

**FLASH POINT
AND
FIRE ANALYSIS**

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Patrick M. Kennedy

Many times the flash point of an ignitable liquid fuel is a key consideration in fire case litigations, civil and criminal. Litigation in fire or explosion incident cases is often a matter of the relative flammability of the fuels involved. When fuel flammability characteristics become the main issue at the heart of a litigation, the subject of "materials science" comes into play. Materials science deals with the various properties and characteristics of substances, particularly with those characteristics which have an impact on their use by a consumer.

Materials science dealing with flammability properties encompasses elements from a variety of the scientific and engineering disciplines. Unlike pure scientific or engineering fields, such as chemistry, the study of the flammability characteristics of materials is a separate discipline, not entirely within the province of chemistry, physics or engineering. In recent trial testimony involving a \$32,000,000 lawsuit over the explosion of a crude oil barge, a Ph.D. in chemistry described the Tag Closed Cup flash point test as having an electrical arc as the test ignition source. This sadly typifies the general lack of accurate knowledge of the flammability characteristics of materials, even among those who profess great knowledge in related fields. Flash point is a physical flammability characteristic, not a chemical property. Few practitioners in the theoretical sciences possess sufficient practical knowledge of flammability characteristics to accurately represent the true significance to a court and jury.

Relative Flammability

Definitions of the relative flammability of a substance can emphasize one or more specific properties of the material. Two general classes of flammability characteristics are used in these definitions: the first dealing with the ignition characteristics (ease of ignition) and the second dealing with the burning characteristics of the fuels themselves (fuel characteristics).

Properties of materials dealing with Ignition Charac-

Ignition Temperature
Autogenous Ignition Temperature
Minimum Ignition Energy
Thermal Conductivity
Specific Heat
Thermal Inertia
Surface to Mass Ratio

Fuel characteristics of materials include the following:

Melting Temperature
Vapor Pressure
Boiling Point
Flammable/Explosive Range
Lower Flammability/Explosive Limit (LEL)
Upper Flammability/Explosive Limit (UEL)
Stoichiometric Mixture
Flash Point
Fire Point
Burning Temperature
Heat of Combustion

Of these various ignition and fuel characteristics, the flash points of ignitable liquids are the most easily determined and widely reported. Because of this, flash point is the most often used as a consideration of the relative danger of such ignitable liquids. This being the case, many products liability law suits hinge upon the determination of flash point or the true significance of a liquid's reported flash point.

Definition of Flash Point

Flash point is the temperature of an ignitable liquid at which it gives off vapors at a rate capable of fueling a momentary flash of flame across the surface of the liquid in a specific laboratory test protocol.

Key to the definition of the flash point of a liquid is the specific test which was used. There are several different types of flash point tests. Each individual test type may produce slightly differing flash points for the same liquid. When reporting the flash point, it is important to specify exactly which test was used.

Though the individual flash point tests differ in the exact apparatus and test protocol, the same basic method is used in all tests to determine flash point. The temperature of a liquid specimen is controlled, determined or monitored and a small gas ignition flame is introduced in proximity to

flash of flame is transmitted within the vapor across the surface of liquid specimen, the temperature is recorded. The lowest temperature of the liquid at which this flash occurs is the flash point. This recorded temperature is then adjusted to standard sea level atmospheric pressure of 760 mm of mercury.

Equilibrium and Non-Equilibrium Tests

Two different kinds of basic tests, equilibrium or non-equilibrium tests, are used, depending upon the purpose for which the determination of flash point is required.

Equilibrium tests, sometimes called "flash/no flash" tests, are made at a specific set temperature. These tests are usually used when a basic minimum or maximum flash point is required for compliance with a code or regulation, such as for products which have labeling or warning restrictions set by law.

Non-equilibrium tests are made by slowly raising the temperature of the specimen liquid at a specified rate and periodically introducing the ignition flame to the vapor space at specific intervals (usually every 2 degrees Fahrenheit). This is done to determine the minimum temperature of the liquid at which the flash occurs. Non-equilibrium tests are most often used when the exact flash point of the liquid is not known.

