions, and emulsions; flow through strainers and filters; and are splashed or sprayed. A hazardous level of electrostatic charge is evidenced by an electric field strength exceeding 3×10^6 V/m, which is referred to as the breakdown strength of air. For an electric field strength exceeding this threshold, the air adjacent to a charged liquid or solid surface is ionized, a phenomenon that immediately precedes an electrostatic discharge.

Pipeline flow

For conductive liquids, such as alcohols and ketones, in grounded conductive piping, the charge on both the piping and liquid is instantaneously dissipated to electrical ground, since both are conductive and charge is readily mobile through them. However, for insulating liquids, such as heptane, hexane, xylene, toluene and other non-polar solvents, the charge on the liquid is relatively less mobile. As a result, the rate of charge generation due to liquid flow often exceeds the rate at which charge can be dissipated from the liquid, even in grounded conductive piping. Thus, even though charge is dissipated from the grounded conductive piping, charge accumulates on the insulating liquid.

For liquids in piping that is made from an electrically insulating material such as plastic, or conductive piping that is lined with PTFE or another electrically insulating material, the insulating piping or lining causes the liquid to be isolated from electrical ground. Thus, even if the charge is mobile

through the liquid, the dissipation of electrostatic charge is limited by the insulating piping or lining. As a result, charge accumulates on both the liquid and the insulating piping or lining. Even if the conductive substrate piping is electrically grounded, the insulating lining of a lined pipe will remain electrostatically charged because the charge on it is not mobile. Thus, electrical grounding of conductive piping, while necessary, may not be enough to minimize the potential electrostatic hazard posed by insulating liquids or liquids in conductive piping with an insulating lining, and additional precautions may be required.

Mixing

The stirring and mixing of liquids can generate electrostatic charge due to contact between the liquid and the vessel walls and agitator, and between the liquid and any undissolved or immiscible solids or liquids. When agitation is discontinued, an insulating liquid can remain electrostatically charged, even if it is contained in a grounded conductive vessel. Charge can even continue to be generated on an insulating liquid as solids settle.

When all charge-generating operations have ceased, the liquid will remain charged for a period of time corresponding to its charge-relaxation time as long as the liquid is in contact with electrical ground, *e.g.*, a grounded metal vessel. The τ for a substance is related to its electrical conductivity and is a measure of the time required for the electrostatic charge to be dissipated by conduction to electrical ground. For conductive liquids, the charge-relaxation time is typically much less than 1 s. For insulating liquids, it can be as long as 100 s.

The dissipation of charge from the liquid in an insulating or lined vessel will be primarily a factor of the charge-relaxation time of the vessel or lining material rather than of the liquid itself. In this regard, the charge-relaxation time for electrically insulating materials, such as plastics, is typically on the order of hours or even days.

Electrostatic discharges

The generation and accumulation of electrostatic charge is not generally in and of itself hazardous. Rather, a hazard is created when accumulated charge gives rise to electrostatic discharges sufficiently energetic to ignite a proximate flammable atmosphere or cause pinholing in electrically insulating vessels, piping or linings. The processing of liquids can give rise to several types of electrostatic discharges, including spark discharges, brush discharges, propagating brush discharges and discharges from the liquid itself.

Spark discharges

The charge generated by the flow and agitation of liquids can cause conductors isolated from electrical ground — such as conductive plant and equipment — to become electrostatically charged. For example, an operator may leave a conductive pail ungrounded while he or she is filling it. The charge on the liquid can cause the conductive

pail to become electrostatically charged.

A section of piping can be isolated from ground if electrical continuity is lost at a flange connection. Flanges can be isolated from ground by insulating gaskets, bushings and paint. A pipe section or flange can become charged by the flow of liquid through it. Similarly, conductive pumps, filters, valves, nozzles, couplings and other fittings can become electrostatically charged if isolated from ground. An agitator can be isolated from ground by insulating bushings or lubricants in the bearings and become electrostatically charged during mixing.

Charge accumulated on isolated conductive plant and equipment can give rise to spark-type electrostatic discharges when exposed to another proximate conductor at a lower electrical potential (voltage), such as adjacent conductive plant and equipment that is electrically grounded, *i.e.*, at zero electrical potential. For example, a spark discharge could occur between an electrostatically charged metal pail, if isolated from ground and a metal nozzle from which a liquid is being dispensed.

