

SOME MYTHS ON HAZARDOUS MATERIALS

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Summary

This paper describes some myths about hazardous materials, that is, deeply ingrained beliefs that are not wholly true. Thus many people believe that explosive mixtures are not dangerous if everything possible has been done to remove known sources of ignition, that non-sparking tools are useful, that if a combustible gas detector reads zero it is safe to introduce a source of ignition, that a pressure of 10 pounds is too small to cause injury and that ton for ton, toxic gases cause more harm than flammable gases.

*"It ain't so much the things we don't know that get us in trouble.
It's the things we know that ain't so."*

Artemus Ward
(1834-1867)

Introduction

In 1974 I wrote a paper on some myths of the chemical industry [1], deeply ingrained beliefs that are not wholly true. This paper describes some more myths, those concerning hazardous materials.

Myths are not incorrect beliefs — there is usually some truth in them — but neither are they wholly true. They are often more true of the past than of the present and they are usually deeply ingrained; they "cannot be destroyed by the presentation of contrary evidence" and they justify "practices whose continuance is independent of their efficacy" [2].

Most people who would admit that myths exist in many walks of life, even perhaps in management [2], nevertheless believe that scientists and engineers decide their views and actions on rational grounds alone. As I shall show, we are not entirely free from a belief in myths.

Myth no. 1

Flammable mixtures are safe and will not catch fire or explode if everything possible has been done to remove known sources of ignition

We are brought up to believe in the fire triangle: Air, fuel and a source of ignition are necessary for a fire or explosion to occur; take one away and an explosion is impossible.

When flammable gases or vapours are handled on an industrial scale this view, though theoretically true, is misleading. If flammable gases or vapours are mixed with air in flammable concentrations, then experience shows that sources of ignition are likely to turn up. They are one of the few things in life we get free.

In many investigations of fires and explosions the source of ignition is not found. Sometimes the investigator attributes the ignition to static electricity but without demonstrating the precise way in which static electricity might have been responsible.

The amount of energy required to ignite a flammable mixture can be very small, 0.2 millijoule. This is the energy produced when a mass of 1 gram falls 20 mm, though it has, of course, to be concentrated into a small time and space. It is, perhaps, therefore not surprising that we cannot completely eliminate all sources of ignition.

As an alternative to the fire triangle, I suggest:

AIR + FUEL → BANG or
AIR + FUEL → FLASH

What are these mysterious sources of ignition that seem to turn up? Sometimes it is genuinely static electricity. A steam or gas leak, if it contains liquid droplets or particles of dust, produces static electricity which can accumulate on an unearthed conductor, such as a piece of wire netting, a scaffold pole or a tool. Discharges may perhaps occur from the cloud itself. In other cases ignition may be due to traces of pyrophoric material, to traces of catalyst on which reactions leading to local high temperature may occur, to friction [3] or to impact of steel on concrete (but not to impact of steel on steel, see Myth no. 3).

The only safe rule is to assume that mixtures of flammable vapour in air in the explosive range will sooner or later catch fire or explode and should never be deliberately permitted, except under carefully defined circumstances where the risk is accepted. One such set of circumstances is in the vapour space of a fixed roof storage tank containing a flammable conducting liquid such as acetone or methanol. Static electricity is not a serious risk, provided splash filling is not allowed, and experience shows that explosions are very rare. The same is not true of tanks containing flammable hydrocarbons with low flash points and additional precautions such as nitrogen blanketing are necessary to reduce the risk of explosion to an acceptable level [4].

Here are just two examples of fires or explosions caused by unusual sources of ignition.

An explosion occurred in a fixed-roof storage tank. The liquid had a high conductivity, so static electricity could be ruled out as the source of igni-

tion. The only source that could be found was frictional heating caused by a taut vibrating wire, which supported a swing arm, rubbing against a pulley which had seized on its bearing and was not free to move; experiments have shown that steel wires subject to friction can produce glowing filaments of thin wire which cannot ignite methane but might ignite other gases. For a fuller account see [3].

Ref. 5 describes a fire in an open tank which occurred while a mechanic was tightening a screwed fitting which was leaking. The tank had been emptied but still contained flammable vapour. The tank was made from aluminium but the fitting — a valve — was made from steel. According to the report friction between the steel and aluminium caused oxidation of aluminium to aluminium oxide, a reaction which is exothermic. Alternatively a thermite reaction between aluminium and rusty iron might have occurred.

