

DISCUSSION - SESSION ONE

ASSESSMENT OF REACTIVE CHEMICAL HAZARDS: SOURCES OF INFORMATION L. Bretherick

Dr Napier (Imperial College):

How far can a catalogue of properties of chemicals and chemical mixtures be used in avoiding dangers that may arise from effects of scale, or of particular experimental or engineering arrangement? Is there a danger that the uninitiated may be led into a false sense of security?

Mr L Bretherick:

There is a real possibility of people extrapolating erroneously from small-scale data and there are very many reported incidents which have happened as a result of this. To counteract this tendency, I have gone to considerable trouble to point out that there are all sorts of effects, including the presence of various contaminants or impurities, and have urged the reader to use his imagination and take all considerations of this nature into account. If people will take the trouble to report these incidents I will try to analyse them and include them in the appropriate place. The main problem has been to locate the information which exists.

THE DETECTION AND MONITORING OF OZONE IN INDUSTRIAL ENVIRONMENTS

V. Visanunimol and D.H. Slater

Dr W D Rees (BP Research Centre, Sunbury-on-Thames):

High levels of ozone, well above the TLV were measured in high voltage test areas, in the vicinity of ultra violet sources and air deodoriser. Did any of the personnel undertaking the tests, and/or equipment operators, therefore, experience any side effects due to ozone?

Mr V Visanuvimol:

No, we did not experience any marked side effects as we were aware of the toxicity of ozone and took care to minimise the exposure of the operators to high ozone level.

Mr H A Duxbury (ICI, Plastics Division):

Is ozone produced from low voltage sparks, for example, in motors with worn brushes?

Mr V Visanuvimol:

We did not find that much ozone was produced in low voltage sparks. We were unable to produce detectable ozone levels from sparks of under 1 kV.

Mr A H Searson (Esso Engineering Services Ltd, New Malden):

The voltages quoted in the author's experimental work are modest compared with voltages common in the power generation and distribution industry, including power supply to industrial plants such as oil refineries.

Can the authors or anyone in the audience comment on the extent to which ozone is recognised as a specific hazard in the power industry as regards the design of enclosed buildings containing high voltage equipment?

Mr J Nixon (H.M. Factory Inspectorate):

As far as I know there have been no cases of ozone poisoning reported but one would expect the effect to be short term.

The Chairman asked; are precautions normally demanded, and is ventilation normally demanded?

There is a section of the Act which says that all noxious or toxic fumes should be removed from the work area, and ventilation would probably be required in confined areas.

Dr D H Napier (Imperial College, Dept of Chemical Engineering):

Mr Visanuvimol has made some reference to and laid some stress on ventilation, with which I agree, but we have had some experience of difficulties with ventilation systems that are lined with foamed plastics. These organic materials react with ozone and it is quite possible for a ventilation system to suffer blockage by this method by the simple means of the organic material falling from the duct and blocking it; we have had difficulty with this particular happening.

Dr G W Stewart (Burmah Oil Trading Ltd):

Can anyone comment on the problems involved with the use of tonnage quantities of ozone in the Chemical Industry, e.g.

in the oxidation of vinyl aromatic compounds to the corresponding aldehydes? Such processes are operated in the U.S.A.

Mr V Visanuvimol:

The problems of handling ozone on a large-scale are much greater than that just the toxicity problems of trace atmospheric levels with which we have been wholly concerned.

Dr H S Eisner (Safety in Mines Research Establishment):

Some years ago ozone was deliberately added to air for germicidal or deodorizing purposes. Is this still carried on? An example was the London Underground Railway.

Mr G Taylor (Greater London Council Scientific Branch):

I have always understood that in fact ozone was at one time added to the air issuing from the underground in order to make the odours less objectionable to passers-by. This procedure was, I think, discontinued many years ago.

An extensive investigation of the intrinsic ozone concentrations inside the underground was carried out by LT some years ago in order to ascertain to what level of O_3 the public and personnel were subjected as a result of the various electrical discharges which inevitably take place within an electrified underground transport system. The levels found were very low but details could be obtained from London Transport.

Mr K Shaw (Glaxo Laboratories):

I am interested in very low concentration of ozone such as might arise during welding. I wonder if any work has been done in measuring ozone concentrations either in the open or in confined spaces; where welding operations are being carried out?

Mr V Visanuvimol:

To my knowledge I do not think any special measurements have been made. The concentration of ozone depends on the extent of the welding operation and the degree of ventilation. In an enclosed and poorly ventilated area the level of the accumulated ozone could rise considerably as ozone has a relatively long life-time as investigated by Nederbragt et al (Nature 206 87 (1965)).

Mr J Nixon (H.M. Factory Inspectorate):

In a lot of cases where ozone is given off nitrous fumes are also involved. How specific are these analytical methods for ozone?

Mr V Visanuvimol:

The classical KI method is normally used for the determination of total oxidants in the atmosphere but it can be used to measure only ozone if precautions to eliminate other oxidants are taken, as outlined in ASTM D1609 - 60.

The Draeger method is claimed by the manufacturers to be adequately specific, interference by other gases such as nitrous oxides and chlorine occur at concentration (of the interfering gas) greater than 5ppm.

The chemiluminescent method is highly specific since no other reagent is known to react with ethylene and produce the same result as that of ethylene-ozone. The wavelength of light emitted by the above reaction is its inherent characteristic.

The ultra-violet absorption method is very specific as it incorporates an ozone scrubber. Hence measurements of the absorption at 254 nm of sample and scrubbed sample streams can be subtracted to cancel out the effect of interfering gases.

