# IMPERIAL CHEMICAL INDUSTRIES HEAVY ORGANICS DIVISION

# SAFETY NEWSLETTER NUMBER 7

# By Trevor Kletz

# 7/1 A STORAGE TANK IS SUCK IN

Welding had to take place near the roof of a storage tank containing volatile flammable liquid which is soluble in water. There was an open vent protected by a flame arrestor on the roof of the tank. The supervisors concerned therefore decided to connect a flex to this flame arrestor and dip the other end of the flex in a drum of water on the ground.

When a movement was made <u>out</u> of the tank the water rose up the flex until sufficient vacuum was developed in the tank to cause the roof to collapse inwards. The tank was designed to withstand  $2^{1}/_{2}$  ins. water gauge vacuum only.

If a movement had been made into the tank it might still have been damaged as the tank was designed to withstand only 8 ins. of water gauge pressure and the flex was immersed in the liquid to a depth of 1 ft.

This is a good example of an accident which occurred not because precautions were neglected or danger was not foreseen, but because the men concerned failed to understand two of the elementary principles of process operation:

(1) That tanks are very fragile and will stand only a very slight pressure or vacuum. The supervisor did not appreciate that  $2^{1}/_{2}$  ins. water gauge is no more than the pressure at the bottom of a cup of tea and that 8 ins. water gauge is the pressure at the bottom of a pint of beer. (Newsletter No. 5, Item 2, described, two other tank collapses in which similar ignorance may have been a contributory factor),

(2) The supervisor did not understand the way a lute works. He did not realise that water could rise up the flex and support a vacuum of 1 atmosphere in the tank.

There is a danger that our training of process workers may be too sophisticated. We try and teach them elementary chemistry and chemical engineering, and it is right that we should do so, but not before we have taught them that tanks and other vessels are not always designed to withstand the pressure to which they can be subjected, that air and fuel mixed together will go "bang" and that addition of hot oil to water will cause steam to be formed, with explosive violence.

## 7/2 WHAT HAPPENS TO LIQUID THAT CONDENSES IN A STACK?

In almost all flare and vent stacks some liquid may collect at the bottom of' the stack. Even if a knock-out drum is fitted some liquid spray may get past or vapour may condense on the sides of the stack; so-called dry flare stacks often contain materials which condense in cold weather.

What happens to liquid which collects at the base of the stack? Two recent incidents in the Division have shown the importance of knowing the answer to this question.

The first incident occurred on a flare stack which is fitted with a few trays at the base for washing the flare gases with water. The water overflows through a lute into a sump from which it is pumped out to drain. Traces of oil which get past the knock-out drum end up on top of the water in the sump. If the oil is volatile an explosive vapour is present in the sump.

This explosive vapour ignited and the man-hole cover was thrown 60 feet. The source of ignition may have been overheating on the pump, which was found to be damaged, or static resulting from the splashing of a two-phase mixture.

The ideal way of preventing a repetition would be to purge the sump with nitrogen. This would be difficult as it is not air-tight and as no nitrogen is available in the area. It has therefore been decided to fence off the man-hole and replace the steel man-hole cover by a light plastic one which can be shattered harmlessly by an explosion - a sort of bursting disc or explosion door. Calculations show that the man-hole is big enough to relieve any explosions which might occur.

The second incident occurred on a flare-stack which sits on top of a concrete sump. The sump was originally fitted with a water inlet line and overflow to drain to wash out any liquid which collected. These were both blanked off when the stack was changed onto a "dry" duty. Some oil nevertheless collected, dissolved the bitumen which sealed the sump cover plates and. overflowed onto the surrounding ground where it was ignited by a spark from the stack.

The overflow line has now been brought back into use.

On your flare and vent-stacks, what happens to any liquid that accumulates? If it overflows through a lute, how do you check that the lute is full and not choked? If there is a water flow into the stack, how do you check that it is flowing?

The second fire, incidentally, showed the value of the foam monitors. Ordinary foam branches failed to put out the fire; after an hour a large monitor was brought into use. It put the fire out in five minutes.