Flash Point Test Apparatus

There are five main test apparatus designs in general use for flash point testing: Tag (Tagliabue) Open Cup, Tag (Tagliabue) Closed Cup, Cleveland Open Cup, Pensky-Martens Closed Cup, and Setaflash (sometimes called the rapid tester). These test apparatus fall into two categories determined by the nature of the exposure of the liquid vapors during the test, open cup or closed cup. In the open cup tests the vapors are totally exposed to the atmosphere. In the closed cup tests the vapors are confined within the test apparatus and the test flame is introduced into the vapors near the surface of the liquid through a small mechanical door or gate. Because of the relative exposure of the vapors during testing, the open cup flash point of a liquid will necessarily be a few degrees higher than for the same liquid in a closed cup tester.

The selection of which flash point test will be used is based upon such considerations as the maximum temperature capabilities of the various apparatus, the particular properties of the liquid (i.e. high viscosity), or the specifications of the code with which the liquid must comply.

ASTM

Though many code and regulation promulgating authorities specify protocols for flash point tests called for in their standards, nearly all current flash point tests in use are based upon the tenets of the American Society for Testing and Materials (ASTM). ASTM is a voluntary society which sets standards for the properties and performance of materials, products, and assemblies.

It is the policy of ASTM to establish procedures and terminology which will maintain a distinction between fire risk assessment standards which are deemed appropriate to describe, measure or control the behavior of materials,

products, and assemblies under actual fire conditions, and fire test standards which provide a means for measuring and describing the response of materials to heat or flame under controlled conditions of testing, including flash point.

The ASTM Coordinating Committee on Flash Point

Several committees within ASTM promulgate flash point or related standards for various types of materials (i.e., petroleum products, chemicals). In order to coordinate the activities of these various committees, the ASTM Coordinating Committee on Flash Point was formed. Among the work of the Coordinating Committee on Flash Point is the production of manuals and reference works such as the ASTM Manual on Flash Point and Related Tests and a collection of the various governmental flash point regulations, Flash Point Regulations.

The committee also sets standards for flash point terminology and on occasion promulgates suggested new standards such as a new proposed "ASTM Standard Practice for Sampling for Flash Point and Related Tests."

Significance of Flash Point in Fire Investigations

The ignition sequence of a fire involves the contemporaneous presence of a competent ignition source and a competent fuel. With liquid fuels, one of the prerequisites for ignitability (fuel competence) is that the liquid be at a temperature high enough to give off sufficient vapors to form an ignitable mixture. This is a practical, if not technical, definition of flash point. If the liquid fuel has not sufficient heat, there would be no fuel vapor to be ignited.

For example, if the fuel source is #2 fuel oil (Tag closed cup flash point 125 F.), and the ambient temperature is only 70 F., it is impossible that the fuel oil can be ignited unless it is heated above its flash point. So it is incumbent upon the fire investigator to determine if the liquid fuel source is or was capable of being ignited in his theory of the ignition sequence.

The very definition which separates combustible from flammable liquids is based upon the flash point of the liquids, the cut off being above or below a maximum temperature which can normally be expected to be encountered, 100 degrees Fahrenheit. The relative danger of a flammable liquid over a combustible liquid is that combustible liquids are not considered competent fuel sources at normal ambient temperatures.

A number of state and federal regulations and industry standards deal with the appropriate labels and warnings on flammable or combustible liquid products based upon flash point. The responsibility for a fire or explosion incident may well rest with the producer or seller of such a liquid if the ultimate user had not been sufficiently warned of the product's danger.

Misconceptions About Flash Point

Some investigators have such a poor education in basic fire science that they do not know the definitions of even the most basic materials science flammability terms. It is not uncommon to read the discovery deposition of a fire investigator who confuses the flash point of a liquid with its boiling point or even its ignition temperature.

Another common misconception about flash point is that the atomization of an ignitable liquid will lower its flash point. While it is true that the atomization of a liquid may allow it to be ignited when the ambient temperature is too low, a lowering of the flash point is not the mechanism by which ignition can be accomplished.

