SAFETY OF ETHOXYLATION REACTIONS
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Ethylene Oxide (EO) is a reactive monomer obtained by oxidation of ethylene. In ethoxylation processes, EO is reacted with various chemicals such as alcohols, phenols, acids, fatty alcohols and fatty acids, ammonia, amines, mercaptans, to produce a wide range of surfactants, solvents and specialty chemicals. Ethoxylation processes operate at temperatures between 40°C and 200°C under pressures ranging from atmospheric to 100 bar, mostly in the presence of a catalyst. The reaction of EO is exothermic. In continuous processes, a tube reactor or a series of stirred reactors or a combination of these, are used to produce solvents or commodities. Semi-batch ethoxylation processes are carried out in stirred reactors or in different types of loop-reactors to produce long chain ethoxylates. Liquid EO is injected in the process and dissolves in the liquid reaction mixture where the ethoxylation reaction takes place. A partial pressure of EO is also present in the gas phase if any. Due to the many accidents that have occurred in processing EO, related with its dangerous properties, the process design and operating conditions of ethoxylation processes may create important safety issues. In this paper, the standards in this field are discussed on the basis of:
- the case histories collected from the literature,
- the data available on interaction of EO with construction materials and gaskets,
- the data on gas phase instability, limiting nitrogen concentration, MIE, explosion overpressure and the methods to control gas phase explosion hazard.
- the literature on EO accumulation, runaway reaction hazard in ethoxylation processes and how to control it.
A full review of the literature in this field is given.

Keywords: Ethylene oxide, ethoxylation reaction, process safety.

INTRODUCTION
Ethylene Oxide (EO) is a reactive monomer obtained by oxidation of ethylene. In ethoxylation processes, EO is reacted with various chemicals to produce surfactants, solvents and specialty chemicals. Due to the thermal instability of EO in the liquid phase and in the gas phase and to the high reactivity of the monomer with other chemicals including water, many accidents have occurred in both the manufacture and the processing of ethylene oxide. The hazards of processing ethylene oxide include:
- A gas phase explosion hazard related to the flammability of EO in the presence of air or oxygen.
- A gas phase explosion hazard due to EO vapour instability. Similar to acetylene, propargyl chloride, nitrous oxide, nitrogen trichloride, chlorine oxides, hydrogen azide or chlorine azide, EO gives decomposition flames with pressure effects in vessels, even in the absence of oxygen.
- A liquid phase decomposition hazard, since the decomposition of liquid EO may be initiated by high temperatures, hot spots or catalysts. The reaction or decomposition of EO can propagate in the liquid phase if a high concentration of EO is present. The thermal stability of liquid EO is influenced by the temperature, the material of construction and the presence of impurities.
- A runaway reaction hazard when EO is reacted with other chemicals in ethoxylation processes, if EO is allowed to accumulate in reaction vessels, due to improper operating
conditions. Also concentrated EO solutions may self-heat and runaway if the temperature is not controlled or if a catalyst is present.

- A toxic hazard since EO is highly toxic and may cause cancer. Diluted EO solutions may also cause severe burns.

It is therefore of interest to review the various process conditions where the processing of ethylene oxide may cause problems and explain how to achieve safe process conditions.

DIFFERENT TYPES OF ETHOXYLATION PLANTS

Depending on the ethoxylation plant distance from EO suppliers, the facility may include a pipe-line to feed EO to feed EO to the storage tank of the ethoxylation unit. The EO feed may also be by a pressure loop not necessitating a local EO storage if the EO supplier plant is not too far from the ethoxylation consumer plant. If there is no local EO supply, EO delivery is by rail or road tank to an unloading station to feed the local EO storage.

It is reasonable to consider that a large production of common ethoxylates may be conveniently situated near an EO supply facility whereas an ethoxylation plant to produce specialty chemical ethoxylates in smaller quantities may be situated near its consumer market.

