Loss Case Histories in Pressurized Ethylene Systems

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This paper addresses a number of accident case histories in pressurized ethylene systems comprising heaters, driers, purifiers and High Pressure Polyethylene product receivers. Also covered are compression-heating accidents in pipelines and compressors, and decomposition via external fire exposure of piping. Several companies contributed accounts; few of these have been reported in the open literature. The probable event scenarios are discussed with reference to safety information that in many cases postdates the contemporary loss reports. While there may be room for some debate over probable causes, insight can be gained simply by reading the accounts.

The objective is to provide real examples of design and operational oversights contributing to preventable losses. As usual in Loss Prevention case histories, an important lesson is that years of uneventful operation often pass before a problem is recognized, and that subsequent investigation often uncovers the potential for other failure routes and possibly worse outcomes.

INTRODUCTION

This paper discusses ethylene loss histories abstracted from various documented sources. The companies involved are not identified, although references are given where accounts have been published. Reference [1] provides a background to the discussion. The losses are placed in six categories:

(1) Drier and Regeneration Systems: Cases A-D
(2) Heaters: Cases E-G
(3) Purifier Vessels: Cases H-M
(4) High Pressure Polyethylene Product Receivers: Cases N-Q
(5) Sudden Compression: Cases R-U
(6) External Fire Exposure: Case V

DISCUSSION OF INCIDENTS (1): DRIER + REGENERATION SYSTEMS

Case A: 1971 Molecular Sieve Drier

System

An underground storage facility had an associated twin drier system. Each four foot diameter, twenty foot high drying tower, constructed of 2½ inch thick SA-212B, FBX steel contained 9000 lb of 3A molecular sieves. The driers operated on alternate cycles of 16 hours heating, 8 hours cooling and 24 hours of drying ethylene feed gas. To regenerate the sieves after a drying cycle, hot ethylene was used as the regeneration gas. Ethylene at a nominal 1340 psia was passed through a salt bath heater at a design flow rate of 7000 lb/hr. Maximum regeneration gas temperature entering the drier was 232°C at the design flow rate. The line between heater and drier was uninsulated. The salt bath temperature was not known accurately. The regeneration gas temperature was measured by a thermocouple mounted in a thermowell in the drier inlet pipe. Temperatures in the bed were not measured. Figures 1 and 2 show typical heater-drier configurations for this type of system.

Failure

On Christmas Day 1971 at approximately 6:30 a.m. the 2-inch diameter regeneration gas inlet and outlet lines on the South drier ruptured releasing high pressure ethylene with an attendant explosion and fire. The ruptures were caused by high temperature metal failure due to an ethylene decomposition flame in the piping. Damage also occurred in the South drier in the area of flame impingement from the outlet line fire. Operational records were destroyed by the fire, but analysis of previous cycle profiles suggested that the incident occurred 4.5 hours into the heating cycle of the South drier. The system was operated as designed except that the regeneration feed rate was low (3830 lb/hr) and this would have increased the regeneration gas temperature. The facility was unattended at the time of the explosion. [illegible] was estimated at $150,000 in 1972 dollars.

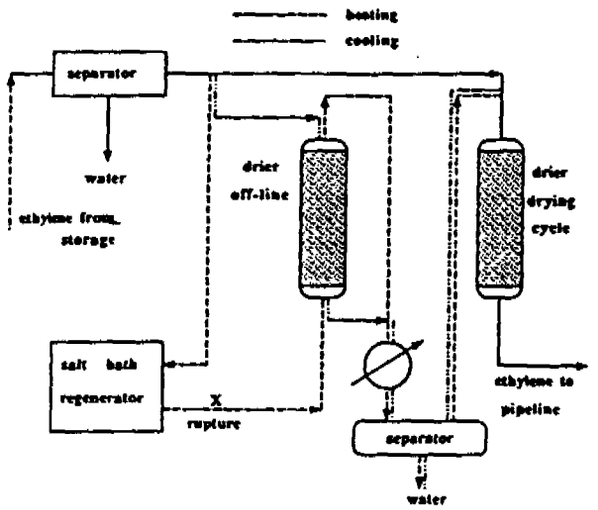

FIGURE 1. Heater outlet pipe rupture.

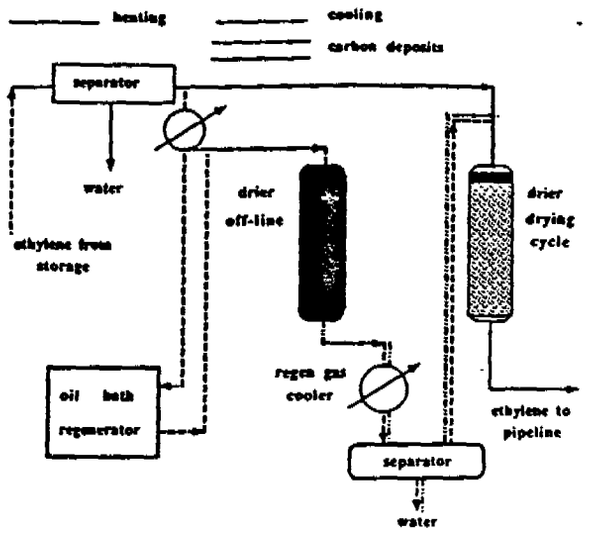

FIGURE 2. Drier inlet pipe rupture.

Causes

The accident investigators concluded that although the full story would never be known there were strong indications that the decomposition was initiated in the heater due to localized hot spots, low salt levels and possible aggravation by low regeneration gas feed rate. This explanation is, however, unlikely.

As shown in [1] the decomposition was instead more likely to have been initiated in the molecular sieve bed than in the heater. There was no evidence that salt levels in the heater had been low and no evidence cited of soot being found in either the heater or the regeneration line upstream of where the inlet pipe ruptured. For stagnant conditions in the drier bed at 1340 psia, runaway oligomerization/polymerization of ethylene can occur at about 275°C and the runaway timescale is about 3 hours if adiabatic conditions are assumed [1]. While records indicate that flow was not lost prior to the event it is possible for channeling of flow to occur in large sieve beds (sieves can clump together), and parts of the bed could have been effectively stagnant.

After the event it was found that the upper 80% of the bed was glued together by a matrix of sieves and carbonaceous material and the sieve crystal structure was destroyed, indicating temperatures above 540°C. Other evidence showed that internal temperatures had reached 650-700°C prior to the external fire. It appears likely that owing to low flow rates the inlet temperature to the drier exceeded about 275°C and runaway occurred in the bed. No records of inlet temperature were available, although the outlet temperature prior to the event was about 150°C at the measuring point some 100 feet downstream. This monitoring point showed a small but steady increase after about 5:00 a.m. which is consistent with the fact that the slow reactions leading to fast runaway typically cause a temperature increase of 40–60°C; only a fraction of this temperature increase need appear at the downstream monitoring point. Since the salt bath heater temperature was not measured, but was likely well in excess of 300°C, any upset in fuelling rate or convective conditions in the bath might have contributed to unusually high regeneration gas temperatures during this particular heating cycle.

Once runaway in the bed had proceeded to decomposition, flames were established in the free gas spaces at the top and bottom of the drier. At the inlet pipe, the decomposition flame stabilized against the regeneration gas flow and heated the pipe, causing it to rupture. The downgoing outlet pipe also ruptured, which is consistent with the fact that ethylene decomposition flames tend to burn upwards and stabilization of the flame front in a downgoing section of the pipe is likely [1]. The metal at the pipe failures showed severe distortion and thinning down to knife-edge sharpness, indicating the good ductility associated with high temperature failure. Microscopic examination of the pipe failures showed a partially recrystallized grain structure without grain elongation, indicating a temperature of 815–870°C (this was attained after rupture as the hot gases escaped through the failure—the temperature prior to failure could not be determined). Measured ethylene decomposition flame temperatures are in the range 1000–1100°C [1]. The metal microstructures were normal nine and eighteen inches away from the ruptures, indicating a thin zone of heating. Thus, the facts are consistent with runaway in the bed and the formation of simultaneous decomposition flame fronts that stabilized, heated and ruptured the inlet and outlet regeneration gas lines.

An alternative cause for high bed temperatures during this cycle was the possibility of water carryover through the feed knockout into the heating gas. In the range of 3% water the bed temperature would be raised about 38°C; much higher temperatures would have been attained if a slug of water had been carried over.

A final observation was that brine in the feed was found to have enlarged the effective pore size of the sieves, meaning that some ethylene would be adsorbed. Sodium levels in the sieves were high indicating that brine carryover might have been a regular event. It was discovered subsequently that 13X sieves catalyze ethylene polymerization and so 3A sieves with enlarged pores would be expected to be slightly catalytic. This would reduce the temperature needed to initiate runaway.

Changes

The principal concern was the fact that hot ethylene rather than nitrogen or natural gas was being used to regenerate the sieve bed. A Design Team succeeded in defining safe operating temperatures but a number of operational and design changes were necessary to assure safe, unattended operation. Risk (including fault tree) analyses were carried out to identify these changes. Briefly, the changes comprised:

(i) Comprehensive monitoring of temperatures throughout the bed using thermocouples with d response time. ESD at prescribed temperature.