The process of atomization breaks up the liquid into small droplets and suspends them in the air. In doing so the surface-to-mass ratio of the fuel is greatly increased. With the increased surface and low mass of each droplet completely surrounded by air, even an ignition source of moderate energy can locally raise the temperature of individual fuel droplets above the flash point of the liquid and ignite them. Each burning droplet then heats other droplets, in turn eventually allowing most of the mass of atomized liquid to burn when the original temperature of the liquid is well below its flash point. The closer that the original liquid's temperature was to its flash point, the less energy is required for ignition and the more efficient the reaction. However, the basic flash point of the ignitable liquid remains the same.

The fact that the ambient air temperature may be below the flash point of the liquid fuel is not a guarantee that ignition of the liquid cannot and will not occur even in the absence of atomization. It is the temperature of the liquid itself, not just the ambient temperature, which is the determining factor in whether there are sufficient vapors for ignition.

Many industrial settings have ignitable liquids in tanks, processing equipment, and pipelines at elevated temperatures higher than their flash points and pressures higher than the ambient conditions. These liquids may have already produced more than sufficient vapors to fuel significant fires and explosions when released.

In such confined conditions as tanks, pipelines and processing equipment, even some liquids at temperatures below their flash points can, over time, produce sufficient quantities of vapors to form mixtures above their lower explosive limits and be ignited. This is especially true if the pressures in the confined spaces are elevated, thus widening the liquids' flammable ranges.

Federal Hazardous Substances Act Regulations - 1990

The Hazardous Substances Act is part of the same federal law which created the Consumer Products Safety Commission. One of the key elements of the Act is its prescriptions dealing with the classification and labeling of consumer products based upon their relative flammability as defined by flash points. The Hazardous Substances Act currently lists three classifications of flammability:

"extremely flammable" - liquids with flash points at or below 20 degrees Fahrenheit;

"flammable" - liquids with flash points above 20 degrees Fahrenheit and below 100 degrees Fahrenheit; and

"combustible" - liquids with flash points at or above 100 degrees Fahrenheit to and including 150 degrees Fahrenheit;

Liquids with flash points above 150 degrees Fahrenheit are not classified as hazardous substances under the Act.

These flash points are determined by the Setafash Closed Cup tester according to 16 CFR 1500.43a.

An exception to this rule states that flash points and the definitions of "extremely flammable," "flammable," and "combustible" may be determined by the Tag Open Cup tester for products whose formulation has not changed since the effective date of 16 CFR 1500.43a, August 10, 1987.

Under these previous definitions, liquids with flash points at or below 20 degrees Fahrenheit were termed "extremely flammable"; liquids with flash points above 20 degrees Fahrenheit and below 80 degrees Fahrenheit were termed "flammable"; and at or above 80 degrees Fahrenheit to and including 150 degrees Fahrenheit were termed "combustible."

These flash points are to be determined by the Tagliabue [Tag] Open Cup tester according to 16 CFR 1500.43.

The Act also states that the labels of ignitable hazardous substances containers must have the following components:

- (A) *The name and place of business of the manufacturer, packer, distributor or seller;*
- (B) *The common or usual name or chemical name of the hazardous substance or of each component which contributes substantially to its hazard;*
- (C) *The signal word "DANGER" on substances which are extremely flammable;*

- (D) The signal word "WARNING" or "CAUTION" on all other hazardous substances;
- (E) An affirmative statement of the principal hazard or hazards, such as "Extremely Flammable," "Flammable," or "Combustible;"
- (F) Precautionary measures describing the action to be followed or avoided;
- (G) Instructions for handling and storage of packages which require special care in handling or storage;
- (H) The statement "Keep out of the reach of children;"
- (I) Such labeling components must be located prominently and in the English language in conspicuous and legible type in contrast by typography, layout, or color with other printed matter on the label.