Ethoxylation reactors may be of different types depending on the plant capacity and on the type and number of different ethoxylates made. Short chain ethoxylated solvents such as ethanolamines, ethyl glycols, diethylene glycol, ... can be manufactured in continuous tube reactors where EO and the substrate, ammonia, water, ethanol, glycol are fed under pressure with some catalyst if necessary. Large productions of ethylene glycol and poly-ethylene glycol (PEG) are obtained in series of continuous stirred reactors where EO is injected in the liquid or in the gas phase. The operating pressure is above atmospheric pressure to enhance EO absorption and reaction, since the reaction rate is proportional to EO partial pressure. A combination of a tube reactor and a stirred reactor is also suitable for continuous production of short chain ethoxylates.

For the production of long chain ethoxylates, the use of semi-batch processes where EO is fed continuously to the reaction mixture containing the substrate and the catalyst is suitable. The most current type of reactor is a simple stirred reactor equipped sometimes with an external circulation loop to increase the reactor heat exchange capacity. In the Pressindustria reactors, the reaction mixture is pumped in a circulation loop through a heat-exchanger and sprayed in a gas/liquid contactor to enhance EO vapour absorption in the reaction mixture droplets. The advantage of this reactor design compared to the common stirred reactor is explained by E. Santacesaria et al.\(^1\)

The usual operating pressure of these two semi-batch processes is up to 4-5 bar abs. Recently Buss loop reactors, similar to Buss hydrogenation reactors, were installed for the production of ethoxylates. Their operating pressure is up to 14 bar abs.

In semi-batch processes, as the ethoxylation reaction proceeds, the reaction mixture volume increases causing a compression of the gas phase. The process initial pressure and the gas phase compression ratio are limited by the maximum allowable working pressure of the reactor. The inert gas pad pressure increases with increasing liquid level and the possible EO partial pressure decreases accordingly causing the reaction rate to slow-down. The excess pressure may be released to a scrubber with the drawback of not keeping the gas phase composition under control.

The many different reactor designs may be explained by the fact that the reaction rate is controlled by EO mass transfer to the reaction mixture which is also influenced by EO partial
pressure. The other operating conditions i.e. substrate, catalyst, process temperature, growth ratio, depend on the recipe considered and on the reactor used.

**REVIEW OF CASE HISTORIES CONCERNING EO PRODUCTION AND ETHOXYLATION PROCESSES**

**ACCIDENTS OCCURRED IN EO PRODUCTION PLANTS**

It is of interest to review accidents occurred in EO production plants because they may have common causes with accidents occurred in ethoxylation plants.

A long known ethylene oxide plant accident is the explosion at Doe Run Olin Mathieson plant on April 17, 1962\(^{2}\). In this accident, a 26 m\(^3\) EO storage tank ruptured violently. The domino effects involved a vapour cloud explosion and severe mechanical damages to the neighbouring installations. The cause of the EO violent reaction is a back-flow of aqueous ammonia from an ethanolamine tube reactor to the EO storage tank.

As EO reacts violently in the presence of small amounts of ammonia, it is necessary to install reliable back-flow prevention from the ethoxylation reactor to the EO feed tank. Also the EO feed is best located in the reactor gas phase. Any back-flow of ethoxylation reaction mixture to an EO storage tank would induce a similar runaway reaction hazard.

Explosion at BASF Antwerp (BASANT) EO/Glycol plant.\(^{3}\)

A severe explosion occurred at the Basant plant on March 7, 1989 causing extensive destructions. The reconstruction of the accident circumstances proved that the explosion originated in an insulated level indicator of the aldehyde column. An EO leak in a wet insulating material with rust deposits produced polyethylene glycols at temperatures of 80°C-120°C. It was shown later that PEG with a chain length greater than four monomers can oxidise in glass wool and produce a hot spot above 600°C. A temperature high enough to initiate the decomposition of EO in vessels and pipes.\(^{4}\) The lessons learned from the BASANT explosion were to use high integrity piping and vessels of welded construction in EO plants, to check carefully for leaks after maintenance, to avoid stagnant liquid in small pipes if temperature is above 80°C, to choose carefully insulation material, to check that pipes and insulation are rust-free, to use stainless steel for EO duty and to simplify the process as far as possible.