Myth no. 2

The worst crime or mistake one can make on a plant handling flammable liquids or gases is to introduce a source of ignition

This is related to the first myth.

Reports on fires and explosions often show an excessive concern with the source of ignition. If it is discovered it is often listed as the “cause”. But since sources of ignition usually turn up once a flammable mixture is formed, the real cause of the fire or explosion is the failure which allowed the flammable mixture to form, either by letting liquid or gas out of the plant or by letting air in. The only sure way of preventing fires and explosions is to keep the fuel inside the plant and the air out of it.

I do not suggest that we should allow indiscriminate smoking, welding, etc. in our plants. Obviously we must do what we can to remove known sources of ignition, so that those leaks that do occur are less likely to ignite. But this is our second line of defence. The first line is to prevent the formation of a flammable mixture.

Myth no. 3

Non-sparking tools should be used on plants which handle flammable liquids or gases

Non-sparking tools seem to be regarded as a sort of magic charm to ward off explosions, though a series of reports over thirty years has shown that they have little value.

The American Petroleum Institute has published a Safety Data Sheet [6], which summarises these reports. It does not say when the tools were first introduced, but as far back as 1930 a number of engineers were asking if they were really necessary. In 1941 an API report showed that it was very unlikely that petroleum vapour could be ignited by the impact of steel on steel produced by hand, and that power operation is required to produce an

incendive spark. It may be possible to ignite hydrogen, ethylene, acetylene and carbon disulphide by the impact of steel on steel using hand tools, but we should never let anyone carry out a maintenance job in an explosive atmosphere of hydrogen, ethylene or anything else.

I suggest that non-sparking spanners should never be used as they are poor as spanners, but that where hydrogen, ethylene, acetylene and carbon disulphide are handled, non-sparking hammers should be available for use in hardening up leaking joints. If possible the use of hammers of any sort for this purpose should be avoided. Non-sparking spanners should not be used even for hardening up leaking joints; it is better to use a good solid spanner and harden up the joint as quickly and effectively as possible.

There is no harm in using non-sparking hammers for all purposes but it is an unnecessary expense. Care must be taken that small particles of grit do not get embedded in the hammers or they will be more dangerous than steel ones.

Myth no. 4

If a combustible gas detector reads zero then there is no flammable gas or vapour present and it is safe to introduce a source of ignition

Combustible gas detectors, both fixed and portable, are some of the most useful instruments we possess and have made a big contribution to safety. However, a knowledge of their limitations is essential if we are not to be misled by them [7,8]. Unfortunately operators are often too willing to believe a zero reading, perhaps because that is the reading they would like to see.

Some of the causes of incorrect readings are:

(1) *The instrument is out of order.* When the instruments fail they do not always fail safe. Portable instruments should therefore be tested every day or, better still, immediately before use every time they are used. A useful test material is 30% isopropanol in water, as it normally produces a low reading (57% of the LEL at 65°F) and will thus detect loss of sensitivity. It also prevents damage to the filament of the instrument by repeated exposure to rich mixtures.

(2) *The vapours may be absorbed by the sample tube.* For this reason we prefer instruments in which the detecting element is placed at the point of test.

(3) *The sample tube may be choked* as a result of the swelling caused by absorption of vapours or in other ways.

(4) *The element may have been poisoned by exposure*, for example, to halogenated hydrocarbons or silicones. Poisoning by the former is temporary, by the latter permanent.

(5) *The substance being detected may form a flammable mixture with air only when hot* and may cool down in the instrument. This is the most common cause of failure to detect explosive mixtures and one explosion which occurred as a result will therefore be described in detail.

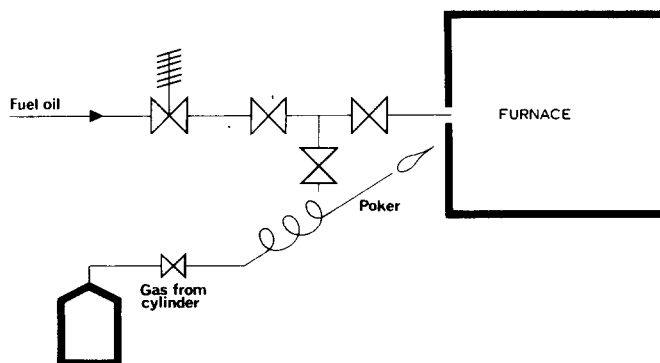


Fig. 1.