The name of these discharges is derived from the distinct and singular discharge channel that is observed for spark discharges under low-light conditions. This may be attributed to the fact that the charge on a conductor is mobile and much if not all of the charge on the conductor propagates to the discharge site. The effective energy, E , of spark discharges is approximated as the energy stored on the isolated conductor, which can be modeled as a simple capacitor, as shown in Eq. 3:

$$E = 0.5CV^2 \quad (3)$$

where, E is energy in J; C is capacitance in F; and V is voltage in V.

While dependent on the capability of the isolated conductor to store charge and the extent to which it becomes charged (*i.e.*, its capacitance and voltage), the effective energy of spark discharges is often sufficient to ignite flammable atmospheres, including vapor evolved from flammable or combustible liquids that are at or above their flash point or in the form of a spray or mist.

Flammable vapor atmospheres may exist within process equipment or piping or be evolved into the process area from open vessels, open transfers or leaks. Sprays and mists of combustible liquids can be flammable at temperatures less than their respective flash points because the fuel is dispersed into the air mechanically or physically, such as when ejected from a nozzle or when condensed, rather than having to rely on temperature to evaporate or volatilize the liquid.

ELECTROSTATIC HAZARD ASSESSMENT

Electrostatic hazard assessment involves the comparison of the effective energy, E , of possible electrostatic discharges with the minimum ignition energy (MIE) of the prevailing flammable atmosphere(s). Let's continue with our example of a metal pail. A 1-gal metal pail might have a capacitance of approximately 10 picofarads (pF). Let's assume that it is iso-

Table 3. Minimum ignition energies of gases and vapors evolved from selected liquids.

Liquid	Minimum Ignition Energy, mJ
Acetone	1.15 @ 4.5 vol.%
Benzene	0.2 @ 4.7 vol.%
Butane	0.25 @ 4.7 vol.%
Carbon disulfide	0.009 @ 7.8 vol.%
Heptane	0.24 @ 3.4 vol.%
Hexane	0.24 @ 3.8 vol.%
Isopropyl alcohol (IPA)	0.65
Methyl alcohol	0.14 @ 14.7 vol.%
Propane	0.25 @ 5.2 vol.%
Tetrahydrofuran (THF)	0.54
Toluene	0.24 @ 4.1 vol.%
Xylene	0.2

lated from ground such that its resistance-to-ground exceeds $1 \times 10^{11} \Omega$ (100 G Ω). If a toluene slurry is being dispensed into the pail, a streaming current on the order of 1 μ A could be reasonably expected. From Ohm's Law, we know that:

$$V = IR \quad (4)$$

where R is resistance in Ω .

Substituting Eq. 4 into Eq. 3 for V and solving the resulting equation using the aforementioned values yields an estimated effective energy of 0.5 mJ. This energy exceeds the minimum ignition energy (MIE) of toluene vapor (0.24 mJ). Thus, a spark discharge from the ungrounded pail would be sufficient to ignite it.

Minimum ignition energy

The minimum ignition energy (MIE) for selected flammable liquids are shown in Table 3 along with the vapor concentration where this MIE may be observed (12). The tabulated data suggest that the MIE of a flammable atmosphere is a factor of its concentration and the prevailing environmental conditions. There is an optimal concentration at which the lowest MIE — sometimes called the LMIE — occurs. Typically, this concentration is slightly greater than the stoichiometric concentration, which is the relative concentration of fuel in oxidant where complete combustion occurs.

For concentrations less than and greater than the optimal concentration, the MIE of the flammable atmosphere generally increases and thus the flammable atmosphere becomes less ignition sensitive. Nevertheless, it is generally recommended that the lowest expected value of the MIE at the prevailing temperature and pressure be used to specify precautions for purposes of minimizing the potential fire and explosion hazard, since the possibility of forming localized concentrations at the optimal value often cannot be discounted with certainty.

With regards to the effects of environmental conditions, the MIEs of flammable atmospheres generally decrease as the prevailing temperature increases because less heat input is required from the electrostatic discharge to create the activation energy needed to initiate the combustion reaction.