Molecular sieve beds are thermally insulating and may develop hot spots. Monitoring of only vapor-space temperatures is inadequate for potentially self-heating systems of this kind, and temperatures should ideally be monitored throughout the bed. In common with purifier beds (see Part 3), thermocouples mounted in thermowells close to the vessel wall may not respond to exotherms closer to the vessel axis. For this reason special designs for thermocouple arrays having relatively fast response have been adopted.

(ii) Replace salt bath with gas convection heater equipped with comprehensive temperature and flow rate monitoring. ESD at prescribed temperature. Loss of flow to switch off heat (note that a salt bath has too much thermal inertia to do this rapidly).
(iii) Engineer changes to ensure that water slugs cannot be carried into the beds and cause sudden exotherms due to adsorption heating by the 3A sieve.
(iv) Ensure that 13X or other sieves capable of adsorbing ethylene cannot be mistakenly used instead of 3A (3A sieves do not adsorb ethylene but 13X will both adsorb ethylene and catalyze polymerization reactions).
(v) Change the MOC of the driers to ensure that embrittlement will not occur during sudden ESD decompression and cooling of the system. Alternatively, ensure that decompression ratio and rate are limited to avoid this effect.
(vi) Insulate regeneration line both to increase fire resistance and to minimize heat losses, thus enabling the heater to be operated at a lower temperature.

Case (B): Heater Outlet Pipe Rupture [2]

System

The system was similar to Case (A) and had run without incident for ten years. A salt bath was used to heat ethylene regeneration gas (1100 psig) to about 230°C (Figure 1). The drying medium was an unspecified molecular sieve. The salt bath had been run at 343-371°C in earlier years but this had been reduced to 302°C. It was normal practice to stop the flow through the heater for 2-3 hours every 12 hours. Thus, ethylene in the heater would periodically heat up to the salt bath temperature, while ethylene in both heater and drier would be stagnant.

Failure

One drier was about six hours into the heating cycle and showing an outlet temperature of 190-205°C just prior to the event. The salt bath was being increased to the target of 302°C when without warning the 3-inch heater outlet pipe ruptured about ten feet from the heater. There were no injuries but the explosion was heard 5 miles away. A large fire resulted which was extinguished once the system was isolated. All conditions had been normal prior to the event with the exception of the regeneration gas flow rate, which had been varying considerably over the previous 30 minutes. Thus, the hot ethylene feed would have approached salt bath temperature during the periods of low flow. The safety valve did not operate during the event, which is consistent with the slow propagation of an ethylene decomposition in a large system [1]; pressure would be relieved into associated piping which provides a large buffer, and the bed would tend to quench the flame.

Causes

Two possible explanations were given in [2]. The first was heater malfunction due to the absence of a fail-safe temperature control system (TRC). Two failures were found after the event. One was short circuiting of exposed thermocouple leads due to insulation damage and the other was failure of the pneumatic tubing between the transducer and the controller. Either of these would have led to overfiring of the heater, but either or both failures could have been the result of heat from the fire [2]. The second possible explanation involved possible impurities such as oxygen, metal oxides or salts, copper acetylides and carbon. However there was no evidence found to support this thesis. It was tentatively concluded that the incident was the result of excessive temperature in the heater due to TRC failure (tacitly that the decomposition originated in the heater).

After the incident one drier was opened and was found to be severely fouled, principally by polyethylene (it was unspecified if this was the drier being heated at the time of the incident). Molecular sieves with pore sizes larger than 3A (such as 13X) adsorb ethylene and also catalyze ethylene polymerization. Heat alone tends to form oligomers (green oils) and carbon [1]. Thus it is quite likely that the sieves were inappropriate for ethylene service, or that the crystal structure had been compromised by brine (as discussed under Case A). This suggests that again, runaway in the sieve bed probably occurred and the flame stabilized against flow in the piping going back to the heater. Contributory causes were the erratic flow which would have caused excessive bed temperatures during periods of low flow. The erratic flow would be consistent with the flame being able to travel so far upstream. As shown in [1], even were the sieve bed not catalytic the heater bath temperature (302°C) exceeded the predictable runaway temperature for the sieve bed and it was only a matter of time before some minor upset occurred which would trigger the decomposition event. The surprising aspect of this event is that it did not occur earlier when the heater bath was normally maintained at 343-371°C, and this might indicate the importance of low flow rate and/or sieve catalysis as contributing factors.

Changes

Owing to the proximity of the system to operating plant it was decided [2] to completely revamp the regeneration system and do away with the salt bath heater. The changes were not specified. However, it was stated that if it had not been practical to do away with the salt bath, the following would probably have been recommended:

(i) Provide automatic shutdown at a maximum salt bath temperature of 288°C, and provide an independent backup system to limit temperatures to this value. Ensure that both normal and backup systems are failsafe.
(ii) Eliminate copper or its alloys from the system (sources of copper acetylide) and take every measure to exclude oxygen from the system.
(iii) Relocate heater to a site at least 50 feet from other processing facilities.
(iv) Inspect tube bundle periodically for erosion—tube failure and contact of ethylene with hot heat transfer salt (a powerful oxidizer) could lead to an explosion.

These recommendations do not address the most probable causes of the incident. If the decomposition indeed resulted from runaway in the drier bed, focus should be given on the type of sieve being used and the possibility of brine or water carryover. Stagnation of hot ethylene (above about 200°C) in the system should be eliminated. The regeneration gas temperature should be measured and its temperature kept at no more than 230°C. To reduce the hazard associated with stagnation of hot ethylene it would be possible, for example, to lower the bath temperature to less than about 200°C prior to ending the heating cycle (and stopping flow). ESD could be arranged should low or no flow conditions be detected in the heater during periods of maximum temperature in the heating cycle.

Case (C): Drier Inlet Pipe Rupture and Fatality [2]

System

The system was conventional and used an oil bath to heat ethylene regeneration gas at 1300 psig to a drier inlet target temperature of 204°C (Figure 2). Both regeneration and drying were downflow. The temperature of the hot oil is believed to have been about 260°C at the time of the incident. The facilities had been out of service and in indoor storage for several years. A similar drying system had been in uneventful service for eleven years. New silica gel desiccant had been charged to the dryers and the unit was commissioned following standard procedures. These comprised purging with nitrogen at low pressure for about ten hours at 270 cubic meters per hour (100,000 SCF/hr). The system was then pressurized and depressurized twice with ethylene, then the pressure was slowly increased to line conditions.

Failure

Both beds were then regenerated. The first drier was heated for about 75 minutes at which time the drier inlet and outlet temperatures reached 185 and 130°C respectively. About 15 minutes later the regeneration cycle was started on the second drier. The inlet temperature rose to about 200°C in 45 minutes, then fell at a rate of 0.3°C/minute for 45 minutes. The bed outlet temperature reached 163°C after 90 minutes of regeneration. 15 minutes after start of cool down of the second drier bed, nearby operators heard "popping" sounds after which the 6 inch inlet pipe to the drier ruptured. There was a fireball which caused the death of one operator and property damage to a distance of 150 feet from the rupture. Inlet conditions were 1300 psig and 185°C at the end of the heating cycle.

Causes

The fall-off of inlet temperature noted above during the heating of the second bed was attributed [2] to a drop flow rate caused by excessive manual throttling, hydrate formation or silica gel "caking." Whatever the reason, there was evidently an initially high temperature established relative to the first drier inlet temperature.

After the incident the first drier was found to be full of large chunks of silica gel, carbon and unknown binder (presumably a low grade polyethylene). The second drier had 1–2 inches of carbon on top of the bed. The liner inside the first drier was collapsed radially inwards with block deposits on the top 4–5 feet of the liner. The bottom three feet had a heavy rust scale. The pipe that failed did so due to internal heating to 700–870°C (cf. Case A), and there were also three bulges caused by overheating in the piping upstream of the rupture.

The investigation concluded [2] that the ethylene decomposition was initiated about five minutes before the pipe ruptured due to a stationary flame front, that is, when the flame stabilized against the flow speed of the inlet ethylene. Initiation was thought to be either in the space behind the internal liner (a possible source of unpurged air and catalysis by rust), in the heater (when stagnant gas would be present at the end of the heating cycle) or at the top of the desiccant bed (aided by accumulation of rust there by the downflow operation mode).

As shown in [1], none of these initiation explanations is probable. The heater had too small a volume to allow runaway at 260°C even under no flow conditions. Rust is a feeble catalyst and quickly becomes poisoned with carbon. It is unlikely that significant concentrations of oxygen would be trapped behind the vessel liner, and even in the presence of rust the small space involved should absorb any reaction heat evolved.

The most probable explanation might be as follows. The silica gel loaded was most likely a polymerization catalyst, which would account for the binder (presumably polyethylene) found in the first bed. There was the possibility of residual oxygen in the gel pore structure, since this was a new bed and chemisorbed oxygen might not have been removed by the nitrogen purge. Silica gel is likely to be analogous to 13X sieve in adsorbing ethylene. Discounting possible upsets, sources of heat would be in the ethylene pressurization step (via heat of adsorption in the silica gel), then in the heating step at which stage polymerization in the bed might begin. Because runaway in a bed at less than 200°C is not predicted [1] in the absence of catalysts, it is reasonable to assume that the silica gel was the major catalyst and secondary effects only would be attributable to the rust found. The presence of oxygen in the pore system might have been the significant factor in this incident, accepting that previous operating experience in a similar system involved the use of the same desiccant. Since the bed temperatures were nowhere monitored, there would be no advance warning of any runaway.