Ethylene oxide plant explosion at BP Chemical Antwerp on July 3, 1987.\(^{5}\)

In this accident, an EO plant was destroyed by a violent explosion originating on the EO purification column. The cause of the explosion is a leak of EO from a man-hole flange into the insulation packing at the base of the column. PEG formation and oxidation with air, produced a hot spot which initiated EO decomposition in a stagnant area inside of the column. The lessons learned from this accident are similar to those of the Basant accident. In addition, it was considered not insulating large flanges for EO duty.

Ethylene oxide plant explosion at Seadrift Texas, on March 12, 1991.\(^{6}\)

The explosion of an oxide redistillation still was carefully investigated. It was shown that after a tube dry-out, EO vapour could react with rust deposits at the temperature of the steam used, to produce a hot spot to above 500°C which could initiate EO vapour decomposition.
A collection of accidents involving ethylene oxide is given by Trevor Kletz in a paper published in 1988. Among the most characteristic case histories reported are the followings:

- A flame impingement on an EO pipe-line connected to a distillation column caused the column explosion (1955).
- A dead-headed reflux pump caused the liquid EO overheat, the decomposition propagated back in the line (1962).
- A tank-car decomposed due to fire exposure. Several tank-car explosions are reported with various causes.
- A leak from pump caught fire. The flame impingement on equipment caused explosion.

ACCIDENTS IN ETHOXYLATION PLANTS
Some other accidents are known involving ethoxylation facilities but they are poorly documented, or their detailed circumstances are unpublished.
The Basle accident of December 7, 1987 occurred on a Pressindustria process. A leak of fatty alcohol and EO caught fire and caused an explosion in the open air production facility.
In Switzerland, two gas phase explosions were recently reported concerning stirred reactor ethoxylation facilities.
The explosion of a tube reactor to manufacture ethanolamine from EO and ammonia was described in Germany. The failure was attributed to the presence of a local gas pocket in the tube.
An accident in Italy is known to be related with the ethoxylation of an amine in a stirred reactor process. There was an unexpected accumulation of EO when a runaway reaction occurred.

A delay in the reaction initiation of an uncatalysed process caused excessive pressure in the reaction vessel protected against overpressure by a rupture disk. The disk rupture was followed by a two phase release of the vessel inventory into a catch tank. The reaction vessel was found empty.
This accident recalls that in case of rapid depressurisation of a pressure ethoxylation process through a rupture disc, large enough to allow liquid carry-over, a two phase release of the reaction mixture will occur due to dissolved EO. Therefore the protection of reactors by only rupture disks for a runaway reaction case or any other reason, is not adequate unless a proper collection system for a two-phase release is provided. The occurrence of a two-phase release may be predicted using vapour/liquid disengagement correlations. However there is no correlation to prove that a two-phase release will not occur. Therefore a proper emergency relief system design should include a release containment system.

In EO production processes and in other circumstances, EO aqueous solutions are produced and stored under temperatures of 40°C-50°C. For concentrations above 10 % wt, the liquid happened to self-heat. Such solutions are reactive and their temperature should be kept under control.

INFLUENCE OF THE VESSEL MATERIAL OF CONSTRUCTION AND OF IMPURITIES ON THE THERMAL STABILITY OF EO
The thermal stability of EO in the presence of various construction materials was investigated by different authors to check the compatibility of these materials with EO. Also of interest are studies on the thermal stability of EO in the presence of impurities like water or caustic soda.
Of particular interest are thermal stability studies carried out using the Accelerating Rate Calorimeter (ARC). B.G. Freeder and T.J. Snee (8) studied the thermal stability of 1.8 g samples EO mixed with 0.2 g aqueous sodium hydroxide solutions with mole concentrations between 0.125 and 1.0 NaOH. The polymerisation exotherm onset detection temperature was found to rise from 2.5°C for 1.0 NaOH mole concentration to 55°C for 0.125 NaOH mole concentration.

