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Explosion Protection according to the EU Directives using the Data from CHEMSAFE Database

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Abstract

For international trade and production of machinery used in potentially explosive atmospheres it is important to know about the regulations within the European Union. This paper presents an application of CHEMSAFE flammability data for fulfilling the requirements of the EU explosion protection directives. Most of the published data for flammability of substances are measured under atmospheric conditions although chemical processes operate often under non-atmospheric conditions. A couple of R&D projects were initiated in Germany to get more knowledge on explosion characteristics for non-atmospheric conditions. The explosion protection for machinery operated under non-atmospheric conditions is defined in the 2006/42/EU Directive. CHEMSAFE fulfills this requirement while it contains data of flammable compounds measured under non-atmospheric conditions and with other oxidizers than air. Furthermore it includes flammability data for gas mixtures consisting of flammable, inert, and different oxidizing components and most of the data are measured according to international standards. Safety data on flammable dusts - such as minimum ignition energy, maximum explosion pressure, ignition temperatures - represents also an important part of the database. The potentially explosive atmospheres are defined in revised Directive 2014/34/EU. For preparing risk assessment documents the following data for flammable gases and vapors, relating to the use of equipment, among others are necessary: Flammability limit, flash point, temperature class - auto-ignition temperature, maximum experimental safe gap. CHEMSAFE’2013 includes not only these data but also more than 200 triangular explosion diagrams, e.g. the newly measured methane/nitrogen/oxygen system under pressures up to 50 bars. The international standard Draft of IEC 80079-1-1 publishes data tables for flammable substances originated from CHEMSAFE which represents the international acceptance of these data.

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1. Introduction

According to the European Occupation Safety and Health guideline (especially the EC hazardous materials Directive 98/24/EC on the protection of the health and safety of workers from the risks related to chemical agents at work and Directive 1999/92/EC of the European Parliament and of the Council of the European Union on minimum requirements for improving the safety and health protection of workers potentially at risk from explosive atmospheres) the employer is obliged to identify and evaluate the risk of fire, explosion and exposure to dangerous substances at the working place. For this purpose they need reliable, easily available and expert-evaluated data to estimate the risk not only of toxicity but also fire and explosion. The CHEMSAFE database [1] delivers these data, mostly for pure flammable substances, but also for a number of mixtures. These data can be applied not only for primary and secondary explosion protections, but for constructive explosion protection e.g. for designing explosion protection measures: explosion proof construction, explosion venting. For these purposes the maximum explosion pressure and the maximum pressure rise per time unit for a given system should be known.

2. Safety Characteristics

European, US and international standards describe the test methods for safety characteristics, such as explosion limits, maximum explosion pressures and maximum rates of pressure rises. In the US the wording “flammability limits” is used instead of the European terminology “explosion limits” to describe the same safety characteristics. Nevertheless, the term “explosion” is preferred in this paper to describe the explosive properties of gas mixtures according to the European standard EN 1127 to avoid misunderstanding.

Strictly speaking, an explosion limit refers to the limiting flammable gas fraction in the mixture with air where a combustion reaction (flame) just fails to propagate (see also [2]). The range between the “lower explosion limit” (LEL) and “upper explosion limit” (UEL) is the so-called explosion range. To analyze flammable gas/oxidizing gas/inert gas mixtures it is useful to extend the terms "explosion limit“ and "explosion range". In the broader sense, the explosion limit refers to the flammable gas fraction of a three-component system that consists of a flammable gas, an inert gas, and an oxidizing gas. Therefore in this paper the term “explosion region” is being used instead of “explosion range” to distinguish between 2- and 3-component systems. Inside the explosion region the gas mixture is explosive and can be ignited by ignition sources.

In a graphical representation of such a 3-component system, the explosion limits form a boundary line that embraces all explosive compositions. The enclosed area is the explosion region.

