The Role of ASTM E27 Methods in Hazard Assessment Part II: Flammability and Ignitability

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Accurate flammability and ignitability data for chemicals form the cornerstone of procedures used to assess the hazards associated with commercial chemical production and use. Since 1967 the ASTM E27 Committee on the Hazard Potential of Chemicals has issued numerous, widely used consensus standards dealing with diverse testing and predictive procedures used to obtain relevant chemical hazard properties. The decision to issue a standard rests solely with the membership, which consists of representatives from industry, testing laboratories, consulting firms, government, academia, and instrument suppliers. Consequently, the procedures are automatically relevant, timely, and widely applicable. The purpose of this paper is to highlight some of the widely used standards, complemented with hypothetical but relevant examples describing the testing strategy, interpretation, and application of the results. A further goal of this paper is to encourage participation in the consensus standards development process.

The paper is published in two parts. The first part (in the preceding issue of Process Safety Progress) dealt with the E27 standards pertaining to thermodynamics, thermal stability, and chemical compatibility. The second part, published here, focuses on the flammability, ignitability, and explosibility of fuel and air mixtures. © 2005 American Institute of Chemical Engineers Process Saf Prog 24: 12–28, 2005

1. INTRODUCTION

Committee E27 of ASTM International, which deals with the Hazard Potential of Chemicals, has been in existence since 1967. During that time, its members have developed and approved over 20 consensus standards relating to ignitability, flammability, and chemical reactivity. The Committee was formed because of the need for consistent, scientifically based, accurate, easy to apply, and most of all, consensus methodologies for the determination of parameters and properties that allow industry to design safe processes properly. The E27 standards are widely recognized and used in hazard assessment and loss prevention engineering.

This paper[1] is published in two parts. Part I dealt with the E27 methods pertaining to thermal stability, compatibility, and energy release estimation [1]. Part I also included a background description of the E27 committee including its scope, membership, and organization. Part II, published here, focuses on the ignitability, flammability, and explosibility of fuel and air mixtures. In this paper and in the E27 standards, the terms "flammability" and "explosibility" are used inter-

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[1] The two parts of this paper are based on a presentation at the 38th Loss Prevention Symposium held at the AIChE Spring National Meeting in New Orleans, LA, in April 2004.

Table 1A. Standard test methods currently administered by ASTM Subcommittee E27.04 on the Flammability and Ignitability of Chemicals.

ASTM Designation	Title	Scope, Citations, Applications, or General Comments
E 502	Selection and Use of ASTM Standards for the Determination of Flash Point of Chemicals by Closed Cup Methods	Guides in the selection of the appropriate ASTM closed-cup flash-point test method. Repeatability and reproducibility for different test methods. Effect of ambient pressure on flash point. Referenced in NFPA 30, 49, 77, 325, 497, and 704.
E 582	Minimum Ignition Energy and Quenching Distance in Gaseous Mixtures	Tests are performed on specified gas mixtures in a 1-L vessel using capacitance sparks and flanged electrodes. Cited in NFPA 77 and 497.
E 659	Autoignition Temperature of Liquid Chemicals	Vapor–air mixtures are tested in 0.5-L heated glass flask. Cited in NFPA 70, 497, and 921.
E 681	Concentration Limits of Flammability of Chemicals (Vapors and Gases)	Lower flammable limit (LFL) and upper flammable limit (UFL) are determined in 5-L spherical vessel. Cited in NFPA 69 and 921.
E 918	Determining Limits of Flammability of Chemicals at Elevated Temperature and Pressure	This practice covers the determination of the lower and upper concentration limits of flammability of combustible vapor–oxidant mixtures at temperatures up to 200° C and initial pressures up to 1.38 MPa (200 psia).
E 1232	Temperature Limit of Flammability of Chemicals	Minimum temperature at which a liquid in equilibrium with its vapor forms a flammable mixture with air at atmospheric pressure. The lower temperature limit of flammability (LTL) is more relevant than flash point for large process vessels.
E 2021	Hot-Surface Ignition Temperature of Dust Layers	Minimum surface temperature capable of igniting a dust layer. Cited in NFPA 70, 499, and 654.
E 2079	Limiting Oxygen (Oxidant) Concentration in Gases and Vapors	Limiting oxidant concentration (LOC) determined in 5-L vessel. Cited in NFPA 69.

Note: These standards are available from ASTM online (**www.astm.org**) or in print in reference 2.

changeably to refer to the ability of a gas mixture or dust cloud to propagate a deflagration after it has been initiated by a sufficiently strong ignition source. Historically, the term "flammability" has been used more often for gases, and "explosibility" more often for dusts.

A comprehensive listing of the various active standards currently administered by E27 was previously given in Tables 1A, 1B, and 1C of Part I. ASTM E27 standards [2] relevant to this Part are recapitulated in Table 1A, which lists the standards of Subcommittee E27.04, and Table 1B, which lists the standards of Subcommittee E27.05. Subcommittee E27.04 on the Flammability and Ignitability of Chemicals deals with gases, vapors from liquids and solids, and nondispersed dusts, such as layers. Subcommittee E27.05 on the Explosibility and Ignitability of Dust Clouds deals only with dispersed dust clouds. In addition to the ASTM numerical designation and title, the tables include a short description of the scope of each standard and some of the citations where the standard may be recommended for use. (These standards are available from ASTM International at the website **www. astm.org.**) International consensus standards such as NFPA 69, Standard on Explosion Prevention Systems, and other NFPA documents [3] provide guidance for

the practical application of the data from the ASTM E27 test methods.

To give the reader a further sense of the general applicability of E27 standards, Figure 1 shows a flowchart for dust explosion protection, which was modified from Figure 7.2 of Eckhoff [4]. Within each appropriate box, relevant ASTM E27 test methods are listed. Clearly, the methods administered by ASTM E27 are well aligned with these and other commonly used hazard/consequence evaluation methodologies.

These ASTM E27 ignitability, flammability, and explosibility standards are used to assess the gas, vapor, and dust explosion hazard properties of materials; to establish safe operating conditions; and to perform consequence analysis for hypothesized accidents. Generally speaking:

- Ignitability test methods determine the minimum energy or temperature required to ignite the most sensitive mixture of fuel, air (oxidant), and diluent.
- Flammability limit test methods determine the concentration limits of fuel, air (oxidant), or diluent (suppressant) in the presence of a sufficiently strong ignition source. The flammability

Table 1B. Standard test methods currently administered by ASTM Subcommittee E27.05 on Explosibility and Ignitability of Dust Clouds.

ASTM Designation	Title	Scope, Citations, Applications, or General Comments
E 789	Dust Explosions in a 1.2-L Closed Cylindrical Vessel	Historical value only, obsolete for design. Occasionally used as a qualitative screening tool.
E 1226	Pressure and Rate of Pressure Rise for Combustible Dusts	Maximum pressure, P_{max}, and maximum rate of pressure rise, dP/dt_{max}, in closed vessel of at least 20-L volume. Cited in NFPA 68, 69, 484, 654, 921.
E 1491	Minimum Autoignition Temperature of Dust Clouds	Minimum temperature at which a dust cloud will autoignite when exposed to air heated in a furnace at local atmospheric pressure. Cited by NFPA 654.
E 1515	Minimum Explosible Concentration of Combustible Dusts	Minimum concentration of dust dispersed in air that will propagate a flame. Cited in NFPA 69, 77, 484, 654, and 664.
E 2019	Minimum Ignition Energy of a Dust Cloud in Air	Minimum ignition energy (MIE) of dust cloud in air. Cited in NFPA 61, 77, 654, and 921.
WK1680	Limiting Oxygen (Oxidant) Concentration of Combustible Dust Clouds	Draft test method that will apply to NFPA 69, 484, 654. *Note: WK1680 refers to the ASTM Work Item of the E27.05 Subcommittee.*

Note: These standards are available from ASTM online (**www.astm.org**) or in print in reference 2.

limit is the boundary between regions that can propagate a flame and regions that cannot. As will be seen below, this concept can also be extended to temperature limits of flammability, as related to commonly used flash-point values.

- The test methods for maximum explosion pressure and rate of pressure rise assume the presence of both a sufficiently strong ignition source and the worst case or most energetic mixture of fuel and oxidizer. They aim to characterize how fast the combustion reaction can proceed in a particular combination of fuel, air (oxidant), and diluent.

