



## Flammability of Halogenated Liquids: Flash Points Limits

Benoit Tribouilloy<sup>a\*</sup>, Esteban Paillery, Ghislain Binotto, Guy Marlair

Ineris, Institut national de l'environnement industriel et des risques, Parc Technologique ALATA BP 2 60550 Verneuil-en-Halatte.  
 benoit.tribouilloy@ineris.fr

The flash point and the boiling point are the regulatory-driven criteria (as referred to in the Globally Harmonized System of Classification and Labelling of Chemicals, known as GHS) on which the classification for the flammability of liquids shall be based in all classification systems of hazardous materials. Some liquids or mixtures of liquids do not have a flash point but can nevertheless generate explosive atmospheres (ATEX). For halogenated liquids, flammability is not necessarily correctly evaluated by use of flash point measurement methods, all based on very small test vessels, sometimes leading to "false negatives" results (no flash detected). The alternative way to solve the flash point issue is the measurement of the Lower Explosion Point (LEP) (also call lower temperature limit of flammability) or the lower explosive limits (LEL). This paper reports on an experimental work to illustrate the issue, by a case study focusing on ethoxy-nonafluorobutane (a fluorinated degreasing solvent whose flash point is non-existent according to published material safety data sheets and therefore classified as 'non-flammable' according to CLP). However, real flammability of this substance is shown by use of European standard methods for the determination of the LEP and the LEL.

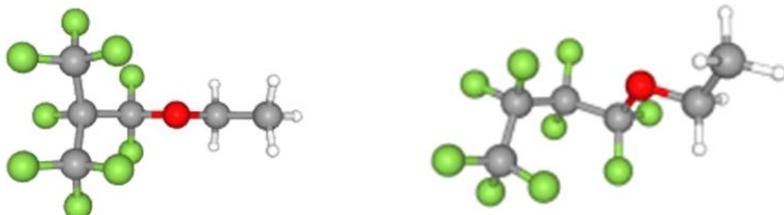
### 1. Introduction

New cleaning and degreasing solvents have been developed in recent years to timely replace those that no longer meet newly worldwide established targets regarding safe and environment-friendly chemicals, such as trichloroethylene and n-propyl bromide banned for their toxicity, hydrofluorocarbons (HFCs) progressively forbidden due to their high global warming potential or hydrochlorofluorocarbons (HCFCs) presenting environmental issues for their impact on the ozone layer. These new products are subject to regulatory testing when they are placed on the market to assess the associated risks (and provide relevant information in safety data sheets). Among the physical hazards to be assessed is flammability mainly defined, as official schemes of classification of hazards are dealt with, by the flash point. However, existing standard methods for measuring flash points are not suitable for many halogenated liquids, resulting sometimes in an underestimation of the fire and explosion risks pertaining to these chemicals and subsequently this may lead to a misleading understanding of the apparent 'non-flammable' character as a result of conventional hazard classification.). In fact, the absence of the hazard statement "flammable" on the SDS or on the bottle (pictogram) does not mean that the liquid contained is incapable of generating vapours that can be ignited, in mixture with air, by a sufficient source of ignition. By the way, this is also true for other categories of difficult to ignite chemicals like ionic liquids (see Diallo et al, 2012) Standard test alternatives do exist to overcome this shortcoming in order to optimise their characterisation and therefore the prevention of risks when used in industrial processes. The presented experimental work discusses futher the issue by a case study focused on ethoxy-nonafluorobutane. At first the open-cup flash point method was used to illustrate the observed phenomenon when this liquid chemical is the test substance, and then the same substance was further tested in accordance with standards EN 15794, for the measurement of the LEP, and EN 1839/Annex A, for the measurement of the LEL, dedicated to the determination of the explosive limits of substances that are not easily flammable (among which halogenated compounds).

## 2. Materials and methods

### 2.1 Basic information on ethoxy-nonafluorobutane

The ethoxy-nonafluorobutane (commercial name: Novec® 7200, manufacturer: 3M Company) is an hydrofluoroether of formula C<sub>4</sub>F<sub>9</sub>OC<sub>2</sub>H<sub>5</sub> comprising two isomers (see Figure 1).