Changes

The following general recommendations were made [2] following this accident:

(i) Where feasible, ethylene should not be used as regeneration medium, especially at high pressures.
(ii) Temperature limits should be reduced to allow for the effects of oxygen and rust, of stagnant gas, and of temperature control tolerances.
(iii) Prior to startup after exposure to air, the drier and associated piping must be properly purged of oxygen, preferably with nitrogen. Dead ends and internal liners (with the possibility of a hazardous dead region behind the liner) should be avoided.
(iv) Redundant and fail-safe features should be provided for temperature control of the heater.
(v) Facilities should be designed and procedures developed to avoid stagnant ethylene at high temperatures.
(vi) Rapid isolation and depressurizing appear to be the most effective actions to stop a thermal decomposition.

The first recommendation is clearly a desirable approach where practical (better still is to use nitrogen to purge the ethylene prior to beginning the heating cycle). The second and third recommendations do not address the possibility of oxygen and ethylene being sorbed in the desiccant and reacting there, nor is a safe temperature specified. The fourth through sixth recommendations are sound, although it is important to depressurize {(vi) above} such that metal embrittlement due to decompression cooling does not occur. This is partly dependent upon the metallurgy of the system, but as shown in [1] a final pressure of about 200 psi should quench any decomposition while not unduly cooling the system during depressurization. A similar recommendation was previously made by Kuhre [9].

Case (D): 1963 Heater Outlet Rupture (Private Communication)

System

Hot ethylene at 1100 psi was used as regeneration medium for an ethylene drying system using silica gel desiccant. The ethylene was heated to 240°C in a salt bath heater with salt control temperature of 329°C.

Failure

Four and one quarter hours into the heating cycle the regeneration gas flow started to fall. After a further half hour there was no flow. Five hours into the heating cycle, after 15

minutes of zero flow, the heater outlet pipe ruptured. After the equipment was dismantled for inspection and repair a deep layer of soot was found in the bed concerned and the inlet line from the heater was covered with carbon deposits. Large "concreted" chunks of sooty material were found at several locations. On opening pig traps at the site, a deposit of sooty material reacted immediately with the air. It turned from black to gray, crackled, pores "opened up" and heat was given off. Subsequent tests made on the salt bath showed regions at 427°C for a control temperature of 260°C.

Causes

The cause of the incident was unknown at the time of occurrence. As shown in [1] the probable cause was runaway in the drier under conditions of low/no flow and compounded with excessive temperatures plus probable catalysis by the silica gel. The loss of flow shortly before the incident might have been the result of polymerization in the bed (formation of polyethylene via silica gel catalysis), and this would account for the chunks of material found after the event. The reactive material found in the pig traps is not relevant to the incident and probably reflects rapid oxidation of finely divided metals/reduced metal oxides in the presence of some combustible organic material (oils and low polymers) on sudden exposure to air. As shown in [1] the incident would be predictable after 10 minutes of stagnation in the drier at the nominal salt bath temperature (329°C). Since the bed temperature was not monitored, and there was the potential for catalysis by the silica gel, a single cause of the incident cannot be identified.

Changes

Both short term and long term recommendations were made:

Short Term:

(1) Regenerate at same pressure but limit salt bath temperature to 232°C.
(2) Thoroughly clean heater tubes. Clean drier system piping. Remove top portion of drier bed to depth where gel is free of aromatic compounds.
(3) Install low flow alarm on regeneration gas flow.
(4) Depressurize heater circuit to 30–40 psig when regeneration is complete.
(5) Remove and inspect 6 inch line to drier inlet and clean thoroughly.
(6) Pig 3 inch line from the heater to the drier vessels.

Long Term:

(1) Provide more heat transfer surface to permit design rates of operation at much milder conditions.
(2) Integrate low regeneration flow alarm, automatic shut off and automatic venting of heater circuit.
(3) Regenerate at lower pressure and higher temperature.
(4) Consider dual cycle operation to minimize severity of operating conditions.
(5) Use a different regeneration gas in a closed recirculating system. Natural gas is one gas to consider.

Long term measure number 3 appears unfavorable unless pressures are reduced to below 200 psi [1] to prevent a propagating decomposition. Even were the pressure reduced to this level or lower, the potential catalytic effects of silica gel might give problems due to polyme formation over time, and higher heater temperatures could lead to oil and carbon formation [1].

DISCUSSION OF INCIDENTS (2): HEATERS

There is no direct evidence for pure ethylene decompositions occurring as a result of initiation in heaters. Although heaters are usually the hottest components in ethylene handling systems, they are relatively small in volume and therefore have high threshold temperatures for runaway. The representative dimension [1] of a heater should in most cases be determined by its outlet head space rather than by tube radius, since it is in the outlet head space that stagnant ethylene is most likely to self heat. Should catalytic material be present, it is likely to accumulate in this space. Heaters have been involved in minor losses due to fouling and formation of soot. The latter has raised concerns over possible "decompositions" although its formation is most likely related to slow reactions involving catalysis by metals and metal oxides.

Case E: Steam Heater Fouling [3]

System

A G-fin exchanger using nominal saturated 300 psia steam at 217°C on the inner pipe was used to heat filtered ethylene at 800 psig for metering. Outlet ethylene temperature was 27°C nominal. Operating data indicated that actual steam pressure downstream of the control valve might have been as low as 270 psig with a steam temperature of about 210°C upstream of the control valve. The ethylene-containing annulus in the heater had a hydraulic diameter of 5 inches.

Failure

An operator noticed that the heater was unable to maintain the normal outlet temperature. After checking that a malfunctioning controller or steam trap was not the cause, a temporary switch was made to a spare heater and the exchanger was inspected. The heater was found to be fouled with a black, sticky material estimated to be 70–80% rust together with some fine carbon. Within the ethylene-containing annulus there was more carbon on the inner surface than on the outer. The safety valve (925 psig) had not opened. The ethylene outlet temperature had remained steady at 27°C for several days and had increased to 49°C over a five minute interval of low flow immediately prior to the shutdown.

Causes

The source of the rust was traced to a collapsed cartridge filter element allowing carry-over of scale from a 25–30 year old piping system which had never been cleaned. No oily residue was found in the heater. When the heater was next cleaned the solids found were primarily ferrous oxide. The investigation concluded that a decomposition might have occurred in the heater. As shown in [1] the event was more likely caused by relatively slow catalytic oligomerization/dehydrogenation of ethylene following the dumping of large amounts of scale into the heated system when the filter element failed. Iron and rust are relatively poor oligomerization catalysts, the former being poisoned by carbon formation on its active sites. Both iron and iron oxides can catalyze these reactions at rates that become observable via calorimetry at less than about 150°C. In the heater, deposited scale would greatly exceed the temperature of the flowing ethylene and might approach wall temperature. It is unlikely that these reactions would proceed to a "decomposition" owing to heat losses and the relatively weak catalytic effects involved. However, the heavy reaction products of the slow reactions would be similar to those from a decomposition.

Changes

Steps taken to eliminate the problem included:

(1) Increase size and strengthen mechanical integrity of filters.
(2) Increase cleaning frequency to reduce risk of element failure and subsequent risk of accumulation of rust (catalyst) in the heater.
(3) Provide system to block off steam flow to the heater if ethylene flow falls to less than 3 ft/s, so reducing the risk of combining low flow with maximum condensing steam temperature.
(4) Reduce normal steam pressure. Since the steam temperature was more than 180°C above the heated ethylene temperature it was recognized that reduction of steam pressure to about 150 psig (185°C) could significantly reduce the risk of reoccurrence.

Case F: Steam Heater and Pipeline Fouling [*1*, *3*]

An unnamed company experienced periodic fouling of an ethylene steam heater operating at 300 psig (216°C). This was prevented by reducing steam pressure to 150 psig (185°C). The fouling was polymeric rather than carbonaceous [*3*]. The actual nature of the residue was not described. This problem appears to have originated in the heater, although if the residue was in fact polymeric rather than carbonaceous it indicates that catalysis was occurring, possibly as a result of rust and pipeline scale being carried into the heater by the gas flow.

As discussed in [*1*] a number of companies have experienced fouling in heaters where the problem was not related specifically to the heaters concerned. Fouling was also experienced in filters in the lines involved. Slow catalytic reactions in the ethylene pipelines due to pipeline scale may cause small whiskers or nuclei of low grade polyethylene to form. The nuclei are observed to grow around core material of metals and oxides. During major flow rate changes the polymeric material is convected downstream to collection points such as filters and heat exchanger tubes. Factors involved might include ground temperature, pipeline metallurgy and frequency of line cleaning. Also, the phenomenon might be linked with the concentration of trace impurities in the ethylene. For example, assuming the catalytic medium is a supported metal oxide of some type, it is not unreasonable to expect that carbon dioxide and possibly water might act as chain terminating agents and limit the catalysis. Experiments by South Texas Pipeline Company [private communication] showed that polymer formation appeared only below a certain threshold (0.8–1.0 ppm) of carbon dioxide in the ethylene entering the pipeline. This suggested that the problem is more likely to be experienced by newer olefin units or those with superior controls/ethylene specifications, since they should produce lower levels of CO_2.

Case G: 1984 Soot Formation in Heater Outlet

2–3 mm layers of soot were found in the outlet plenum of an ethylene letdown preheater. 1 mm layers were found immediately downstream. An oily fouling was found upstream and downstream of the hydrogen inlet to an acetylene removal bed downstream of the heater. Upstream of the heater was very clean. The heater temperature was 160°C (75 psig steam) and the upstream piping was not regularly cleaned. As in Case F this problem appears to have been the result of low level catalysis in the heater, presumably by pipeline scale carried there.

