OUTGASSING PHENOMENON IN FLASH POINT TESTING FOR FIRE SAFETY EVALUATION

Gregory E. Gorbett CFEI, CVFI, Christine Kennedy CFEI,
Kathryn C. Kennedy CFEI, Patrick M. Kennedy CFEI, CFPS
John A. Kennedy and Associates Fire and Explosion Analysis Experts
Sarasota, Florida United States

ABSTRACT

Accurate ignitable liquid flash point testing provides an important component in the evaluation of a liquid material’s relative flammability danger.

Government regulations and industry standards dealing with labeling, warnings, Material Safety Data Sheets (MSDS’s), and transportation and handling of ignitable liquids are frequently based on the physical property of flash point.

“Outgassing” in flash point testing is the condition in a flash point test in which nonflammable components of a liquid mixture tend to inert the vapor space being tested, while the evolution of gasses to the atmosphere outside the test cup are ignitable. Outgassing can mask the true flammable nature of a substance. When outgassing occurs during flash point testing, products capable of producing dangerously flammable atmospheres are frequently listed as having no flash point and thereby are classified as non-flammable.

This outgassing phenomenon most frequently occurs with liquids that contain certain halogenated hydrocarbons such as Dichloromethane (Methylene Chloride) in mixtures of ignitable liquids. When using industry standard flash point tests in the fire safety evaluation of certain common consumer and industrial products, the phenomenon of outgassing has long been known but frequently overlooked. Improper understanding of this flash point behavior and the inappropriate application of the standards has led to the dangerous mislabeling of consumer products and undue public safety risks.

The importance of truly recognizing and understanding the outgassing phenomenon becomes of critical importance when ignitable liquid manufacturers use halogenated hydrocarbon liquids, such as methylene chloride, in an attempt to “inert” an otherwise flammable liquid product.

The current research reported here was undertaken in order to provide further study and publicize this phenomenon. In this work the authors produced a detailed search of the current literature and test standards and performed a series of laboratory tests on outgassing-type ignitable liquids.

A series of laboratory tests were conducted on commercially available products containing halogenated hydrocarbons, as well as on pure methylene chloride. Each material was tested by ASTM standards D56 tag closed tester; D1310 tag open cup; D93 Pensky-Martens Closed Tester; D3278 and 3828 Setaflash; E1232 Temperature limit of Flammability of Chemicals; UL 340 Test for Comparative Flammability of Liquids; and NFPA 321 Standard on Basic Classification of Flammable and Combustible Liquids.
INTRODUCTION

Accurate ignitable liquid flash point testing provides an important component in the evaluation of a liquid material’s relative flammability danger. The phenomenon known as “outgassing” produces vapors that inert the chamber of the testing apparatus which prevents the accurate determination of a material’s flash point. Improper understanding of the aspects of flash point determination, as well as the related phenomena’s, results in an incorrect evaluation of a liquid material’s relative flammability danger.

The purpose of the current research was to provide further study on this phenomenon. In this work, the authors produced a detailed review of the literature and test standards and performed a series of laboratory tests on outgassing-type ignitable liquids. In order to fully understand the concept and dangers associated with outgassing, some prerequisite knowledge is required. The initial objective of this paper is to provide a thorough discussion of the important terms and concepts that are necessary and helpful in developing a better understanding of the test results and discussion of outgassing. First, there will be a discussion on the current method of determining the relative flammability danger of materials, including flammability characteristics, current test methods for determining the flash point of a material, the significance of flash point tests, and the relationship between the flammability characteristics and required warnings and labels. This initial information will then be followed by an explanation of the outgassing phenomenon, including the importance and dangers of outgassing. Finally, results of the experiments and a discussion will follow.

RELATIVE FLAMMABILITY DANGER OF MATERIALS

DETERMINATION OF FLAMMABILITY

The relative flammability of a material is defined by the physical properties of the material. Properties of materials dealing with ignition characteristics include ignition temperature, autogenous ignition temperature, minimum ignition energy, specific heat, and surface to mass ratio. Fuel characteristics of materials include flash point, vapor pressure, flammability limits, flame point or fire point, vapor densities, and boiling points. These combined properties will reveal how a liquid material will behave in a fire.

However, there are a few properties that should be given more weight when attempting to determine the relative flammability danger of materials including vapor pressure, flammability limits, flash point, and boiling points. Each are fundamental physical properties that influence the flammability of a liquid fuel.