3. CHEMSAFE Database

Hazardous properties of different substances can be only compared when using the same test methods. This has been the main goal for collecting, evaluating and storing these measured data in a database for twenty five years. Now the CHEMSAFE database [1] contains rated safety characteristics on fire and explosion protection for approximately 3000 different flammable gases, liquids and dusts and over 2800 mixtures of gases, vapors, and dusts, such as explosion limits, flash points, ignition temperatures, limiting oxygen concentration, ignition energy, maximum experimental safe gap, etc. These data are necessary for explosion protection purposes. CHEMSAFE is a joint project involving three project partners from Germany: BAM, Berlin, PTB (Physikalisch-Technische Bundesanstalt) in Braunschweig, and DEHEMA (Gesellschaft für Chemische Technik und Biotechnologie e. V.) in Frankfurt am Main. The recommendations in the database are given by the experts of two German federal institutes: BAM and PTB. These institutes also publish their own measured data. The database is available all over the world online on the internet (see http://www.dechema.de) and as an in-house version in German and English, developed by the DEHEMA, Frankfurt/Main (see Fig. 1).
4. Explosion Protection

There are uniform requirements for explosion protection within the European Union (EU) for machinery and equipments used in explosive atmospheres, see Directives 2006/42/EC [3] and 2014/34/EU [4]. These correspond to the CHEMSAFE temperature classes (see Table 1) and explosion groups of substances and machinery (see Table 2), respectively [2].

<table>
<thead>
<tr>
<th>Temperature class</th>
<th>Auto ignition temperature ($T_{AIT}$) in °C</th>
<th>Maximum surface temperature in °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1</td>
<td>$T_{AIT} &gt; 450$</td>
<td>450</td>
</tr>
<tr>
<td>T2</td>
<td>$300 &lt; T_{AIT} \leq 450$</td>
<td>300</td>
</tr>
<tr>
<td>T3</td>
<td>$200 &lt; T_{AIT} \leq 300$</td>
<td>200</td>
</tr>
<tr>
<td>T4</td>
<td>$135 \leq T_{AIT} \leq 200$</td>
<td>135</td>
</tr>
<tr>
<td>T5</td>
<td>$100 \leq T_{AIT} \leq 135$</td>
<td>100</td>
</tr>
<tr>
<td>T6</td>
<td>$85 &lt; T_{AIT} \leq 100$</td>
<td>85</td>
</tr>
</tbody>
</table>

The auto ignition temperatures stated in the table relate to an initial pressure of the mixture of 101.3 kPa (ambient pressure). The temperature classes specify the allowed surface temperatures for electrical and non-electrical equipment with respect to the flammable substance used (see European standards EN 13463-1, EN 60079-0, EN 60079-14).

Flammable gases and vapors are classified into explosion groups according to their experimental safe gap. The measured data in CHEMSAFE and the test methods will be discussed later on.

The determination of the safety characteristics for classifying of substances in temperature classes and explosion groups based on harmonized international standards.
Table 2. Classification of substances in explosion groups according its maximum experimental safe gap values.

<table>
<thead>
<tr>
<th>Explosion group</th>
<th>Maximum experimental safe gap (MESG) in mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>IIA</td>
<td>MESG &gt; 0.9</td>
</tr>
<tr>
<td>IIB</td>
<td>0.5 ≤ MESG ≤ 0.9</td>
</tr>
<tr>
<td>IIC</td>
<td>MESG &lt; 0.5</td>
</tr>
</tbody>
</table>

Safety of workplaces is regulated by the Directive 1999/92/EC [5] and Directive 2009/104/EC [6]. Every member state of EU has to specify technical rules in order to implement these directives into the national laws. In Germany the Federal Ministry of Labor and Social Affairs is responsible for regulation of industrial safety and health. The Federal Institute for Occupational Safety and Health (BAuA) as a federal authority belongs to the Federal Ministry of Labor and Social Affairs (BMAS) and as a major governmental research institution advises the Federal Ministry of Labor and Social Affairs in all matters of safety and health and of the humane design of working conditions. This institute is responsible for these technical regulations for safety in the workplace and in its home page (www.baua.de) one can find the German technical rules for operating safety (Technische Regeln für Betriebssicherheit - TRBS). For explosion protection in operational safety the following technical rules are responsible: TRBS 2152 ff, TRBS 2153. The topics of these technical rules are the primary, secondary, and constructive explosion protections.