The thermal stability of pure and contaminated EO was investigated by L.G. Britton (9) also in ARC tests. Pure EO was found to exhibit the threshold self-heat rate of 0.02°C/min. at 210°C-220°C in titanium bombs and at 200°C in Hastelloy bombs. In the presence of water, the ARC threshold self-heat rate of 0.02°C/min. was obtained at 150°C with 10 % wt. water, 70°C with 40 % wt. water and 50°C with 90 % wt. water. See also the curve in ref. 10.

EO with 1 % wt. dimethylamine exhibited a threshold onset temperature of 33°C. Ammonia is known to react with EO as in the reactors to manufacture ethanolamines. Therefore, the presence of water, amines and ammonia, and any other alcaline contaminant should be excluded in bulk EO storages.

Rust is known to induce slow EO polymerisation at storage temperature and is supposed to have initiated a runaway polymerisation at higher temperature (7). High surface area iron oxide caused the initiation of EO decomposition with an onset temperature of 98°C. So did aluminium chloride. Chlorides of Sn, Ti, and Fe are said to reduce EO thermal stability. Insulation materials present also a detrimental effect on EO thermal stability. ARC tests on a charge of 2 g EO and 2 g insulation materials have been performed. A threshold heat-rate of 0.02°C/min. was found at 70°C for asbestos, 85°C for calcium silicate insulation, 120°C for expanded perlite, 150°C for mineral wool.

FIRES IN INSULATION MATERIALS
Fires in insulation materials was a frequent cause of explosion in EO production plants and ethoxylation plants. Leaks of EO in the insulation material have been shown to form polyethylene glycols (PEG). The insulation material and traces of rust are known to catalyse EO polymerisation at temperature below 100°C. (See above). Very divided PEG in insulation material can then oxidise and self-heat to above 500°C, a temperature high enough to initiate the violent decomposition of EO on the process side. The key literature references on this phenomenon are the papers of Laurence G. Britton (9)(10) and H. Giesbrecht et al. (4) related to the BASANT explosion. In ref. (4) it was shown that a leak of EO in wet glass wool would give PEG at temperature down to 80°C-120°C especially if the insulation material is impregnated with Fe₂O₃ + 1 % Cr O. 50 % of the PEG produced have a chain length of four monomers or more. These PEG's could oxidise in glass wool and self-heat to above 600°C, a temperature high enough to initiate EO decomposition.

The practical conclusions on the experimental results found in the literature are that a construction material which does not give rust would be preferable for EO duty, i.e. stainless steel. The best choice for the insulation material is foam glass with closed porosity, which would not enhance PEG oxidation. As pointed out earlier, large flanges should not be covered by the insulation to avoid leaks into the insulation material. The choice of flanges and gaskets is very important. First quality equipment should be used. Gasket materials which react with
EO at process temperature should be excluded. Gaskets which would swell or yield at the process temperature should not be used. Gasket which would be immediately destroyed in case of fire should be avoided. In European countries, spiral wound graphite gaskets are installed, which provide a good resistance in case of fire. If composite gaskets are used, one should check that components of the gasket do not dissolve in EO over time.

CHOICE OF CONSTRUCTION MATERIAL FOR EO STORAGE

The above considerations may result in decisions made concerning the design on construction material for EO storages. Depending on the date of construction and on the location, the design of EO storages may be quite different. Probably, large storage vessels near EO production plants or even in ethoxylation facilities are made of carbon steel to lower their cost of construction. Carbon steel vessels should be cleaned and treated to exclude the presence of iron oxide which would promote the formation of PEG. For the same reasons and for safety considerations, these storage vessels are cooled and insulated. From time to time, it may be necessary to remove the insulation for corrosion and thickness inspection.

If the construction material is stainless steel, both the refrigeration and the insulation are less necessary. There is less need for inspection and inspection is easier. The storage vessels are smaller and located in a pool, completely submerged with water or partly submerged with their top cooled by a water spray. Old storage vessels made of carbon steel kept under the sun and without refrigeration are of a lower standard.

