

HAZARDS OF HIGH FLASH POINT LIQUIDS IN RELATION TO THE ATEX 137 DIRECTIVE

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Since 1st July 2006 all employers in the EU have to comply with the minimum requirements of "ATEX" Directive 1999/92/EC, commonly known as the ATEX 137 Directive. From Chilworth Technology's experience it appears that most employers have identified that the risks associated with flammable liquids and combustible dusts need to be assessed under ATEX 137. However, experience also suggests that many employers have not identified that higher flash point liquids can also create explosive atmospheres under certain circumstances: for example, when they are heated, condensed or sprayed to form an aerosol or mist, fractionated, mixed with residues of lower flash point liquids; or undergo reaction or decomposition.

The aim of this paper is therefore to raise awareness of the circumstances where high flash point liquids can form explosive atmospheres, and hence are covered by the ATEX 137 Directive. It also aims to provide guidance on carrying out the appropriate explosion risk assessments on the handling of high flash point liquids. To do this it describes incidents involving high flash point liquids, as well as other circumstances where the potential presence of an explosive atmosphere has been overlooked, e.g. in heat transfer fluid and fuel systems.

The conclusion is that the ATEX 137 Directive does apply to high flash point liquids in the circumstances described. In conclusion the paper also mentions that, in circumstances where ATEX 137 does not apply (i.e. non-atmospheric conditions), explosion risks would still need to be assessed under the Chemical Agents Directive (CAD) and Machinery Directive.

INTRODUCTION

On 16th December 1999 the European Union adopted Directive 1999/92/EC, entitled "minimum requirements for improving the safety and health protection of workers potentially at risk from explosive atmospheres" [EC 2000]. This has become commonly known as the **ATEX 137 Directive**, after Article 137 of the Treaty of Rome under which it was adopted. As the ATEX 137 Directive's title suggests, it is concerned with the risks to people associated with the presence of explosive atmospheres in the workplace. In summary it requires that employers:

1. In order of preference, take technical and/or organisational measures to prevent the formation of, avoid the ignition of, and/or mitigate the effects of, an explosive atmosphere.
2. Carry out an assessment of explosion risks to establish the measures that are in place and any further measures that are required.
3. Carry out hazardous area classification, and then adopt minimum requirements laid down in the directive in the areas identified; e.g. selection of appropriate equipment and protective systems as defined in Directive 94/9/EC [EC 1994], commonly known as the "ATEX 100a Directive" or "ATEX 95 Directive".
4. Draw up an Explosion Protection Document (EPD)¹; which contains the risk assessment, hazardous area classification, and organisational and/or technical measures taken.

¹The UK has incorporated the ATEX 137 Directive into the Dangerous Substances and Explosive Atmospheres Regulations (DSEAR) 2002. These regulations require that a risk assessment document be drafted, with is equivalent to an "EPD".

As part of the ATEX 137 Directive's obligations, the European Union has since developed a non-binding Guide of Good Practice [EC 2003] for implementing the Directive. Other member states such as the UK have also developed their own guidance and codes of practice to help employers implement ATEX 137.

One of the most important definitions associated with the ATEX 137 Directive is that for an "explosive atmosphere". This is defined in Article 2 of the Directive as

"... a mixture with air, under atmospheric conditions, of flammable substances in the form of gases, vapours, mists or dusts in which, after ignition has occurred, combustion spreads to the entire unburned mixture."

A precise definition for "atmospheric conditions" is not given in the Directive; but from the Guide of Good Practice this is generally understood to mean air (20.8% v/v oxygen) at pressures and temperatures between 0.8 and 1.1 bara and -20 and 60°C respectively.

Chilworth Technology have carried out fire and explosion risk assessments in the UK and elsewhere both before and after the introduction of ATEX 137. The experience gained from carrying out these assessments has indicated that the majority of employers understand the hazards associated with flammable substances (liquids, gases and dusts) that can form explosive atmospheres under atmospheric conditions. For example, liquids that have a closed cup flash point below 40°C are often identified as being flammable liquids to which the ATEX 137 Directive applies.