*Figure 1: The two isomers of ethoxy-nonafluorobutane: a) ethyl nonafluoroisobutyl ether, b) ethyl nonafluorobutyl ether*

Published flammability data from a supplier of this chemical are accessible on the web and are reported in Table 1.

*Table 1: Reported flammability volatility and flammability parameters of ethoxy-nonafluorobutane*

Name	Boiling (°C)	Flash Point	Flammability Range in Air (%vol)
ethoxy-nonafluorobutane	76°C	None	2,4 – 12,5

### 2.2 Flash Point

In the American guidance document for the selection of closed cup flash point methods (ASTM E502-07, 2013), it is stated that some liquids, such as trichloroethylene, cannot propagate the flame due to the small volume of the test vessels (about 10 ml). To illustrate the phenomenon encountered when measuring flash points on halogenated or partially halogenated liquids, open cup tests (Cleveland open-cup apparatus described in ISO 2592) were carried out on ethoxy-nonafluorobutane. There is a normative consensus that this phenomenon, called "halo", defined as an increase in the pilot flame (see Figure 2), should not be considered as a criterion of flammability. The only ignition criterion to be retained, which is a normative criterion, is the observation, or detection, of a flame propagation on the surface of the liquid (called "flash") according to the criteria for determining the flash point.



*Figure 2: Pilot flame above the liquid ethoxy-nonafluorobutane at a temperature of 32°C (Open cup test performed at Ineris)*

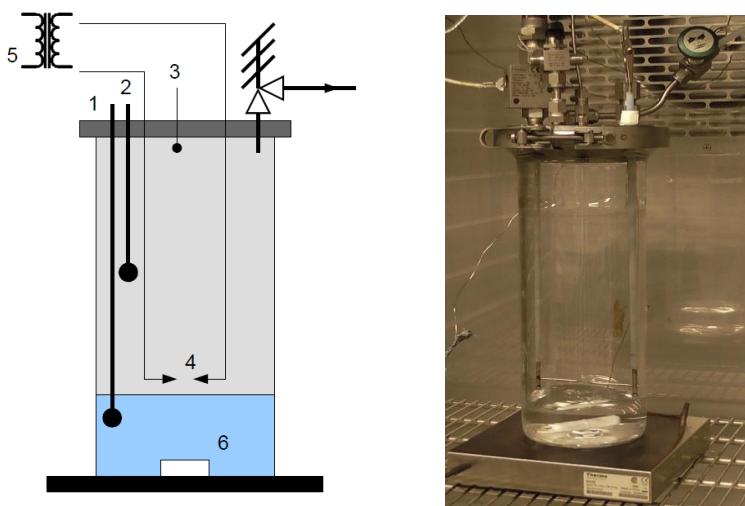
Based solely on flash point measurements, the tested product is considered non-flammable

### 2.3 LEP

The 'lower explosion point' (LEP) is the term used in the European standard EN 15794 (2009), whilst the American standard ASTM E1232, 2019 uses the term 'lower flammable temperature limit' (LTL). These two

terms are synonymous since they are consistently defined as the minimum temperature at which a liquid gives off enough vapour to form a flammable mixture with air under equilibrium conditions.

The LEP of ethoxy-nonafluorobutane was determined according to the method described in EN 15794 in a tube of 100 mm inner diameter and of 290 mm height. The temperatures of the liquid and gas phase are measured by type K thermocouples of 1 mm diameter (marked 1 and 2 on Figure 3a). A third 0.5 mm diameter K-type thermocouple (3) placed just below the lid allows early detection of any temperature rise. About 10 mm above the surface of the liquid, two stainless steel electrodes (4) are placed opposite each other at a distance of 5 mm and connected to a high voltage transformer (5) (effective voltage between 13 kV and 16 kV and short circuit current between 20 mA and 30 mA). A magnetic bar is added to agitate the liquid (6). This tube is placed in a climate chamber capable of varying from -20 °C to 200 °C. The duration of the arc generated between the two electrodes is set at 0.2 s and 0.5 s if the first test is negative (no ignition).