The following year there was a major decomposition incident in this system and the heater was an initial suspect in the investigation. This is discussed in Case I.

DISCUSSION OF INCIDENTS (3): PURIFIER VESSELS

The purifier vessels discussed here comprise molecular sieves and catalytic beds for removal of trace impurities (excluding water, which is covered above under "Driers"). Usually these purifiers involve ethylene at lower pressures (250–750 psi) than the drier vessel associated with cavern storage described above (typically 1100–1500 psi). An important point about ethylene at the lower pressures (less than 750–900 psi) is that it will not propagate a decomposition flame at ambient temperature. For a decomposition to be supported, the gas must be hot. Thus, in a flowing system involving runaway in a purifier, a flame can only exit the vessel in the direction of gas flow, following the hot gas. More usually, the flame will be confined to the heated vessel where the runaway takes place. Often, incidents in purifiers do not involve a decomposition. Instead, catalysis by the bed packing results in formation of polymer which can bind the bed together into one or more resilient chunks.

Work conducted by Union Carbide in 1986 (unpublished) showed that 13X molecular sieve is an ethylene polymerization catalyst with an ARC adiabatic threshold temperature of 190°C, indicating a maximum acceptable bed temperature of about 140°C (allowing for temperature monitoring difficulties and possible variability of catalytic activity, a figure of 100°C might be used in practice). This finding explains many of the following cases. Other studies conducted at about the same time identified many commercial bed materials as ethylene hydrogenation catalysts, including 13X molecular sieve. This finding explained incidents involving hydrogen ingress at either end of purification trains producing high purity ethylene for low pressure polymerization.

Case H: 1967 Purifier Vessel Rupture

System

Ethylene was purified in a bed containing 700 lb of 13X molecular sieve. The bed was regenerated using hydrogen-methane gas at 260°C, then flow purged with nitrogen. The temperature was allowed to drop to 170°C then the bed was pressurized to 200 psig with nitrogen. 3–5 SCF/min of ethylene was then introduced to the top of the bed and pressure built up to 280 psig.

Failure

At this point in the preloading sequence the temperature recorded 20 inches above the bed rose to 180°C. No temperatures in the bed were being measured. The pressure was then increased to 300 psig ethylene, blown to 250 psig and repressurized (these steps being to displace nitrogen). Following 7 hours of loading with the bed open to a line pressure of 280–295 psig the above bed temperature had dropped to 130°C. A small flow of 2 SCF/min was then started off the top with ethylene going in at the bottom. The above bed temperature rose to 180°C in 3½ hours and over the next 4 hours the flow was adjusted to maintain this temperature. Shortly afterwards the shell ruptured creating a longitudinal ⅜ inch by 32 inch hole. The gas caught fire immediately and burned for 25–30 minutes. The fire was not controlled since the heat prevented the inlet valves from being closed; all the gas up to the closed feed valve at the gas plant was burned. Total loss to the purifier and areas of flame impingement was limited to $6,000.

Causes

The principal cause of this incident was the failure to measure temperatures in the bed during regeneration and preloading

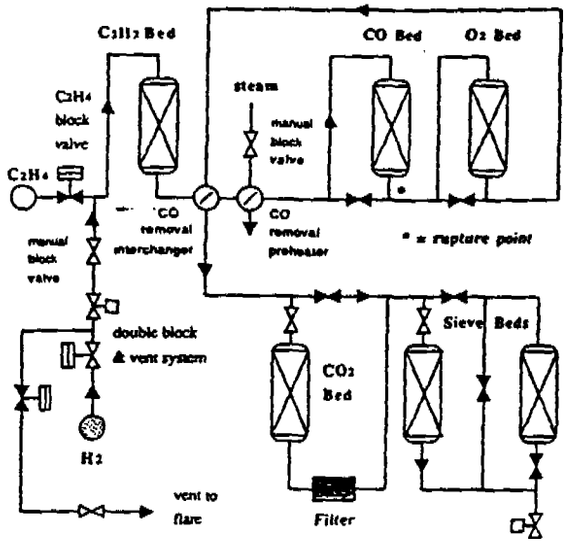

FIGURE 3. Purification system basic schematic.

with ethylene, since 13X sieve is a polymerization catalyst. Owing to its large pore size, 13X also adsorbs ethylene and releases heat. The temperature measured above the bed gave no measure of the temperature anywhere within the bed where these exothermic processes would occur. Even though the pressure of ethylene involved in this incident was unusually low (280 psig), there was evidently enough potential (via adsorption and polymerization) to generate the temperature required to cause thermal failure of the vessel. Had the bed temperature been comprehensively measured, any shortcomings in the purging and preloading procedures should have become apparent in time to take action. Such temperature measurement should be via fast acting thermocouples distributed throughout the bed and not via thermocouples mounted in heavy thermowells located near the walls, since the sieves are effective thermal insulators.

Changes

Recommended changes and actions were:

(1) Heat sensing devices to be relocated to inside the bed and additional sensors installed.
(2) Shut off valve to be installed in the ethylene feed line at the inlet to the area.
(3) Regenerating and preloading procedures to be reviewed.
(4) Inspect second sieve bed for flaws before restarting.
(5) Obtain further information on 13X sieves before reusing them in this service.
(6) Metallurgist to examine damaged bed for flaws.

Case I: 1985 Purification Train Decomposition [*1*]

System

Ethylene was let down to 400 psig via a preheater. Normally it was then mixed with a small flow of hydrogen and passed to a palladium catalyst bed to remove acetylene, and then to other impurity removal beds downstream. The system schematic is shown in Figure 3. Owing to contaminants in the stream, the palladium bed had earlier become inactive. Normally, the hydrogen flow was shut off automatically if the ethylene flow fell below a predetermined level of 8000 lb/hr. The unit was shut down on January 26.

Failure

The ethylene flow meter was improperly calibrated (indicated 12000 lb/hr at actual flow rate of zero) and so during a system outage the hydrogen valve did not receive a signal to fully close. Thus, hydrogen flowed into the acetylene removal vessel at a low rate during the system outage. Because the bed was inactive, no temperature rise due to ethylene hydrogenation occurred and the interlock which would normally have closed the hydrogen feed valve was not tripped. At this time the acetylene removal bed contained ethylene plus hydrogen in perhaps a 80:20 mole ratio, at about 400 psig and a temperature of 30–40°C.

On startup (January 29) the flow pushed this mixture through the CO removal preheater into the CO removal bed. This heater was at about 150°C, and owing to the initially low flow rate the initial gas temperature may have been about 120°C or more instead of the nominal 50°C. The CO removal bed contained a catalyst comprising copper plus copper oxides ($Cu + CuO + Cu_2O$) supported on zinc oxide. A runaway reaction occurred in the CO removal bed and a decomposition flame emerged and stabilized in the 8 inch outlet pipe, causing high temperature failure. The CO removal bed was melted down and the subsequent O_2 removal bed was overheated (both vessels were replaced). The escaping gas ignited and deflagrated. Copper was found plated onto piping downstream of the CO removal bed. Analysis of products collected downstream showed that reactions included hydration and aromatization.

Causes

The cause of the runaway was initially demonstrated using a small reactor. It was shown that an 80:20 ethylene:hydrogen mixture at 180 psig would undergo runaway reaction over the CO removal bed catalyst at about 100°C. Later calorimetric studies showed that under adiabatic conditions the starting temperature for runaway was roughly ambient. The mechanism of the runaway has been given [*1*] in terms of a series of reactions beginning either with reduction of copper oxides or ethylene hydrogenation over zinc oxide catalyst. In any case, the following series of reactions is inferred from both the chemistry of the process and an analysis of products collected downstream in the system:

$$2CuO + H_2 \xrightarrow{(<100^\circ C)} Cu_2O + H_2O \quad [-34\ kcal] \quad \text{reduction} \qquad [1]$$

$$Cu_2O + H_2 \xrightarrow{(<100^\circ C)} 2Cu + H_2O \quad [-25\ kcal] \quad \text{reduction} \qquad [2]$$

$$C_2H_4 + H_2 \xrightarrow{(<100^\circ C)} C_2H_6 \quad [-33\ kcal] \quad \text{hydrogenation} \qquad [3]$$

$$C_2H_4 + H_2O \xrightarrow{(>250^\circ C)} C_2H_5OH \quad [-10.6\ kcal] \quad \text{hydration} \qquad [4]$$

$$nC_2H_4 \xrightarrow{(>350^\circ C)} \text{oils, etc} \quad [-25.5\ kcal] \quad \text{oligomerization} \qquad [5]$$

$$nC_2H_4 \xrightarrow{(>350^\circ C)} \text{aromatics} \quad \text{aromatization} \qquad [6]$$

$$C_2H_4 \xrightarrow{(>1000^\circ C)} C + CH_4 + H_2 \quad \text{decomposition} \qquad [7]$$

The final reaction (flame reaction) has a heat of about 25 kcal/mol ethylene as discussed in [1]. The copper deposited in the piping downstream of the CO removal bed was probably formed via the "copper mirror" reaction, where copper hydride is formed then sublimes and decomposes.