## 7/3 MOLECULAR SEALS

In these Newsletters I have several times referred to the importance of keeping a regular flow of' gas (preferably inert gas) up a stack in order to prevent air diffusing down, and. to sweep away any small leaks of air that occur. (See Newsletter 5, Item 3). Very large flow rates are needed when the stack contains lighter-than-air-gases.

One method for reducing the rate at which air diffuses down the stack and thus saving inert gas is to install a molecular seal near the top of the stack. This is a system of baffles, as shown below.



Water might accumulate in the seal and create a back-pressure on the flare header, which could be dangerous. For this reason a  $1^{1}/_{2}$  inch diameter drain line and lute are fitted - lagged to the steam pipes to prevent freezing - and also a small hole (say  $1^{1}/_{2}$  inch diameter) in the position shown.

On one of the HOC Division flare stacks the drain line was recently found to be choked. If the  $1^{1}/_{2}$  inch hole had choked as well the plant could have been over-pressured. The molecular seal has therefore been removed.

It is clear that molecular seals are undesirable where they could create a dangerous back pressure unless much more effective measures can be taken than in our design to prevent choking of the lute drain line.

## 7/4 THE POSITIONING OF RELIEF VALVES

If a vessel is protected against overpressure by a relief valve, the valve is sometimes placed on the vessel itself, sometimes immediately before or after. Three incidents have drawn attention to the need to consider critically where the relief valve is placed - it can matter.

In the first incident, which happened a few years ago, a furnace was protected by a. relief valve in the inlet line. A restriction developed after the furnace and the relief valve lifted and took most of the flow. The flow through the furnace tubes fell to a low level so they overheated the and burst. The low flow trip and alarm did not operate as the flow through them was normal.



The second incident occurred recently on the bottom line of a distillation column containing cold LPG.



The two heat exchangers A and B are designed to withstand 150 psi and, to protect them from the still pressure if the motor valve opens fully, a relief valve is fitted in the position shown.

A leak in exchanger C, coinciding with a low pressure in the process line, resulted in a slug of water entering the process line and forming a plug of ice in a dip in the line between A and B. As a result A was isolated from its relief valve and overpressured.

These circumstances are rather difficult to foresee in detail, but in general whenever there is any chance of a vessel being isolated from its relief valve by chokes in a line caused by ice, solidified process material, catalyst dust or any other source, then a relief valve must be placed on the vessel itself, or alternatively, the vessel must be made capable of withstanding the full pressure to which it can be subjected.

In the present case the latter would probably have been the easiest course to adopt at the design stage. It would not have cost much more to make A and B capable of withstanding 300 psi.

#### 7/5 FAULTY EXPLOSIMETERS

In Safety Newsletter No. 6, Item 3, I said that many explosimeters brought in for overhaul are found to be faulty and that they should, therefore, always be checked on a sample of flammable vapour, such as fuel gas, before use. It has now been pointed out to me that if fuel gas is used a grossly insensitive meter would respond but would still he of little use afterwards. In addition, if a meter is repeatedly used in an over-rich atmosphere the activated filament may fail early. Meters should therefore be tested with a flammable liquid which gives off only a lower concentration of vapour.

A mixture of xylenes is suitable and a. sketch of simple apparatus for testing explosimeters is attached. I suggest that one of these is kept in every Control Room or Supervisor's office



As stated in Newsletter No. 3, Item 9, the sample lines to explosimeters must be made of a material which will not absorb the vapours that might be present. Many synthetic rubber tubes, <u>including</u>, <u>some supplied by the manufacturers of explosimeters</u>, will absorb vapours. Nitrile and Silicon rubbers are suitable for most of the materials we use; "Neoprene" and "Thickol" are not.

When testing explosimeters the tubing should therefore be tested as well as the meter itself.

#### 7/6 ANALYSER ENCLOSURE.

Many of the automatic analysers installed on our plants are enclosed in flame-proof housings. If there is a leak of liquid or vapour inside the housing it does not matter as the housing will stand any explosion that results.

Before an analysis housing is opened the power should be switched off. Otherwise any vapour inside can spread into the building and be ignited by a spark form the electrics inside the case.