MIEs generally decrease as the prevailing pressure increases because the flammable atmosphere has more potential energy at higher pressures; thus, less energy is required from the electrostatic discharge to create the activation energy needed to initiate the combustion reaction. The presence of an alternative oxidant such as pure oxygen, as opposed to air, can also affect MIEs. For example, the MIE of diethyl ether is 0.19 mJ at a concentration of 5.1 vol.% in air (21 vol.% oxygen), but only 0.0012 mJ in pure oxygen.

Brush discharges

Brush-type electrostatic discharges arise from charged items made from materials that are insulating in electrostatic terms, such as plastics, to proximate conductors at a lower electrical potential (voltage), such as grounded conductive plant equipment and personnel. Brush discharges can have an effective energy (E) of as much as 4 mJ, and thus can be sufficiently energetic to ignite vapors evolved from flammable liquids, many of which have MIEs less than 4 mJ, as shown in Table 3.

Examples of plastic items that can become electrostatically charged during the processing of liquids include piping, tubing, containers, funnels, pumps, filter media and filter housings. These items can become electrostatically charged: (a) by contact with an electrically insulating liquid during filling, pouring (emptying), and stirring; and (b) when handled, wiped or rubbed by personnel. For example, a plastic container may become electrostatically charged during the pouring of an insulating liquid, such as toluene. The charged plastic container could give rise to a brush discharge as it is brought close to the vessel into which the liquid is being poured.

Unlike spark discharges, no satisfactory model has yet been proposed for estimating the effective energy of brush discharges, and their maximum effective energy (4 mJ) is known only empirically. The name of these discharges is derived from the multiple brush-like discharge channels that are observed for brush discharges under low-light conditions. This is attributed to the fact that the charge on an insulating surface is not mobile and cannot form a singular discharge channel. For this same reason, only a limited area of the insulating surface is discharged during any one discharge event. Thus, a charged insulator can give rise to multiple brush discharges until all of the charge on its surface(s) has been discharged or dissipated.

Operations during which flash fire incidents caused by brush discharges have occurred include: the use of plastic containers and funnels in the open transfer of flammable liquids; the replacement of synthetic filter media; and the breaking (disconnecting or opening) of PTFE-lined piping containing residual flammable liquid, among others. Brush discharges can also pose an ignition hazard in the event of a leak or spill around a plastic item, or when plastic items such as containers, plastic sheeting, and drum pumps are used to clean up spills and leaks of flammable liquids.

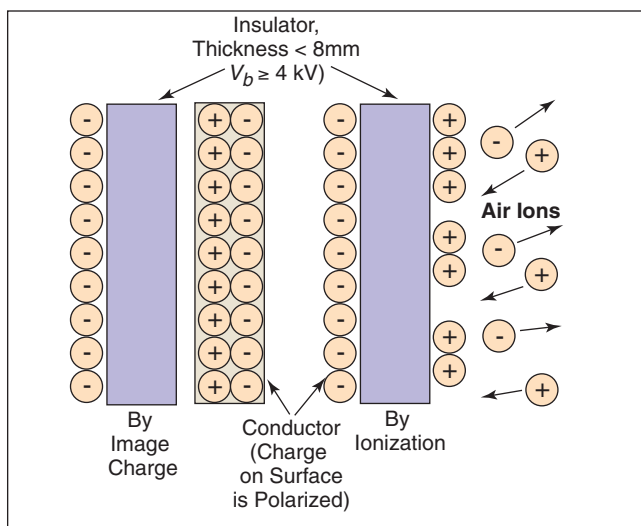
Propagating brush discharges

Breakdown voltage, V_b , is the voltage at which the insulating property of a material breaks down and an electrical arc is able to puncture or cause a pinhole in the material. In glass-lined vessels and PTFE-lined piping, if the potential difference between the liquid and the conductive substrate vessel or piping exceeds the breakdown voltage of the lining, a propagating brush-type electrostatic discharge can occur. These highly energetic discharges, which have effective energies of as much as 2–3 J, not only can cause leaks by puncturing glass and PTFE linings, but also ignite flammable atmospheres, including vapors evolved from flammable liquids. Leaks can pose a risk of fire and explosion if the liquid is flammable or combustible, or a risk of injury to personnel and damage to equipment if the liquid is also corrosive.