EO storage vessels are pressure vessel since a nitrogen pressure is applied to prevent boiling, to exclude gas phase decomposition explosion and to make pump feed easier. The request for a storage pressure higher than the ethoxylation reactor pressure to prevent back-flow from the reactor to the storage vessel, is only realistic for low pressure ethoxylation processes up to 4-5 bar. For high pressure processes, above 10 bar, the drawback of having a high pressure storage may overcome the benefit of that type of back-flow prevention.

GAS PHASE EXPLOSION HAZARD

The explosive range of EO vapour in air under atmospheric pressure is 2.6 vol. % to 100 vol. % and the minimum ignition energy is 0.065 mJ. Pure EO vapour is flammable per se, without air, giving a decomposition flame.

The Minimum Decomposition Energy (MDE) of pure EO vapour depends on the temperature, the pressure and on other factors. The MDE of pure EO vapour was investigated by M. Glor and R. Siwek.\(^\text{(11)}\) It was found that the MDE of pure EO vapour by a purely capacitive electric discharge was 200 mJ under a pressure of 3.5 bar abs. This value could be reduced to 10 mJ by the introduction of inductance or ohmic resistance in the circuit. The authors concluded that up to ca 4 bar, the initiation of EO vapour decomposition by brush discharges was improbable. The temperature had no influence on the MDE of EO between 25°C and 100°C.

According to ref.\(^\text{(12)}\) for an initial temperature of 60°C and a pressure of 25 PSIG (2.7 bar abs.), the dilution of EO with nitrogen increases the mixture ignition energy. With 10 vol. % nitrogen, the ignition energy is one joule, with 40 vol. % nitrogen, no ignition was obtained even with a discharge energy of 1000 J. The nitrogen concentration to prevent ignition with a 45 joule capacitive discharge, of EO + nitrogen mixtures, for temperatures between 60°C and
190°C and pressures of 10 - 25 - 45 - 80 PSIG i.e. 1.7 - 2.7 - 4 - 6.4 bar abs., was obtained in ref. (12). This data is well in the operating range of most ethoxylation plants. A figure is provided where the necessary concentration of nitrogen to raise the MDE of the gas phase to above 45 J is given. For example, to safely operate a process at 160°C under 4 bar abs., 54 vol. % nitrogen would be necessary in the reactor gas phase. With increasing pressure and increasing temperature the nitrogen concentration requested would increase continuously.

Fairly compatible results were obtained by R. Siwek and E. Rosenberg (1989). (13) in a 20 litre sphere at temperatures of 100°C and 200°C and pressures up to 7 bar abs. In this paper, the limiting nitrogen concentration for a 250 J ignition source would be 60 vol. % for current operating pressures. A figure providing the safe nitrogen concentration as a function of temperature up to 300°C and pressure up to 5 bar abs. is given. Also of interest is a figure giving the gas phase explosion overpressure of pure EO vapour as a function of temperature up to 300°C and initial pressure up to 5 bar abs. This figure allows the estimation of the reactor pressure resistance necessary to contain a pure EO vapour explosion. The same authors suggest that an EO vapour explosion could be suppressed by the action of explosion suppressors as shown in their paper.

To our knowledge, the most wide-spread explosion prevention and protection measures are nitrogen blanketing and the construction of pressure resistant reaction vessels to contain the most severe gas phase explosion, the later measure being applied only in the most recently built plants. An interesting review of EO gas phase explosive properties is given by Bartknecht. (14)

One should note that the published data does not cover pressures between 7 bar abs. and 15 bar abs., a pressure at which some ethoxylators operate. The necessary data is unpublished. As pointed out by several authors (11) (12) (13), the presence of a high concentration of nitrogen in ethoxylation reactor gas phase will reduce the reaction rate and the plant productivity. Therefore it is of interest to adjust with precision the nitrogen concentration to the actual gas phase composition, eventually taking into account the substrate vapour pressure. This is generally possible for large productions of a limited number of ethoxylates. This is not realistic for small productions of a great number of different products.