*Figure 3: a) a schematic diagram of the setup described in EN 15794, b) a view of the Tube – see details about numbered marks in section 2.3*

#### 2.4 LEL

The LEL of ethoxy-nonafluorobutane was determined by applying the method described in Annex A of EN 1839 (2017), for substances that are difficult to ignite due to large quenching distances but also their ability to generate flame inhibitors during combustion. For halogenated hydrocarbons with a degree of halogenation (that is the number of halogen atoms in the molecular structure divided by the number of H-atoms in the molecular structure) greater than 0.8, the explosion limits and limiting oxygen concentration shall be determined with moist air (RH 50 % at ambient temperature) to avoid the formation of flame inhibitors (such as CF<sub>3</sub>H, C<sub>2</sub>F<sub>5</sub>H, etc) through the formation of hydrogen fluoride, which testing condition was indeed applied for testing ethoxy-nonafluorobutane, since this chemical has a degree of halogenation equal to 1.8.

The tests are performed in a vertical glass tube (marked 1 on Figure 4) of 80 mm inner diameter and 500 mm height (for standard gases, the tube can be 300 mm high). At its base, 60 mm from the bottom, the same electrodes (2) described in paragraph 2.3. are connected to the same high voltage transformer (3). At the top and bottom of the tube are two 1mm diameter type K thermocouples (4) (5). The base of the tube is connected to an evaporator (6) for the evaporation of the liquid to be tested. Between the two pieces of equipment, a pneumatic valve (7) is installed to direct the air/vapour flow towards the test tube or the evacuation (to avoid stopping the flowmeter between two tests, thus ensuring the stability of the air/vapour mixture). The assembly is placed in an oven (8). The composition of the air/steam gas mixture is prepared by flow measurement. The air flow rate is adjusted with a mass flow controller (9) and the liquid with a syringe pump (10). The air flow is saturated with water by bubbling through a flask (11) containing glass beads and filled with water. At its exit, the air stream is sent to an identical flask (12), without water, placed in a cooling bath (13) whose temperature is adjusted to achieve a relative humidity of 50% (as determined at room temperature) at its exit (marked (14) in Figure 4).

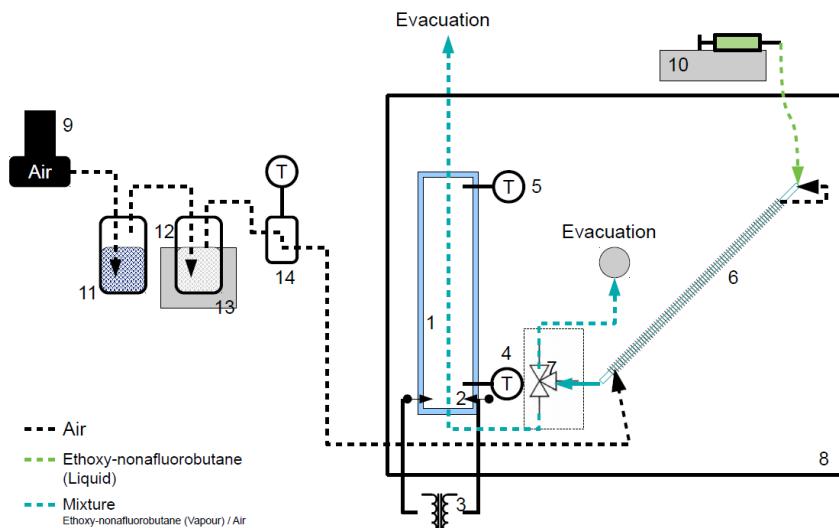


Figure 4: Schematic diagram of the setup described in annex A of EN 1819 - Tube method -See details about numbered marks in section 2.4

### 3. Experimental Results

#### 3.1 LEP

The tests were carried out with a filling rate of 20% by volume. Table 1 shows the results obtained on a sample. This first test is primarily used to determine whether liquid ethoxy-nonafluorobutane can generate vapours which, when mixed with air, can be ignited by an ignition source. Ignition is occurring at a liquid phase temperature of 7.5°C.

