

Liquid Hydrogen Cyanide Polymerisation Hazards

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The HCN Industry Safety Conference was initiated in 1981 to provide a free and open exchange of safety information between companies involved in the production, handling, distribution and use of hydrogen cyanide and related chemicals. The annual conference addresses a broad range of safety issues including prevention of the extremely hazardous HCN polymerisation reaction. HCN polymerises rapidly and exothermically under basic conditions – or via autocatalysis – and the resultant HCN polymer subsequently decomposes violently from around 100 °C. If allowed to continue unchecked, polymerisation can proceed to an explosion.

In 1985, the member companies commissioned a major safety study of the HCN polymerisation reaction. Now referred to as “The Fauske Studies”, the comprehensive experimental programme determined that reactor relief is not a feasible protective basis of safety for the rapid, gaseous polymerisation/decomposition runaway, and quenching (e.g. with SO₂) was recommended as an effective alternative. However, as the experiments utilised contaminants to accelerate the reaction, the study was unable to determine an accurate induction (or incubation) time for pure or acid stabilised HCN.

No further significant study of the HCN polymerisation reaction has been presented to the HCN Safety Conference since the Fauske Studies in 1985.

Syngenta has a large HCN manufacturing facility in Louisiana, USA and have active representatives on the HCN Safety Conference. The manufacturing plant produces several thousand tonnes of HCN per annum and transports a small amount to external end users in mild steel railcars. Stabilised HCN can be held in a railcar (in transit or temporary storage) for several weeks or months.

This paper details a current ongoing study of the induction time for HCN polymerisation, carried out by Syngenta Process Hazards group in Huddersfield. The study utilised small scale thermal methods including DSC and Phi-Tec I to predict the likely induction time of HCN in a 40 te HCN railcar, considering the effects of acid stabiliser and likely contaminants, including water.

Introduction

HCN is a highly valuable precursor to many chemical products and is produced on an industrial scale with over 1 million tons per annum being produced and consumed worldwide. Bulk HCN has been stored as a liquid at ambient conditions for over 80 years. In 1952 when DuPont started up their Memphis plant, storage quantities increased significantly to as much as 100m³ and storage volumes have increased since. Shipping liquid HCN in railcars was also started in 1952. The risk of exothermic runaway polymerisation and the need to stabilise HCN to make it safe for storage and shipment was recognised from the beginning. HCN has been well studied in terms of its hazards, chemical and physical properties, best handling practices, and incidents which are widely shared within the HCN industry, primarily via the HCN Industry Safety Conference.

In 1981 the Safety Conference began and provided the forum for exchange of safety information between those companies and their designated representatives involved in the production, handling, distribution and use of hydrogen cyanide, acetone cyanohydrin, sodium cyanide and related chemicals. Annual meetings are held at various locations throughout North America with attendees from all over the world. The annual meetings are arranged by a Board of Directors (HCN Safety Board) composed of volunteers from the various companies that attend the Conference (Participating Companies).

The annual meetings address a broad range of safety issues including HCN safety incidents, medical protocols, personal protective equipment, HCN detection, polymerisation prevention, equipment selection, design principles and other special topics. The Agenda is determined by the HCN Safety Board. In the mid 1980's a number of companies that comprised the HCN Safety board sponsored a major safety study (Fauske and Associates Inc. 1985-1988)^{1,2,3}, which was the first real study of HCN polymerisation rates, to determine if storage relief systems were adequate.

This paper looks in detail at HCN polymerisation in terms of the mechanism, the hazards and methods of stabilisation and quenching, and a number of industrial incidents, as documented by the HCN Safety Conference, are reviewed. The main findings of the Fauske data are also reviewed and the limitations discussed. The results of a recent safety study of the polymerisation by Syngenta, looking specifically at induction time are detailed.