A furnace tripped out on flame failure as the result of a reduction in fuel oil pressure. The operator closed the two isolation valves and opened the bleed (Fig.1).

When the oil supply pressure had been restored the supervisor tested the inside of the furnace with a combustible gas detector. He got no response and, therefore, inserted a lighted poker; a bang occurred, damaging the brickwork and slightly injuring the supervisor.

When the burner went out, it took a few seconds for the solenoid valve to close and during this time oil entered the furnace. In addition, the line between the valve and the burner may have drained into the furnace. The vapour from this oil (flashpoint 150°F, 65°C) was too heavy to be detected by the combustible gas detector, as it condensed out in the sample tube. If a detector in which the detector head is placed at the point of test had been used the vapour might have condensed out on the sintered metal that surrounds the detector head.

When relighting a hot furnace burning fuel with a flash point above ambient temperature, we cannot rely on a combustible gas detector to detect a flammable mixture. We should therefore sweep out the furnace for a long enough period of time to be certain that any unburnt oil has evaporated. Operators should know the reason for purging so that they are less likely to reduce the purge time to avoid delay.

It is not a bad rule to say, "If a furnace burning fuel oil trips, have a cup of tea before relighting it". This will give most furnaces time to purge. If the delay is unacceptable then permanent pilot burners, supplied from a separate fuel supply, may be used.

To keep the purge time as short as possible, the solenoid valve should close quickly, it should be close to the burner and the line in between should be sloped so that it does not drain into the furnace.

There is a need for a gas detector which can detect vapour which is explosive when hot but safe at atmospheric temperature, for example, a detector with a heated sample tube.

For many years the furnace on which the explosion occurred and other furnaces burning heavy oils had been tested with detectors which were incapable of detecting the vapour of the fuel. Often we disbelieve instruments; we believe them uncritically when they tell us the answer we want.

Myth no. 5

If the pressure on a liquefied gas is reduced the amount of liquid remaining can be calculated by heat balance

If a liquid is under pressure at a temperature above its atmospheric pressure boiling point and the pressure is reduced, then some of the liquid will flash and the rest will fall to its boiling point at the new pressure. It is easy to calculate the amount that will flash and the amount of liquid that remains. However, the flash is accompanied by the production of a great deal of spray and experiments have shown that under the right conditions all the liquid may form a mixture of vapour and spray [9,10]. This phenomenon is well known to anyone who has removed the cap from the radiator of their car while the engine was hot. In this case the spray consists of large droplets which soon fall to the ground. In other cases the spray may be fine.

No-one, so far as I know, understands the factors controlling the amount or fineness of the spray. Does it depend on the liquid density, its surface tension, its degree of superheat or the geometry of the vessel or the aperture causing the reduction in pressure?

Note that if the vapour is flammable a fine liquid spray is also flammable and remains flammable below the flash point [11,12].

Myth no. 6

A pressure of 10 pounds is small and will not cause injury

There is not a printer's misprint in the heading. I wrote it that way because that is how we usually speak. We say, "The pressure in the vessel is 10 pounds" because "10 pounds per square inch" is too much to say.

Unfortunately this leads to a belief that, as 10 pounds is not much, so a pressure of 10 pounds is not much. Once we analyse the myth we see it is wrong, but it is still hard to get the idea out of our heads. Whenever people have been injured or plant damaged by pressure, surprise is expressed — by technically qualified people as well as operators — that so little pressure could cause so much damage or injury.

For example, some years ago an operator opened the door, 3 feet 6 inches diameter, of a steam filter before blowing off the pressure. The operator was crushed by the door against the frame of the filter and was killed instantly. During the investigation, surprise was expressed that such a small pressure (30 p.s.i.g.) could cause the injuries and damage that occurred and a chemical explosion in the filter was suggested. In fact, simple calculation shows that

the force acting on the door was 18 tons — and it is not surprising that when the holding bars were released it flew open with great violence.

In another incident a driver opened the manhole on top of a pressure road tank wagon while there was 10 p.s.i.g. air pressure in the tank. He was blown off the top. Surprise was expressed that the pressure was sufficient to do this.

On several occasions tankers have been emptied with the manhole and vents shut and have collapsed. Surprise has been expressed that the atmospheric pressure is sufficient. In fact, atmospheric pressure acting over the surface area of even a small tanker can amount to 200 tons. No-one would expect the tanker to survive if a railway engine was lowered on to it.