POSSIBLE IGNITION SOURCES FOR GAS PHASE EXPLOSION

In general, the accidents where an EO vapour gas phase explosion is believed to have occurred, the gas phase contained probably pure EO vapour with limited or no nitrogen concentration as in EO production plant distillation columns. The ignition sources mentioned are hot spots caused by insulation fires. These hot spots are energetic ignition sources. The prevention of such hot spots and the presence of the proper nitrogen partial pressure in the gas phase reduce to a very low level the probability of having a gas phase explosion. The prevention of electrostatic discharges is also important i.e. by providing electric continuity between all the metallic parts of the plant and earthing. The electric resistivity of EO is low, of the order of $10^6$ $\Omega$.m so that the build-up of electrostatic charges does not occur. In general, the usual limitation of the circulation velocity is applied to EO while unnecessary. The mechanical dispersion of liquid EO into droplets does not occur in ethoxylation reactors since EO is vaporised completely when introduced in the gas phase.

Charge generation is very limited. This reduces the probability of the gas phase ignition with a MDE of 45 joules, 250 joules or more.
RUNAWAY REACTION HAZARD IN ETHOXYLATION PROCESSES

Runaway reaction hazard in ethoxylation processes may be caused by the decomposition of the substrate, the decomposition of the ethoxylate and the runaway of the ethoxylation reaction. The problems induced by the thermal instability of the substrate is not specific of ethoxylation reactions. One should check as in any chemical process that the substrate is stable under process conditions. Most ethoxylates may show some degree of decomposition above 200°C. The decomposition may become fast above 250°C especially in alkaline conditions and may present autocatalytic behaviour. This reaction is well known and must not be overlooked.\textsuperscript{(15)(16)(17)}

Unless a particular instability of the ethoxylates is the result of the substrate own instability, a runaway reaction caused only by the decomposition of the ethoxylate is unlikely under usual process conditions. The runaway of the desired ethoxylation reaction may be due to the controlling reactant (EO) accumulation in the reaction mixture. In normal process conditions, EO is continuously fed to the reactor and there is a stationary quantity of unreacted (accumulated) EO present in the reactor. In case of cooling failure, the accumulated quantity of EO will react and cause a temperature increase and possibly a pressure increase. In well designed processes, the process temperature, pressure and the EO feed rate are chosen and controlled to minimise EO accumulation and thus optimise the process productivity. To study the consequences of a sudden cooling failure under such normal process conditions, VSP tests were carried out on a series of ethoxylation reactions to experimentally simulate a cooling failure in semi-batch processes, both at the beginning of EO injection where the reaction is fast and at the end of EO injection where the reaction is slower. The processes considered covered the ethoxylation of saturated and unsaturated alcohols, fatty alcohols, fatty acids and glycols. VSP is for "Vent Sizing Package", the DIERS bench-scale apparatus. The VSP is a pseudo adiabatic calorimeter to study runaway reactions under conditions close to adiabatic conditions thus providing a good representation of the consequences of a runaway reaction at industrial scale.

In these experiments, the substrate or reaction mixture was charged to a stainless steel closed VSP test cell. The gas phase was inerted with the requested nitrogen pressure and the temperature was raised to the normal process temperature. Then EO was injected to obtain the usual total pressure at the normal process temperature. Then the catalyst was injected to initiate EO reaction. In all the tests made on initial reaction mixtures the catalyst injection was followed by a temperature increase of a few degrees Celsius and a decrease of the pressure corresponding to EO consumption.

In the tests made on the final reaction mixtures, the EO injected reacted immediately slowly due to the catalyst already present. For this reason, it was impossible to adjust the test cell pressure to the normal process pressure.

The above testing procedure may be applied to detect processes where a cooling failure would induce a runaway reaction hazard due to the controlling reactant accumulation under normal process conditions. In addition, the following precautions are necessary to keep the process under safe conditions:

- the EO feed must be interrupted immediately in case of cooling failure,
- the process must be under normal conditions before the cooling failure.

To ensure that EO accumulation is restricted to a safe concentration, it is necessary to limit the process total pressure by process control and safety interlocks and as a third barrier by
collected pressure safety valves. It is also necessary to control the process temperature to exclude too low a temperature.