Piping made from plastics and other electrically insulating materials can also give rise to propagating brush discharges. This can occur when the electric field associated with the charge generated by the flow of the material inside the piping is sufficiently strong to ionize the air outside the piping — *i.e.*, if the electric field strength exceeds the breakdown strength of air (3×10^6 V/m). Upon ionization, opposite polarity ions are attracted by the electric field associated with the charge inside the piping. These oppositely charged ions accumulate on the outside wall of the piping, forming a double-layer charge with the charge on the inside wall. If the potential difference between the charge layers exceeds the breakdown voltage of the pipe wall, or if a conductor at a lower electrical potential approaches the layer of charge on the outside wall, a propagating brush-type electrostatic discharge can occur.

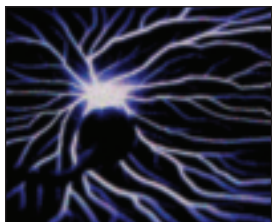
Both propagating and brush-type discharges arise from electrostatically charged insulators. The difference is that brush discharges arise when there is a single-layer charge on one side of the insulator, while propagating brush discharges arise when there is a double-layer charge — *i.e.*, charge on both sides of the insulating surface. As shown in Figure 1, the second layer of charge can be provided either by image charge or by ionization of the atmosphere on the opposite side of the insulator. The image charge is the opposite-polarity charge attracted to the charge on an insulator that results from the polarization of the otherwise balanced charge in the conductor. The double-layer charge enables more of the charge to “propagate” to the primary discharge channel, and accounts for the higher energy of propagating brush discharges. A propagating brush discharge under low light conditions is shown in Figure 2.

While no data on the dimensions of pinholes caused by propagating brush discharges or the resulting leak rates could be found, pinholes are often undetectable by the naked eye. They may appear as little more than discolorations in the glass or on the surface of the insulator, as shown in Figure 3. For this reason, pinholes are typically detected through spark testing rather than visual inspection. Spark testing involves the use of a conductive brush



■ Figure 1. Double-layer charge. In the absence of the adjacent charged insulator, the charge on the conductor would be balanced, i.e., all mixed-up and an equal number of positive and negative charges. In the presence of the charged insulator, there is still the same amount of positive and negative charge on the conductor, but the charges are polarized.

electrode charged to 15–20 kV using a high-voltage power source. The brush is guided over the insulating surface and creates a spark discharge to the grounded conductive substrate vessel or piping when a pinhole is detected.



■ Figure 2. Propagating brush-type electrostatic discharge that causes pinholes in glass-lined vessels, viewed under low light.



■ Figure 3. Pinhole damage to the glass lining of a reactor due to propagating brush discharges. The pinhole damage is indicated by the white spots on the blue background. Courtesy of the Institution of Chemical Engineers (Rugby, U.K.).

dielectric strength, characteristics associated with plastic piping and vessels, the PTFE in lined conductive piping, and the glass in lined conductive vessels.

For example, one manufacturer of glass-lined vessels indicates that the thickness of the glass lining in a typical reactor may range from 35 to 95 mil (1 mil = 1/1,000 in.) and averages 60 mil. Since the breakdown strength of the ceramic-like glass lining is reported to be 0.50 kV/mil, the breakdown voltage of the glass lining in a typical glass-lined reactor ranges from 17.5–47.5 kV and averages 30 kV. Notably, the manufacturer suggests that the thickness of the glass-lining on agitator blades, nozzles, and other vessel appurtenances may be as much as 5 kV lower on average.

Another manufacturer reports that the thickness of the lining in typical PTFE-lined pipe may range from 130 mil

in 1-in. dia. (nominal) pipe to 160 mil in 4-in. dia. pipe. Since the breakdown strength of PTFE is reported to be 0.48 kV/mil (14), the breakdown voltage of the PTFE linings may range from 62.4–76.8 kV. Like the glass-lined vessels and appurtenances, however, the breakdown voltage of the PTFE-lining can be less at the point where the pipe and lining bend to form a flange face. The pinholes reported in glass and PTFE linings from incidents of propagating brush discharges confirm that voltages exceeding these breakdown voltages can be reached.

Discharges from liquids

Charge accumulated on insulating liquids can give rise to electrostatic discharges from the surface of the liquid, even in the absence of an electrode at a lower electrical potential. These discharges, known as surface streamers or go-devils, can be sufficiently energetic to ignite vapor evolved from the liquid, if flammable (15). Surface streamers and go-devils are believed to occur due to potential (voltage) gradients in the liquid. Rather than requiring an electrode at a lower electrical potential to induce the discharges, the discharges occur from points in the liquid at a relatively high electrical potential, to points at a relatively lower electrical potential. Different electrical potentials exist at different locations and times throughout the agitation of an insulating liquid, depending upon the rate of agitation and the location in the liquid relative to the agitator blades, baffles and vessel walls.