NFPA Flammable and Combustible Liquids Codes

The National Fire Codes as promulgated by the National Fire Protection Association (NFPA) distinguishes classes of ignitable liquids as Flammable or Combustible with a cut off flash point of 100 degrees Fahrenheit. Under National Fire Code, NFPA 321 - "Standard on Basic Classifications of Flammable and Combustible Liquids," there are six classifications for ignitable liquids as determined by their Tag Closed Cup flash points (ASTM D-56).

Flammable Liquids

- Class IA- liquids with flash points below 73 degrees and boiling points below 100 degrees Fahrenheit
- Class IB- liquids with flash points below 73 degrees and boiling points above 100 degrees Fahrenheit
- Class IC- liquids with flash points at or above 73 degrees and below 100 degrees Fahrenheit

Combustible Liquids

- Class II- liquids with flash points at or above 100 degrees and below 140 Fahrenheit
- Class IIIA- liquids with flash points at or above 140 degrees and below 200 degrees Fahrenheit
- Class IIIB- liquids with flash points at or above 200 degrees Fahrenheit

NFPA 325M, "Fire Hazard Properties of Flammable Liquids, Gases, Volatile Solids" lists the flash points as well as several other flammability characteristics of commonly encountered fuels.

Errors in Determining Flash Point

Erroneous flash points are often reported when testing procedures are not followed accurately or completely, or when operator inexperience creates errors in interpretation of observed flash point results.

In closed cup flash point tests, as the temperature of the liquid approaches the flash point, the test ignition flame often becomes enlarged when applied to the vapor space. This enlarged flame takes on a "halo" effect around the actual flame itself. This "halo" is sometimes identified as a flash by an inexperienced operator. This results in a too low flash point being reported.

Errors in filling the flash point cup are also common problems. Too much liquid in the cup will result in the test ignition flame being applied too closely to the surface of the liquid. This creates erroneous flash points which are too low. Conversely, if too little liquid is used, the observed flash point will be higher than accurate.

If the specimen liquid is allowed to be sloshed onto the inner sides of cup, the observed flash point will also be too low because of the increased surface area from which the liquid is giving off vapors.

Bubbles which are allowed to remain on the surface of the liquid during testing or the loss of ignitable volatile light ends from the liquid prior to testing can alter tests results and produce observed flash points at too high a temperature.

If the rate of heating is too fast or slow, or excessive air turbulence is present during the test procedure, erroneous flash points can also be reported.

When liquids being tested for closed cup flash points are mixtures containing significant percentages of water or other compounds which give off large quantities of non-flammable gases during heating, the phenomenon known as "outgassing" often occurs.

Outgassing is a condition in which the flammable portions of the vapors given off by a liquid are inerted by the non-flammable vapors and do not ignite within the closed cup. Instead they burn outside of the closed cup apparatus and are manifested in enlarged igniter flames but no flash. This condition is often confused with the "halo" effect that is commonly seen when testing at temperatures just below the flash point. In fact, the outgassing occurs at temperatures just above the closed cup flash point of the sample's ignitable liquid components.

Outgassing can occur with both Tag and Setaflash closed tests, though it is more prevalent in the Setaflash apparatus because of its much smaller headspace.

Often the outgassing condition can mask or prevent the accurate determination of the liquid's true flash point in a closed cup apparatus. This condition is sometimes circumvented by retesting a specimen of the sample in the Tag or Cleveland open cup apparatus.

As many erroneous flash point results stem from errors in the sampling of liquids for testing, the Coordinating Committee on Flash Point has promulgated a new proposed "ASTM Standard Practice for Sampling for Flash Point and Related Tests." The practice covers procedures involved in obtaining, preserving, storing, and handling samples intended for use in tests to determine the flash point or fire point of liquids. The reliability and reproducibility of flash point and related test results is dependent upon the representativeness and integrity of the samples upon which the tests are conducted.

Variances and anomalies in the taking of samples can affect flash point and related test results. Such test results will be limited to the actual samples themselves unless a uniform sampling process is used. Test results can only be considered representative for the actual samples themselves unless the sampling process is conducted in accordance with this standard.