Usage Survey of ASTM E27 Standards

In preparation of this paper, an informal survey was conducted in 2003–2004 to estimate the frequency of use of ASTM E27 test methods for ignitability, flammability, and explosibility. The survey was sent to E27 committee members, which included commercial testing laboratories, government laboratories, chemical manufacturers' laboratories, and explosion protection equipment manufacturers' laboratories. These laboratories include most of the major U.S. facilities for testing the ignitability, flammability, and explosibility of chemicals, particularly for dusts. The results are listed in Table 2 in terms of total number of times a method was used per year by all the laboratories, using the past 3–4 years as a base. (Note that this table has been updated from the one in the Loss Prevention Symposium paper.) The results are listed by ASTM standard number and abbreviated title. It appears from Table 2 that the dust test methods are used more frequently than the methods for gases. Of the E27.04 standards, E 502 for flash point is used most extensively. This particular standard is probably also used by numerous industrial laboratories that we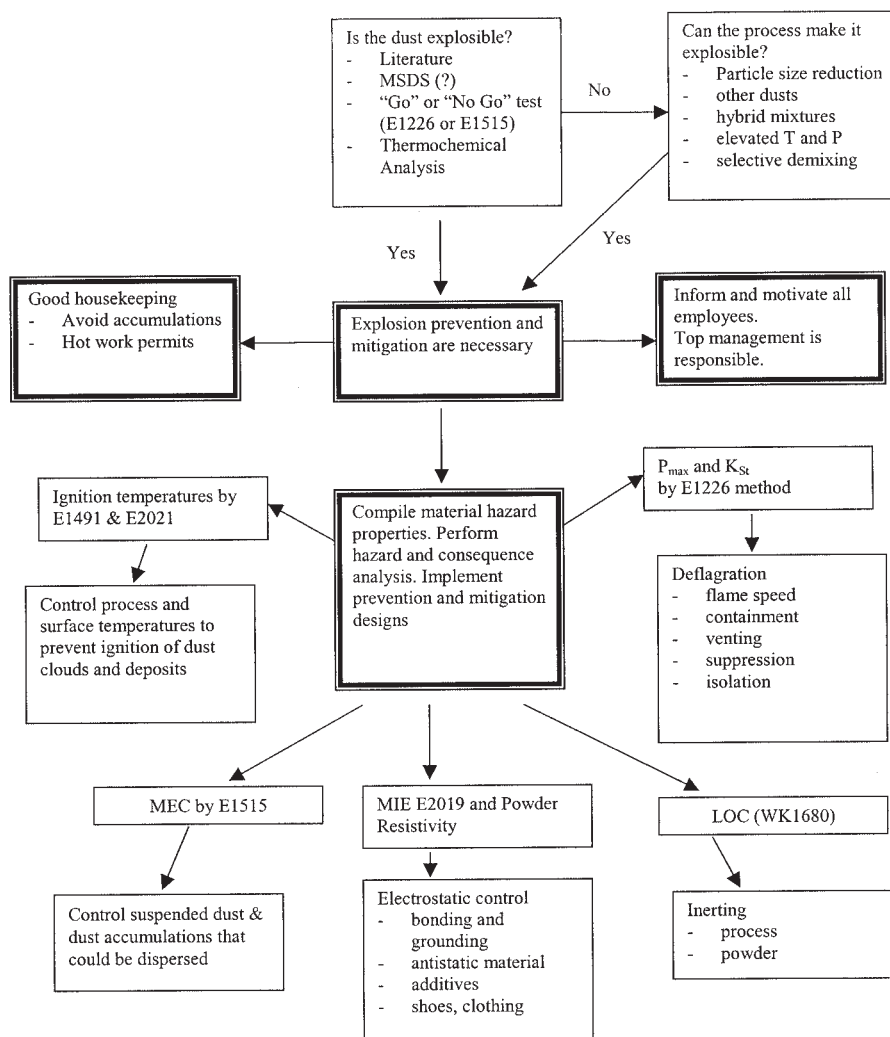re not part of the survey. For the E27.05 standards, E 1226 on pressure and rate of pressure rise and E 2019 for minimum ignition energy of dusts are used very extensively.

There are two apparent reasons for the greater use of E27.05 standards than E27.04 standards. First, the gas and vapor test methods have been around for a long time, and test data have been compiled and published for a large number of pure chemicals (for example, NFPA 325, Fire Hazard Properties of Flammable Liquids, Gases, and Volatile Solids). In addition, existing mixing rules or correlations (for example, Le Chatelier's linear mixing law; see Kuchta [5], p. 14) are considered adequate for most loss prevention applications involving gaseous fuel mixtures. On the other hand, a large database for dusts that had been obtained using E 789 is now considered obsolete, and is being regenerated using E 1226. The second reason for the large frequency of dust cloud tests is the strong sensitivity of flammability, ignitability, and explosibility values to the particle size distribution of the sample. That is why different powder products made up of the same pure chemical need to be tested individually.

2. IGNITABILITY TEST METHODS

Minimum Ignition Energy (MIE)

Measured MIE values are highly sensitive to the test method, particularly the spark electrode geometry and the characteristics of the electrical discharge circuit. Therefore, standard test methods had to be developed so that comparable data could be obtained by different laboratories. ASTM standard test methods E 582 and E 2019 determine the lowest energy (stored by a capacitor and released as a spark) that will ignite gas–oxidant and dust cloud–oxidant mixtures, respectively. At any given fuel concentration, the minimum energy to ignite can be determined. By testing over a range of fuel

Is the dust explosible?
- Literature
- MSDS (?)
- "Go" or "No Go" test (E1226 or E1515)
- Thermochemical Analysis

Can the process make it explosible?
- Particle size reduction
- other dusts
- hybrid mixtures
- elevated T and P
- selective demixing

No

Yes   Yes

Good housekeeping
- Avoid accumulations
- Hot work permits

Explosion prevention and mitigation are necessary

Inform and motivate all employees.
Top management is responsible.

Ignition temperatures by E1491 & E2021

Compile material hazard properties. Perform hazard and consequence analysis. Implement prevention and mitigation designs

P_{max} and K_{St} by E1226 method

Control process and surface temperatures to prevent ignition of dust clouds and deposits

Deflagration
- flame speed
- containment
- venting
- suppression
- isolation

MEC by E1515

MIE E2019 and Powder Resistivity

LOC (WK1680)

Control suspended dust & dust accumulations that could be dispersed

Electrostatic control
- bonding and grounding
- antistatic material
- additives
- shoes, clothing

Inerting
- process
- powder

Figure 1. Dust explosion protection philosophy (adapted from Figure 7.2 of Eckhoff [4]).

concentrations, the lowest MIE for a material can be determined for the optimum or most easily ignited mixture.

Minimum Ignition Energy of Gaseous Mixtures—E 582

The ASTM standard test method E 582 for "Minimum Ignition Energy and Quenching Distance in Gaseous Mixtures" is based on research conducted at the U.S. Bureau of Mines in the 1950s and 1960s. E 582 for gases uses a simple high voltage (up to 30 kV) spark circuit designed to minimize inductance, stray capacitance, and current leakage from the power supply. These design features are implicit in the procedure described in the Bureau of Mines publication by Litchfield et al. [6].

The test procedure starts with addition of gases into the test vessel. When the proper gas mixture has been formed, a spark is generated between electrodes. The spark gap distance can also be varied. Ignition or non-ignition is determined by visual observation. A series of tests over a range of fuel concentrations determines the MIE at the most easily ignited concentration. The test

method also allows determination of the parallel-plate ignition quenching distance, which is comparable in magnitude to the quenching diameter and the maximum experimental safe gap ("MESG"). Among various provisions of the ASTM E 582 standard method is that the spark circuit should have negligible inductance and low capacitance. The smallest MIE values are typically found using low-capacitance circuits with correspondingly low time constants. A discussion of these features, with reference to experimental data, can be found in Chapter 3-5.4 of a recent CCPS Concept Book by Britton [7]. It is also shown that, although the lowest MIE values should in principle be obtained with pointed electrodes and a very low circuit capacitance, the higher voltages needed to compensate for a very low capacitance tend to cause corona losses from pointed electrodes. Thus, pointed electrodes are not generally used for MIE measurements of gases.

The reported MIE is normally the stored energy that is just sufficient to ignite the optimum mixture at the optimum gap length, although the option exists to also report the MIE calculated by integrating the measured voltage and current across the spark gap. In principle,

Table 2. Survey results of ASTM E27 method usage by 14 laboratories.

ASTM Method	Title	Average Annual Use
Subcommittee E27.04 on the Flammability and Ignitability of Chemicals		
E 502	Flash Point of Chemicals by Closed Cup Methods	212
E 582	Minimum Ignition Energy and Quenching Distance	11
E 659	Autoignition Temperature of Liquid Chemicals	56
E 681	Concentration Limits of Flammability	34
E 918	Limits of Flammability at Elevated Temperature and Pressure	8
E 1232	Temperature Limit of Flammability of Chemicals	2
E 2021	Hot-Surface Ignition Temperature of Dust Layers	59
E 2079	Limiting Oxygen (Oxidant) Concentration in Gases and Vapors	8
Subcommittee E27.05 on Explosibility and Ignitability of Dust Clouds		
E 789	Dust Explosions in a 1.2-L Closed Cylindrical Vessel	118
E 1226	Pressure and Rate of Pressure Rise for Combustible Dusts	797
E 1491	Minimum Autoignition Temperature of Dust Clouds	155
E 1515	Minimum Explosible Concentration of Combustible Dusts	189
E 2019	Minimum Ignition Energy of a Dust Cloud in Air	650
WK1680*	Limiting Oxygen Concentration in Dust Clouds	56

*Note: WK1680 is not a currently published standard, but a working draft.

this would yield a smaller MIE value because of energy losses in the circuit.

For most fuel gases and vapors, the MIE is <1 mJ, and therefore ignition control strategies cannot be used as the sole means of explosion protection. A paper by Ural [8] discussed how the commercial aviation sector, after a series of deadly fuel tank explosions, has rediscovered how very difficult it is to limit the spark energy in practice. Commercial airplane manufacturers had been attempting to design fuel tanks so that the maximum credible electrical spark energy is less than one-tenth the jet fuel MIE, and relying on the lack of ignition sources as the sole means of fire prevention. Jet fuel has an MIE of <1 mJ.

For low MIE gases and vapors, ignition control efforts are still useful because they may reduce the frequency of ignition incidents. The MIE can vary by several orders of magnitude, depending on the types and concentrations of fuel and oxidant, plus the temperature and pressure. Further, the operating conditions might be such that the optimum mixture cannot form, in which case some higher MIE value might be taken to represent worst-case conditions for a particular process.

Example of Evaluating the Ignition Hazard of a Gas Mixture

There is no accepted method of calculating the ignition energy of a mixture of two or more fuel gases from the values corresponding to the separate components. A possible method for determining MIEs for mixtures of "C + H + O + N" organic fuels has been developed, but has not yet been fully evaluated [9]. If, for example, the mixture contains easily ignited components such as hydrogen, plus hard-to-ignite components, such as ammonia, ASTM E 582 should be used to determine at what hydrogen concentration the mixture

becomes ignitable at an assumed effective energy level. For example, the latter might be taken as 10 mJ to represent corona and brush discharges from plastic surfaces, or 25 mJ to represent sparks from ungrounded personnel [7].

Alternatively, ASTM E 582 might be used to evaluate the benefits of reducing the oxygen concentration relative to that available from ambient air. As nitrogen or other inert gas is added to air, its strength as an oxidizer diminishes, and the MIE of optimum fuel–oxidant mixtures increases by orders of magnitude. If the maximum effective energy of ignition sources present in a system can be determined, partial inerting might be used to complement existing explosion protection systems. For instance, the frequency of activation of a suppression system might be minimized. Alternatively, the ignition hazard resulting from an upset in a nitrogen–air mixer serving an inhibited monomer storage tank might be assessed.