Recently when the cover was removed from a flash-point analyser case it vas found to be half full of naphtha and two gallons were spilt on the floor; fortunately the power had been switched off beforehand.

These facts should be made known to the artificers who service the analysis instruments and, in addition, I suggest that a reminder to switch off the power before opening the case should be fixed on the outside of each case.

If the power has to be switched on with the case open then a Red Permit-to-Work (Fire Permit) should be obtained.

Many of the housings are purged with nitrogen. This will prevent an internal fire but will not prevent a fire or explosion if the housing is opened with the power connected.

## 7/7 OXYGEN CYLINDERS

In Newsletter No. 5, Item 5, I described a fire which had occurred on an oxygen cylinder and the precautions that should be taken when the valves on oxygen cylinders are opened. A note dated 14th November described these precautions in more detail. Another point has now been brought to our attention. The plastic caps which cover the nozzles on refilled oxygen cylinders will burn readily in oxygen and therefore care must be taken to see that they are completely removed and that no bits are trapped in the oxygen stream when cylinders are connected up.

An accident involving oxygen is described in the October 1968 issue of "Accidents", published by the Factory Inspectorate. Welding was taking place inside a tank. The cylinders were outside and flexible hoses led to the welding set. One of the men lit a cigarette and noticed that it burned away more quickly than normal and that his lighter-flame was longer than usual. He did not, however, realise what this meant. When the welder started to weld a spark fell onto another man's pullover; it immediately caught fire and spread to his entire clothing. He later died from his injuries.

It is clear that oxygen had leaked into the vessel through flexes which were not in first class condition. If there is the remotest chance that oxygen can accumulate in a confined space then the atmosphere must be tested for oxygen as well as for flammable vapour before welding starts. Is this covered in your fire-permit and vessel entry instructions?

On some Works welders' torches must be lit outside the vessel.

# 7/8 TEMPERATURE POINTS WITH SHEATHS

An artificer was called to check a faulty Rototherm. He decided to remove the Rototherm and when he did so oil spurted out from the pocket. He thought the Rototherm was in a sheath but it was not.

If some of the Rototherms on a Works are in sheaths and some are not, then those without sheaths should be clearly marked in some way on or near the Rototherm itself.

## 7/9 SOURCES OF IGNITION

We are all familiar with the three sides of the fire triangle - air, fuel, and a source of ignition. Take one away and an explosion cannot occur.

We also know that in practice this is incorrect. If air and fuel are mixed, a source of ignition will ultimately turn up and ignite the mixture. Air and fuel should never be allowed to mix, except under rigidly defined circumstances where the risk is accepted, such as in the vapour space of a fixed roof tank containing non-hydrocarbons.

The ease with which a source of ignition can turn up is illustrated by a recent report on fires at petrol filling stations during the off-loading of petrol from road tankers. All the fires occurred after the hose had been dismantled.

Eleven fires were investigated and no definite causes of ignition could be found. Static discharges seemed unlikely as no static could be detected in trial experiments. Sparks might have been generated by dropping the end of the hose on concrete but the hoses are usually not treated roughly enough for this to occur. The only recommendation made is to avoid projections on the ends of hoses, such as occur on some types of clip. (see also 16/7)

## 7/10 LABELLING OF ROAD TANKERS

In Newsletter No. 6, Item 6, I referred to a road accident involving a phenol tanker (not ICI.). The tanker was labelled "Phenol" but no details were given about its properties or the precautions to be taken. An item in "Fire" December 1968, p. 325, described the result. The Fire Service found on arrival that police and. other people were not aware of the dangers and were walking around in the spilt phenol. Subsequently the soles of three policemen rotted away. Hoses were used to spray the phenol on the road. The outside of the hoses were allowed to come into contact with the phenol and within five minutes of use four hoses had burst.

In HOC Division for some years all tankers have carried labels describing briefly the properties of the contents and the action to be taken if a spillage occurs. The phenol incident emphasises the need for this and the need for checking from time to time that the labels are being fitted.