Erroneous test results may be obtained if precautions are not taken to avoid the loss of volatile material between the taking of the sample and the testing. Highly volatile materials may be present in the form of gases, vapors, foams, or as mixtures in samples. These volatile materials may not be detected by testing because of losses during sampling, storage, or handling and transfer in the loading of test apparatus. For example, this is especially evident with heavy residues, crude oils, asphalts from solvent extraction processes, or waste streams.

Samples and specimens which have a froth or foam on their surface will also produce erroneous test results. Care must be taken to avoid any foaming or frothing of samples before testing.

The fire investigator should exercise particular care in the interpretation of test results from samples which have been taken under field conditions. Field samples are particularly subject to weathering (the loss of lighter end components to the atmosphere) and to contamination by foreign substances.

Dissolved light ends may be released from the sample matrix if a liquid sample is allowed to solidify. For most accurate results, samples should be prevented from going through a phase change between sampling and testing.

Safety in Sampling

Consideration should be given to the safety of the atmosphere in which the sample may be taken. Such atmospheres may be flammable, toxic, corrosive, or oxygen deficient.

The person taking the sample should avoid the production of an ignition source by static electricity, arcs, sparks, heat, or open flames. There should be no smoking in the area at the time that the samples are taken. Specialized breathing apparatus and/or protective clothing may be necessary.

Sampling Procedures

Sampling devices and sample containers used to acquire samples should be clean, dry, and free of previous samples' residues or extraneous or foreign substances. Sampling devices and sample containers should be constructed of materials which will not be dissolved, oxidized, or otherwise react with the material being sampled. Sample containers should be promptly and securely sealed, airtight, immediately after the samples have been taken.

Materials which are not uniform or homogeneous may require that multiple samples be taken from various levels or areas within the volume of material being sampled. Such samples may be susceptible to variances caused by the stratification of materials, sedimentary deposits and variations caused by incomplete mixing or by separation of components.

If possible, sufficient quantities of each sample should be taken to fulfill the prescriptions of the appropriate test standards, as well as enough for subsequent tests to recheck test results. A sample size of approximately 500 ml (one pint) is recommended.

Approximate Specimen Size for ASTM Flash Point Tests

<u>ASTM Number</u>	<u>Test Name</u>	<u>Sample Size</u>
D56	Tag Closed Cup	50ml
D92	Cleveland Open Cup	75ml
D93	Pensky-Martens Closed Cup	70ml
D1310	Tag Open-Cup	90ml
D3143	Cutback Asphalt Tag Open-Cup	90ml
D3278	Setaflash Closed-Cup	50ml*
D3828	Setaflash Closed	50ml*
D3934	Flash/No Flash Closed Cup	70ml
D3941	Equilibrium Closed-Cup	70ml

*Though only 2-4ml of material is used for actual testing, the standard requires that 50ml be drawn as a specimen.

Preserving Samples

Sample containers should be new, clean, dry, and free of foreign or extraneous substances. They should be filled as nearly full as is practicable, in order to reduce or prevent the production of vapor headspaces which may contain volatilized sample material. However, adequate room should be allowed for expansion of the sample, taking into consideration the temperature of the liquid at the time of filling and the probable maximum temperature to which the filled sample container may be subjected.

Samples should also be matched to the appropriate sample container materials. Natural or synthetic seals, gaskets, or container materials, particularly metals or plastics, may dissolve, oxidize, allow vapors to permeate container walls, or chemically react with certain samples. Samples should not be stored in plastic (i.e., polyethylene, polypropylene) containers unless the container material has been shown to be impermeable. Volatile materials may diffuse through the walls of plastic containers.

Each sample should be properly identified and labeled immediately after a sample is taken. Pertinent information about each sample should be recorded:

Date, time, and exact location where the sample was taken;

Nature of the sample, if known, (including safety or warning information);

Identity of the person taking the sample;

Approximate temperature of sample at the time of collection;

Chain of custody of the sample from the time it was collected, through the testing, and post-testing storage, and disposal;

Date, time, and circumstances of each instance that the sample container is opened.