Case J: 1985 Reactor Gas Backflow into Molecular Sieve Bed

Failure

The ethylene supplier went down and the 1 mile long pipeline header pressure fell below the reactor pressure. The reactor gas containing ethylene and hydrogen at about 85°C flowed past a check valve into the last bed in the purification train, which was a 13X molecular sieve bed. Some time later an operator noticed paint that was blistering and changing color upstream of the 13X bed. The burned pipe was about 10 meters long. Not much soot was subsequently found and no rupture occurred.

Causes

Backflow of the hot reactor gas caused rapid hydrogenation over 13X catalyst raising the temperature to above 300°C, the estimated temperature attained by the pipe wall. The pipe wall was heated either by hot gas leaving the back-flowing 13X bed or by a hydrogenation-decomposition flame of ethylene. No data are available on the existence of such a "hybrid" flame. As hypothesized by the author, the presence of hydrogen would slightly increase the theoretical flame temperature but might greatly increase the reaction rate. Subsequent tests using an adiabatic calorimeter revealed that ethylene with hydrogen levels similar to those involved would undergo exothermic reaction over 13X sieve with an adiabatic reaction threshold of only 90°C. Since other reactant ratios were not tested and because a safety factor of at least 50°C is desirable this result adequately explains the observed event. It can be assumed that with a greater system pressure, pipe rupture and a major fire would have been possible.

Changes

Possible changes suggested at the time included the use of safety systems to complement the use of check valves, such as an automatic double valve and vent. As in the other 13X bed incidents more comprehensive bed temperature monitoring should be used, since in this incident the bed high temperature alarm (100°C) did not sound until after the blistering paint had already been observed and the event was already underway. The reason for backflow was a check valve which was stuck in the open position, possibly with resin.

Case K: Hydrogenation Incident [8]

A report of this incident [8] identified iron rust as a hydrogenation catalyst responsible for a decomposition. This occurred in a small shell-and-tube heat exchanger upstream of a CO methanator reactor in an ethane cracking plant.

System

Cracked gas from ethane pyrolysis contains mainly hydrogen, ethylene, unreacted ethane plus methane, acetylene, carbon oxides and other minor components. The ethylene product is purified by cryogenic fractionation in a demethanizer with "back-end" acetylene hydrogenation on the feed to the ethylene splitter. Hydrogen is separated from the cracked gas in the demethanizer feed chilling train. A small hydrogen slip stream is further purified to 98% for use in the acetylene hydrogenation step; this slipstream is further purified by chilling and addition of ethylene as a methane absorber. This step is followed by methanation of the small amount of CO present in the hydrogen. To assure that no acetylene can accumulate in the cold spots ethylene is also used to absorb acetylene from the purified hydrogen separator drum. The system design anticipated that were ethylene carried over in the hydrogen from the separator drum, the CO methanator catalyst would catalyze the exothermic hydrogenation of ethylene. Thus the separator (containing over 70 mol% ethylene in the liquid) contained numerous safeguards. Methanator reactor feed was heated in a small shell-and-tube type heat exchanger followed by a double pipe 600 psig steam heater. The unexpected runaway occurred in the reactor feed-effluent exchanger on the shell side handling reactor feed. The incident occurred shortly after initial plant start-up while the system was still being debugged. The plant had been in production about one week.

Failure

Without warning the heat exchanger shell ruptured releasing gas at about 450 psig. The gas ignited in the air. Flames were initially about 30 feet high but died down to 3 feet within 5 minutes of the rupture, which was caused by excessive temperatures. Subsequent examination showed that 35 minutes before the incident the temperature downstream of the feed/effluent exchanger began to climb and pegged out (400°C) 15–20 minutes before the rupture, at which point it was rising at roughly 15°C/minute. This was not a normally monitored temperature (provided only for exchanger performance evaluation) and was not the bed inlet temperature. It was also found that the ethylene concentration going to the CO methanator rose from less than 0.1% to at least 6% shortly before the event. There was no observed temperature rise in the methanator, although inlet temperature rose from 250 to 290°C during the event, suggesting that the hydrogen and ethylene had reacted upstream.

Causes

The rupture was caused by excessive temperatures due to uncontrolled hydrogenation of ethylene. However, the noncatalyzed reaction does not proceed below about 300°C. The exchanger had been heating feed from 5°C using hot fluid at a tube side temperature of about 260°C, and failed about one-third the way from the inlet end. Although no rust was found in the exchanger, it was concluded that this was the catalyst responsible. It was hypothesized that the high pressure venting following rupture effectively cleaned the exchanger of deposits. A test program using DSC showed that Fe_3O_4 is a hydrogenation catalyst with activity beginning in the range 100–150°C and strong activity above 200°C. The temperature in the exchanger was in the lower range identified with catalytic activity. It was hypothesized that operation of the methanator under 32 bar pressure of hydrogen caused the production of the reduced iron oxide catalyst. Note: iron oxide catalysts are extremely variable with respect to structure and surface area, hence their catalytic activity.

Postscripts

It was noted [8] that 3A driers had given unexpected exotherms during regeneration whenever the hydrogen-rich regeneration gas contained above normal concentrations of ethylene. This suggests that either the sieve structure was accessible to ethylene (or the reaction is sufficiently fast to occur

on the geometrical surface), or the sieve had become contaminated with a catalyst. 3A sieve should have a pore structure which is inaccessible to ethylene, although ion exchange and other processes can open the pores. The driers operated at about 50 psig and normal inlet temperatures of 210–230°C. The reaction was confirmed by the appearance of effluent ethane at the expense of ethylene and hydrogen. The problem was avoided by limiting drier inlet temperature to 190°C and taking additional measures such as further temperature lowering upon detection of any exotherm in the bed. The phenomenon was not observed after the first desiccant change, and it was concluded that rust had accumulated in the drier bed. Laboratory tests showed no activity of new 3A sieve up to 350°C.

Case L: 1984 Molecular Sieve Bed Chunking

System

The North Molecular Sieve Bed in a purification train was regenerated, preloaded and pressured up after changing the 13X sieves. It was placed on standby under about 420 psig ethylene pressure for 15 days before returning to service.

Failure

A 50–60 psi pressure drop instead of the normal 5 psi was observed across the bed. Three days later the North vessel outlet was opened. The vessel contained a 5000–6000 lb chunk of 13X sieve bound together with polyethylene, surrounded with free-flowing 13X. The material could not be jack-hammered out and high pressure water jets had to be used to free it. The only damage to the vessel was a bent support beam and screen, plus broken welds in the beam support clips. The maximum recorded temperature was 100°C at thermocouples about 8 inches from the vessel wall. No decomposition occurred although an odor of pyrolyzed ethylene was noted on samples from the bottom of the bed.

Causes

The presumed cause of the incident was inadequate preloading owing to an undersized restrictive orifice in the preload station. Contributing factors were the placement of bed thermocouples which were close to the wall and insulated by the sieves, the new 13X load which might be more active than conditioned sieves, and a long period of stagnation following loading.

Test work has demonstrated that 13X sieve is a polymerization catalyst. The pore system is large enough to allow access to ethylene and also to other molecules such as hydrogen with which ethylene can react. In this incident, the bed was evidently hot enough at some stage to allow polymerization to proceed, but there was either insufficient temperature, pressure or ethylene to cause a runaway to decomposition. The thermocouples were entirely inadequate to monitor the bed temperature and it is probable that farther into the bed the temperatures were well above 100°C. Wall mounted thermocouples in thermowells are slow acting and will not give an indication of axial temperature in the bed. This may allow high temperatures to persist after regeneration or after preloading, and may fail to give warning of a runaway event during pressurization.

Case M: 1982 Sieve Bed Decomposition

System

The South olecular Sieve Bed was being placed in service after 1 week of shutdown. At this time the bed pressure was being raised from 270 to 460 psig.

Failure

During pressurization the bed outlet was seen to be red hot. Blow down was however completed without equipment rupture.

Causes

It was thought that faulty heat tracing caused the incident, which seemed possible because several defects were subsequently found in the control systems. Transition to runaway was presumably caused by increased reaction rate when the pressure was increased to 460 psig. After a week of standby at 270 psig, heat generated by adsorption alone was calculated to have the potential only for a 20°C exotherm on pressuring to 460 psig. Approximate calculations suggested that at least 500°C could have been attained by the effects of two heaters over one week. At the higher pressure, models [1] have indicated a runaway temperature of 350–400°C in a stagnant system of this size in the absence of catalysis. However, as discussed above, 13X sieve is a polymerization catalyst and runaway can develop at significantly lower temperatures.

DISCUSSION OF INCIDENTS (4): HIGH PRESSURE POLYETHYLENE

These incidents occurred during or shortly after an extended period of stagnation in high pressure polyethylene (HPPE) product receivers, caused by pump or other failures. These product receivers are heated, high pressure vessels collecting molten polyethylene from the HPPE reactor. Their vapor spaces and associated lines contain heated ethylene at high pressure.

Cases N–P: Miscellaneous Product Receiver Decompositions

Two of the available HPPE system decomposition case histories (N, O) considered the possibility of catalyst carry-over from the reactor. In a third (P) the decomposition occurred three and one-half hours after a pumping shutdown with a receiver heating medium temperature of about 285°C and system pressure of about 3000 psig. In this case the cause of the decomposition could be confidently attributed to thermal runaway. A computer model based on the type of thermokinetic equation given in [1] predicted that at temperatures above 276°C the runaway reaction would attain maximum rate in the given timeframe.