- The vapor pressure of a material is defined as the equilibrium pressure exerted by the vapor of a liquid at a given temperature, reached when the number of molecules escaping from the liquid equals the number returning.\(^1\)

- The flammability limit is the upper or lower concentration limit at a specified temperature and pressure of a flammable gas or a vapor of an ignitable liquid and air, expressed as a percentage of fuel by volume that can be ignited.\(^2\) Flammability limits are key in defining the percentage of a vapor concentration required at upper and lower limits for combustion to occur.

- The boiling point of a liquid fuel is defined as the temperature at which liquid becomes a vapor or gas.\(^1\)

The relationship of the material’s danger to its vapor pressure is directly related to its boiling point and flammability limits. When the vapor pressure of a liquid reaches 760 mmHg (1 atm), the liquid is at its boiling point, so the temperature at which that occurs is recorded as its
boiling temperature. When the temperature of a liquid is such that its vapor pressure reaches the percentage of 760 mm/Hg (1 atm) that is equivalent to the lower flammability limit of the fuel, the fuel is said to be at its flash point.  

**FLASH POINT**

Flash point of a liquid is the lowest temperature of a liquid, as determined by specific laboratory tests, at which the liquid gives off vapors at a sufficient rate to support a momentary flame across its surface. Flash points are determined by specific laboratory test protocols that produce a momentary flash of flame across the surface of the liquid (fig. 1 & 2). There are several different types of flash point tests. Each individual test method may produce slightly different flash points for the same liquid. When reporting the flash point, it is important to specify exactly which test was used.

The test apparatus fall into two categories determined by the construction of the test chamber, either open cup or closed cup. In the open cup tests the vapors are totally exposed to the atmosphere (fig. 1). In the closed cup tests, the test vapors are confined within the test apparatus and the test igniter flame is introduced into the vapors near the surface of the liquid through a small mechanical door (fig. 2). There are five main test apparatus designs in general use for flash point testing: Tag (Tagliabue) Closed Cup, Tag Open Cup, Cleveland Open Cup, Pensky-Martens Closed Cup, and Setagash (rapid tester).

Though the individual flash point tests differ by the apparatus and test protocol, the same basic method is used in all tests to determine flash point. The temperature of the liquid specimen is gradually increased in a controlled manner and a small gas ignition flame is introduced into the vapor space just above the surface of the liquid. If a momentary flash of flame is transmitted within the vapors across the surface of the 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 mmHg (1 atm).

Test method selection 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.

![Figure 1: Closed Cup Flash (Paraxylene)](image1.png)  ![Figure 2: Open Cup Flash (Paraxylene)](image2.png)

**SIGNIFICANCE OF FLASH POINT TESTS**

The significance of proper flash point testing can not be overstated. Flash point of ignitable liquids are often times used as the main consideration when determining the relative danger of the liquid. There are two standard flammability classification systems in use today, NFPA 30: Flammable and Combustible Liquids Code (National Fire Protection Association) and The Federal Hazardous Substances Act enacted in 1990. Each of the systems provide uniform classifications for the labeling of ignitable liquids according to their flash point.
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 (37.8°C). Under National Fire Code, NFPA 30 – *Flammable and Combustible Liquids Code*, there are six classifications for ignitable liquids as determined by their TAG Closed Cup flash points.

**Flammable Liquids**
- **Class IA** – liquids with flash points below 73 degrees and boiling points below 100 degrees Fahrenheit (22.8 – 37.8 degrees Celsius)
- **Class IB** – liquids with flash points below 73 degrees and boiling points above 100 degrees Fahrenheit (22.8 – 37.8 degrees Celsius)
- **Class IC** – liquids with flash points at or above 73 degrees and below 100 degrees Fahrenheit (22.8 – 37.8 degrees Celsius)

**Combustible Liquids**
- **Class II** – liquids with flash points at or above 100 degrees and below 140 degrees Fahrenheit (37.8 – 60.5 degrees Celsius)
- **Class IIIA** – liquids with flash points at or above 140 degrees and below 200 degrees Fahrenheit (60.5 – 93.3 degrees Celsius)
- **Class IIIB** – liquids with flash points at or above 200 degrees Fahrenheit (93.3 degrees Celsius)

The Federal Hazardous Substances Act enacted in 1990, is part of the same federal law which created the Consumer Products Safety Commission. It distinguishes classes of ignitable liquids as Extremely Flammable, Flammable, or Combustible. The Hazardous Substances Act currently lists three classifications of flammability as determined by their Setaflash Closed Cup tester.