E 582 can also be used to assess the increased hazards if the oxygen concentration is increased. As additional oxygen is added to air, for example by decomposition of a peroxide, the MIE of optimum fuel–oxidant mixtures decreases by orders of magnitude. Difficult-to-ignite gases may ignite readily and common solvents may be ignited by corona discharges and other very weak sources. NFPA 53 on "Recommended Practice on Materials, Equipment and Systems Used in Oxygen Enriched Atmospheres" and a series of ASTM publications, such as G-128 "Standard Guide for Control of Hazards and Risks in Oxygen Enriched Systems," provide detailed information on the hazards of oxygen-enriched systems.

Minimum Ignition Energy of Dust Clouds— E 2019

Test method E 2019 for "Minimum Ignition Energy of a Dust Cloud in Air" describes several electrical spark
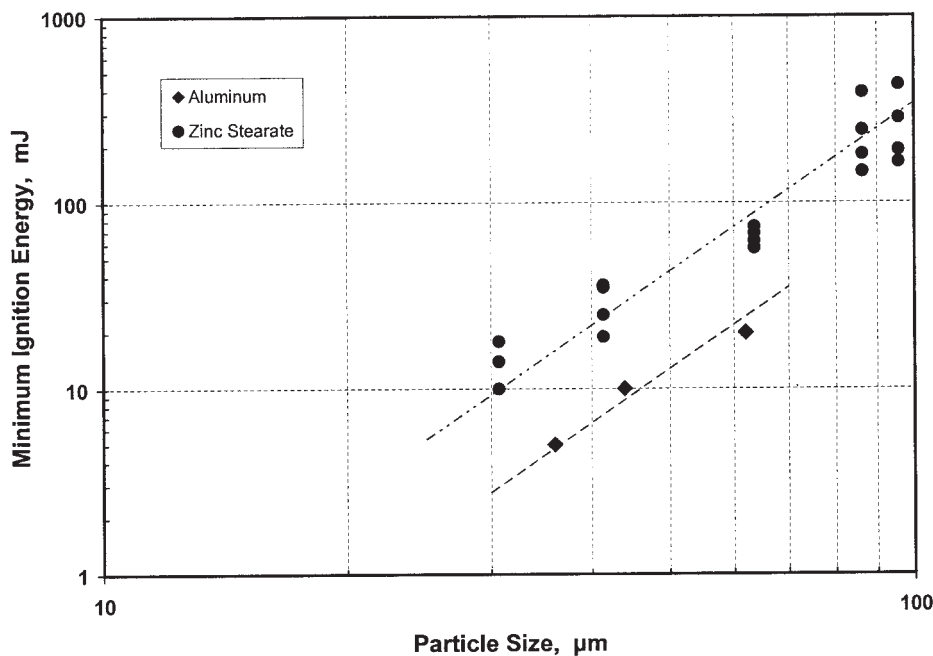
Figure 2. MIE data from E 2019 showing effect of particle size for two materials.

circuits in current use that have been found to yield comparable MIE results. Unlike E 582 for gases, E 2019 is a "performance standard," whereby the methodology adopted must produce data within the expected range for a series of reference dusts. E 2019 describes several suitable spark generating systems in an appendix, but other circuits may be used if they produce the same MIE values for the reference dusts. Attributed in part to the high dependency of dust MIE on physical characteristics such as particle size distribution and (in some cases) moisture content, plus the large ignition energies involved relative to most gases, there has been considerable variability in published "dust ignition energy" data even for pure chemicals such as sulfur. Apart from physical differences between samples of the "same" dust, the cause of much of the data scatter has been the design of the electrical circuit and the calculation of the energy released by the spark. It has been found that, unlike the case with most gases, the ignitability of dusts is dependent on the spark duration, which is directly affected by the spark-generating system (see Eckhoff [4], p. 407; and Eckhoff and Enstad [10]).

As alluded to above, many parameters affect the measured MIE value. These include concentration, electrical circuit, capacitors, inductance, electrodes/ spacing, ignition timing, turbulence, and the physical characteristics of the dust (surface area, moisture level, particle size). Therefore, it would be virtually impossible to find the absolute minimum energy required for ignition. Given that, for all practical purposes, there is no "absolute" value for dust MIE, it is difficult to assess the accuracy of a particular value except by reference to other values measured for an identical sample. Thus, E 2019 is a performance-based standard to measure the relative MIE of dusts. Calibration tests for each apparatus and circuit must be performed with at least three

different reference dusts. Reference data for four dusts are listed in E 2019. The range of MIE values listed for each dust provides some information on the typical scatter in the data for different MIE circuits. With some circuits, dust MIE values are determined only to within a factor of about three. E 2019 allows the reporting of a specific MIE value or the reporting of an MIE range, whose ratio is a factor of about 3. For example, the MIE of lycopodium powder can be reported as either about 20 mJ or 10–30 mJ, using one of the circuits listed in E 2019. The method does permit interlaboratory differences as large as a factor of 10.

Examples of four suitable spark-generating systems are described in Appendix X1 of E 2019. Three of these are high-voltage capacitance circuits (10–30 kV) triggered by (1) an auxiliary spark in a three-electrode system, (2) a moving electrode, or (3) a slowly increasing voltage across the gap. The fourth circuit involves energy storage at a lower voltage (<2.5 kV) and triggering by a low-energy, high-voltage pulse applied across the gap. This pulse is generated by discharging a small capacitor through a transformer whose secondary winding is connected in series with the spark gap.

Figure 2 shows the effect of particle size on the MIE of a dust. The aluminum MIE data (diamonds) are from Eckhoff ([4], p. 33), and are plotted vs. the particle size of the samples. The zinc stearate data (circles) are from an unpublished ASTM E27.05 round-robin study among four different labs, all using the slightly modified Eckhoff circuit, which is referred to in E 2019 as the "Triggering by Auxiliary Spark." The scatter of the data points in Figure 2 is a good indication of the interlaboratory reproducibility of the MIE test results for samples with narrow particle size distributions. A polydisperse sample can be expected to show a wider range of MIE values. As illustrated by the dashed lines through the

data points in Figure 2, the data sets for both dusts appear to support the theoretical expectation that MIE is proportional to approximately the cube of the particle size (see Eckhoff [4], p. 32).

Examples of Safety of Additives and Special Procedures

A choice of antioxidants for a granular polyolefin production facility may represent different chemical and physical options. One consideration is the MIE of the additive compared with that of the polymer. If the MIE is less than that of the polymer, the likelihood of ignition will be increased in accumulation sites such as baghouses. The likelihood of ignition may also increase in bins, especially if the additive MIE is <10 mJ. Options include a different additive whose MIE is greater when tested at the same particle size, or to purchase an additive that is coarser. For example, a sub-400 mesh additive, whose MIE is <10 mJ, could be replaced by a coarser additive that contains no material having an MIE < 20 mJ.

Many companies have adopted policies to restrict handling of dusts below some prescribed MIE value. They may also inert conveying systems and storage bins for a dust with MIE below some value. The "action level" adopted varies with operating experience but is typically ≤10 mJ. This is the effective energy normally ascribed to bulking brush discharges, which are believed responsible for dust ignition in properly grounded equipment [11, 12].

Autoignition or Spontaneous Combustion

A series of ASTM E27 standards address spontaneous combustion of gas mixtures (E 659), dust clouds (E 1491), and dust layers (E 2021). There is no ASTM test addressing spontaneous ignition of bulk solids. The principal application of these test methods is to define the maximum acceptable surface temperature in a particular area, usually for electrical classification purposes. Other applications include qualitative assessment of hazards inside process equipment rather than external to it (such as bucket elevator bearings).

Autoignition Temperature of Liquids—E 659

ASTM standard test method E 659 measures the "Autoignition Temperature of Liquid Chemicals." A liquid or adequately volatile solid sample is added to an open-neck glass flask held inside a furnace. The quantity of added sample is systematically varied to determine the lowest temperature at which hot-flame ignition occurs, based on visual observation. This is the autoignition temperature (AIT). Additional test observations that may be reported are the lowest temperature at which cool flames are observed (cool flame temperature (CFT) [13]) and the lowest temperature at which exothermic, nonluminous preflame reactions are observed [reaction threshold temperature (RTT)]. The AIT is the most widely used of these parameters and is commonly listed in data compilations.

Approximately 30 years ago, ASTM E 659, which uses a spherical 500-mL flask, replaced ASTM D 2155, which used a smaller 200-mL flask. AIT values measured in the 500-mL flask can be ≥10° C lower, largely because of a higher ratio of heat generation to heat removal in the larger flask. However, another reason for adopting the larger 500-mL borosilicate glass flask was to reduce catalytic wall effects, which could lead to spuriously low AIT values for certain chemicals. Because the 500-mL flask size has not been adopted everywhere, two disparate databases continue to be generated.

In practice the AIT is affected by any factor altering the relative rates of heat generation and removal, such as the size, shape and surface material of an enclosure, convective conditions and residence time, plus the composition and pressure of the reacting mixture. Therefore autoignition data must be applied carefully. Several papers have been written on this subject [14–22]. Large-scale equipment presents a greater hazard than small-scale equipment because heat generation increases faster than heat removal (or natural losses) as the scale increases. For large-scale chemical processes, the CFT and RTT parameters may also need to be considered. For instance, if a solvent vapor–air mixture is heated in a large atmospheric process vessel, "cool flames" might trigger two-stage ignition at much less than the "standard" AIT. The CFT may be on the order 50–100° C less than the AIT, whereas exothermic preflame reactions may occur at appreciable rates at still lower temperatures. The situation becomes more complicated if pressures other than atmospheric are involved because the effect of pressure can be highly irregular. In general, expert advice should be taken when assessing situations involving large scale or high pressure.

Example of Applying Equipment "T Code" for Gases and Vapors

Article 500.8 of NFPA 70, also known as the National Electrical Code, provides that "Class I equipment shall not have any exposed surface that operates at a temperature in excess of the ignition temperature of the specific gas or vapor." The AIT measured using E 659 is often used directly for evaluating the hazard of autoignition arising from electrical equipment. In this case the measured AIT is considered synonymous with "ignition temperature" in the field because it is tacitly assumed that hot surfaces in a classified area cannot trap stagnant volumes of gas–air mixture significantly larger than those used in the standard test and that no significant surface catalysis occurs.