Discharges can also be induced from the liquid surface by an electrode at a lower electrical potential, such as the vessel wall, agitator, sampling rods, gauging rods, thermocouples, level indicators and other conductive items extending into a vessel. The rate of charge generation can be aggravated by the presence of solids and immiscibles in the liquid, since these provide additional surfaces for contact charging.

Electrostatically charged conductive liquids may produce spark discharges when isolated from ground, such as when they are resident in plastic vessels or containers or glass-lined vessels. In contrast, electrostatic discharges from electrically insulating liquids have not yet been well described. However, since even the most insulating liquids are more conductive than insulating solids, it is likely that discharges from insulating liquids may exhibit the characteristics of both spark and brush discharges. As described above, both spark-type and brush-type electrostatic discharges are often sufficiently energetic to ignite flammable vapor atmospheres, such as those that may be evolved from the liquid itself.

Discharges from charged sprays and mists

It has been theorized that lightning-like electrostatic discharges may occur on an industrial scale in large clouds of highly charged sprays and mists (16). If the charge exceeds the breakdown strength of air, 3×10^6 V/m, the air within the cloud will begin to ionize. The surface-charge density

on a particular droplet may become sufficient to overcome the breakdown strength of air and produce a discharge to the vessel wall or to an adjacent droplet at a lower electrical potential.

While the discharge energy from any one droplet may be small, the effect may be to create a cascade of discharges from the others and thereby simultaneously release substantially more of the energy of the cloud. It has been speculated that such a discharge may be sufficiently energetic to ignite a flammable spray or mist.

Notably, lightning bolts during thunderstorms are produced by clouds, millions of cubic meters in volume. In contrast, in industrial processes and even in large-scale experiments with clouds of sprays and mists as large as 60 m³, there is no record that these theorized lightning-like discharges have ever been observed (17). Further, there is no record that these discharges have been observed from sprays or mists, even during the washing of 30,000 ft³ compartments in ocean-going tankers (18). Consequently, the probability that lightning-like discharges from an electrostatically charged spray or mist will occur in industrial-scale process vessels and equipment is considered remote.

CONTROLLING THE HAZARDS

A number of approaches are available for controlling electrostatic hazards associated with liquid processing, including raising the conductivity of the liquid, providing a pathway to electrical ground to dissipate charge from the liquid, and limiting the flow and agitation velocity, among others.

Increasing conductivity

The electrostatic hazard posed by insulating liquids, such as toluene, hexane, heptane, xylene and other non-polar solvents, can be decreased dramatically by increasing their electrical conductivity. The conductivity of an insulating liquid can be increased through the addition of an antistatic additive or a more-conductive liquid. These additives typically do not affect the rate of charge generation, rather the increased conductivity enables charge to be more readily dissipated from the liquid.

Antistatic additives, also known as conductivity improvers, have the advantage of requiring the addition of only a few parts-per-million (ppm) to increase the conductivity of an insulating liquid by several orders of magnitude (19). While the chemistry of these additives is proprietary, it appears that there are principally two mechanisms by which they accomplish this feat. First, the additives contain multiple salts that are dissolved within the insulating liquid, with at least one of the salts being sufficiently strong to remain capable of providing free ions in the solution. The second mechanism is electron transfer. Certain polymers, such as some sulfonic and acrylate polymers are capable of transferring electrons from the end of one chain to the end of an adjacent chain.

While these mechanisms are believed common to commercially available antistatic additives, the use of these ad-

ditives is also highly empirical. That is, performance often cannot be predicted theoretically, and instead requires laboratory-scale testing to determine whether an additive will be effective at increasing the conductivity of a particular liquid or mixture. Ultimately, testing of field samples also may be required to verify that the additive is having the desired effect in full-scale equipment.

One disadvantage of antistatic additives is that the salts, polymers, and other ingredients that comprise them are sometimes incompatible with pharmaceutical and food applications. In these instances, the use of a conductive liquid, such as an alcohol or ketone, may be considered. However, these liquids have the disadvantage of needing to be added in much greater concentration (*e.g.*, on the order of 10–20 vol.% or more), which may be disruptive to the process chemistry. Further, these liquids also must be miscible in the insulating liquid in order to increase the liquid's electrical conductivity. Lastly, if the conductive liquids are flammable, they may increase the flammability of the insulating liquid, such as by lowering the flash point.