However, there are other substances that can also form explosive atmospheres in certain circumstances and which are not always identified as requiring a risk assessment under ATEX 137. These include “high flash point” liquids: namely, liquids with closed cup flash points measured as being above 40°C; both those classed as flammable under EU Directive 67/548/EEC [EEC 1967] and amending Directives and those that are not.

From experience Chilworth Technology has identified circumstances where these high flash point liquids can potentially generate explosive atmospheres. These are as follows:

1. Heating above the flash point in normal operation e.g. thermal oils.
2. Heating above the flash point due to a deviation from normal operation.
3. Formation of a spray, mist or aerosol.
4. Fractionation of liquid blends, leading to a concentration of lighter fractions.
5. Reaction or decomposition leading to a lowering of the flash point.
6. Presence of contaminants that have a lower flash point or generate flammable gases.

On many occasions these potential hazards are identified and the associated risks assessed before they lead to fires and explosions. However, there are circumstances where accidents or incidents have occurred, often because a hazard has not been identified.

The following sections elaborate on all the above circumstances, with extensive use being made of actual fire/explosion incidents and other examples.

HEATING ABOVE THE FLASH POINT (NORMAL OPERATION)

HEAT TRANSFER FLUIDS

Many sites use oils or fluids (e.g. “hot oils”) as heat transfer media. Examples of their uses encountered during ATEX assessments include:

1. Heaters for air feeding dryers (spray, fluidised bed etc.).
2. Heated drums for drying adhesives, laminates or fibres.
3. Heating and cooling of vessel jackets.

Heat transfer fluids can have flash points that are relatively low (40–60°C); though where heating to temperatures above 150°C is required the fluids can have flash points in the range 190–220°C. The latter are often called “hot oil” systems, and generally consist of a recirculation loop with a pump and heater (often gas or oil fired) that feeds heat exchangers, heating coils, heated drums or other heating devices, with a high-level expansion tank connected to the suction side of the pump to provide a reservoir of cold oil. The schematic below describes a typical system.

Whereas hot process fluids, even those with high flash points, tend to be identified as requiring assessment in terms of ATEX 137, heat transfer fluids are sometimes overlooked because, for example:

1. Heat transfer fluids are service rather than process fluids, and so do not tend to receive the same attention.
2. The heat transfer fluid systems are often “turnkey” systems that have been designed and installed by contractors, who often maintain the systems as well e.g. replace spent fluid. Therefore, a site operator often

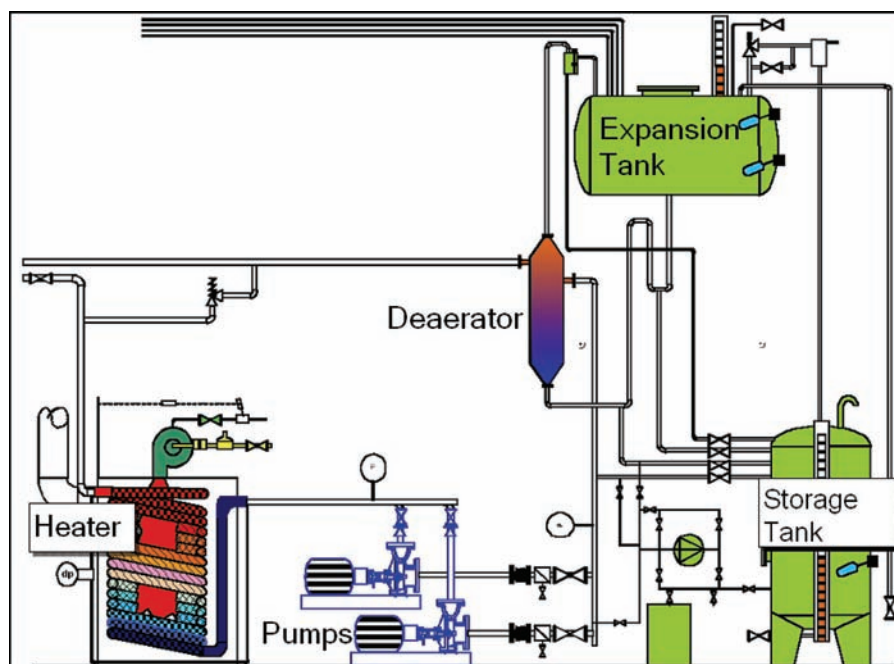


Figure 1. Process schematic of a typical thermal fluid system (reproduced by permission of Heat Transfer Systems Ltd.)