Myth no. 7

Blast walls provide the ultimate protection against explosions

Despite all our precautions, explosions may occur inside or outside the plant equipment. Certain equipment, in which the chance of an explosion occurring has been judged to be greater than normal, for example, certain oxidation reactors, have been surrounded by blast walls to protect people and other equipment from missiles and blast.

The walls may give some people a feeling of security but that is about all. To withstand the sort of pressures that might be developed, especially in a confined explosion, the walls would have to be so thick that they would cost as much as the plant. If an explosion occurred inside many so-called blast walls, the result would be that people would be hit by a stream of moving concrete instead of a stream of moving air. Even if the wall withstands the shock wave it may deflect pressure onto people sheltering behind it.

Instead of building blast walls we would do better to spend our money on reducing the probability that an explosion will occur. The high-integrity protective system described by Stewart [13] is better value for money than a blast wall as it will prevent explosions in oxidation reactors instead of providing doubtful protection against the consequences.

Equipment which is particularly liable to leak and fire is sometimes surrounded by fire walls which prevent the fire reaching other equipment. These walls serve a useful purpose. They are often spoken of loosely as blast walls but they are really fire walls.

In small research plants where the maximum energy release is equivalent to a few kg of TNT, construction of reliable blast walls is feasible and is the recommended solution, as a high integrity protective system would be too expensive and often we do not have the knowledge needed to design one correctly. A method of designing blast walls for small units has been described by High [14].

Myth no. 8

Ton for ton toxic gases produce more casualties than flammable gases or liquids

The concentrations of toxic vapour which can cause sudden death or injury are much lower than lower flammable limits. The spread of toxic vapours cannot be cut short by ignition. Hence we would expect sudden releases of toxic vapours to produce many more casualties than sudden releases of flammable vapours.

In practice, however, this is not the case. For the period 1970–75 the press, including the trade press, reported 34 fires or explosions in the oil and chemical industries (including transport) throughout the World which resulted in 5 or more fatalities; these amounted to about 600 fatalities in total. I know of only two comparable toxic incidents in the same period causing a total of 28 fatalities. They were: (a) an explosion in a refrigerated store which was caused by a leak of natural gas and which resulted in rupture of several ammonia tanks. It is not clear from the report whether the ten fatalities were caused by the explosion or the ammonia [15] and (b) a tank burst which killed 18 people [16].

Simons [17] has compared fatalities caused by the transport of flammable and toxic gases in the U.S.

“During the period 1931 to 1961 37 persons (non-workers) were killed in LP-Gas flash fires and explosions from accidents involving tank trucks (i.e. road tankers). This is an average of 1.23 fatalities per year ... For the years since 1961, an exact tally has not been made, but the annual average is believed to be in the range 1 to 2 fatalities per year.”

In addition, an unknown number of people were killed in accidents involving LP-Gas tank cars (i.e. rail tankers).

In contrast, during the same period five people were killed in the U.S. as the result of accidents involving road and rail tankers of chlorine. So far as is known, the transport of other toxic gases caused no fatalities in the U.S. in this period. Five deaths in 45 years is an average of 0.1 death/year.

The total quantity of flammable flashing liquid in stores, process plants and transport containers probably exceeds the total quantity of toxic flashing liquid, but this is not sufficient to explain the difference. Marshall [18] has compared the average number of fatalities actively caused by the explosion of various amounts of hydrocarbon vapour and the release of various amounts of chlorine. He states that 1.27 people will be killed for each ton of hydrocarbon vapour that explodes.

For chlorine the data (taken mainly from [19]) are sparse, but Marshall suggests one fatality per 2,000 lb of chlorine. We thus see that, ton for ton, chlorine produces about the same number of casualties as explosive vapours although much higher figures are widely believed to be possible.

Why do sudden releases of toxic vapours kill so many fewer people than expected, despite the serious results that are theoretically possible?

The explanation may be that, while in theory a toxic vapour can spread a very long way and cause many casualties, weather conditions have to be exactly right and this rarely coincides with a leak. In addition, people can often escape; Simons [17], discussing chlorine, writes: "People flee instinctively when confronted by the greenish, choking cloud. Flammable gas clouds do not provide such a clear warning of danger." Furthermore, if windows are closed a toxic gas cloud can pass over houses without causing casualties. On average, therefore, toxic vapours produce fewer casualties than expected.