4.1. Primary explosion protection

In order to avoid explosive atmospheres in the presence of flammable substances and mixtures, the generally applied solution in industrial processes is purging the system with an inert gas. Reliable measurement data are required concerning the explosion range of such ternary systems. The limiting values of a ternary system can be determined from the measured explosion limits data obtained from different inert gas concentrations in air - e.g. limiting oxygen concentration (LOC) or, more generally, “maximum oxidizing gas concentration” (MOC) in the case of using oxidizing gases other than air, the “maximum permissible amount of flammable gas concentration” (MXC) and “maximum required inert gas concentration” (MAI), (see [7] for further information). These values can be shown in a so-called explosion diagram using a triangle plot (see Fig. 2).

These diagrams can be used, for example, for the estimation of flammability of gas mixtures in different process conditions. Flammability is very important information for customers from chemical and process industries or transport companies. With the help of limiting values, e.g. LOC, a process engineer can control the oxygen amount in the gas mixture in order to avoid the dangerous explosive atmosphere in an industrial process. Most chemical processes are carried out at elevated temperatures and/or pressures. In these cases measured data are required in these conditions.

The in-house version of the database CHEMSAFE provides a graphical representation of these data in x-y or in triangular diagrams (see Fig. 3) which makes easily understandable the influence of these parameters. The temperature dependence of the explosion limits of the system hydrogen/nitrogen/air can be seen from this diagram. At elevated temperatures the explosion regions expand for all flammable gases, i.e. the upper explosion limits are increased whereas the lower explosion limits are lowered. This can be understood as less combustion energy is required at higher temperatures to heat the reactive gas mixture to reach the flame temperature. For many flammable gases the relative change of explosion limits is lower and upper similar.

Fig. 4 shows the pressure dependence of the explosion limits of methane as a typical example for a variety of flammable gases.

For the majority of flammable gases, explosion regions expand with increasing pressure. While the lower explosion limits remain nearly constant, the upper explosion limits are shifted towards much higher values of the flammable gas fraction.
Fig. 2. Safety characteristics derived from the explosion diagram [7].

Fig. 3. Explosion region of the ternary system H₂/N₂/air at temperatures at 20 and 400 °C [1]
Although interpolation of temperature dependence between measured explosion limit curves is normally allowed, but this kind of interpolation in the case of the pressure dependence can cause fairly big mistakes. Extrapolation of the pressure dependence is a particularly dangerous task for chemically unstable gases. For example ethene decomposes at higher pressures and two reactions take place in the system: combustion and decomposition (see Fig. 5a).

Ethene and other chemically unstable gases like ethylene oxide have caused serious accidents in the past. That’s why BAM has carried out many tests on these systems and published these data in CHEMSAFE for practical use e.g. in sterilization processes (see Fig. 5b).
Many industrial processes need data for the explosion region of a flammable gas with an inert gas not only in air but also in pure oxygen atmospheres; such data can also be taken from CHEMSAFE. The newly measured explosion diagram of methane/nitrogen/oxygen system under pressures up to 50 bars (see Fig. 6) can be compared with the explosion diagram of methane/nitrogen/air system in Fig. 4 and e.g. the upper explosion limits at 10 bar initial pressure values are much larger in oxygen than in air.

Fig. 6. Explosion regions of the ternary system CH₄/N₂/O₂ at 20 °C and 1 bar, 10 bar and 50 bar initial pressures [1]

Different inert gases exert different influence on the shape and size of the explosion region of a flammable gas. The European legislation for hazardous substances and dangerous goods allow the application of a calculation method in accordance with International Standard ISO 10156: 2010 No. 3.3, for the classification of small amounts of gas mixtures [8, 9]. When results are interpreted, it must also be taken into account that nitrogen equivalence coefficients themselves are influenced to a certain extent by the flammable gas. It is therefore not possible to specify exact numbers that are valid for any flammable gas. This ISO standard from 2010 uses many experimental values from CHEMSAFE as a base of the calculation method for flammability and oxidizing ability of gases. These calculation methods are used for classification and labelling for gases in the GHS system in Europe (see CLP Regulation [10]). This influences not only transport classification but also the Safety Data Sheets and occupation safety.