The drivers of tankers containing phenol and eleven other products are now being issued with Hazard Cards which provide more details of the hazards, the action to be taken if an accident occurs and the first-aid treatment. These are issued to the drivers with their papers. If the driver is killed or unconscious are these kept in a place where they can be seen by the police?

# 7/11 RECENT NOTES

The following have been issued recently. For copies of them or any further information on any other item please telephone B.3927.

"Discharges of Static Electricity from Ball Valves.". 5.1 2,68.

Under certain conditions sparks have been observed jumping between the handle and body of a ball valve. The note describes the conditions under which this can occur and makes recommendations for prevention.

<u>"A Review of Explosions on Chemical Plant Furnaces – Some Comments on their Design and Operation"</u> 13.12.68.

Details of 12 explosions are listed, almost all of which occurred during light-up or while running on low rate. The recommendations that result from a study of the explosions are listed.

# "Welding on Live Equipment – Olefines". 17.12.68

For some time welding has not been permitted in the Division or lines containing olefins as there is a danger that explosive decomposition might be initiated by a "hot spot". It has now been agreed that direct welding is permissible on lines containing ethylene or propylene or mixtures of either of these with inert gas, provided the total pressure is about atmospheric. Oxygen, of course, must not be present in explosive proportions and there must be no dienes or acetylenes present.

Under-pressure connections using clamps are now possible and may be considered if the "carrot" is large enough.

#### "A Review of LPG Fire and Explosions", 13.9.68.

Brief details are given on 44 fires that have occurred on equipment handling LPG, in refineries, chemical works, and LPG distribution plants.

#### "Hazard Analysis – A Quantitative Approach to Safety".

Report No. 0.200.611/A. A revised and expanded version of a report already issued.

#### "Electrostatic Hazards"

Three reports describing the results of surveys of the Division's three large Chemicals Works. (North Tees Development Report No. 122, 26.9.68, Oil Works Technical Memorandum No. 717, 7.11.68 and Olefine Works Report dated 15.11.68).

#### "Crankcase Explosions"

Agricultural Division Report No. EDN 1239 by D. Summers-Smith, 30.12.68 shows that crankcase explosions occur at the rate of once in 420 years per machine and that the best method of protection is to fit BICERI relief valves.

Unless some form of protection is fitted, the risk to men working near the machines is unacceptably high.

## 7/12 ANOTHER OFFICL REPORT ON A MAJOR FIRE

The Stationery Office have re-issued the "London Gazette" for September 3rd - 10th 1666, describing the Great Fire of London. The view taken of the causes of the fire is somewhat different to that given in present day reports.

"Divers Strangers, Dutch and French, were during the Fire, apprehended upon suspicion that they contributed mischievously to it, who are all imprisoned, and information prepared to make a severe inquisition thereupon by my Lord. Chief Justice Kreling, assisted by some of the Lords of the Privy Council, and some principal Members of the City; notwithstanding which suspicions, the manner of the burning all along in a Train, and so blown forwards in all its way by strong winds, makes us conclude the whole was an effect of an. unhappy chance, or to speak better, the heavy hand of God upon us for our Sins, showing us the terror of his Judgment in thus raising the fire, and immediately after, his miraculous and never enough to be acknowledged Mercy, in putting a stop to it, when we were in the last despair, and that all attempts for the quenching it, however, industriously pursued, seemed insufficient .....

...... And we have further this infinite cause particularly to give God thanks that the fire did. not happen in any of those places where his Majesties Naval Stores are kept; so as though it hath pleased God to visit us with his own hand, he hath not, by disfurnishing us with the means of carrying on the War, subjected us to our Enemies ....

..... though some think, that if the whole industry of the Inhabitants had been applied to the stopping of the Fire, and not to the saving of their particular goods, the success might have been better, not only to the Public, but to many of them in their own Particulars."

Our first thoughts after reading these quotations is to be amused at their quaintness. Will our accident reports seem as amusing in 2266? We do not now blame God and the foreigners for our fires but we do blame most of them on "human failing" and use that as an excuse for taking no

action to improve our hardware, instructions, operating methods and so on. Perhaps we have not changed so much.

22 January 1969