AIT data compilations are given in NFPA 325 and NFPA 497, "Recommended Practice for the Classification of Flammable Liquids, Gases, or Vapors and of Hazardous (Classified) Locations for Electrical Installations in Chemical Process Areas." However, these data compilations do not address mixtures and there is no available method for combining individual component data. Also, data compilations often use the lowest published AIT value, which can unnecessarily increase operational costs in cases where a commercial-grade chemical (such as hexane) displays a range of AIT values, depending on the components actually present. Finally, most of the compiled data predate the current ASTM E 659 method and can involve tests conducted in either larger or smaller vessels. It is therefore assumed

here that a new AIT determination is conducted using ASTM E 659.

Table 500.8(B) of Article 500.8 of NFPA 70 shows a list of 14 possible temperature classes (T codes) that are to be marked on nameplates for Class 1 equipment. Each T code has a corresponding "maximum safe operating temperature." For example, code "T1" corresponds to a temperature of 450° C and code T6 to 85° C. Article 500.8 provides that the maximum equipment temperature, as indicated by the T code, not exceed the ignition temperature of the specific gas or vapor to be encountered. A particular item of equipment is often available with a range of different T codes, depending on the needs of the purchaser. Thus, the AIT of the specific gas, vapor, or mixture present in an area can determine which manufacturer or style of equipment is purchased and at what cost.

A similar AIT application is to determine the maximum safe operating temperature of other hot surfaces in a classified area, such as process or utility pipelines. It might be determined that additional insulation is required to reduce the external temperature. Provided large stagnant pockets of gas–air mixture are not trapped by the hot surfaces involved, the AIT is normally a conservative measure of the ignition temperature. Exceptions include certain reactive chemicals whose ignition temperatures are lowered by rusty surfaces.

Dust Cloud Autoignition Temperature—E 1491

In ASTM standard test method E 1491 for "Minimum Autoignition Temperature (MAIT) of Dust Clouds," dust is dispersed into a heated furnace set at a predetermined temperature. The dust cloud is exposed to the heated furnace walls for several seconds. A visible flame exiting the furnace provides evidence for ignition. The dust concentration and temperature are systematically varied to find the lowest temperature at which self-ignition occurs for the most easily ignited dust concentration. Four different furnaces are described in ASTM E 1491 as suitable for MAIT measurement: the 0.27-L Godbert–Greenwald Furnace, the 0.35-L BAM Oven, the 1.2-L Bureau of Mines Furnace, and the 6.8-L Bureau of Mines Furnace. As for the dust MIE standard, this is a performance standard. Any apparatus used must produce MAIT values within the range of data listed for several standard reference dusts. Each furnace yields slightly different MAIT data, with the largest deviations occurring at the greatest MAIT values. However, the lower MAIT range is of more practical importance and here the agreement is much better (for example, 265 ± 25° C for sulfur). Comparison MAIT data for the four furnaces are listed in E 1491 and in publications by Conti et al. [23, 24]. In most practical cases, such as dryers, the operating temperature is significantly below the measured MAIT of the dust cloud.

Dust Layer Ignition—E 2021

ASTM standard test method E 2021 for "Hot-Surface Ignition Temperature of Dust Layers" uses a constant-temperature hot plate to heat the dust layer on one side only. It is based mainly on a test method described in
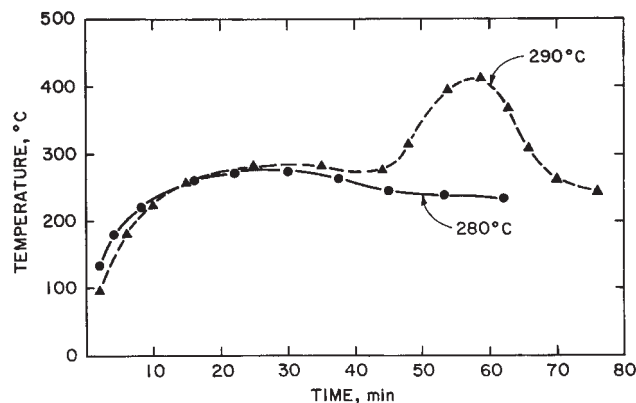

Figure 3. Example data from hot surface ignition temperature test E 2021.

a publication by Miron and Lazzara [25]. Routine tests use a 12.7-mm (0.5-in.) thick layer, which might simulate a substantial build-up of dust on the outside of hot equipment. However, because the ignition temperature normally decreases substantially with increasing dust layer thickness, the method allows layer thickness to be varied according to the application. This can depend on the user's housekeeping standards. Typical hot-plate data are shown in Figure 3. In E 2021, ignition is defined as a temperature rise in the dust layer of at least 50° C above the hot-plate temperature or visible evidence of combustion, such as a red glow or flame. In Figure 3, the dust layer did not ignite in a test starting at an initial temperature of 280° C, but did ignite at an initial test temperature of 290° C.

The dust layer ignition temperature measured with E 2021 is usually less than the dust cloud MAIT measured with E 1491. This is because the duration of the layer test may be hours as opposed to the few seconds that a dust cloud is suspended in a furnace. However, some exceptions occur. One possible reason for the cloud MAIT being less than the layer ignition temperature is if melting occurs. This excludes combustion air from a layer but not from a suspension of dust particles. If the layer ignition temperature is near the softening or melting point, increasing the layer thickness may promote ignition rather than melting. Another possible reason for a lower cloud ignition temperature is a dust with a high thermal conductivity, such as some metal powders [26]. The high thermal conductivity prevents the localized build-up of temperature within the layer.

Because of the great dependency of dust layer ignition temperature on test conditions, especially layer thickness, data of uncertain origin should not be used for direct comparison purposes. Indeed, many "dust layer ignition temperature" data reported in older publications were determined using a basket held in the so-called modified Godbert–Greenwald furnace [27], in which a small sample was heated from all sides.

It should be noted that the lowest ignition temperature for a dust corresponds to bulk heating under conditions that cause the dust to be heated from all sides. This is the situation for very thick dust layers, accumulations inside heated equipment such as dryers,

or large piles of dust. Neither the dust cloud MAIT nor the dust layer hot-surface ignition temperature is appropriate for these scenarios. Instead, either scaled isothermal basket tests or adiabatic calorimetry (with an appropriate mathematical model tying the reaction rate to heat and air flow) should be used. The Frank–Kamenetskii equation is often used to model this situation [28].

Example of Applying Equipment "T Code" for Dusts

This is similar to the example for gas/vapor T code but with two important differences affecting data application. These involve first, the definition of "ignition temperature," and second, the provision of a maximum allowable surface temperature for dusts that may dehydrate or carbonize.

Article 500.8 of NFPA 70 provides that "The temperature marking specified in 500.8(B) shall be less than the ignition temperature of the specific dust to be encountered. For organic dusts that may dehydrate or carbonize, the temperature marking shall not exceed the lower of either the ignition temperature or 165° C (329° F)."

The user of NFPA 70 is referred to a compilation of "dust ignition temperatures" presented in Table 2-5 of NFPA 499, Recommended Practice for the Classification of Combustible Dusts and of Hazardous (Classified) Locations for Electrical Installations in Chemical Process Areas, which states: "The ignition temperature of a dust layer is a function of the type of dust and its physical and chemical properties and is often less than the cloud ignition temperature. The ignition temperature shown in Table 2-5 is the lower of the two." The data compiled in Table 2-5 of NFPA 499 are not derived from consistent test methods nor were both dust cloud and layer ignition temperatures available in all cases. Ideally, both ASTM E 1491 and E 2021 should be run to determine the lowest ignition temperature of a representative dust sample, addressing both chemical and physical properties. Assuming that the layer ignition temperature is less than the cloud MAIT, the layer tested should be thick enough to represent "worst credible case" accumulations. There is, however, no formal guidance with respect to dust layer thickness used in either NFPA 70 or NFPA 499. This is attributed to the fact that, until recently, the majority of dust layer ignition temperature data were generated using the "modified Godbert–Greenwald furnace," where the layer thickness was not a test parameter.

3. FLAMMABILITY LIMIT TEST METHODS

The ASTM E27 Committee developed and now maintains separate flammability test standards for gas/vapor–air and dust–air mixtures. For gaseous fuel concentration limits, there is a lower flammability limit (LFL) and upper flammability limit (UFL). For dusts, only the lower flammability limit or minimum explosible concentration (MEC) is of practical importance [29]. Although the term "LFL" has been more commonly used for gases and the term "MEC" used for dusts, they both refer to the lowest concentration of fuel that can propagate a flame when mixed with air or another oxidizer. In addition to the fuel concentration limits,

E27 has a standard for the limiting oxygen concentration (LOC). Oxygen concentrations above the LOC allow flame propagation and oxygen values below the LOC prevent flame propagation. For the LFL, UFL, MEC, or LOC, the flammability limit occurs when the heat release rate is insufficient to allow self-sustaining flame propagation through the fuel–air mixture. The object of these E27 test methods is to determine scientifically sound values for flammability limits of materials. To apply these values to practical situations, appropriate safety margins are available in NFPA 69.

Flammability Limits of Gases and Vapors—E 681 and E 918

ASTM standard test method E 681 determines the "Concentration Limits of Flammability of Chemicals (Vapors and Gases)" at atmospheric pressure and temperatures up to 150° C. It aims to simulate the behavior of large volumes of test mixture with respect to the lowest (LFL) and highest (UFL) fuel concentrations that can propagate a flame through a homogeneous mixture with air (or other oxidant no stronger than air). For most fuels, a 5-L spherical glass test vessel is used. For fuels that have large quenching distances and that may be difficult to ignite, a special procedure in Annex A1 of E 681 recommends the use of a 12-L spherical flask. The gaseous mixtures are subjected to electrical spark ignition source, and the absence or the presence of flame propagation is determined visually. Recognizing the subjectivity of the visual flame propagation assessment for near-limit mixtures, some laboratories use video-recording systems for subsequent analysis. Although lower and upper flammability limits have already been determined for many common fuels (see NFPA 325 or MSDSs), the method is still useful for new products, such as the new ozone-friendly refrigerants, and for some mixtures. In many cases, Le Chatelier's linear mixing law (see Kuchta [5], p. 14) is appropriate for estimating the LFL values of gas mixtures. Appropriate safety margins for the practical application of LFL and UFL data are available in NFPA 69.