Grounding plant equipment

All conductive plant and equipment associated with the processing of flammable liquids should be electrically grounded in order to prevent the accumulation of electrostatic charge, and thereby minimize the probability of ignition from spark-type electrostatic discharges. Conductive plant and equipment that should be grounded include piping, vessels, containers, agitators, pumps, valves, other fittings, flanges and couplings, among others.

Suitable reference grounds for fixed conductive plant components, vessels and equipment are identified in the National Electrical Code (NEC) or NFPA 70 (20), and include the plant superstructure. The grounding of conductive plant and equipment should be verified regularly by measurement.

Efforts should be made to keep flammable liquids in continuous contact with electrical ground, even in glass-lined vessels and PTFE-lined piping, in order to minimize the accumulation of electrostatic charge on the liquid. Only piping and hose made from antistatic or conductive materials should be used with flammable liquids in order to minimize the probability of ignition from brush-type and propagating brush-type electrostatic discharges. Such piping and hose should be electrically grounded during use.

Limiting flow and agitation velocity

The free fall of flammable and combustible liquids during the filling of vessels and containers causes splashing and spraying, with the consequent generation of electrostatic charge on the liquid. Splashing of flammable and combustible liquids can also result in the formation of flammable and electrostatically charged sprays and mists.

To minimize the potential electrostatic hazard, flammable and combustible liquids should instead be intro-

Table 4. Electrostatic discharge energies.

Discharge Type	Discharge Energy
Spark discharges	$0.5CV^2$ J
Brush discharges	4 mJ, maximum
Propagating brush discharges	~3,000 mJ
Liquid discharges	
• Conductive liquids	$0.5CV^2$ J
• Insulating liquids	~4 mJ

duced to vessels and containers through either bottom filling (*i.e.*, the introduction of a liquid through a port located at the bottom of the vessel) or a grounded conductive dip pipe. A dip pipe is a pipe that extends from the inlet port on top of a vessel or container to near the bottom.

A dip pipe should extend sufficiently close to the bottom of the vessel or container such that its outlet or discharge end is almost immediately submerged beneath the liquid during filling. The end should be cut at an angle, fitted with a baffle plate, or otherwise designed to minimize splashing and spraying of the liquid. For removable dip pipes used with drums and other small containers, the end of the dip pipe should also be blunted or otherwise designed to minimize the possibility of puncturing the container.

Limiting the liquid velocity during vessel and container filling operations helps to limit electrostatic charge generation in the transfer piping and minimize splashing and spraying in the receiving vessel or container. Approaches for limiting the liquid flow velocity include reducing the pumping rate or transfer pressure and using control valves. Similarly, the rate of electrostatic charge generation during the mixing of liquids can be controlled by limiting the speed of agitation. Of course, this option is available only when a variable-speed agitator is used.

If limiting the liquid velocity and agitation rate are impracticable, it may be impossible to dissipate electrostatic charge from the liquid at a rate sufficient to prevent the accumulation of a hazardous level of charge ($< 3 \times 10^6$ V/m). In such cases, inerting of the vessel or container before and during filling and agitation should be considered in order to minimize the fire and explosion risk.

Inerting

Safety during the transfer and mixing of flammable liquids is frequently based on inerting, since even if the probability of ignition from electrostatic discharges from the liquid can be minimized by controlling the flow and agitation rates, the consequences of ignition are often significant. If properly implemented, inerting may represent the primary basis of safety and, if the flow and agitation rates can be limited as described above, control of ignition sources may be considered a secondary basis of safety, such as in the event inertion is lost.

Inerting is the introduction of an inert gas, such as nitrogen, argon or carbon dioxide, to a vessel or container in order to reduce the relative oxidant concentration below the limiting oxidant concentration (LOC). The LOC is the oxidant concentration below which combustion — and therefore a fire or explosion — cannot occur. The oxidant of con-

cern during vessel and container filling is generally the oxygen in air, and in such cases the LOC is referred to as the limiting oxygen concentration. The LOC is a property of each flammable and combustible material, and is a factor of the oxidant present and the inert gas that will be used.