- **“extremely flammable”** – liquids with flash points at or below 20 degrees Fahrenheit (-6 degrees Celsius),
- **“flammable”** – liquids with flash points above 20 degrees Fahrenheit and below 100 degrees Fahrenheit (38 degrees Celsius), and
- **“combustible”** – liquids with flash points at or above 100 degrees Fahrenheit to and including 150 degrees Fahrenheit (65 degrees Celsius),
  - Liquids with flash points above 150 degrees Fahrenheit are not classified as hazardous substances under the Act.

Numerous state and federal regulations and industry standards deal with the appropriate labels and warnings on flammable or combustible liquid products based upon these classification systems. Therefore, it can be deduced that the classification, labeling, and warning of a material’s relative flammability danger is established solely by its flash point. A more detailed discussion of the hazards and safety concerns when material’s are mislabeled can be found in the discussion and conclusion sections of this paper.

**“OUTGASSING”**

“Outgassing” is the condition in a flash point test in which the vapors of nonflammable components of a liquid mixture tend to inert the vapor of the testing apparatus, while the gasses evolved to the atmosphere outside the test cup are ignitable.
This outgassing phenomenon most frequently occurs with liquids that contain certain halogenated hydrocarbons such as Dichloromethane (Methylene Chloride) in mixtures of ignitable liquids. When using industry standard flash point tests in the fire safety evaluation of certain common consumer and industrial products, the phenomenon of outgassing has long been known but frequently overlooked. Outgassing has been documented in both open and closed cup apparatuses, though it appears to be more prevalent in the closed cup apparatuses. This is due to a greater restriction of the inert gases by the closed cup apparatuses.

During a test with outgassing present flammable vapors are forced out of the closed cup and into the atmosphere enlarging the igniter flame. This enlargement is frequently confused with the “halo” effect that is commonly seen during normal testing at temperatures just below the flash point (fig. 3). The “halo” is a small blue outer edge of the igniter flame observed when lowering the igniter flame into the apparatus cup as the sample nears its flash point. Enlarged igniter flames are considerably larger in size and vary in shape and color from those caused by the “halo” effect (fig. 4). Enlarged igniter flames are indicative of outgassing occurring.

![Figure 3: Closed Cup Normal Supply Flame](image1)
![Figure 1: Closed Cup Outgassing – (Halogenated Hydrocarbon)](image2)

**TESTING**

The purpose of this study was to provide further investigation of the outgassing phenomenon. A series of laboratory tests were conducted on commercially available products containing halogenated hydrocarbons, as well as on pure methylene chloride, pure p-xylene, and a mixture of p-xylene with methylene chloride. A list of products tested as well as a breakdown of individual substances by percentages is illustrated in figure 5.

![Figure 5: Percentages of substances contained in each product tested](image3)

<table>
<thead>
<tr>
<th>PRODUCTS TESTED</th>
<th>SUBSTANCES (BY PERCENTAGE)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Xylene</td>
</tr>
<tr>
<td>p-Xylene</td>
<td>100%</td>
</tr>
<tr>
<td>Commercial Product – A^1</td>
<td>10%</td>
</tr>
<tr>
<td>Commercial Product – B^4</td>
<td>--</td>
</tr>
<tr>
<td>Commercial Product – C^9</td>
<td>--</td>
</tr>
<tr>
<td>Methylene Chloride (CH₂Cl₂)</td>
<td>--</td>
</tr>
<tr>
<td>p-Xylene with 10% CH₂Cl₂</td>
<td>90%</td>
</tr>
</tbody>
</table>

The calibration of each test apparatus was performed prior to proceeding with any series of tests. This calibration was performed according to the specifications of the individual
standard. Pure p-xylene was used for the calibration and control sample for each test apparatus as specified in the standards. The laboratory tests performed consists of four different testing apparatuses, which include: 1) Tag Closed Tester, 2) Tag Open Cup, 3) Pensky-Martens Closed Tester, and 4) Setaflash. Each laboratory test was performed in compliance according to its individual approved test standard. These standards include:

1. ASTM D56\textsuperscript{10} Tag Closed Tester
2. ASTM D1310\textsuperscript{11} Tag Open Cup
3. ASTM D93\textsuperscript{12} Pensky-Martens Closed Tester
4. ASTM D3278\textsuperscript{13} and ASTM 3828 Setaflash (rapid tester)

RESULTS

Fig. 6 shows the flash point and outgassing results from each test performed.

Calibration/Control

Pure p-xylene was used as a control sample and to calibrate each test apparatus. When the test apparatus is operating properly, a flash point for p-xylene is $81\pm2$ degrees Fahrenheit ($27.2\pm1.1$ degrees Celsius). Fig. 6 illustrates that all test apparatuses were well within the limits of calibration.