has little knowledge about the heat transfer fluids themselves. For example, when carrying out site assessments, it has been found that a material safety datasheet was not available or even the name of the fluid used was not known.

3. The site employing a hot oil system did not routinely handle flammable liquids e.g. food processing sites.

On a number of sites, inspection of areas where hot oil was used revealed that no hazardous areas had been defined, even though the hot oil was handled above its flash point; and hence there were no controls on ignition sources local to where leaks of hot oil could occur.

However, as the following incident reveals, even if suitable equipment has been specified there could still be a fire and explosion risk due to the emission of liquid as well as vapour at high temperature. On a chemical site hot oil at 300°C and 4 barg leaked from a 12 mm orifice in a pipe, creating a dense white fume comprising both vapour and liquid droplets [Anon 1997]. Evidence suggests that lagging was either absent, damaged or not fitted correctly. The sprayed oil droplets hit both a local flameproof light fitting and a water sprinkler head, activating the latter. The combined effects of cold water and hot fluid impinging on the light fitting cracked the glass casing, leading to vapour/mist reaching the hot filament and igniting. This incident not only illustrates that hot oils can form explosive atmospheres but also the benefits of lagging hot oil lines.

As well as being above their flash point, some thermal fluids can be handled close to their auto-ignition temperature, thus making them susceptible to self-ignition when in contact with air. For example, on one site an oil temperature of up to 300°C could be set when the fluid auto-ignition temperature was quoted as 315°C. Hot oil systems are often equipped with high temperature and low flow alarms, but these do not always automatically shut down the heater and on one site the company concerned did not know what the high temperature alarm was set at.

HEAVY FUEL OIL

Heavy fuel oil is sometimes employed as a fuel in steam boilers and other combustion devices. It is normally heated above its flash point of 80–130°C to reduce its viscosity and hence improve atomisation at the burner, with typical temperatures being above 90°C. This often means that heavy fuel oil above its flash point is transported through non-hazardous areas such as boiler houses. One safeguard in these cases is that a high density of line joints is often restricted to the heater (heat exchanger) area, and that the area near the boiler(s) is often protected by a fusible link mechanism that shuts off the fuel oil supply in the event of an external fire. In addition, lines are normally lagged, so spraying of fuel oil is unlikely. Therefore, the only area where a Zone 2 area is justifiable is the around the heaters, which are often in a separate area or room attached to the boiler house. From experience, though, the heater area can be both poorly ventilated

(in a small room adjacent to a boiler house) and unlikely to contain any equipment that is suitable for Zone 1 or 2 areas.

HEATING ABOVE THE FLASH POINT (DEVIATIONS FROM NORMAL OPERATION)

LOSS OF TEMPERATURE CONTROL

This is especially significant when the system concerned is open and there are known ignition sources such as mills in the area. For example, a fire occurred at an ink manufacturer, where carbon black was milled in an oil with a flash point of 130°C. The incident occurred when there was a loss of cooling water to the mill's water jacket, which caused the oil to be heated above its flash point. The oil vapour then ignited, probably at the mill outlet which was open. The lack of any means of detecting a loss of cooling water (e.g. a high temperature or loss of coolant alarm that shuts off the mill on activation) was one of the main causes of the fire.