Table 1: LEP estimation of ethoxy-nonafluorobutane on first sample

Ignition test n°	1	2	3	4	5	6	7	8	9	10	11
Liquid phase temperature (°C)	- 8,9	- 7,7	- 5,9	- 4,8	- 2,3	0,1	1,7	3,4	5,6	6,7	7,5
Gaseous phase temperature (°C)	- 10,5	- 8,5	- 6,6	- 4,5	- 2,6	- 0,7	1,2	3,2	5,2	4,2	5,5
Ignition?	No	No	No	No	No	No	No	No	No	No	Yes

A second test with a second sample was performed to confirm the first value obtained (see Table 2). Ignition was observed at 3.3°C (no ignition at 3.0°C). Figure 5 shows the development of the flame in the test vessel (video captures).

Table 2: LEP determination of ethoxy-nonafluorobutane on second sample

Ignition test n°	1	2	3
Liquid phase temperature (°C)	3,3	2,7	3,0
Gaseous phase temperature (°C)	1,7	1,7	2,1
Ignition?	Yes	No	No

Figure 5 shows the flame development in the test vessel (video captures) performed at 3.3°C.

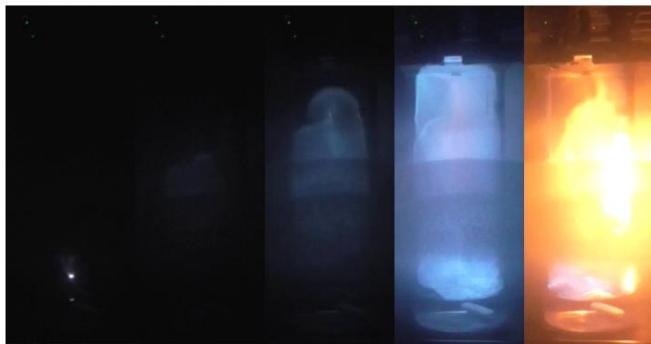


Figure 5: LEP: Flame development (left to right) in the gas phase (liquid temperature: 3.3°C) after spark generation

Figure 5 clearly shows the phenomenon of self-sustained combustion (flame detachment, ignition criterion) and not a halo phenomenon as in the case of flash point ignition test. It should be noted that prior to these tests targeting the assessment of LEP of the studied chemical, other tests were carried out at higher temperatures, always with the aim of observing potential ignition. From the results presented in Table 3, this temperature range appears to correspond to the upper explosion point (UEP) zone, i.e. between 12.5°C and 17.3°C.

Table 3: UEP estimation of ethoxy-nonafluorobutane

Ignition test n°	1	2	3	4
Liquid phase temperature (°C)	17,3	22,7	28,5	12,5
Gaseous phase temperature (°C)	15,7	23,0	29,7	9,4
Ignition?	No	No	No	Yes

Figure 6 shows the flame development in the test vessel (video captures) performed at 12.5°C.



Figure 6: UEP: Flame development (left to right) in the gas phase (liquid temperature: 12.5°C) after spark generation

### 3.2 LEL

To ensure evaporation of the liquid at the evaporator outlet, we had to work at 38°C. The different concentrations of the vapours of the solvent in air tested, with a relative humidity close to 50% at ambient temperature, are presented in Table 4. The LEL is equal to 3.4%vol by applying annex A of the EN 1839 standard, with an ignition observed at 3.6%vol.