LAGGING FIRES: THE PRESENT POSITION

K. Guban

Dr E Hutton (Laporte Industries Ltd):

In areas of high risk plant regarding lagging fires, the presence of conventional lagging is regarded as an unacceptable risk. What is the best alternative if some degree of risk can be accepted? In order to maintain process control some insulation needs to be provided for some sections of outdoor plant - we have used in the past a form of several layers of crimped aluminium sheeting which give a limited efficiency of insulation but offer low heat and liquid hold up within the insulation system.

Mr M Kneale (Lankro Chemicals Ltd):

Foam glass has been found to be very effective and is now appreciably cheaper than 2 or 3 years ago. Fitting of the foam glass can be easily achieved after a short period of

employee training.

Mr J M Alexander (ICI, Petrochemicals Division):

The only solution we have found with some persistent problems with lagging fires has been to remove the lagging and use expanded metal 'stand-offs' to protect the plant operators against burns. Dr Hutton's comments on the use of crimped aluminium as a low grade insulating material are interesting. Some people may argue, however, that the risk of a thermite reaction on hitting aluminium smeared on mild steel, is not acceptable.

Mr J R Stirzaker (ICI, Organics Division):

Many instances of lagging contamination are caused by leaking pipe flanges. Prevention being better than cure, the principle of eliminating as many flanges as possible is pertinent here, i.e. welded runs of piping. Where flanges cannot conveniently be eliminated why not leave them unlagged? This would be a compromise to leaving the whole pipe run unlagged.

Dr Guban agreed that there was a lot to be said for leaving flanges unlagged.

Mr K N Palmer (Fire Research Station, Building Research Establishment):

A method of test for ignition temperature of oils on lagging is described in reference 12 to the paper. Results of tests show that ignition temperature of an oil depends to some extent on the composition of the lagging, even though it is non-combustible, and that a benefit of 20 to 30°C can be obtained by choosing a favourable material. P C Bowes has recently produced a Building Research Establishment Current Paper (No. 35/74) on fires in oil-soaked lagging.

A prerequisite for an oil to cause a lagging fire may be that its boiling point should be sufficiently high to prevent it being evaporated quickly and also that it should deposit solid materials, eg due to cracking, in the lagging to enable smouldering to proceed.

Dr Guban:

It would seem to be the case in that aliphatic oils which are moderately stable at high temperatures perform less well than oils of the Thermex type which are very much more stable at elevated temperatures. In general the more dense the lagging the better its performance with the same contaminant.

Mr R G Collis (Admiralty Oil Laboratory):

What is the experience of fires caused by accidental spillage of so-called fire resistant hydraulic fluids, particularly of the aqueous polyglycol or water/oil emulsion type.

Dr Gugan:

I am aware of the chlorinated straight chain paraffins as well as the phosphate esters but I am less familiar with hydraulic fluids involving solution or suspension of organic materials in water. These fluids will be fire resistant if the proportion of water is high enough but, should the fluid escape on to lagging, then the more volatile constituent - almost certainly the water - will evaporate preferentially and a problem would arise similar to that which may occur with a conventional hydraulic fluid.

Dr I E Eastham (Rohm & Haas (UK) Ltd):

Is there any experience with lagging fires initiated by reaction other than air oxidation, eg polymerisation of monomers, clearly later sustained by air.

Dr Gugan:

I have never come across it in a lagging situation. The presence of air is always necessary for spontaneous ignition to occur.

Mr D G Wilde (Safety in Mines Research Establishment):

There are some grounds for supposing that a test for the flammability of liquids dispersed in laggings would be useful. Such a test would eventually lead to a body of knowledge that would enable plant operators to place a specific risk within the list.

Would the author like to comment on this view, and discuss the usefulness of a test from other points of view, and comment on the practicality of the devising of a test.

Dr Gugan:

I would very much like to see a test devised. What is missing is a unifying test procedure which would enable a quantitative assessment of the hazard as well as a ready comparison of the relative hazards of combustible liquids. It is important however that the results produced by such equipment should be

accompanied by some guidance as to how they are to be used. As the paper I hope has made clear, single spontaneous ignition results are available; what has hitherto been difficult is in extrapolating these single results to different systems of geometry and heat flow. It is right that I should indicate, through my personal experience, that any research which would give a meaningful result in this field is costly and time consuming. Nevertheless Mr Wilde's suggestion has great attraction and would, if pursued rigorously, create a useful body of information which could be of great assistance to designers.

Mr J A Dukes (UKAEA):

There are two hazards:

- (i) having a lagging fire and not knowing of it;
- (ii) knowing or suspecting then taking the wrong action.

Is it true that temperature sensitive paints are useless as indicators on surfaces, since surface temperature of lagging is not very dependent on whether or not there is a fire? Is smoke the main evidence of danger, apart from inexplicable rise in fluid temperature?

Dr Gugan:

Temperature sensitive paints are not satisfactory as indicators for lagging fires because the surface to which they are applied - the outer surface of the lagging - is relatively insensitive to wide variations of temperature within the lagging. Even if these paints were improved in sensitivity to respond to very small changes in temperature, it is unlikely that they could ever detect and indicate an incipient lagging fire. Copious fuming remains the single most characteristic attribute of the early stages of lagging fires. This in many respects is the most sensitive indicator since fuming precedes the development of incandescence within the lagging, although of course it also accompanies incandescence and it is often a matter of chance at which stage of fire development the fuming is observed.