Case Q: 1989 Product Receiver Decomposition: External Fire Impingement

Failure

A product receiver top flange leak was ignited externally, presumably by a static discharge, and the flame impinged on instrument lines 2–3 feet away, comprising plastic tubing inside aluminum conduit. This caused the reactor reject valve to open, releasing high pressure gas which immediately ignited. The subsequent large flame impinged on 2–3 feet of uninsulated pipe going to the safety valve atop the receiver, which was operating at 900 psi and 285°C. The pipe wall was raised above the autodecomposition temperature of ethylene and this caused a decomposition flame to propagate into the receiver some five minutes after the reject valve opened. The instrument line damage disabled the dump valve and this led to rupture disc operation. The safety valve operated correctly.

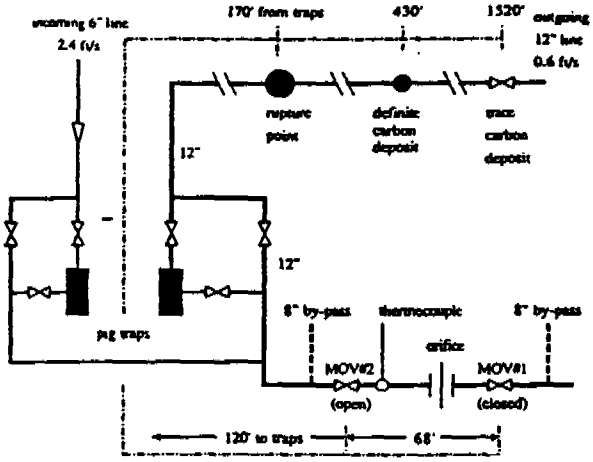

FIGURE 4. Piping system.

Causes

It was hypothesized that the initial flange leak was caused by bolt loosening following a number of process interruptions prior to the event, which would have caused hot-cold temperature "cycling" at the flange. The ignition source might have been static electricity accumulation on an ungrounded aluminum weather barrier caused by impingement of debris from the high pressure gas stream. Causal factors include the aluminum conduit and plastic lines, which had almost no fire resistance (the plastic lines were subsequently replaced with copper), and the uninsulated pipe going to the safety valve. The weather barriers should ideally have been grounded stainless steel both to add fire endurance and prevent static sparks.

DISCUSSION OF INCIDENTS (5): SUDDEN COMPRESSION

These incidents involve compressors or sudden compression in pipelines. All the incidents involve the presence of a diatomic gas (nitrogen or more likely air). Two cases involved compressors used in HPPE systems.

In the first (R), a double-valve-and-vent that had been used to isolate the compressor during maintenance was purged in preparation for start-up and then the pressure was raised to 3000 psi. A decomposition occurred which was confined to the double-valve-and-vent piping. It was suspected that purging had been incomplete and residual air was present. For adiabatic compression:

$$T_2/T_1 = R^{[(\gamma-1)/\gamma]}$$

where

T_2 = final temperature (K)
T_1 = initial temperature (K)
R = ratio of final-to-initial absolute pressures
γ = ratio of specific heats of gas

Whereas γ for ethylene is about 1.2, that for oxygen or nitrogens is about 1.4. This elevates the final temperature by hundreds of degrees. An additional effect of oxygen is to lower the ignition temperature of ethylene, so some residual air was likely to have been present. However, as shown in [*1*], mild decompositions can occur in the absence of air even for greatly diluted ethylene. Given the very large compression ratio available here, it is not possible to discount the event in the absence of residual air. In the second compressor incident (S), a full isolating blank had been left in place in the discharge line, and a decomposition occurred upon start-up. Residual air was considered a contributing factor.

Case T: Meter Run Decomposition [*4, 5, 6*]

System

The piping system is shown in Figure 4. The orifice box was removed from a 12 inch diameter, 68 foot long meter run for maintenance, leaving a two foot gap in the line which was open to the air for 45 ± 15 minutes. After reinstallation of the box, the power was returned to the motor operated valves. In order to check the MOV limit switches, one valve (#2) was opened completely. This caused sudden compression of an ethylene-air mixture from zero to 1320 psig. The valve took 20 seconds to open completely, although later calculations indicated that the 91:1 pressurization only took about 3–4 seconds, occurring when the valve was about 15% open.

Failure

A decomposition was initiated in the stagnant 12" line due to sudden compression of the original gas in the pipe by high pressure ethylene acting as a piston. There was sufficient air present both to greatly raise the temperature (adiabatic compression) and lower the ignition temperature of back-mixed ethylene at the interface with the gas entering the meter run. A decomposition flame propagated out of the meter run through MOV #2 and traveled several hundred feet before stabilizing against the gas flow. At the point of stabilization, the pipe wall was softened by the flame temperature and ruptured under pressure.

After flame initiation at MOV #1, it traveled into the outgoing 12" line. It did not propagate into the 8" by-pass connection, which went vertically down into the ground, showing that ethylene decomposition flames tend to burn at the pipe roof and will not usually burn into down-going pipe unless carried by gas flow. This is also supported by the fact that paint only peeled from the top third of the meter run piping and pig trap lines. At the rupture point, metal thinning and a longitudinal split were observed, typical for decomposition failures. The estimated failure temperature was 620 ± 30°C at 1320 psig. Carbon was found in the 6" incoming line and at least 260 feet beyond the rupture point in the 12" line.

This incident gave rise to the concept of "leading" and "trailing" decomposition flame fronts. The former leads the decomposition zone and travels with its velocity superimposed on the gas flow velocity. The latter burns against the flow and may become stationary under the correct conditions. From an analysis of carbon deposits it was estimated that the leading flame front traveled 430–1520 feet into the outgoing line in 7–10 minutes, giving an estimated flame speed of 0.7–3.6 feet per second. Relative to the 0.6 ft/s gas flow, the flame speed was thus 0.1–3 ft/s. The number 3 ft/s (often used to estimate ethylene flame speeds) derives from this analysis. The trailing flame front reached the point of stabilization (170 feet) after 7–10 minutes, giving an apparent flame speed of 0.3–0.4 ft/s. Allowing for gas flow, the relative flame velocity was thus 0.2–0.3 ft/s. The trailing flame either stabilized completely against the flow or the flame zone was long and slow moving enough to heat the wall to thermal failure. Had the flow velocity been greater the flame system might have traveled indefinitely into the line, perhaps all the way to a storage cavern.

Causes

The event was evidently caused by too-rapid compression of diatomic gas in a line closed at one end. Later modeling of

the incident [1] estimated a pressurization time of 4.2 seconds and a maximum temperature of 740±5°C in the end-gas with a temperature of 560±5°C at the interface with the ethylene. A temperature of 450–560°C would have been sustained for about 3 seconds. To correctly pressurize a line, nitrogen purging should have been carried out and the line then pressurized slowly. Ideally, flow purging with ethylene using a bypass should be used to sweep out the diatomic gas. Normally, slow pressurization of long lines is done by "cracking" the valve and keeping the flow rate slow enough to prevent icing and possible embrittlement. This is not practical for short lines and a restrictive by-pass is preferred. So long as all air or nitrogen is removed, there is little practical risk of ethylene decomposition at compression ratios of up to 100:1.

CASE U: VALVE STATION DECOMPOSITION

In Brief

A by-pass line at a valve station in a cross-country pipeline was pressurized and a decomposition was valved in manually by the operator after observing blistering paint on the line. Residual air at above 4–6% oxygen caused the decomposition, as demonstrated by a full-scale simulation [1]. Correct purging had not been carried out. This event could have been far more serious had the decomposition propagated into the major cross-country line. Another sudden compression incident was said to have occurred some years ago at another company location involving several hundred feet of pipe.

Other accounts of decompositions during pipeline pressurization are incomplete. In one case the decomposition was reported to have been arrested at a valve which was only partially opened (this is consistent with the observed tendency of ethylene decomposition flames to travel close to a pipe roof). The decomposition flame stabilized at the valve and overheated the wall causing an explosion but no injuries.

DISCUSSION OF INCIDENTS (6): EXTERNAL FIRE EXPOSURE

One incident in a return gas system was covered above (Case Q). Only one additional case history is available, but in view of the miles of intermediate pressure ethylene piping susceptible to third party fire damage, ignited leaks etc., the hazard is ever-present.

Case V: Pipe Impingement Fire

In Brief

A pipeline carrying ethylene at 2200 psig pressure and a nominal temperature of 246°C received an impingement fire from a leaking hot oil line. The line was valved in but underwent an internal decomposition and ruptured. After the event the line was filled with carbon [10]. The rupture might in part have been due to heat from the external fire, since the pipe was seen to be red hot prior to the explosion.

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CAUTION

This database is intended only for use within Dow by Dow employees for educational purposes and to increase safety awareness. The information reported is the best currently available to Dow regarding the incident, however, some facts may be speculative and some descriptions incomplete. Laboratory results reported may not present what would occur in actual field applications. A thorough review of all other available data and a thoughtful review of your applications should be made before using or relying upon this information.