Suitability of the inert gas must be checked for individual cases: Metal dusts react with carbon dioxide, water vapour, or nitrogen (titanium, magnesium).

4.2. Secondary explosion protection

If an explosive atmosphere cannot be prevented from emerging, the avoidance of the ignition sources plays an important role. For combustible dusts it is more difficult to avoid an explosive mixture by limiting of the concentration than in case of gases or vapors. The minimum ignition energy is one of the most important safety characteristics of these substances in order to assess the risk of an explosion. Minimum ignition energy (MIE) values of dust samples are usually determined by the modified Hartmann apparatus in BAM. The CHEMSAFE database contains approximately 500 minimum ignition energy values for dust samples some of which are very different, so the experts of BAM and other institutes are about to check all the data for dusts in CHEMSAFE, in the available literature and data collections in order to provide more adequate information to users of this database. It is really dangerous to choose only one value from a safety characteristic of a dust sample without taking into account all the other values for this characteristic.
The auto ignition temperature is the basis for the explosion prevention measure “Avoidance of ignition sources” by limiting the temperatures of hot surfaces [2]. In case of auto ignition temperatures of vapors and gases one can trust the published recommended values in the database. There are the basic data for avoiding ignition sources e. g. hot surfaces. The test apparatus is demonstrated in Fig. 7.

Fig. 7. Test apparatus for auto ignition temperatures (\(T_z\)) of flammable gases and liquids according to DIN 51794 and IEC 60079-20-1 [11].

If the operational conditions of the process plant are not atmospheric, then it is important in many cases to know the influence of pressure on the auto ignition temperatures for chemical substances. Some examples taken from CHEMSAFE can be seen in Fig. 8.

Fig. 8. Auto ignition temperatures (\(T_z\)) of flammable liquids as a function of pressure, measured in autoclave. (Source: PTB) [1]
It can be seen from this example that the auto ignition temperatures are strongly influenced by pressure. Therefore it is dangerous to use data which are measured at ambient pressure for process conditions at elevated pressures. The auto ignition temperature’s ranges for temperature classes are demonstrated as dotted lines in the Figure 8.

4.3. Constructive explosion protection

It is not always possible to reduce the risk of an explosion by avoiding occurrence of explosive mixtures and ignition sources. In those cases the effects of an explosion should be minimized to an acceptable level by constructive measures in order to mitigate the damage and losses of and eliminate the injuries of working personals.

The following safety characteristics are necessary to quantify the effect of an explosion: Maximum explosion pressure, maximum rate of pressure rise, Kst value for dust, MESG, etc. These data are the bases for explosion-proof, explosion shock resistant constructions of equipments or designing explosion venting, decoupling or suppression measures, and flame arresters. Maximum explosion pressure (CHEMSAFE contains absolute pressure and not gauge pressure) and maximum rate of pressure rise for a dust cloud are measured in BAM either in a 20 dm³ sphere or in a 1 m³ explosion chamber (see Fig. 9a and 9b). For example in search for acetyl cellulose one can find two maximum rate of pressure rise, \((dp/dt)_{\text{max}}\) values in the CHEMSAFE database: 625 bar m/s and 595 bar m/s. Both these data are displayed together with information about particle size distribution and/or median value of the investigated dust sample (see Fig. 10). Nevertheless dust safety characteristics data in CHEMSAFE have to be used as approximate information about this type of substance. There are not as precise data as a flash point of a pure flammable liquid.

In the case of gases and vapors not only explosion pressures, but some other characteristics also provide important information for the mitigation of the detrimental effects of an explosion. One of the characteristic data for explosion-proof equipment is the maximum experimental safe gap (MESG). This is the gap which prevents flame transmission for all concentrations of the respective flammable substance/air mixture determined under defined test conditions. The test conditions are standardized in IEC 60079-20-1. A schematic view of the apparatus is shown in Fig. 11.