ASTM standard practice E 918 is used for "Determining Limits of Flammability of Chemicals at Elevated Temperature and Pressure." It can be used at initial temperatures up to 200° C and initial pressures to 1.38 MPa (200 psia). The pressure resistant metal test vessel is a vertical cylinder, 1-L in size, which is smaller than that used in E 681. However, vessel size effect may not be as important for tests at high initial pressure because the quenching distance decreases with increasing initial pressure. Electrically exploding fuse wire is used as an ignition source. E 918 uses a pressure criterion for flame propagation, which is much less subjective than the visual method used in E 681. Flame propagation is defined as a combustion reaction that produces at least a 7% rise above the initial absolute test pressure. The data from this test can be useful for evaluating the hazards in process vessels that operate at elevated temperature and pressure.

A review article describing the evolution of flammability test methods, recently published by Britton [30], indicates that current European test methods are generating erroneously wide "flammable limits" by "over-

driving" small, vertical test vessels. The lower flammable limits (LFLs) of organic fuels in air agree quite well with the predictions of a "heat of oxidation" model [9], provided the LFL data are generated in a vessel of adequate size such as required in ASTM E 681. The absolute error caused by "overdriving" the ignition process in small test vessels is far greater at the UFL than at the LFL. This can cause unnecessary expense when the data are applied to large or high-throughput systems that are intentionally operated above the UFL.

Example of Deflagration Prevention by Control of Combustible Concentration

The objective is to operate outside the flammable range (below the LFL or above the UFL) using appropriate safety factors (such as those in NFPA 69) to mitigate errors in either the gas concentration monitoring or the flammable limit measurements. In some process systems, the composition may vary both spatially and temporally, whereas there may be additional monitoring instrumentation errors caused by calibration offset and/or time lag. Where such effects make it impractical to operate above the gas mixture UFL, such as in some vent-collection headers, it is common practice to add a sufficient concentration of "enrichment gas" to cause the net fuel composition to always be above the UFL, regardless of how the vent stream composition may change. Similarly, some early suppression systems used fuel as the suppressant.

Chapter 6 of NFPA 69 provides that after the appropriate LFL for the combustible components has been determined, addressing all operating conditions, the combustible concentration shall be maintained at or below 25% of the LFL. The exception for gas-phase systems is where automatic instrumentation with safety interlocks is provided, in which case the concentration shall be maintained at or below 60% of the LFL. This method is termed "deflagration prevention by combustible concentration reduction."

An alternative control method described in Chapter 5.7.3 of NFPA 69 permits operation above the UFL. This is a common strategy for atmospheric storage of liquids whose vapor pressures are high enough to maintain vapor concentrations above the UFL under all operating conditions. This method is included under "deflagration prevention by oxidant concentration reduction" in NFPA 69 because, arguably, when operating above the UFL the concentration of oxygen available from ambient air is insufficient to produce an ignitable mixture.

Specific guidance is given for near-atmospheric vent-collection headers in Chapter 5.7.3.2 of NFPA 69. Addition of at least 25 vol % of methane or natural gas can be used to render the gas stream nonflammable, provided no component of the stream has a UFL greater than that of hydrogen in air (75 vol %) and the vent header does not contain oxygen at a concentration greater than can be derived from ambient air. Marine vent-collection headers can also be rendered nonflammable by the addition of enrichment gas but the precise requirements are covered separately in Title 33.CFR (Part 154).

Flammability Limits of Dust Clouds—E 1515

ASTM standard test method E 1515 determines the "Minimum Explosible Concentration (MEC) of Combustible Dusts." Flammability limits, such as the MEC, are used to characterize safe operating conditions in industrial processes or plants. If the operating conditions and maintenance procedures can be maintained well below the MEC, then the hazard may be considered to be minimal. In the extreme, the E 1515 test may identify a dust as being inert or nonignitable at any concentration at the energy level used in the test. In practice, the MEC can be used to indicate the likelihood of explosions arising from accumulations of fugitive dust. These dust accumulations, if dispersed, may create a significant dust explosion hazard.

The testing procedure for E 1515 involves the dispersion of dust into a ≥20-L vessel and the initiation of a pyrotechnic ignitor. To determine the MEC, the dust concentration is reduced systematically until no deflagration occurs. The criterion for significant flame propagation is a pressure rise of at least 1 bar. This pressure criterion for dusts is much higher than that for gases in E 918 because a much stronger ignitor is used for the dust tests. The stronger ignitor is required because dusts are intrinsically much more difficult to ignite than gases. The criterion used in the 20-L chambers is based on comparison MEC tests in a much larger 1-m^3 (1000-L) chamber in a publication by Cashdollar and Chatrathi [31]. Examples of E 1515 data for two different dust samples are shown in Figure 4, where the corresponding MEC values are 30 and 80 g/m^3.

In MEC testing, the selection of the appropriate ignitor energy can be difficult, especially for hard-to-ignite materials. The importance of differentiating flammability limits from ignitability limits is discussed in E 1515 and Cashdollar and Chatrathi [31]. Therefore, tests may need to be repeated using different energy ignitors. If there is an uncertainty whether a strong ignition source is overdriving a deflagration in a 20-L chamber, E 1515 recommends that additional tests be conducted in a larger 1-m^3 chamber.

As seen in Table 2, the MEC method enjoys frequent use. Chapter 6 of NFPA 69 discusses explosion protection by control of dust concentration, including the appropriate safety margin below the measured MEC. Although it does not specifically reference E 1515, this would be the applicable test method for the MEC of the dust cloud for NFPA 69. E 1515 is identified as the standard test method in NFPA 654, Standard for the Prevention of Fire and Dust Explosions from the Manufacturing, Processing, and Handling of Combustible Particulate Solids; NFPA 664, Standard for the Prevention of Fires and Explosions in Wood Processing and Woodworking Facilities; and FM Data Sheet 7-76.

Example

Before installing vents in their dust collector, a company desired to determine whether an explosion hazard did exist. An MEC test was conducted on the explosive ingredient being used, and a value of 30 g/m^3 was found (see Figure 4). This is relatively low for a MEC and indicates the high hazard associated with this material. Engineering calculations and material recov-
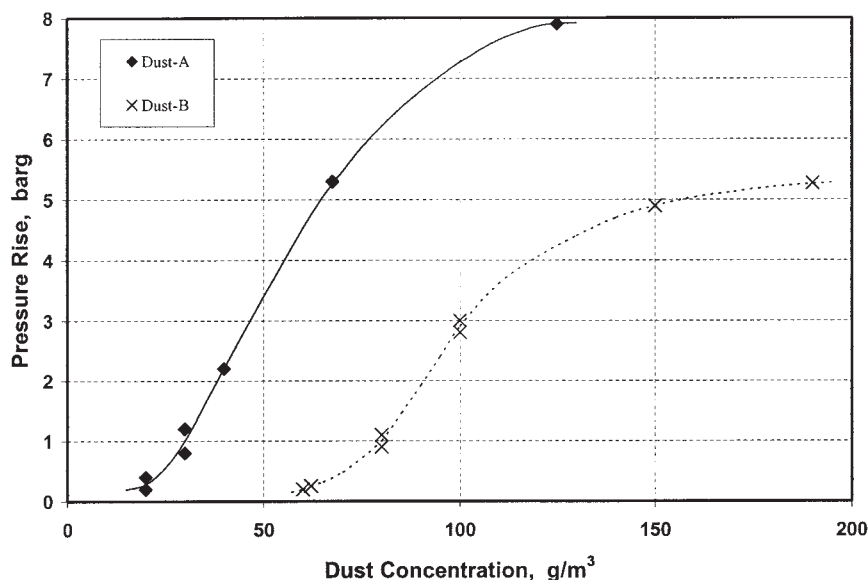
Figure 4. Typical data for determination of MEC for two dusts, using E 1515.

ery data indicated that the dust concentration in the collector could exceed this level, particularly during pulsing. Consequently, the decision was made to install explosion vents on the dust collector.

Limiting Oxygen Concentration for Gases— E 2079

ASTM standard test method E 2079 was published recently to measure the "Limiting Oxygen (Oxidant) Concentration in Gases and Vapors." Being a new method, E 2079 has been designed to address some problems associated with the E 681 and E 918 test methods [32]. E 2079 requires the test vessel to be at least 4 L in volume and to be nearly spherical. The ignition sources include a 10-J electric spark, a continuous electric arc, and a fuse wire. Where necessary, the use of stronger igniters is permitted. A 7% pressure rise criterion is generally used to establish flammability. E 2079 also provides advice on how to modify this pressure criterion when using the stronger igniters.

To determine the LOC, the fuel gas concentration and the oxygen concentration are systematically varied to find the limiting oxygen value at the most easily ignited gas mixture. The reported LOC value is the average of the lowest oxygen concentration that produced a deflagration and the highest oxygen concentration that did not. Chapter 5 of NFPA 69 addresses deflagration prevention by oxygen control, specifying appropriate safety factors when using LOC data, and it references E 2079.

The E27.04 subcommittee is also considering the development of a new standard test method to determine the lower and upper flammability limits of gases by using vessel size, ignition strength, and pressure criteria concepts similar to those in E 2079.

Limiting Oxygen Concentration of Dust Clouds—WK1680

ASTM Work Item WK1680 is a proposed or draft standard test method for "Limiting Oxygen (Oxidant) Concentration of Dust Clouds." A brief description and rationale for the LOC Work Item are listed at the ASTM E27 website. The proposed LOC for dusts is a working draft document available only to E27.05 subcommittee members. The LOC method is used to identify safe operating conditions for dusts when the oxygen concentration is controlled. In brief, the test method involves the dispersion of a dust into a chamber containing a gas mixture with a reduced oxygen concentration. The test procedures and propagation criterion are similar to those in E 1515. When determining the LOC, the oxygen concentration is gradually reduced until the dust cloud no longer ignites. To determine the LOC, the dust concentration and the oxygen concentration are systematically varied to find the limiting oxygen value at the most easily ignited dust concentration. The proposed method is based on comparison LOC data from 20-L and 1-m^3 chambers in a publication by Going et al. [33]. For dust systems where explosion venting or suppression is not practical, the reduction of the oxygen level below the LOC can be a useful protection measure. Advice on the appropriate safety margin to use in industrial plants is available in NFPA 69.