Incident No. 81-0028 Date 05/81

Title

Glowing Embers Fire in Vacuum Truck Hopper

Summary

While dry vacuuming solids that were plugging a cracked gas quench column, a glowing embers type fire was discovered in the vacuum truck hopper. Analysis of the solid prior to this operation had shown it to be a hydrocarbon polymer with a flash point in excess of 500 deg.C. Explosimeter readings taken after the incident, performed on sealed fiberpaks of the material that had been removed manually, showed it to be hot. Apparently the sample brought to the lab had devolatilized, giving an erroneous high flash point. No one was hurt and the only damage was a burned filter bag. If it is necessary to remove this material in the future, it will be degassed and vacuumed wet.

Chemical Indexing Terms

HYDROCARBONS
POLYMERS
HYDROCARBON POLYMER

Incident No. 81-0084 Date 11/81

Title

Autoignition of Polybutadiene In Insulation

Summary

While cleaning a reboiler in the Butadiene Plant, some material got into the insulation. Later, a small fire started due to autoignition of the polymer in the insulation. It was extinguished by a hand extinguisher.

Chemical Indexing Terms

POLYBUTADIENE
BUTADIENE
INSULATION

REACTIVE CHEMICALS INCIDENTS
Heading, Summary, and Indexing Terms

Hydrocarbons Technology Center

Incident No. 82-0046 Date 05/82

Title

Benzene Plant Temperature Excursion

Summary

A temperature excursion occurred in the Benzene Plant when an upset caused the ethylene concentration in the hydrogen feed to the methanator, used to catalytically remove CO from the stream, to rise from 1% to near 25%. The trip on the methanator is normally set at 400 deg.C. However, the trip had been manually bypassed and the temperature climbed to over 700 deg.C before being brought under control.

Chemical Indexing Terms

BENZENE
HYDROGEN
ETHYLENE
CARBON MONOXIDE

REACTIVE CHEMICALS INCIDENTS
Heading, Summary, and Indexing Terms

Hydrocarbons Technology Center

Incident No. 82-0075 Date 10/82

Title

Plugging and Pressure Rise of Feed Chiller to Methane Stripper

Summary

The feed chiller to the methane stripper in the light hydrocarbons plant was plugging due to ice formation. To dissolve the ice, 1.5 drums of propanol were added. However, this resulted in complete plugging and a pressure rise which was released by the safety. Deplugging was th n accomplished by adding methanol. Analysis of the propanol drums showed that one contained 60 wt. percent water. In the future, all propanol will be checked for water content and only new full drums used for deplugging.

Chemical Indexing Terms

METHANOL
WATER
METHANE
PROPANOL
HYDROCARBONS
PROPYL ALCOHOL
N-PROPNOL

REACTIVE CHEMICALS INCIDENTS
Heading, Summary, and Indexing Terms

Hydrocarbons Technology Center

Incident No. 82-0083 Date 11/82

Title

Back Pressure of Fuel Gas at Acetylene Plant

Summary

Fuel gas (methane) back pressured from the off gas system in the flare line at the Acetylene Plant through a check valve into the carbon monoxide product line going to the TDI Plant. Two rupture discs blew in the phosgene reactor and shut the plant down without further consequences. The complex series of events started when Acetylene asked for clearance from Utilities Distribution to start adding fuel gas to enrich their off gas so that it could be burned at Power II instead of flared. Utilities Distribution gave clearance without realizing LHC #6 had closed a valve where this line passes through their plant. The back pressure caused the overpressure of the CO line for a short time. After the event the check valve worked perfectly.

Chemical Indexing Terms

FUEL GAS
ACETYLENE
METHANE
PHOSGENE
CARBON MONOXIDE

Incident No. 82-0097 Date 07/82

Title

Altered Piping Traps 1,3-Butadiene

Summary

A several hundred foot section of piping had been altered during the recent Plant I modernization so as to trap the contents of the line, 1,3-butadiene, between block valves with no means of relieving the line for liquid expansion. The situation was discovered prior to any significant release of the material when a small leak at a flanged connection was discovered. The line was manually relieved to the plant "day tanks."

Chemical Indexing Terms

1,3-BUTADIENE

Incident No. 83-0035 Date 07/83

Title

Light Hydrocarbons Filter Pot Fire

Summary

The instrument air cleanup system at the Light Hydrocarbons II Plant consists of dual alumina beds for drying plus a final filter pot made of multiple elements in a manifold. During regeneration of one of the alumina beds, hot air at 90 psiq and up to 600 deg.F was mistakenly switched through the filter system, which apparently ignited and scorched paint on the pot and the outlet line 15 feet downstream. It was found that cotton filter elements had been substituted for the fiberglass elements used in the past.

Chemical Indexing Terms

AIR
COTTON
ALUMINA
FIBERGLASS

REACTIVE CHEMICALS INCIDENTS
Heading, Summary, and Indexing Terms

Hydrocarbons Technology Center

Incident No. 84-0009 Date 02/84

Title

Exotherm in Ethylene Reactor

Summary

AFTER THE REACTOR WAS COOLED TO AMBIENT TEMPERATURE AND PADDED WITH NITROGEN, LIQUID CRUDE C4 WAS INTRODUCED. WITHIN ONE MINUTE AN EXOTHERM OCCURED AND THE TEMPERATURE WENT TO 650 DEG C. THE FEED WAS STOPPED AND THE REACTOR WAS DRAINED INTO THE SURGE TANK. IT IS THOUGHT THAT AFTER HYDROSTATIC TESTING AND PURGING SOME RESIDUAL WATER MAY HAVE REMAINED IN THE FEEDLINE AND WAS PUSHED IN FRONT OF THE C4 CRUDE INTO THE REACTOR. THE WATER AND CRUDE C4 ABSORBED ON THE HIGH SURFACE AREA DRY ALUMINA CATALYST AND GENERATED HEAT WHICH CAUSED THE C4 VAPOR TO AUTOPOLYMERIZE OR REACT WITH THE RESIDUAL HYDROGEN ON THE SURFACE OF THE CATALYST. THIS LIBERATED MORE HEAT WHICH PROPAGATED THE EXOTHERM.

Chemical Indexing Terms

NITROGEN
HYDROGEN
WATER
ALUMINA
HYDROCARBONS

Incident No. 85-0036 Date 08/85

Title

Fire in Butadiene Plant Alumina Bed

Summary

A liquid C2 hydrogenation reactor at the butadiene plant was shut down for removal of catalyst on alumina. After purging with steam a forced air flow was used for cooling the reactor. When the airflow was started, a barbeque type fire was observed. The fire was probably cause by finely divided carbon particles on alumina and some hot spots in the alumina.

Chemical Indexing Terms

BUTADIENE
CARBON
ETHYLENE
ALUMINA

Incident No. 85-0037 Date 08/85

Title

Exotherm in Hydrocarbon Hydrogenation Reactor

Summary

Just after start-up of a liquid crude C4 hydrogenation reactor at the butadiene plant, an exotherm occurred which caused a large temperature increase. It is thought that a small amount of free water in the crude C4 feed led to the incident.

Chemical Indexing Terms

WATER
HYDROCARBONS
BUTADIENE

REACTIVE CHEMICALS INCIDENTS
Heading, Summary, and Indexing Terms

Hydrocarbons Technology Center

Incident No. 85-0039 Date 08/85

Title

Pyrophoric Polymer Fire

Summary

While cleaning a condensate stripper at the ethylene plant, a fragment of pyrophoric polymer was removed and not properly stored under water. After lying in the sun for a day, the material caught fire.

Chemical Indexing Terms

ETHYLENE
POLYMERS

Incident No. 87-0013 Date 02/87

Title

Explosion and Flame While Loading Tank With Caustic

Summary

An operator opened a valve on a two inch 50% caustic line to fill a day tank at the LHC II Plant. After a flow was started, the operator turned away and walked a few steps before he heard a moderate explosion. He described a confined yellow flame of a few seconds duration in and above the tank. The hinged lid on the tank blew open and fell back closed. Two investigative meetings have failed to define a resonable explanation. No injuries and no equipment damage resulted. Investigation is continuing and results will be reported at a later date.

Chemical Indexing Terms

CAUSTIC

Hydrocarbons Technology Center

Incident No. 87-0019 Date 03/87

Title

Naphtha Furnace Transfer Line Fire

Summary

A fire was detected inside a transfer line to a naphtha furnace. The line had been left open to the atmosphere while hydrojetting other equipment. This had become a routine operation. Although the possibility of autoignition had never been considered, everything indicates that autoignition of a pyrophoric material took place. In the future, the transfer line will be flooded prior to the hydrojetting operation.

Chemical Indexing Terms

NAPHTHA

Incident No. 87-0096 Date 11/87

Title

Flames Erupt From Reboiler Tubes Following Removal of Exchanger Head In LHC-6 Plant

Summary

A reboiler in the LHC-6 Plant had been taken out of service for cleaning. Following the removal of the exchanger head, flames started coming from the reboiler tubes. No damage resulted.

Chemical Indexing Terms

Incident No. 88-0010 Date 02/88

Title

Exotherm During Regeneration of Acetylene Converter as Result of Incorrect Line Set-up

Summary

During regeneration of the acetylene converter, an exotherm occurred as a result of incorrect line set-up. During the reduction phase with hydrogen, the bottom product in the depropanizer entered the acetylene converter and caused a temperature rise of 600 deg.C. The hydrogen flow was stopped immediately and methane was used to wash the converter.