Table 4: LEL determination of ethoxy-nonafluorobutane in according to annex A EN 1839 / 50% HR

Concentration (%vol)	4,0	3,0	3,4	3,6	3,8
Tube temperature (°C)	22	38	38	38	38
Moisture (%HR)	47,5	49,7	50,2	50,9	50,9
Ignition?	Yes	No	No	Yes	Yes

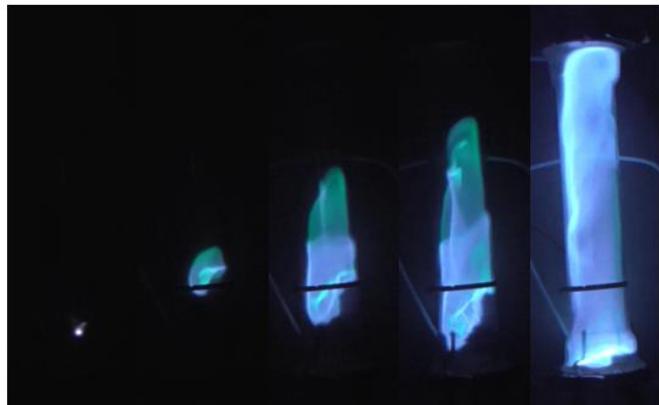


Figure 7: LEL- Flame development (left to right) in the tube of mixture air/ ethoxy-nonafluorobutane (vapour 3,6 %vol in air) after spark generation

#### 4. Interpretations of the results

Tests to determine the LEP of ethoxy-nonafluorobutane show that it can generate flammable vapours in air at low temperatures, well below the flash point of ethanol, which is classified as "highly flammable liquid and vapour". This ability to generate ATEX was confirmed by measuring its LEL according to the method described in Annex A of EN 1839 at 38°C and atmospheric pressure.

#### 5. Conclusions

With this case study, we wanted to highlight the inconsistencies, and subsequently potentially misleading interpretation of information that can be disseminated in safety data sheets or marketing communications from experimental results that are nor properly challenged with alternative tests, in particular with severely halogenated substances: How can a liquid classified as non-flammable generate an explosive atmosphere? The standard methods for determining flash point cited in the Manual of Tests and Criteria (Seventh revised edition – United Nations) do not consider the specificities presented by halogenated liquids with respect to combustion (large reaction quenching distances and influence of humidity). The alternative would be either to determine the LEP (or LTL) by application of EN 15794(2009) or ASTM E502-07(2013) and to classify the liquid according to this temperature or to determine the explosive limits (since these data also concern vapours generated by liquids - a vapour is the gaseous state of a liquid) by application of EN 1839 (2017) or astm E681(2009) in which specific recommendations are given for difficult to ignite gases or vapours. This work also reminds the user that cautions are needed since conventional physical hazard classification schemes do have limitations, and that all flammability rating methods are based on criteria that a) are not referring to intrinsic properties of the chemicals (by contrast to a melting point), and b) are always (flash point, LEP, LEL) apparatus dependant.

#### References

- A-O. Diallo, C. Len, A.B. Morgan, G. Marlair, Revisiting physico-chemical hazards of ionic liquids, Separation and Purification Technology 97 (2012) 228–234, doi:10.1016/j.seppur.2012.02.016.
- ASTM E502-07, 2013, Standard Test Method for Selection and Use of ASTM Standards for the Determination of Flash Point of Chemicals by Closed Cup Methods.
- ASTM E681 - 09(2015) Standard Test Method for Concentration Limits of Flammability of Chemicals (Vapors and Gases).
- ASTM E1232, 2019, Standard Test Method for Temperature Limit of Flammability of Chemicals.
- EN 1839, 2017, Determination of the explosion limits and the limiting oxygen concentration (LOC) for flammable gases and vapours / Annex A: Method for determining the explosive limits and the oxygen concentration of difficult to ignite substances.
- EN 15794, 2009, Determination of explosion points of flammable liquids.
- ISO 2592, 2000, Determination of flash and fire points - Cleveland open cup method.
- 3M™ Novec™ 7200 Engineered Fluid (product information) <https://multimedia.3m.com/mws/media/199819O/3m-novec-7200-engineered-fluid-en.pdf>.