Temperature Limits

Flash point is considered a material hazard property, perhaps the most frequently used in fire protection engineering. ASTM defines flash point as "the lowest temperature, corrected to a pressure of 101.3 kPa, at which application of an ignition source causes the vapors of the specimen to ignite under specified conditions of test." As this definition suggests, the flash-point values can be significantly influenced by the test apparatus and the test method. In general, the open-cup flash-point tests yield higher flash-point values than those in the closed-cup tests. It is also important to recognize that significant differences may exist even among the values obtained from different closed-cup test methods. Unfortunately, flash-point data reference

tables (such as NFPA 325) are populated with values of unknown origin, perhaps because of the varying influences of different industries in the consensus standard-making processes. For example, NFPA 30, Flammable and Combustible Liquids Code, defines flash point as "the minimum temperature of a liquid at which sufficient vapor is given off to form an ignitable mixture with the air, near the surface of the liquid or within the vessel used, as determined by the appropriate test procedure and apparatus specified" in that standard. NFPA 704, Standard System for the Identification of the Hazards of Materials for Emergency response, on the other hand, does not specify a test method, and defines flash point as "the minimum temperature at which a liquid or a solid emits vapor sufficient to form an ignitable mixture with air near the surface of the liquid or the solid." The ASTM E27 Committee has two standards to address some of the problems in this arena.

Flash Point Test Method Selection and Use—E 502

ASTM E27 Standard Test Method E 502 for "Selection and Use of ASTM Standards for the Determination of Flash Point of Chemicals by Closed Cup Methods" gives advice for the use of flash-point methods developed by other ASTM committees. Despite being one of the earlier standards of the E27 Committee, E 502 is still widely used and referenced today (see for example, NFPA 1, 30, 35, 77, 115, 385, and 704). This test method covers the determination of the flash point of liquid and solid chemical compounds flashing from below −10 to 370° C (16–700° F). E 502 uses the procedures and apparatus in ASTM Test Methods D56, D93, D3278, D3828, and D3941. It provides additional explanatory notes and procedure modifications not contained in the individual methods. E 502 also permits determination of flash point for solids and highly viscous liquids. For a given fuel viscosity and anticipated flash-point range, the user is advised which particular test is suitable.

E 502 offers a valuable discussion, providing insight into some of the dangerous or curious results obtained from flash-point tests. First, the flash point does not represent the minimum temperature at which a material can evolve flammable vapors. With the exception of certain equilibrium test methods, most flash-point tests are run at a finite heating rate, and thus vapor concentrations are not representative of equilibrium conditions. Flash-point testing uses downward and horizontal propagation of flame. Flame propagation in these directions generally requires slightly higher vapor concentrations than those required for upward flame propagation. The flame is introduced at a finite distance above the liquid surface. Because the vapors are denser than air, the vapor concentration is slightly higher at the liquid surface than that at the flame position. There are instances with pure materials where the absence of a flash point does not ensure freedom from flammability. Included in this category are materials that have large quenching diameters (such as halogenated hydrocarbons or certain aqueous acetic acid solutions). Such materials will not propagate a flame in any apparatus the size of a flash-point tester. However, its vapors may be flammable and may burn when

ignited in a larger process or storage vessel. Some materials having very dense vapors, a narrow range of flammability, or the requirement for being somewhat superheated to burn will not exhibit a flash point with conventional test methods, but can form flammable vapor–air mixtures if heating and mixing are optimum and the temperatures are raised.

In specific instances, contrary to usual behavior, the open-cup flash point may be at a lower temperature than the closed-cup flash point. Conventional flash-point tests can also introduce large errors when the fuel is a mixture or contains flammable impurities. A liquid containing flammable and nonflammable components can evolve flammable vapors under certain conditions while not exhibiting a closed-cup flash point. This phenomenon is observed when a nonflammable component is sufficiently volatile and present in sufficient quantity to inert the vapor space of the closed cup. In many instances, liquids of this type will exhibit an open-cup flash point. In certain cases the material may exhibit no flash point, either open or closed, but when spilled it may become flammable after the nonflammable component has evaporated. Therefore, it is important to test samples that have been weathered to an extent comparable to the material in the process stream. It is also important to keep in mind that liquids containing a highly volatile nonflammable impurity, which exhibit no flash point because of the influence of the nonflammable material, may form flammable mixtures if totally flash vaporized in air in the proper proportions. Some mixtures of water and hydrocarbons, or low-volatility halogenated hydrocarbons and volatile hydrocarbons, may have low flash points but will not of themselves sustain burning. These materials can present explosion hazards in closed vessels but will not burn as a pool fire out in the open. Therefore, for process and storage vessels, E 502 recommends the use of E 1232, which is described below.

## Temperature Limit of Flammability of Chemicals—E 1232

ASTM standard test method E 1232 measures the "Temperature Limit of Flammability of Chemicals." The temperature limit of flammability test measures the minimum temperature at which liquid or solid chemicals evolve sufficient vapors to form a flammable mixture with air under equilibrium conditions. This test is designed to remedy limitations inherent in flash-point tests, and yields a result closely approaching the minimum temperature of flammable vapor formation for equilibrium situations in the chemical processing industry, such as in process vessels, storage tanks, and similar equipment. This test also allows the use of oxidant/diluent mixtures other than air, which need to be evaluated in cost-saving partial-inerting applications.

The result of the E 1232 test is deliberately differentiated from the flash point by using the term "lower temperature limit of flammability (LTL)." For standard test method E 1232, the LTL is defined as the lowest temperature (corrected to standard atmospheric pressure of 101 kPa) at which application of an ignition source causes a homogeneous mixture of a gaseous

Table 3. Comparison of E 1232 test apparatus with commonly used closed-cup flash-point test apparatuses.

Method/Apparatus	D56 Tag Closed	D93 Pensky–Martens	D3828 Setaflash	E 1232 LTL
Test volume shape	Cylinder	Cylinder	Cylinder	Sphere
Nominal vapor space volume, mL	67	46	19	5000
Sample volume, mL	50	75	2 or 4	50 or more
Stirrer	No	Yes	No	Yes
Heating rate	finite	finite	equilibrium	equilibrium
Ignition source	flame	flame	flame	spark
Ignition location	top	top	top	below center
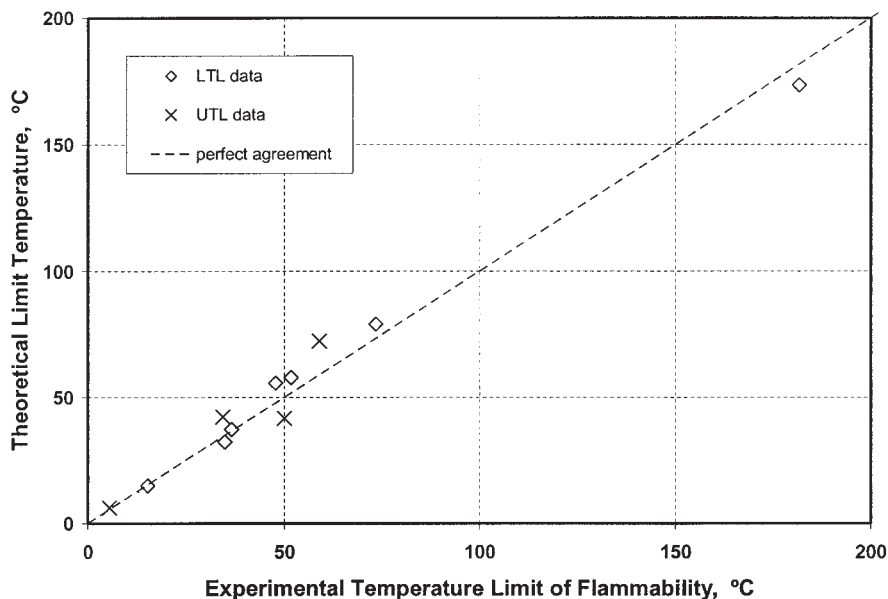
Figure 5. Comparison of experimental LTL values from E 1232 with theoretical values. UTL values are also given, although the method for determining UTLs is not specifically covered by E 1232.

oxidizer and vapors in equilibrium with a liquid (or solid) specimen to ignite and propagate a flame away from the ignition source. Unlike flash point, LTL is a true material property in most circumstances. The difference between the flash point and LTL increases as the flash point increases. It is important to recognize that LTL can be tens of degrees Celsius lower than the closed-cup flash point.

The E 1232 test apparatus is similar to that described in E 681. The 5-L test flask is placed in a heated chamber to ensure a controlled and uniform temperature. A pool of liquid sample is stirred in a closed vessel in an air atmosphere. The vapor–air mixture above this liquid is exposed to an ignition source and the upward and outward propagation of flame away from the ignition source is noted by visual observation. Temperature in the test vessel is varied between trials until the minimum temperature at which flame will propagate away from the ignition source is determined. A striking comparison of this apparatus with the common closed-cup flash-point test apparatuses can be found in Table 3.

Temperature limit of flammability results obtained by E 1232 are consistent with vapor pressure and con-

centration limit of flammability data. This provides a built-in check of results on pure materials that produce vapors obeying the ideal gas law at the test conditions, and leads to a high degree of confidence in the results obtained for mixtures. In Figure 5, from ASTM subcommittee data by Bodman et al. [34], experimental LTL values for a number of pure chemicals obtained using E 1232 show good agreement with the theoretical values, which are the computed temperatures at which the vapor pressure equals the LFL.

Although not specifically listed in the E 1232 test method, a modification of the E 1232 procedures has also been used to measure the upper temperature limit of flammability (UTL). Experimental data for UTL are compared with the calculated values in Figure 5. This capability, which is not available with conventional flash-point test methods, is useful for applications where explosion protection is achieved by operating above the UFL.