Storing Samples

Samples should be stored in a cool, dry, dark location and protected from extremes of temperature, especially from freezing or high heat. Sample containers should be protected from leakage, damage, breakage, or tampering during storage. Local codes and regulations may require that certain quantities of flammable or other dangerous substances be stored in specialized cabinets or storage areas.

Handling Samples

Samples from leaky or poorly sealed containers should not be used for testing. Sample containers should not be opened unnecessarily. Sample containers should be resealed promptly after necessary transfers.

When making necessary transfers, the samples should be at least the equivalent of 10 degrees C. (20 degrees F.) below the expected flash point, before the sample container is opened. Once specimens have been removed from sample containers they should be tested as promptly as possible to prevent the possible loss of volatile fractions or components.

Specimens which have been previously tested may not produce accurate results and should not be retested. New specimens should be transferred from sample containers for each test.

Conclusion

The property of flash point can be a very effective fire investigation analysis tool to the fire investigator and trial lawyer. But, a true understanding of the nature of flash points, proper procedures for determining flash points, and significance of flash point test results is absolutely necessary. As with most things in life, half truths or inadequate understanding of all the aspects of a matter are worse than none.

ASTM Flash Point Standards

- D56 Standard Test Method for Flash Point by Tag Closed Tester
- D92 Test Method for Flash and Fire Points by Cleveland Open Cup
- D93 Test Methods for Flash Point by Pensky-Martens Closed Tester
- D1310 Test Method for Flash Point and Fire Points of Liquids by Tag Open-Cup Apparatus
- D3143 Test Method for Flash Point of Cutback Asphalt with Tag Open-Cup Apparatus
- D3278 Test Method for Flash Point of Liquids by Setaflash Closed-Cup Apparatus
- D3828 Test Methods for Flash Point by Setaflash Closed Tester
- D3934 Method for Determination of Flash/No Flash of Liquids by the Closed-Cup Method
- D3941 Test Method for Flash Point by the Equilibrium Method with a Closed-Cup Apparatus
- D4206 Test Method for Sustained Burning of Liquid Mixtures by the Setaflash Tester (Open Cup)

ASTM Sampling Standards

- D140 Standard Practice for Sampling Bituminous Materials
- D3437 Standard Practice for Sampling and Handling Liquid Cyclic Products
- D4057 Standard Practice for Manual Sampling of Petroleum and Petroleum Products
- E300 Standard Practice for Sampling Industrial Chemicals
- E502 Test Method for Selection and Use of ASTM Standards for the Determination of Flash Point of Chemicals by Closed Cup Methods

NFPA Flammable and Combustible Liquid Standards

- NFPA 30 - Flammable and Combustible Liquids Code
- NFPA 321- Standard on Basic Classifications of Flammable and Combustible Liquids
- NFPA 325M-Fire Hazard Properties of Flammable Liquids, Gases, Volatile Solids

ABOUT THE AUTHOR

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He holds Bachelor of Science Degree in Communications from St. Joseph's College, Liberal Studies (Math/Physics) from the University of the State of New

York and Fire and Safety Engineering Technology from The University of Cincinnati.

He is a member of the American Society for Testing and Materials (ASTM) Committee on Fire Standards, the ASTM Coordinating Committee on Flash Point and Related Tests and the ASTM Committee on Forensic Sciences and its Sub-Committee on the Technical Aspects of Products Liability Litigation. He is the original author of the ASTM Standard on Sampling for Flash Point and Related Tests and a contributing editor to the ASTM Flash Point Manual.

He is the Chairman of the Board of Directors of the National Association of Fire Investigators, the Chairman of the National Fire Protection Association (NFPA) Fire Science and Technology Educators section and a principal member of the NFPA Technical Committee on Fire Investigations.

He is the co-author of two currently available textbooks on fire and explosion investigation:
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to be among the standard texts in the field.

Additional copies of this monograph may be obtained from:

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