Some liquids such as heavy fuel oil have to be heated to keep them mobile when stored or pumped, though the temperature can still be below the flash point if good temperature controls are in place. However, on one site steam was used to heat heavy fuel oil in a storage tank, with a controller apparently regulating the oil temperature to 60°C, i.e. below the flash point of 80–120°C. However, this temperature could not be confirmed because there was no reliable temperature indication (i.e. the local dial indicator appeared to be broken) and there were no records of the controller ever having been calibrated. The site in question appeared to be unaware of the flash point of heavy fuel oil and hence the implications of letting the liquid overheat.

HOT SURFACES

Contact with hot surfaces can also lead to liquids being heated above their flash point. One example is the handling of gas oil (flash point 60°C) in boiler houses, where:

1. Spraying of liquid onto surfaces is a possibility, because gas oil is handled at ambient temperature and hence pipes are rarely lagged.
2. Although the hot surfaces (e.g. boilers) are often insulated, small defects in insulation may be sufficient to raise the gas oil temperature above the flash point.

Thermal insulation checks on hot surfaces and fusible links that shut off the fuel supply if there is an external fire are often the main protection against fires and explosions caused by leaks of gas oil local to the boilers or other burners.

Hot work is another cause of hot surfaces, and has been the cause of fires and explosions involving high flash point liquids such as diesel fuel in the past. In these cases it was not recognised that local heating by the hot work could raise the temperature of any liquid present and create an explosive atmosphere, so the plant was only drained and not cleaned or gas freed.

MISTS, SPRAYS AND AEROSOLS

CONDENSATION MIST

If hot vapour is rapidly cooled, it can condense to form a mist, which can be flammable. The small mist droplets can remain in suspension for a long time.

The hot oil incident described above is perhaps one example where formation of a condensation mist was a contributory factor. Condensation mists have also been responsible for crank case explosions in marine diesel engines, due to oil evaporating on an overheated bearing.

SPRAYING

Spraying of high flash point liquids under pressure can create a mist/aerosol that is flammable, even if the liquid is below its flash point. Research work has been published on modelling of the phenomenon in order to estimate the risks; including the likelihood of mist formation, the effect of impingement and an estimation of the likely minimum ignition energy based on the mean droplet size. This has been documented elsewhere [Bowen and Shirvill 1994] [Krisha et al 2003] [Maragkos and Bowen 2002]. Mists are recognised as a possible cause of an explosive atmosphere in ATEX 137, and are discussed in the latest IEC hazardous area classification standard IEC 60079-10-1 [IEC 2008].

The conclusions of the research work are that the propensity of a system to form mists/aerosols with smaller (i.e. more flammable) droplets will increase as:

1. The liquid density increases.
2. The liquid viscosity decreases.
3. The surface tension decreases.
4. The operating pressure increases.

For example, it appears that mists/aerosols are unlikely to be generated where the internal pressure is less than 1 bar g [Bowen and Shirvill 1994].

The most likely causes of significant flammable mist/aerosol atmospheres that could lead to fires and explosions are when high flash point liquids are deliberately sprayed onto surfaces; e.g. the application of coatings such as paint and solvent cleaning. For example, the spraying of diesel fuel, gas oil and kerosene in order to clean vessels has led to explosions. One incident of note occurred at a road haulier's yard, where a mixture of kerosene, gas oil and diesel fuel was sprayed to clean a bitumen tanker [HSE 2005]. The high-pressure spray generated a flammable mist, probably by impingement on a bitumen spraying bar, which then ignited, fatally burning the person carrying out the spraying. Static electricity was believed to be the most likely ignition source, given the likely low conductivity of the spray mixture, the lack of conductor earthing and the spray velocity used. In another case, kerosene mist ignited when it was sprayed from a fire tender to clean aviation tanks, resulting in three men being killed [HSE 1983].

Mist formation at joints is another possibility; either through leakage under pressure from a joint or in-leakage

of air through a joint when a vacuum is applied. The following incident illustrates both of these scenarios. Two different printing inks (yellow and cyan) were being offloaded into storage tanks from a multi-compartment road tanker at a newspaper publisher. When offloading the yellow ink, a fire occurred at a hose coupling that was quickly extinguished by the tanker driver. Offloading continued, and once the cyan ink had been delivered, the tanker delivery pump was reversed and the hose coupling was loosened to clear the hose. This resulted in smoke being seen at the coupling and damage to the hose, indicating that a fire had occurred inside the hose.