Outgassing and Flash Point

All of the products tested, with the exception of pure p-xylene, produced enlarged igniter flames, thus all tests exhibited some form of outgassing. However, no outgassing was observed while performing the Tag open cup test on commercial product “B”. No closed cup flash points were recorded, due to outgassing. Outgassing was producing inert vapors that restricted the ignition of the ignitable vapors that were also being produced. The phenomenon “outgassing” is evident from the open cup flash point test results. There were recorded flash points for each of the Tag open cup tests except for pure methylene chloride. The open cup test apparatus allowed for the dissipation of the inert gases which enabled the ignition of the underlying ignitable vapors. Note that the open cup flash points for p-xylene: methylene chloride, commercial product “A”, commercial product “B”, and commercial product “C” are all within the range of combustible liquids utilizing the Tag open cup method.

Note the significant difference in flash points between pure p-xylene and the ten percent methylene chloride addition to p-xylene. The addition of methylene chloride to pure p-xylene yields no flash point for any of the closed cup tests. However, a Tag open cup test yields an increase of 25 degrees Fahrenheit (13.8 degrees Celsius), which illustrates the effect that these halogenated hydrocarbons have on typical flammable liquids. Using either of the flammability classification systems this increase has changed the flammability rating of p-xylene from a flammable liquid to a combustible liquid when using the open cup method, and has changed p-xylene to a non-flammable, non-combustible liquid according to the closed cup tests. Bear in mind that this change in flammability is because of the testing apparatuses and not because of a major chemical or physical property change. P-xylene: methylene chloride is still as much a flammability hazard as it was when it was pure p-xylene.

<table>
<thead>
<tr>
<th>PRODUCTS TESTED</th>
<th>TEST APPARATUSES</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TAG Open Cup</td>
</tr>
<tr>
<td>p-Xylene</td>
<td>Flash Point</td>
</tr>
<tr>
<td>Methylene Chloride (CH₂Cl₂)-Pure</td>
<td>Outgassing (YES or NO)</td>
</tr>
<tr>
<td>Flash Point</td>
<td>NO</td>
</tr>
</tbody>
</table>

Figure 6: Results from flash point tests
### DISCUSSION

**DANGERS OF “OUTGASSING” – Mislabeling**

Outgassing produces results that are contrary to the entire purpose of American Society for Testing and Material’s flash point testing standards – “The safety of lives and property from fire.” Further discussion of this contradiction with ASTM’s flash point testing standards follows.

There are many dangers that are associated with the phenomenon of outgassing. For instance, the inaccurate assessments of the minimum flammability dangers of “outgassing” liquids. Outgassing can mask the true flammable nature of a substance. When outgassing occurs during flash point testing, products capable of producing dangerously flammable atmospheres are frequently listed as having no flash point and thereby are classified as non-flammable. The most widespread danger witnessed is the underestimation of the dangers of these liquids by manufacturers, suppliers, shippers, and consumers.

Manufacturers, in erroneous attempts to lower the flash point and relative danger of their products will add halogenated hydrocarbons, however in reality all they accomplish is masking or preventing the accurate flash point of their product. Mislabeling and improper warnings of these products are the result of these flawed tests. Improper understanding of flash point behavior and the inappropriate application of the standards has led to the dangerous mislabeling of consumer products and undue public safety risks. Failure to warn of the true flammability of these liquids creates many hazardous situations that would otherwise be avoidable. Consumers and shippers gain a false sense of security in these products that are based upon inappropriately high reported flash points, which can give rise to numerous unwanted fires, burn injuries, and even deaths.

The Federal Hazardous Substances Act, discussed briefly in the “Significance of Flash Point” section, also outlines the requirements for proper warnings and labeling. This Act specifically 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;

* MSDS - Pensky-Martens Closed Cup Flash Point of 22°F (-5.6°C); No flash was noted in our testing
An affirmative statement of the principal hazard or hazards, such as “Extremely Flammable”, “Flammable”, or “Combustible”;

Precautionary measures describing the action to be followed or avoided;

Instructions for handling and storage of packages which require special care in handling or storage;

The statement “Keep out of reach of children”;

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.