If the estimated LTL is significantly different from the temperature at which the LFL was measured, a correction to LFL may be required in the prediction of LTL. This is because LFL is somewhat dependent on tem-

perature. Certain chemicals (such as organic acids) exhibit a high degree of nonideal vapor-phase behavior, being highly associated in the vapor phase. To properly interpret the vapor pressure/volume percentage/weight percentage/temperature relationships, knowledge of the degree of nonideality (association and molecular weight) is necessary. (Concentration limits of flammability for these materials are generally expressed in terms of weight per unit volume.) The fact that E 1232 combines all-important aspects and bypasses such difficulties associated with predictions makes E 1232 a useful tool for hazard and consequence analysis, particularly for mixtures where accurate estimation of vapor pressure is often difficult.

4. TEST METHODS FOR MAXIMUM EXPLOSION CHARACTERISTICS

There are two ASTM E27 test methods for measuring the maximum pressure and rate of pressure rise (dP/dt) for dusts. The first is E 789, which uses a 1.2-L chamber and spark ignition. It can provide some information on the ignitability of dust clouds by a continuous electric arc, but the data are not recommended for explosion protection design. It has been kept by E27 mainly for historical reasons. The second method is E 1226, which uses a ≥20-L chamber and much stronger ignition sources. The data from it are recommended for use in explosion vent sizing by NFPA 68, Guide for Venting of Deflagrations.

There is currently no comparable ASTM test method for maximum pressure and rate of pressure rise for gases and vapors. Nonetheless, NFPA 68 uses the gas/vapor deflagration index value (K_G) for deflagration vent sizing for gases and vapors. The K_G value depends on dP/dt as does K_{St} for dusts (see the definition of K_{St} below).

It is well known that, when an atmosphere of a fuel and air is ignited, rapid combustion can occur. If this occurs in a confined space, the pressure increases in response to the rapid temperature rise. The result can be a destructive explosion. The requirements for this to occur are well known: fuel, oxidant, mixing, ignition, and confinement. The fuel needs to be dispersed or mixed with the oxidant. In the case of a solid, the fuel must be of sufficiently small particle size to be dispersed and burn rapidly. The maximum pressure developed and the rate of pressure rise are important input data for explosion protection design.

Pressure and Rate of Pressure Rise for Dusts—E 789 and E 1226

ASTM standard test method E 789 for "Dust Explosions in a 1.2-Liter Closed Cylindrical Vessel" is based on a 1950s Bureau of Mines test method described in a report by Dorsett et al. [27]. It is limited by the size and cylindrical shape of the test vessel and by the relatively weak electric ignition source. The data from this method are used as part of the criteria to identify combustible dusts for NFPA 70 area classification for dusts. E 789 says that the data should not be used for vent sizing or explosion containment design.

ASTM test method E 1226 for "Pressure and Rate of Pressure Rise for Combustible Dusts" was developed to correct the limitations of E 789. The data from E 1226

are recommended for deflagration vent design in NFPA 68. The test procedures are similar to those in ASTM E 1515. A well-dispersed dust cloud is formed in a ≥20-L chamber, nearly spherical in shape, and subjected to a strong pyrotechnic ignition source. A dust cloud is formed using the discharge of a small cylinder of compressed air. After a prescribed time delay, the highly turbulent dust cloud is ignited using a strong ignition source of known reproducible energy release characteristics. The pyrotechnic ignitors cause a significant pressure and this must be accounted for, especially when using a strong ignition source in a small chamber. For example, two 5-kJ igniters used in a 20-L chamber by themselves will cause an increase in pressure of about 1 bar. Appendix X1 of E1226 discusses corrections that can be made to P_{max} data generated in 20-L chambers using strong ignition sources. In some cases, it may be necessary to perform larger-scale testing to obtain reliable data.

The resulting pressure and rate of pressure rise are measured by appropriate instrumentation. Figure 6 shows typical test data from E 1226 for an individual test at a particular concentration of a particular dust. The rate of pressure rise and the explosion pressure are plotted vs. time. To obtain the maximum explosion data for the dust, tests are conducted over a wide range of dust concentrations (Figure 7). The peak values of P_{max} and $(dP/dt)_{max}$ from individual tests (for example, as shown in Figure 6, which are from a test at 500 g/m^3) are plotted in Figure 7. Then the explosibility parameters P_{max} (maximum pressure) and $(dP/dt)_{max}$ (maximum rate of pressure rise) are found at the worst-case dust concentration. The rate of pressure rise data are then size-normalized by the following equation:

$$K_{St} = (dP/dt)_{max} V^{1/3}$$

where K_{St} is the deflagration index and V is the chamber volume.

As with the other dust test methods, E 1226 is a performance standard. One suitable test chamber is listed in the appendix, but other chambers can also be used if their data match the data from a series of reference dusts. The test procedures in standard E 1226 are based on extensive comparison data between 20-L and 1-m^3 chambers by Bartknecht [35] and Siwek [36].

The primary use of the test data P_{max} and K_{St} is for the design of explosion protection systems: containment, venting, suppression, or isolation. Vent designs provide a relief area that will eliminate damage or limit damage to the process equipment to an acceptable level. The required vent area is calculated using equations from NFPA 68 and requires knowledge of the process (volume, temperature, operating pressure, design strength, and vent relief pressure) and of the fuel characteristics (P_{max} and K_{St}). The safety of the design is only as good as the explosibility data. Suppression is the active extinguishment of the combustion and again limits the explosion pressure to an acceptable level. Suppression designs require similar process and hazard data to determine the hardware requirements such as size, number, and location of suppressors; detection
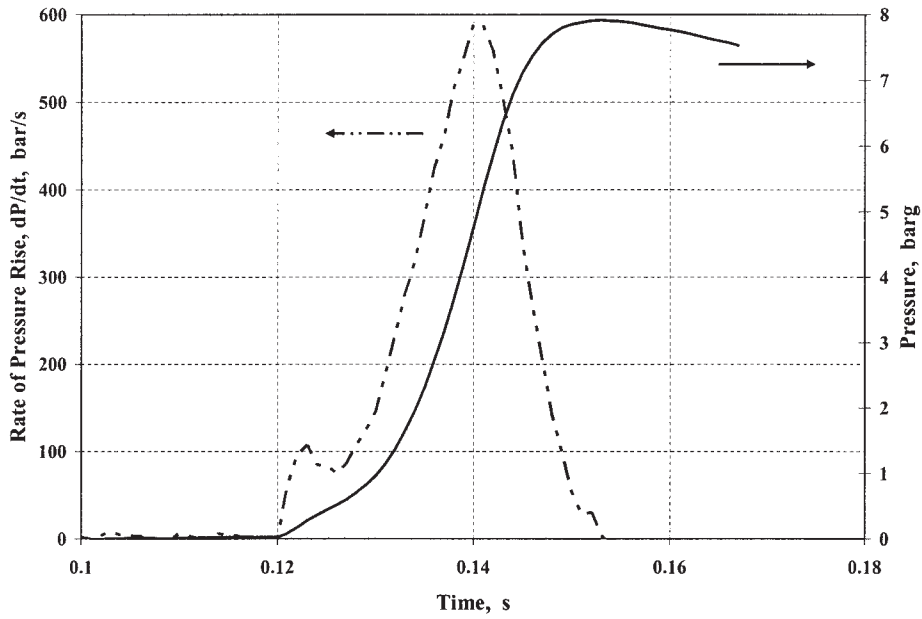
Figure 6. Data from E 1226 for pressure and rate of pressure rise for a dust explosion.
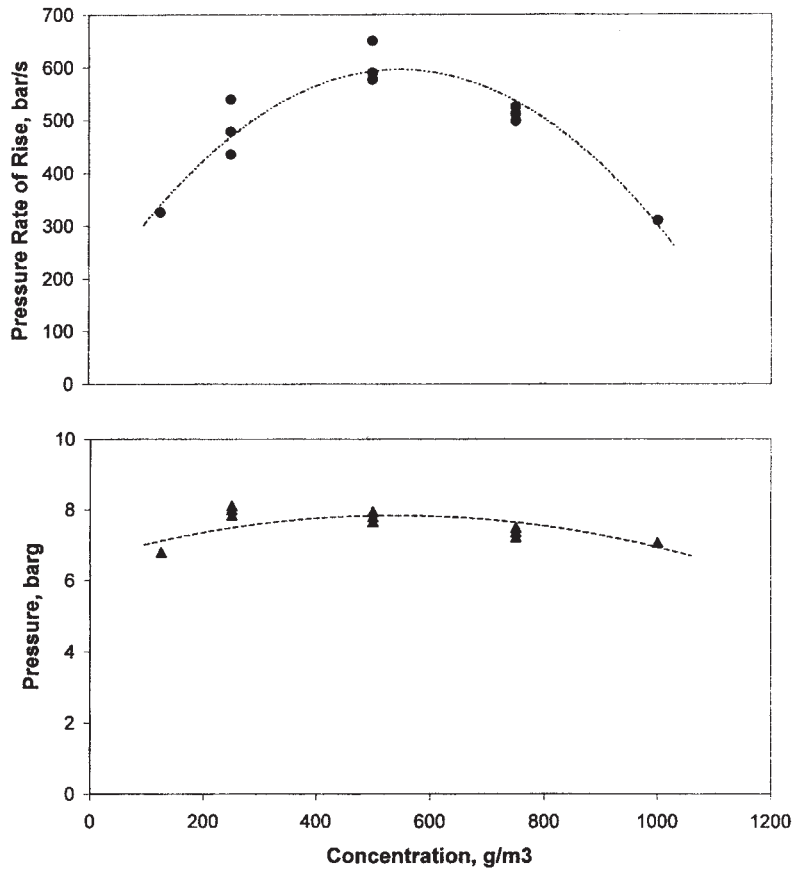

Figure 7. Rate of pressure rise and pressure vs. dust concentration from E 1226.

parameters; and the maximum pressure caused by the protected event. Isolation, which is the prevention of flame propagation through interconnections, requires

the same process and hazard data to determine hardware needs and locations.