The inks had a flash point of 140°C, and although the tanker contents were heated to lower the viscosity of the inks this was to no more than 40°C. The inks were delivered using the tanker's pump and different couplings were used to deliver each ink. It is therefore believed that the following flammable atmospheres caused each of the fires:

1. *First fire:* A flammable spray or mist had occurred local to a hose coupling, due to the pressure inside the hose and a leak at the coupling. Evidence for this included an oil film around the coupling and the poor condition of the coupling seal.
2. *Second fire:* Ingress of air occurred through the loosened coupling when the pump was reversed, causing the formation of a flammable mist inside the hose.

The likely source of ignition for the fires is an interesting one. In common with many road tankers, the tanker pump was powered hydraulically using a separate three-phase electric pump. It was found that the power supply to the electric pump was not adequately earthed (supply earth resistance 5 MOhms), due to a short circuit between one of the phase cables and the earth cable. This probably led to the tanker chassis tending towards phase voltage, which would then have been earthed via the hoses, which had conducting reinforcing metal spirals. A poor or loosened hose coupling would therefore have resulted in sparking across the coupling at the same point where an ink mist was being generated; hence the fires.

However, fires and explosions due to flammable mist/aerosol formation at leaking joints are not common compared to similar leaks involving low flash point liquids or liquids handled above their flash point [Bowen and Shirvill 1994]. The main reason appears to be that the droplet size is often too large for any effective ignition sources to be present, and/or the aerosol disperses to below the lower explosive limit within a short distance of the leak source.

FRACTIONATION

Some high flash point liquids are blends, such as fossil fuel (i.e. petroleum or coal) distillates comprising a number of organic chemicals (mainly hydrocarbons) distilled within a certain boiling range. If these blends or distillates are heated, it is possible that the lower boiling "light" fractions will vaporise in preference to the higher boiling "heavy" fractions, leading to explosive atmospheres due to

concentration of the light fractions in vapour spaces or distillate receivers.

One example of fractionation is in storage tanks containing heated hydrocarbon blends such as heavy fuel oil, bitumen or coal tar pitch. In such tanks light fractions can accumulate in the tank vapour space, leading to an explosive atmosphere both within the tank and around the vent when the tank is filled. From experience, such flammable atmospheres are not always identified, although they have been the cause of fires or explosions in the past. Once such fire occurred in a bitumen tank, and was attributed to a slug of high temperature material (“overheated slug”) being charged to the tank and igniting a flammable atmosphere in the vapour space [Fishwick 2001]. The “overheated slug” was itself attributed to faulty electrical trace heating on the feed line heating a locked-in mass of bitumen.

Another example of fractionation is when petroleum-based blends are recovered by distillation, as the preferential vaporisation of lighter fractions can often lead to the distillate having a lower flash point than the virgin material. At a paint manufacturing site a hydrocarbon cleaning solvent with a flash point of at least 40°C was routinely recovered by distillation, and it was assumed that the recovered solvent would also have the same flash point. However, a test on the recovered solvent revealed that it had a closed cup flash point of 27°C.

CHEMICAL REACTION OR DECOMPOSITION

Some high flash point liquids can either react with other materials or decompose, leading to the generation of flammable gases or liquids with a lower flash point. Some of these reactions or decompositions are relatively easy to spot, while others require detailed technical knowledge of the materials present and their chemistry.

The following examples are illustrative of typical situations based on published literature and experience. They do not cover the whole range of reactions or decompositions that can occur:

1. Some materials are water-reactive. For example, a high flash point silicone-based liquid was found to react with moisture in the air to produce ethanol, which has a flash point of 12°C.
2. Many heat transfer fluids thermally degrade over time, particularly if taken near to or above their recommended maximum temperature. This degradation reduces the flash point. For example, a US chemical company found that the flash point of a heat transfer fluid had dropped from 160°C to 39°C, while a company in Switzerland found that another heat transfer fluid flash point had dropped from 120°C to 60°C after only one year of service [UK CRHF 2009]. Experience has shown that some sites arrange for routine flash point tests on their heat transfer fluid(s) and occasional replenishment of the same based on evidence of degradation from the flash point tests. However, this has not been encountered universally.