It is important to note that the above conclusions on the safe process conditions, also in case of a cooling failure, are restricted to normal process conditions before the cooling failure. If an abnormal high concentration of EO is present in the reaction vessel, the runaway reaction may become violent as shown by the fast reaction of concentrated EO solutions. It is therefore very important to maintain the process under normal conditions all the time. The other possible causes of the controlling reactant (EO) accumulation are common to all semi-batch processes.

No agitation: This is a well known cause of the controlling reactant accumulation. Agitation or circulation should be controlled before allowing EO injection. EO injection should be interrupted in case of agitation failure.

Temperature too low: The reaction is slower than expected and more EO accumulation is possible even if the maximum allowed total pressure is not exceeded. This process deviation is potentially dangerous and should be excluded.

No catalyst: The reaction will not proceed as usual and EO will accumulate until the maximum allowed pressure is reached to cut EO feed. The catalyst should never be added after EO introduction to the reactor. To avoid charging too much EO to the reactor without the reaction initiation, it is recommended to check for the presence of the reaction exotherm and pressure decrease after the injection of a limited amount of EO. Continuous EO feed is only allowed after the reaction initiation. This prereaction procedure would also cover possible delays in the reaction initiation.

Temperature too high: This is not a cause of accumulation but the EO feed should be interrupted because something is wrong somewhere. This may be the result of EO accumulation. EO injection should be stopped immediately.

**SPECIFIC CAUSES OF RUNAWAY REACTION**

There are nevertheless specific causes of EO accumulation in some ethoxylation reactions. In some processes, the ethoxylation is carried out without a catalyst to add one mole of EO on a reactive site and prevent glycol formation. In this case, the reaction initiation may be obtained after a delay and the reaction may become slow requesting an excess of EO to go to completion. This may cause problems. The reaction may start suddenly and pressurise the reaction vessel because of the high concentration of EO present. After the addition of one molecule of EO on the reactive site, it is necessary to add a catalyst to react a second mole of EO on the alcohol function introduced. Before the catalyst introduction, it is necessary to degas the reaction mixture to remove the excess EO present. This is obviously very important.

As pointed out above, there are other sources of runaway reaction hazards, specific of ethoxylation plant operation. The runaway polymerisation / decomposition of an EO storage due to a back-flow of the ethoxylation reaction mixture from the reactor to the storage vessel. This extremely serious accident must be prevented by redundant back-flow prevention, the most effective of which is to provide an EO storage pressure greater than the ethoxylation
reactor operating pressure. This type of accident has occurred in plants manufacturing ethanolamines where the operating pressure may be well above the storage usual pressure, also ethanolamines and ammonia are very effective catalysts of the polymerisation of EO.

In the Doe Run accident(2) the ethoxylation reactor was a tube reactor where EO was fed in the liquid phase thus making the back-flow possible. In the wide spread semi-batch ethoxylation processes the provision of an EO feed in the gas phase and not through a dip pipe in the liquid would prevent a significant back-flow of liquid reaction mixture to the EO storage vessel.

A temperature below the ambient in EO storage vessels could possibly prevent a runaway reaction in case of reaction mixture back-flow to the EO storage vessel since most contaminants would cause EO to react, only at temperatures above the ambient.

Contamination of EO by impurities.

The poor quality of EO delivery may lower its thermal stability and induce self-heating. The most probable contaminants are water, rust, glycols, PEG’s. If the storage temperature is low enough, the impurities will not induce any detectable self-heating. This is a good reason to keep this temperature low. In case of abnormal self-heating, the best solution is to consume the EO stock as soon as possible. Monitoring of the storage temperature to detect self-heating is only effective for significant temperature increases well above the daily variation of the storage temperature which may be of a few degrees Celsius. A good quality control would be more effective to detect contamination of the EO delivered.

Runaway reaction in a scrubber designed to collect EO vents and PSV discharges can be prevented by proper control of the possible discharge to the scrubber, monitoring the scrubber temperature and providing enough cooling capacity to the scrubber.