From Table 2, E 1226 appears to be the most fre-

quently used ASTM E27 method for dusts. It is cited in numerous NFPA documents (1, 61, 68, 484, 654, 664, and 921) and Factory Mutual documents (Data Sheets 7-36 and 7-76). The K_{St} and P_{max} data are also used in hazard assessment, forensic analysis, and consequence modeling. They are also used to estimate the deflagration burning velocity, flame speeds, and induced gas and particle velocities [37, 38].

Example

A pharmaceutical company is processing an explosible ingredient through a spray dryer, cyclone, and dust collector. The cyclone is used for collection of the bulk of the material and the dust collector retains the fines. It is located outdoors and requires protection by venting. The only material available for testing was collected from the cyclone and gave a P_{max} value of 8.1 barg and a K_{St} value of 153 bar·m/s when tested by E 1226. When sieved to sub-200 mesh (<75 μm) and tested, the material gave P_{max} and K_{St} values of 8.3 barg and 242 bar·m/s, respectively. From the dirty volume of the dust collector of 250 ft^3 and a design strength of 3.0 psig, the NFPA 68 equation for $L/D < 2$ was used to calculate the required vent areas using 0.1 bar P_{stat} vents. The required area was 4.5 and 7.2 ft^2 for the coarser and finer material, respectively. Because the finer particles could be expected to be present in the dust collector, the larger vent area was selected for the design.

5. CONCLUSIONS

ASTM Committee E27 has produced and continues to produce important standard methodologies that are used for hazard evaluation. Dedicated use of these standards offers the following benefits:

- More reproducible data as a result of well-defined test methods.
- Reduced probability of incorrect data or data interpretation stemming from warnings on pitfalls that may negatively affect data generation and interpretation.
- The ability to verify adherence to test procedures by comparing test results on standard materials with those published in the Precision and Bias sections of the E27 standards.
- Simpler data interpretation and application attributed to the number of guides, standards (such as NFPA), and technical papers based on data from E27 methods.
- Reduced probability of accidents during testing arising from warnings regarding issues that may negatively affect safety.

The E27 standards greatly enhance the ability of an organization to produce accurate, meaningful data. Consequently, those organizations that practice these methods and apply the data to their processes have a competitive edge in that they are able to avoid reactive chemical accidents, fires, and explosions.

New technologies will require modification of existing test methods and development of new ones, and therefore the E27 Committee will continue to be active. Individuals knowledgeable in process safety testing are encouraged to become part of E27. Individuals that participate in E27 are able to influence the modification and development of standards and, perhaps more important, are able to establish contacts and interactions with individuals at other organizations. These contacts yield ideas on improvement of process safety testing methods and instrumentation. As with any volunteer organization, a key to success is to have active, enthusiastic, dedicated, and knowledgeable members participating. The current emphasis within companies to enhance performance in Environmental Health and Safety coupled with the Process Safety Management regulations (OSHA) makes the relevance of ASTM E27 activities more important than ever.

LITERATURE CITED

1. D. Frurip, L. Britton, W. Fenlon, J. Going, B.K. Harrison, J. Niemeier, and E. Ural, The role of ASTM E27 methods in hazard assessment Part I: Thermal stability, compatibility, and energy release estimation methods, Process Safety Prog 23 (2004), 266–278.
2. ASTM International, "General test methods," Annual Book of ASTM Standards 2004, Vol. 14.02, ASTM, West Conshohocken, PA, 2004. (Individual standards are also available from **http://www.astm.org**)
3. National Fire Protection Association (NFPA), Various publications and standards, including NFPA 1, 30, 35, 49, 53, 61, 68, 69, 70, 77, 115, 325, 385, 484, 497, 499, 654, 664, 704, and 921, NFPA, Quincy, MA. (NFPA publications are also available at **www.nfpa.org**)
4. R.K. Eckhoff, Dust explosions in the process industries, 3rd ed., Gulf Professional Publishing/Elsevier Science, Houston, TX, 2003.
5. J.M. Kuchta, Investigation of fire and explosion accidents in the chemical, mining, and fuel-related industries—A manual, USBM Bulletin 680, U.S. Bureau of Mines, U.S. Department of the Interior, Washington, DC, 1985.
6. E.L. Litchfield, E.L. Hay, T.S. Kubala, and J.S. Monroe, Minimum ignition energy and quenching distance in gaseous mixtures, RI 7009, U.S. Bureau of Mines, U.S. Department of the Interior, Washington, DC, 1967.
7. L. Britton, Avoiding static ignition hazards in chemical operations, American Institute of Chemical Engineers, Center for Chemical Process Safety, AIChE–CCPS Concept Book, New York, NY, 1999.
8. E.A. Ural, Airplane fuel tank explosions, Proc of the 37th Annual Loss Prevention Symposium, American Institute of Chemical Engineers, New Orleans, LA, March 30–April 3, 2003.
9. L. Britton, Using heats of oxidation to evaluate flammability hazards, Process Safety Prog 21 (2002b), 31–54.

10. R.K. Eckhoff and G. Enstad, Why are long electric sparks more effective dust explosion initiators than short ones?, Combust Flame 27 (1976), 129–131.

11. L. Britton, Static hazards using flexible intermediate bulk containers for powder handling, Process Safety Prog 12 (1993), 240–250.

12. T. Hoppe, N. Jaeger, and J. Terry, Safe Handling of Combustible Powders during Transportation, Charging, Discharging and Storage, Journal of Loss Prevention in the Process Industries, 13 (2000), 253–263.

13. B. Lewis and G. von Elbe, Combustion, flames, and explosions of gases, 3rd ed., Academic Press, New York, NY, 1987.

14. Setchkin, N.P. Self-ignition temperatures of combustible liquids, Research Paper 2516, J Res Natl Bur Stand 53 (1954), No. 49.

15. R.D. Coffee, Cool flames and autoignitions: Two oxidation processes, Loss Prev AIChE Tech Manual 13 (1980), 74–82.

16. D.C. Bull, Autoignition at hot surfaces, Proc of 2nd Int Symp on Loss Prevention and Safety Promotion in the Process Industries, Vol. III, 1977, pp. 165–172.

17. D.J. Lewis, Autoignition temperature determinations and their relationship to other types of potential ignition sources and their application to practical situations, Chem Process Hazards (IChemE Symp Series Issue) 58 (1980), 257–273.

18. D.C. Bull, L.R. Cairie, A.J. Harrison, and P.A. Morgan, Influence of natural convection on the critical conditions for hot surface autoignition, Proc of 3rd Int Symp on Loss Prevention and Safety Promotion in the Process Industries, 1980, pp. 8/634–8/646.

19. A.J. Harrison, R.M. Furzeland, R. Summers, and L.R. Cairnie, An experimental and theoretical study of autoignition on a horizontal hot pipe, Combust Flame 72 (1988), 119–129.

20. E.J. D'Onofrio, Cool flame and autoignition in glycols, AIChE Technical Manual: Loss Prevention, Vol. 13, AIChE, New York, NY, 1980.

21. T.J. Snee, Auto-ignition, slow combustion and the variation of minimum ignition temperature with vessel size, Loss Prev Bull 81 (1988), 25–38.

22. A.J. Harrison and L.R. Cairnie, The development and experimental validation of a mathematical model for predicting hot-surface autoignition hazards using complex chemistry, Combust Flame 71 (1988), 1–21.

23. R.S. Conti and M. Hertzberg, "Thermal autoignition temperatures from the 1.2-L furnace and their use in evaluating the explosion potential of dusts," Industrial dust explosions, K.L. Cashdollar and M. Hertzberg (Editors), STP 958, ASTM, West Conshohocken, PA, 1987, pp. 45–59.

24. R.S. Conti, K.L. Cashdollar, and R.A. Thomas, Improved 6.8-L furnace for measuring the autoignition temperatures of dust clouds, RI 9467, U.S. Bureau of Mines, U.S. Department of the Interior, Washington, DC, 1993.

25. Y. Miron and C.P. Lazzara, Hot-surface ignition temperatures of dust layers, Fire Mater 12 (1988), 115–126.

26. Jacobsen M., A.R. Cooper, and J. Nagy, Explosibility of metal powders, RI 6516, U.S. Bureau of Mines, U.S. Department of the Interior, Washington, DC, 1964.

27. H.G. Dorsett Jr., M. Jacobsen, J. Nagy, and R.P. Williams, Laboratory test equipment and test procedures for evaluating explosibility of dusts, RI 5624, U.S. Bureau of Mines, U.S. Department of the Interior, Washington, DC, 1960.

28. P.C. Bowes, Self-heating: Evaluating and controlling the hazards, Elsevier Science Publishers B.V., Amsterdam, 1984.

29. K.L. Cashdollar, Overview of dust explosibility characteristics, J Loss Prev Process Ind 13 (2000), 183–199.

30. L. Britton, Two hundred years of flammable limits, Process Safety Prog 21 (2002a), 1–11.

31. K.L. Cashdollar and K. Chatrathi, Minimum explosible dust concentrations measured in 20-L and 1-m^3 vessels, Combust Sci Technol 87 (1992), 157–171.

32. E.A. Ural, Flammability potential of selected halogenated fire suppression agents and refrigerants, Process Safety Prog 22 (2003), 65–73.

33. J.E. Going, K. Chatrathi, and K.L. Cashdollar, Flammability limit measurements for dusts in 20-L and 1-m^3 vessels, J Loss Prev Process Ind 13 (2000), 209–219.

34. G. Bodman, L. Britton, M. Labarge, and E.A. Ural, A review of the characteristic scatter and bias of ASTM E1232, Standard test method for temperature limit of flammability of chemicals, ASTM Research Report, December 6, 2002 (Available from ASTM as RR: E27-1004).

35. W. Bartknecht, Explosions: Course, prevention, protection, Springer-Verlag, New York/Berlin, 1990.

36. R. Siwek, Experimental methods for the determination of the explosion characteristics of combustible dusts, Loss Prevention and Safety Promotion in the Process Industries, Vol. 3, EFCE, Basel, Switzerland, 1980, p. 1304.

37. E.A. Ural, Dust entrainability and its effect on explosion propagation in elongated structures, Plant/Oper Prog 11 (1992), 176–181.

38. E.A. Ural, A Simplified development of a unified dust explosion vent sizing formula, Process Safety Prog 20 (2001), 136–144.