Taylor [20] discusses the reasons why poison gas was not used in World War II and writes:

"Most probably the explanation was the simple calculation that, weight for weight, high explosive was more effective than gas in killing people."

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DETERMINATION OF THE EFFECT OF A THERMAL EXPLOSION OF ORGANIC PEROXIDES (HOMOGENEOUS EXPLOSION TEST)

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Summary

In this paper an instrument for investigating the pressure effects caused by thermal explosions of such unstable substances as organic peroxides is described.

The design of the instrument makes it possible to simulate situations with a moderate degree of confinement. A number of intermediate scale experiments have been carried out to investigate the applicability of the results of this laboratory instrument for practical purposes. Within the limits of experimental accuracy a good agreement between laboratory and intermediate scale results is obtained. In the employed configurations with moderate confinement the thermal explosion of peroxides is found to give relatively weak pressure effects, the magnitude of which strongly varies in accordance with chemical constitution.

Introduction

The phenomenon of thermal explosion is well known (see for instance [1–3]). In general every exothermal reaction may, depending on the external conditions, lead to a thermal explosion. A good understanding of the thermal explosion is important for the safe handling, storage, production and transportation of many industrial chemicals such as organic peroxides [4]. The initial thermal conditions leading to an explosion are well understood and in principle it is possible to calculate parameters such as critical temperature, critical dimensions and the induction period in which an explosion can be expected. For the determination of the necessary self-heating parameters several test methods are available, for instance the adiabatic storage test [5], isothermal storage test [6] and various practical self-heating tests such as Wärmestau Verfahren [7] and the SADT test [8,9].

More complicated is the description of the thermal explosion itself and the physical events, like pressure and temperature effects, accompanying the explosion. In the past many tests have been developed to assess the behaviour of unstable substances when involved in a fire. The Dutch pressure vessel test [10] and the German steel tube test (Stahlhülsen Verfahren) [11], which are described in RID [12], are well-known. The results of these tests can only

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be used in a comparative way since both techniques do not give values which can be extrapolated to practical conditions.

More quantitative data are obtained with such test methods as the time-pressure test [13] and the Janaf test [14]. These two tests are relatively simple and in concept restricted to the determination of the thermal explosion effect of a sample in a closed pressure vessel.

The present instrument enables one to measure the characteristics of the effect of a thermal explosion under external circumstances simulating conditions which are met in practice. Much attention is paid to the confinement of the substance. Furthermore the instrument is equipped with practical provisions such as a bursting disk, variable heating rates and an outer chamber which serves as an expansion chamber for the explosion products. The extent to which the results of this instrument can be extrapolated to large scale events is discussed. The investigations are restricted to the thermal explosion of solids and liquids, and secondary explosions are explicitly avoided. The latter may occur when the gaseous products of the primary thermal explosion form a combustible mixture with the ambient air.

Apparatus

The apparatus (see Fig. 1) is made of stainless steel and consists of two compartments: a sample holder (1) containing the sample; and an expansion chamber (2) in which the explosion products (foam, gases etc.) are contained. The volumes of these compartments are 10^{-4} and 10^{-2} m³ respectively. The whole apparatus is designed for a working pressure of 3.0 MPa* and a maximum temperature of 600 K and is provided with a rupture disk (3) with a bursting pressure of 3.6 MPa.

To prevent evaporation of the sample and to give the sample a moderate confinement the holder is closed at the top with a teflon-coated aluminium membrane (4). The bursting pressure of this membrane can be varied to simulate different degrees of confinement. A small (capillary) tube (5) connects the sample holder with the expansion chamber. This connection serves as a venting valve to equalize the pressure between the two compartments in the early stages of decomposition. The capillary tube is made of teflon and has an internal diameter of 1.6×10^{-3} m and a length of 2 m so that evaporation is minimal.

The apparatus is provided with an external primary heating coil (7) and an additional secondary heating coil (8) around the sample holder. The primary coil is wound in such a way that a uniform temperature distribution along the whole apparatus is achieved. The temperature of the apparatus is regulated by a programmable temperature control unit. (Haake, type TP 32). The heating rate \dot{T} is a linear function of time and is variable between 0.56 mK/s and 50 mK/s (2 to 180° C/h). The purpose of the secondary heating coil is to

*1 MPa = 10^6 N/m² = 10 bar.