NFPA 69, the U.S. consensus standard on explosion prevention systems, recommends that in order for inerting to be considered a reliable basis of safety, the oxygen concentration in a vessel should be reduced to 2% less than the LOC when oxygen concentration is continuously monitored, unless the LOC is less than 5 vol.%, in which case the oxygen concentration should be reduced to less than 60% of the LOC (21). When oxygen concentration is not continuously monitored, the oxygen concentration should be reduced to less than 60% of the LOC, again unless the LOC is less than 5 vol.%, in which case the oxygen concentration should be reduced to less than 40% of the LOC.

Filtration

Liquids are sometimes passed through filters before they are introduced to a receiving vessel or container. The flow of liquids through fine-particle filters is often characterized by the generation of relatively high levels of electrostatic charge due to the relatively large amount of surface area available for contact in the filter and the consequent double-layer charging (22). Coarser filters can aggravate electrostatic charging in liquids when they become plugged. When the piping and filter are filled with liquid, there is no headspace for a flammable vapor atmosphere to be evolved. However, when the flammable liquid enters a vessel downstream of a filter, a flammable vapor atmosphere may evolve and the charge on the liquid may pose an electrostatic ignition hazard.

Consequently, it is desirable to relax the electrostatic charge from a flammable liquid before it enters a receiving vessel. This is typically accomplished by locating filters as far upstream of the receiving vessel as possible. This does not dissipate charge from the liquid entirely. Rather, the residence time in the piping between the filter and receiving vessel allows the liquid to return to its steady-state streaming current. Alternatively, a charge relaxation tank may be used. A charge relaxation tank is a grounded conductive tank used to provide the required residence time when the length of piping downstream of a filter is insufficient to permit the relaxation of the streaming current back to the steady-state value.

Charge relaxation time is sometimes defined as the time required for the charge on a material to relax to $1/e$ or 37% of its initial value. This is because the relaxation of electrostatic charge from materials that obey Ohm's Law (Eq. 4) is exponential. Since the relaxation of charge from liquids is rarely exponential, the charge-relaxation time for liquids is typically defined as the time required for the charge to relax to 10% of its initial value. The charge-relaxation times for selected liquids are shown in Table 5 (23).

Exclusion of electrically insulating materials

The use of items made from PTFE, polyethylene, polyvinyl chloride and other electrically insulating materials with flammable liquids is generally not recommended due to the risk of ignition from brush-type electrostatic discharges. Such materials can also isolate liquids and conductors from electrical ground, and thus make them susceptible to the accumulation of electrostatic charge. Items of concern include containers, funnels, tools, drum liners and PTFE in lined pipe, among others. Instead, use of comparable items made from antistatic or conductive materials is suggested. Such items should be electrically

Literature Cited

1. Cross, J. A., "Electrostatics – Principles, Problems, and Applications," Adam Hilger, IOP, Bristol, U.K., p. 29 (1987).
2. Glor, M. and G. Luttgens, "Understanding and Controlling Static Electricity," Expert-Verlag, Ehningen bei Boblingen, Federal Republic of Germany (FRG), p. 50 (1989).
3. Eichel, F. G., "Electrostatics," *Chem. Eng.*, McGraw-Hill, New York, **74** (6), pp. 153–167 (March 13, 1967).
4. Crawl, D. A., and F. C. Louvar, "Chemical Process Safety – Fundamentals with Applications," Prentice Hall, Englewood Cliffs, NJ, pp. 201–204 (1990).
5. Schon, G., "Handbuch der Raumexplosionen," Verlag Chemie, Weinheim Bergstr., FRG (1965).
6. Gibson, N. and F. C. Lloyd, "Electrification of Toluene in Large Diameter Metal Pipes," *J. Appl. Phys.*, **3** (1970).
7. Kozman, I. and J. Gavis, "Development of Charge in Low Conductivity Liquids Flowing Past Surfaces – Experimental Verification and Application of the Theory Developed for Tube Flow," *Chem. Eng. Sci.*, **1062** (17), pp. 1,023–1,040 (1962).
8. Britton, L. G., "Avoiding Static Ignition Hazards in Chemical Operations," AIChE Course, New York, pp. 106–110 (1999).
9. British Standard 5958, "Code of Practice for Control of Undesirable Static Electricity – Part 1," British Standards Institute, London, U.K., p. 12 (1991).
10. NFPA 77, "Recommended Practice on Static Electricity," National Fire Protection Assn. (NFPA), Quincy, MA, pp. 45–47 (2000).
11. NFPA 77, pp. 4–5 (2000).
12. NFPA 77, pp. 41–42 (2000).
13. Glor, M. and G. Luttgens, p. 105 (1989).
14. Britton, L. G., p. 235 (1999).
15. NFPA 77, p. 77–10 (2000).
16. Glor, M. and G. Luttgens, pp. 110–111 (1989).
17. Glor, M. and G. Luttgens, p. 111 (1989).
18. Cross, J. A., p. 365 (1987).
19. British Standard 5958, p. 14 (1991).
20. NFPA 70, "National Electrical Code," §250 C, 250–50, Quincy, MA, pp. 70–88 (1999).
21. NFPA 69, "Standard on Explosion Prevention Systems," Quincy, MA, p. 69–8 (2002).
22. Britton, L. G., pp. 116–118 (1999).
23. NFPA 77, pp. 44–47 (2000).