Chemical Indexing Terms

HYDROGEN
METHANE
ACETYLENE

Incident No. 88-0018 Date 03/88

Title

Ignition of Air / Vaporized Hydrocarbon Mixture While Decoking Naphtha Furnace

Summary

While decoking a naphtha furnace, hydrocarbons that were blocked in a line by a valve and a leaking check valve were vaporized by the 200-300 deg.C hot air. The air/vaporized hydrocarbon mixture ignited and the increased temperature and subsequent 4 bar pressure rise was sufficient to rupture the line.

Chemical Indexing Terms

HYDROCARBONS
NAPHTHA

REACTIVE CHEMICALS INCIDENTS
Heading, Summary, and Indexing Terms

Hydrocarbons Technology Center

Incident No. 88-0050 Date 08/88

Title

LHC II Plant Molecular Sieve Column Fire

Summary

A fire occurred in a molecular sieve column at the LHC II Plant. While unloading spent molecular sieve from one of the dehydrators, smoke and fire were noticed coming from the manway. Nitrogen purge, followed by the introduction of water, quenched the fire. An investigation showed the cause to be air oxidation of unsuspected trapped organics in the sieve, initiated by the heat of adsorption of moist air being purged through the bed during dumping. The bed had previously been purged, but channeling had allowed significant quantities of organics to remain in the bed.

Chemical Indexing Terms

NITROGEN
AIR
WATER
MOLECULAR SIEVE

Incident No. 90-0069 Date 09/90

Title

Sulfur / Iron Fire in Reboiler

Summary

A sulfur iron fire occurred when a side stream reboiler of the extraction tower from the aromatics plants was opened.

Chemical Indexing Terms

SULFUR
IRON

REACTIVE CHEMICALS INCIDENTS
Heading, Summary, and Indexing Terms

Hydrocarbons Technology Center

Incident No. 90-0076 Date 10/90

Title

Acetylene Hydrogenation Reactor Exotherm

Summary

During start-up, feed to the acetylene hydrogenation reactor was started before the proper composition from the preceding tower had been achieved. The reactor exothermed, the high temperature alarm engaged, and the reactor was vented to the flare.

Chemical Indexing Terms

ACETYLENE

REACTIVE CHEMICALS INCIDENTS
Heading, Summary, and Indexing Terms

Hydrocarbons Technology Center

Incident No. 90-0087 Date 12/90

Title

Hydrodealkylation Reactor System Shutdown Due To Coke Fouling of Cross Exchanger

Summary

The Hydrodealkylation, HDA, reactor system had been operating for approximately two weeks at capacity within established guidelines for parameters to prevent the formation of coke in the system. The Hydrogenation plant whose H2 offgas feeds the HDA plant was then shut down for a catalyst changeout. After approximately six days of operation the HDA plant had to be shut down due to coke fouling of the cross exchanger. Upon inspection of the equipment a considerable quantity of coke had been formed in the B reactor and in the cross exchanger. The exchanger also showed signs of under deposit corrosion in high coke areas. The H2 offgas from the Hydrogenation plant normally contains 60 - 100 ppm H2S. Recommended operating guidelines had not included the addition or monitoring of sulfur containing compounds in or around the HDA plant. Preliminary analysis of the coke found in the exchanger and reactor indicates that the coke was formed due to a catalytic effect of iron present in the refractory of the reactor. In previous operation the iron had been passivated by the sulfur, and without the presence of sulfur, the iron acted as a catalyst for the formation of coke.

Chemical Indexing Terms

Hydrocarbons Technology Center

Incident No. 91-0018 Date 03/91

Title

Insulation Fire During Cooling of Hydrogenation Reactor

Summary

Because of polymer formation on the methylacetylene/propadiene hydrogenation reactor, the catalyst is regenerated once a month. The normal temperature at the outlet of the reactor during the regeneration is 120 deg.C; however, on this occasion, temperatures above 200 deg.C were observed. To cool the reactor, the shell was partly filled with propylene. Because of the temperature difference between the pipe and the shell wall, a small crack occurred at a weld of the shell wall. This resulted in a small insulation fire which was under control within five minutes.

Chemical Indexing Terms

METHYLACETYLENE
PROPYLENE
PROPADIENE
INSULATION

Incident No. 91-0040 Date 06/91

Title

Nitrogen Supply Contaminated By Hydrocarbons

Summary

The utility nitrogen supply was contaminated by C3-C5 hydrocarbons. This probably happened due to a hose connection to the column, which runs at 15 bars pressure, from the nitrogen supply, which is under 6 bars. A check valve in the line did not prevent the backflow.

Chemical Indexing Terms

NITROGEN
HYDROCARBONS

REACTIVE CHEMICALS INCIDENTS
Heading, Summary, and Indexing Terms

Hydrocarbons Technology Center

Incident No. 91-0054 Date 08/91

Title

Double Feed Of Toluene and Xylene Causes Reactor Runaway Reaction

Summary

After repairing a trip-throttle valve of a reactor feed pump, the pump was started. Due to misoperation of the valve (the governor was stuck), a double amount of toluene and xylene was fed to the reactor. This caused a runaway reaction. No injuries or property losses resulted.

Chemical Indexing Terms

TOLUENE
XYLENE

Incident No. 91-0089 Date 11/91

Title

Polymer Fire In Depentanizer Column Opened For Maintenance and Cleaning

Summary

During the "turnaround" at the LHC/benzene plant the depentanizer column was opened for maintenance and cleaning. After several days, an accumulation of diene polymer in the bottom of the column ignited. Procedures clearly state that the polymer must be kept wet to avoid this problem. In this case the procedures were not followed; in fact, the column and material had not been wetted for approximately five days prior to the incident.

Chemical Indexing Terms

LHC
LIGHT HYDROCARBONS
BENZENE
BUTADIENE POLYMERS
POLYMERS
DIENE POLYMER

Hydrocarbons Technology Center

Incident No. 92-0007 Date 01/92

Title

Exotherm During Catalyst Regeneration In Hydrogenation Reactor

Summary

In preparation to replace the catalyst in the hydrogenation reactor used to convert methylacetylene and propadiene to propylene and propane, air was introduced to burn off pyrophoric polymers which are known to build up on the catalyst. During this operation the reactor got hot. Nitrogen was introduced and the temperature dropped. Procedures and controls are being installed to better control this regeneration cycle.

Chemical Indexing Terms

METHYLACETYLENE
CATALYST
PROPADIENE
PROPYLENE
PROPANE
AIR
POLYMERS

Incident No. 92-0036 Date 05/92

Title

Autoignition Of Polymer Near A Partial Condenser

Summary

Some butadiene polymer was placed in a small trash bin near a partial condenser. The polymer autoignited and socorched the aluminum insulation cover of the condenser. The fire extinguished itself with no subsequent damage.

Chemical Indexing Terms

BUTADIENE
AUTOIGNITION
ALUMINUM INSULATION
INSULATION

REACTIVE CHEMICALS INCIDENTS
Heading, Summary, and Indexing Terms

Hydrocarbons Technology Center

Incident No. 92-0050 Date 07/92

Title

Polymerized Butadiene Deforms Flanges In Air Cooler

Summary

The flanges of the air cooler in butadiene service were deformed because butadiene polymerized in between. By the force of the butadiene popcorn some bolts broke, but as the popcorn sealed the hole, no major leak occurred.

Chemical Indexing Terms

BUTADIENE

Incident No. 92-0061 Date 08/92

Title

Exotherm In Gasoline Fractionator Column

Summary

During the shut down of the gasoline fractionator column, it was cleared by air purging. Smoke was observed accompanied by a temperature increase in the column. Tests done afterwards with the material from the column revealed an exotherm starting at 150 deg.C.

Chemical Indexing Terms

HYDROCARBONS
GASOLINE

Hydrocarbons Technology Center

Incident No. 92-0067 Date 08/92

Title

Temperature Increase In Ethylene Reactor Following Inadequate Hydrogen Separation

Summary

During start-up, the hydrogen separator did not operate adequately, so the feed to the acetylene converters became too rich in hydrogen. Uncontrolled reactions in the following reactor caused temperature increases to 350 deg.C. No injury or loss.

Chemical Indexing Terms

HYDROGENATION
ACETYLENE
ETHYLENE
HYDROGEN

Incident No. 92-0069 Date 08/92

Title

Unloading of Wrong Catalyst Into Tank

Summary

Two catalyst containers had to be unloaded. Written procedures together with correct certificate of analysis and results of positive identification had been given to the operators. Nevertheless, the unloading of the wrong catalyst into the tank was started. No injury or loss.

Chemical Indexing Terms

CATALYST

REACTIVE CHEMICALS INCIDENTS
Heading, Summary, and Indexing Terms

Hydrocarbons Technology Center

Incident No. 92-0071 Date 08/92

Title

Exotherm In Activated Carbon Bed From Vacuum Cleaning Truck Exhaust Vapors Following Time Interruption

Summary

To avoid exposure to the environment with benzene, the exhaust vapors of a vacuum cleaning truck are directed to an activated carbon bed. The day before, this operation took place for 2 to 5 hours without any problems. The day after, the upper part of the bed got hot when the operation started again. No injury or loss. Comment: The same kind of experience was reported two years ago when a vacuum cleaning truck started operation after a weekend break. The supplier of the active carbon mentioned in the investigation that some incidents have been reported to him where, after an interruption, exotherms have been observed. The only explanation for this phenomenon is that unknown reactions, at ambient temperatures, occur on those tremendous large surfaces which produce products triggering that observed exotherm.

Chemical Indexing Terms

ACTIVATED CARBON
BENZENE