3. The following is an example of a reaction/decomposition where more specialised knowledge was required to identify it. There was an explosion at a chemical company that carried out an esterification. Although the reaction was carried out hot (over 160°C), the reaction temperature was below the flash point of the product ester, which was known to be over 200°C. It was therefore assumed to be safe to transfer the hot (i.e. uncooled) ester out of the reactor using compressed air. However, an explosion occurred in the reactor while discharging the hot ester, which resulted in the manway being ejected through the factory roof; and in the subsequent investigation it was found that the flash point of the product ester was actually 160°C, i.e. below the reaction temperature. Through further laboratory investigations, the reduction in the flash point was attributed to a particular starting material for manufacture of a polyol raw material used in the esterifications. The presence of traces of this material was found to cause a partial decomposition of the ester.

CONTAMINATION

FLAMMABLE LIQUID CONTAMINANTS

Flammable liquid contaminants have been a cause of fires and explosions involving high flash point fuels such as diesel fuel and gas oil; in particular where the liquid is handled in pipes and vessels that have previously been used for other low flash point fuels such as petrol (gasoline). The practice of switch loading tanks between high and low flash point fuels routinely occurs in the oil industry, though even when switching is planned explosions still occur [NTSB 2004].

However, fires and explosions have also occurred when switch loading has not been recognised. For example, an explosion occurred when a driver was brazing a leaking diesel tank on his truck. The driver was using a proprietary fuel retriever to store the diesel fuel while he worked, and had refilled the tank after a previous attempt to repair the leak only to find that it was still there. The cause was attributed to the retriever being contaminated with petrol that had previously been stored in it, which was then flushed into the truck’s diesel tank. However, it should be noted that heating of residual diesel fuel in the tank by the brazing operation could also have created an explosive atmosphere in the tank.

FLAMMABLE GAS CONTAMINANTS

Although less common, flammable gases can also create explosive atmospheres where high flash point liquids are being handled. For example, if water contaminated with organic matter is used as a flushing medium, accumulation of water as a second phase in, for example, a storage tank can lead to the creation of flammable marsh gas (methane/ethane and hydrogen). This was concluded to be the fuel for an explosion in a kerosene tank, where river water was used as a line flush [Kletz 1983]. Static electricity,

probably due to a turbulent water/kerosene two-phase mixture in the feed line and tank, was the probable ignition source.

If flammable gases are used in process operations, these may dissolve in a high flash point liquid and then be released when the pressure reduces to atmospheric, e.g. in a storage tank. For example, in a refinery hydrogen was used to desulphurise and then strip gas oil grades [Riezel 2009]. Dissolved hydrogen was carried forward to a bulk storage tank where it exploded, causing a large pool fire involving two large gas oil tanks.

CONCLUSIONS

The conclusion that can be drawn from this paper is that there are a number of circumstances where the storage and handling of high flash point liquids can lead to the formation of explosive atmospheres in atmospheric conditions. Examples described include the presence of liquid above its flash point due to heating, fractionation or chemical reaction; the condensation or release of liquid as a spray or mist; and the presence of lower flash point liquids or flammable gases. The ATEX 137 Directive would apply if these circumstances can occur at a workplace. Therefore, an employer must identify whether or not they can occur on their site(s), and fulfil the requirements of the Directive if they can.

Of course, some explosive atmospheres involving high flash point liquids could occur in non-atmospheric conditions, and hence would be outside the scope of ATEX 137. Examples mentioned above include the inside of reactors and heated storage tanks at high temperatures. However, it should be recognised that these situations are still likely to require a risk assessment under the Chemical Agents Directive (CAD)² [EC 1998] or the Machinery Directive [EEC 1989].

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