Decomposition of liquid EO due to a hot spot or a dead-headed pump:

The accident case histories have shown that the initiation and the propagation of the liquid decomposition assuming a deflagration mode was possible. The initiation of the decomposition occurs if a hot spot is present with a temperature high enough to initiate EO decomposition, above EO autodecomposition temperature.

The propagation is possible in tubes or pressure vessels if the initial temperature and pressure of the unreacted oxide is high enough. This is similar to other unstable chemical deflagration behaviour. Experimental results concerning liquid EO propagating decomposition are given in ref. 9 and 18.

VENTING OF RUNAWAY REACTIONS

The limitation of excessive pressure in ethoxylation reactors using pressure safety valves (PSV) is an effective back-up to prevent EO accumulation. This comes after process control and instrumental safety interlocks. The release should be collected to a catch tank and a scrubber since EO is present.

If the process is well understood, the probability of having a runaway reaction accident is greatly reduced. So there is no need for large emergency relief vents on ethoxylation reactors. This makes the use of PSV quite suitable. The use of PSV may prevent complete pressure blow-down and possibly prevent or limit liquid carry-over in case of the PSV actuation. A combination of a rupture disk and a PSV in series can protect the PSV from the formation of polymers and help to the detection of the vent actuation. This is very important since an
undetected large flow of EO to the scrubber may cause the absorption liquid over-heat and EO emission. The vent line must be nitrogen blanketed to prevent ignition of EO vapours with air.

In one case history mentioned above, an emergency relief vent has proved to be useful in the case of the delayed initiation of an uncatanysed ethoxylation reaction in a continuous process. This was a significant deviation from normal process conditions which could have been detected earlier.

The provision of emergency relief vents for severe runaway reaction scenarios in the case of ethoxylation processes leads to unrealistic, large, containment systems with complex design. Therefore the prevention of process deviations is a more effective policy in this field.

KINETIC AND THERMODYNAMIC MODELS TO REPRESENT ETHOXYLATION PROCESSES
A series of interesting papers was published by Prof. Santacesaria et al. To provide integral models for the ethoxylation of various substrates (1-19-20-21-22-23-24).

In these papers the kinetics of the ethoxylation reaction in the liquid phase is studied as a function of the process conditions. The solubility of EO in the liquid phase is related to EO partial pressure in the gas phase taking into account the liquid changing composition, using thermodynamic models (NRTL). The solubility of EO in final products was also measured. In some papers the influence of EO mass transfer is considered.

These papers may help to estimate the EO stationary concentration in the process and determine the safe operating limits of processes, with some theoretical effort.

TOXIC PROPERTIES OF ETHYLENE OXIDE
Ethylene oxide is toxic. In the United States the average allowable concentration in air specified by OSHA is 1 ppm i.e. 1.8 mg/m$^3$ with possible 15 minute excursions to 5 ppm i.e. 9 mg/m$^3$. The NIOSH specified a IDLH of 800 ppm.

In France, the exposure limiting concentration is 10 ppm and the exposure limiting average concentration is 5 ppm.

Concentrations of the order of 10 ppm are well below the odour detection threshold making the use of instrumental detectors necessary.

The effects of exposure to EO are described in a toxicology data sheet issued by the French INRS\(^{(25)}\).

The contact of EO or EO aqueous solutions with skin may cause severe burns, even for low EO concentrations.

The Conseil Européen de l'Industrie Chimique (CEFIC) has issued a list of papers published on the effects of exposure to ethylene oxide.\(^{(26)}\)

A survey of exposures and exposure control in the EO production and ethoxylation industries was published in 1990 for the USA.\(^{(27)}\)

CONCLUSION
The author hope that this paper addressing the various process safety issues of ethoxylation processes will help understand the relevant literature and contribute to hazard control in this field.

LITERATURE
26. CEFIC, 1998, Compilation of public reports pertaining to EO, EO Production. WG/MEG TOX TF (490) - CEFIC, avenue E. Van Nieuwenhuyse 4, PO Box 2, B-1160 Bruxelles.