In Table 3 a comparison of the minimum ignition energy with the maximum experimental safe gap values for the most frequently used gases indicates that MIE and MESG have the same order of magnitude. The most easily ignitable hydrogen has the smallest MESG value. This information is also very valuable for explosion protection.
Fig. 10. Result of a search of maximum rate of pressure rise for dust Cellulose-2,5-acetate in CHEMSAFE [1].

1 Inner explosion chamber (20 cm³)
2 Outer explosion chamber (2.5 dm³)
3 Gap
4 Window
5 Ignition source
6 Screw

Fig. 11. MESG apparatus according to IEC 60079-20-1 (Source: PTB, Braunschweig) [11].

Test results for safety characteristics of the same compound can sometimes be used to check the reliability of the measured data. In addition to the minimum ignition energy, the maximum experimental safe gap, which in turn is correlated with the maximum normal burning velocity, can also serve as a measure of ignitability at nearly point-ignition sources. It has been proved for a great variety of substances that minimum ignition energy, minimum ignition current and maximum experimental safe gap are correlated with one another so that the classification of substances is preserved when classification is made according to each of these three quantities.
Table 3. Minimum ignition energy of some gases in comparison with their maximum experimental safe gap values.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Minimum ignition energy (MIE) in mJ</th>
<th>Maximum experimental safe gap (MESG) in mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>0.017</td>
<td>0.29</td>
</tr>
<tr>
<td>Acetylene</td>
<td>0.019</td>
<td>0.37</td>
</tr>
<tr>
<td>Diethyl ether</td>
<td>0.19</td>
<td>0.87</td>
</tr>
<tr>
<td>Propane</td>
<td>0.24</td>
<td>0.92</td>
</tr>
<tr>
<td>Methane</td>
<td>0.29</td>
<td>1.14</td>
</tr>
<tr>
<td>Ammonia</td>
<td>14</td>
<td>3.18</td>
</tr>
</tbody>
</table>

The values of MESG are known for numerous pure substances. However, there has been no method for estimating the MESG of mixtures of flammable substances, even when the MESG of the pure components are known. If the MESG of a mixture of flammable substances has not determined experimentally, explosion prevention measures usually choose the lowest MESG of the mixture components. This often makes it necessary to take expensive safety measures.

Based on some 150 measurements of binary and ternary mixtures, Brandes et al. [12, 13] developed a method which allows the MESG for mixtures of flammable substances to be estimated. They proposed an equation which is applicable, if a clearly defined stoichiometric equation is known and there are no further influences on the reaction kinetics:

In CHEMSAFE’s in-house version this calculation method can be used for estimation of MESG of mixtures with a maximum of four components, if the stoichiometry is known.

5. Conclusion

The use of the rated data from CHEMSAFE database is a possibility to fulfill the requirements of the EU explosion protection directives, mentioned before. For effective explosion protection it is necessary to know the safety characteristics of the hazardous substances under atmospheric and also under other process conditions. Constructive explosion protection needs additional information on maximum explosion pressure, maximum rate of explosion pressure rise and maximum experimental safe gap of a hazardous system for designing constructive safety devices and reduces the impact of an explosion on the surroundings. In the CHEMSAFE database one can find both, rated safety characteristics for atmospheric conditions needed for Safety Data Sheets and characteristics for process conditions needed for process design and operation. Most data in CHEMSAFE have been measured according to German and European Standards, but some of them according to ASTM. The user is supported by a help text about the test methods, definitions of safety characteristics and the possibility of the conversion of the units. In addition, CHEMSAFE can handle mixtures and supplies semi-empirical calculation methods for the most important characteristics.

Flammability calculation of gas and vapor mixtures using the ISO 10156 standard and the MESG calculation for flammable mixtures are available in CHEMSAFE. These estimation methods replace the difficult measuring procedures, providing economic advantage.

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References