Inspection of the warnings and labeling of the products used in our testing, notes that only commercial product “B” was properly labeled. Both, commercial product “A” and commercial product “C” were labeled incorrectly. The material safety data sheet (MSDS) for commercial product “C” gives a flammability rating of “one” and notes no flash point when utilizing the Setaflash closed tester. However, open cup tests in fig. 6 illustrates that this product should be labeled as a combustible liquid with a flash point of approximately 110 degrees Fahrenheit (43.3 degrees Celsius). Commercial product “A”, also notes no flash point within its material safety data sheet (MSDS) when utilizing the Tag closed tester, but fig. 6 registers a open cup flash point of 113 degrees Fahrenheit (45 degrees Celsius). Commercial product “A” has another fatal flaw which is found within its title, “Non-Flammable Adhesive Remover”. This title is contrary to what the Federal Hazardous Substance Act requires of warnings and labeling on ignitable hazardous substance containers (see components (D) and (E) above). The Act specifies that a container must possess affirmative statements of the principal hazards and that a signal word must be utilized on the container indicating the hazard of the ignitable substance.

REFERENCES OF OUTGASSING IN STANDARDS

There are no required or mandatory references within the current literature and/or test standards that address this phenomenon. The current literature and test standards fail to adequately address the effects of the outgassing phenomenon. However, many references are made within nonmandatory appendices of these test standards and literature.

The most prevalent standard that should require users to identify possible issues with outgassing is from the American Society for Testing and Materials (ASTM) E 502, Standard Test Method for Selection and Use of ASTM Standards for the Determination of Flash Point of Chemicals by Closed Cup Methods.14 The only references to outgassing-type ignitable liquids can be found in the nonmandatory appendices. The first reference in this appendix is,

1. “flash point does not represent the minimum temperature at which a material can evolve flammable vapors” (X1.1).

This reference identifies that flash point tests are not completely conclusive in determining a products relative danger. More specific references to outgassing, include:

2. “there are instances with pure materials where the absence of a flash point does not ensure freedom from flammability,” and “included in this category are materials that require large diameters for flame propagation, such as trichloroethylene” (X1.2), and

3. “…a single test such as a flash point should not be relied upon to characterize completely the flammability of a material. Process and handling conditions should be carefully considered and additional tests may be warranted” (Note X1.2).

Other test standards and/or current literature making any reference to outgassing-type ignitable liquids can be found in figure 7. The references found within fig. 7, are minor
references typically found within the nonmandatory appendices of the test standard or literature.

**Figure 7: Test standards and/or current literature making minor references to outgassing**

<table>
<thead>
<tr>
<th>ORGANIZATION</th>
<th>DESIGNATION</th>
<th>TITLE</th>
<th>REFERENCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>NFPA**</td>
<td>30-00</td>
<td>Flammable and Combustible Liquids</td>
<td>I.1.2, A.1.1.1, A.1.1.2(3)</td>
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<tr>
<td>NFPA</td>
<td>35-99**</td>
<td>Standard for the Manufacture of Organic Coatings</td>
<td>A-1-6.1.2</td>
</tr>
<tr>
<td>NFPA</td>
<td>53-99†††</td>
<td>Recommended Practices on Materials, Equipment, and Systems Used in Oxygen-Enriched Atmospheres</td>
<td>F-2.4.2</td>
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<tr>
<td>NFPA</td>
<td>77-00††***</td>
<td>Recommended Practice on Static Electricity</td>
<td>A-7.2.1</td>
</tr>
<tr>
<td>UL ***</td>
<td>340†††</td>
<td>Test for Comparative Flammability of Liquids</td>
<td>4.4</td>
</tr>
</tbody>
</table>

*ASTM – American Society for Testing and Materials  
**NFPA – National Fire Protection Association  
***UL – Underwriters Laboratory

**CONCLUSIONS**

A single test such as a flash point should not be completely relied upon to portray the definitive flammability danger of a material. Manufacturers and/or suppliers of such materials should be held accountable to review the process and handling conditions of the material thereby designating any additional testing required. For instance, if a material generates no distinguishable flash point, the manufacturers and/or suppliers should review other physical characteristics of the material to aid in correctly distinguishing the relative flammability danger of the material.

Improper labeling or warning of a material’s relative flammability danger based upon inaccurate flash points or improper flash point testing has been the main issue in many product liability lawsuits. The responsibility for a fire or explosion incident may well rest with the manufacturer or supplier of such a liquid if the ultimate user had not been sufficiently warned of the product’s danger. Responsibility could also be attributed to the current literature and test standards that fail to adequately address the effects of the outgassing phenomenon.

The testing performed reveals that by adding these halogenated hydrocarbons to existing flammable liquids does not inert the flammability of the product, it only side-steps the tests. The test results compared to the inspection of the warnings and labeling from the tested product container’s illustrate the dangers associated with outgassing and improper flash point tests.
REFERENCES