ACKNOWLEDGEMENTS

The author wishes to acknowledge the valuable contributions of Vahid Ebadat, David E. Kaelin, Sr., Victoria Jones and Rita D'Aquino to this article. The author also wishes to thank his wife and family, who have helped make all of his achievements possible.

Table 5. Charge relaxation times for selected liquids.

Liquid	Charge Relaxation Time, s
Conductive liquids ($\gamma > 10^4$ pS/m)	
Acetaldehyde (15°C)	1.1×10^{-6}
Acetonitrile (20°C)	5×10^{-7}
Ethyl acetate (25°C)	1.2×10^{-3}
Ethyl alcohol (25°C)	1.6×10^{-3}
Ethylene glycol	2.9×10^{-6}
Methyl alcohol (18°C)	6.6×10^{-6}
Methyl ethyl ketone (25°C)	1.6×10^{-5}
Methyl isobutyl ketone	$> 2.2 \times 10^{-5}$
Phenol	8.7×10^{-5}
Isopropyl alcohol (25°C)	5×10^{-7}
Water, distilled	7.1×10^{-7}
Semi-conductive liquids ($\gamma = 100$ – 10^4 pS/m)	
Methylene chloride	0.018
Trichloroethylene	0.037
Non-conductive liquids ($\gamma < 100$ pS/m)	
Benzene, purified	~100
Carbon tetrachloride	~100
Heptane, purified	~100
Hexane, purified	~100
Styrene monomer	2.2
Toluene	21
Xylene	~100

grounded when used.

Notably, these precautions are not intended to be exhaustive. Rather, they are the ones most commonly employed. Additional or different precautions may be required depending upon the specific application or conditions that could not have been reasonably foreseen. Expert advice should be sought as necessary.

CEP

Related Courses Offered by AIChE

Course #583: Identifying and Managing Chemical Reactivity Hazards
Houston, TX; Oct. 30–31, 2003

Course #536: Understanding and Preventing Explosions
Las Vegas, NV; Nov. 13–14, 2003

Member fee: \$995, Non-member fee: \$1,155

For more information or to register, visit www.aiche.org/education or call (800) 242-4363.

JAMES C. MULLIGAN is a senior process safety engineer with Chilworth Technology, Inc. (11 Deer Park Drive; Monmouth Junction, NJ 08852; Phone: 732-274-0900; Fax: 732-274-1371; E-mail: jmulligan@chilworth.com) and has been working in the fields of process safety and environmental management for 16 years. His areas of expertise include: fire and explosion hazard assessment, incident investigation, prevention and protection; hazards related to gas and vapor flammability, dust explosions and thermal stability; classification of hazardous materials for transport, process safety management (PSM/HAZOP), regulatory analysis and compliance; and electrostatic hazards. Mulligan was formerly a technical manager with the Chemical Manufacturers Assn. (now American Chemistry Council). He has represented the chemical industry before Congress and U.S. government agencies during the development of numerous safety and environmental laws and regulations. Mulligan is the author of several articles on chemical process safety and is a regular speaker at company and industry training courses and events. He received a BChE from The Catholic Univ. of America and an MBA from Villanova Univ., and is a member of AIChE, NFPA, ASSE, and ASTM.