Hydrogen Cyanide

| | |
|------------------|--------------------------|
| Molecular weight | 27.03 |
| Appearance | Colorless liquid |
| Melting point | -13.4°C |
| Boiling point | 25.7°C |
| Density | 0.6884 g/cm ³ |
| Odour | Bitter almond |
| Taste | Metallic |

Table 1. General Properties of HCN

Hydrogen cyanide, also known as hydrocyanic acid or prussic acid, is a clear liquid, extremely toxic by inhalation, skin absorption, or ingestion, with a weak but identifiable odour. HCN can be ignited by an open flame or spark and will form explosive mixtures in air. It is very volatile and its combustion products are non-toxic: nitrogen, carbon dioxide and water.

HCN manufacture is based primarily by the Andrussov process which involves the oxidation of methane and ammonia at about 1200°C over a platinum catalyst:



Within Syngenta, an average of 110 te of HCN are produced per day, rates fluctuating depending on demand. The primary use is for the onsite production of a triazine herbicide, with approximately 40 te per week sent to an external customer.

HCN Polymerisation

Proposed Mechanism

HCN will polymerise rapidly under basic (pH>7) conditions. At basic pHs, the HCN dissociates to H⁺ and CN⁻. The CN⁻ ion combines with an HCN molecule to form the polymer. The reaction is self-accelerating (autocatalytic), as the polymer and polymer byproducts are also basic:

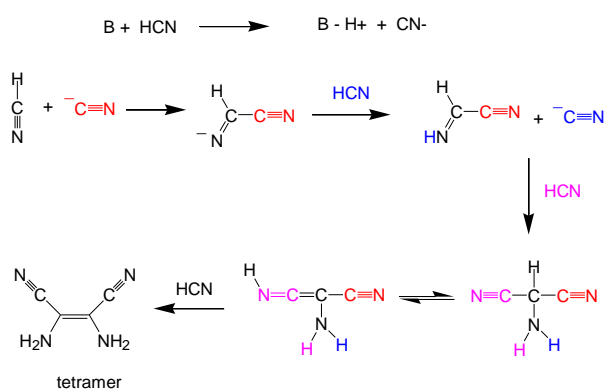


Fig 1. Proposed Initiation Mechanism

A simplistic propagation to polymer can be envisaged from the tetramer formed in this reaction:

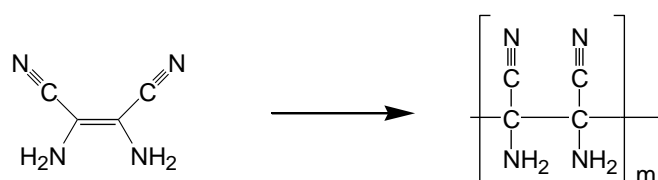


Fig 3. Simplistic Propagation

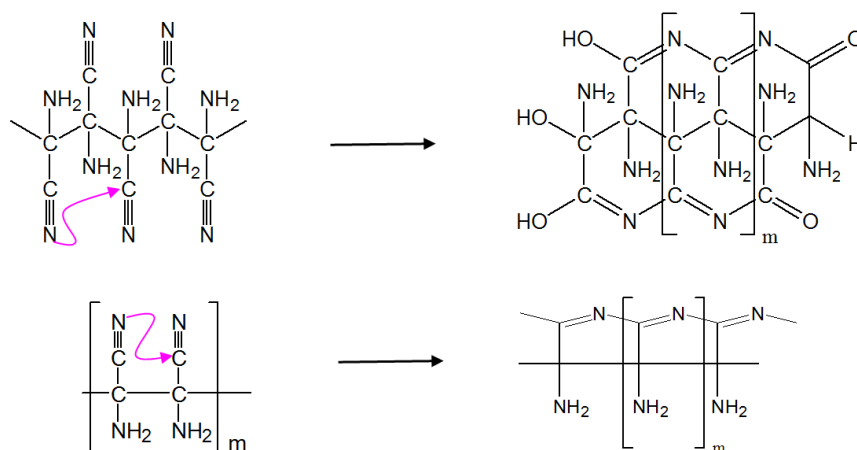


Fig 4. Possible Crosslinking

A host of lower oligomers are present in the polymer, for example the tetramer and pentamer which are always found in the polymer mixture:

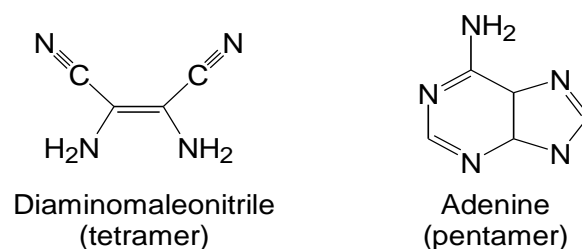


Fig 2. Characterised oligomers found in the polymer

The tetramer is always present and can be polymerised under HCN polymerisation conditions. However, there is no clear evidence that tetramer is a necessary intermediate of the polymer. With intramolecular cross-linking, various polymeric structures can be proposed.

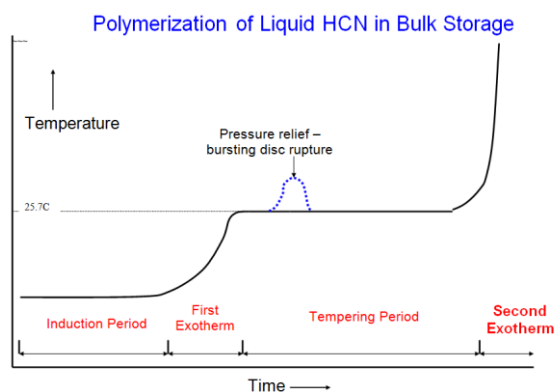
The presence of adenine and other heterocyclic oligomer structures indicates that the polymerisation is actually more complex and many mixed 5, 6, and 7-membered heterocycles, or combinations thereof have also been proposed.

Stabilisation of HCN

Small amounts of acid, e.g. sulphuric acid can be added to HCN as a stabiliser. The acid reacts with any basic materials and keeps the HCN solution acidic. HCN is normally stabilised with 0.06-0.08 wt. % sulphuric acid, keeping the pH of the HCN < 4. However, the use of sulphuric acid needs to be carefully controlled as in excess it can react exothermically and lead to uncontrollable runaway (Banavali, R., 2002)⁴. Most severe reactions are observed at HCN/H₂SO₄ mole ratios of 0.5-1 and at acid concentrations of 99 and 78.4 wt %. If sulphuric acid is the inhibitor of choice, dilute H₂SO₄ (<60%) should be used, and any possible leak of H₂SO₄ into HCN should be prevented.

Hazards of HCN Polymerisation

Polymerisation is an extremely exothermic reaction (-1600 kJ/kg) (Gause & Montgomery 1960)⁵ and self-accelerating (autocatalytic). The HCN polymer decomposes violently from around 100 °C. If allowed to proceed unchecked polymerisation can proceed to an explosion.



Unstable HCN first undergoes an induction period

Very little apparent reaction occurs. In time the liquid turns pale yellow and gradually becomes more brown. Modest heat evolution is masked by installation characteristics (natural heat losses)

Polymerisation rate slowly increases (autocatalytic effect)

Precipitation of finely divided dark polymer occurs and heat evolution rate increases to the point where the temperature starts to increase. This causes further increase in polymerisation rate

Fig 5. Stages of polymerisation

Temperature rises exponentially until it reaches boiling point (25.7°C)

Temperature stabilises while the exotherm causes HCN to boil (tempering). However, reaction rate is still increasing (although not as fast)

In a Constrained Vessel:

- Pressure drop through tank vent increases, causing pressure and temperature to rise again
- Sufficient pressure generated to cause relief device to operate
- If a bursting disc is used, pressure suddenly falls back to near atmospheric with associated temporary decrease in reaction rate
- Liquid continues to boil as reaction rate progressively increases
- Just as it appears that all the fuel is about used up and that things should quiet down, the reaction can suddenly take off.
- Temperature and pressure within vessel rise sharply.

This final reaction (which involves decomposition of polymer) may occur with explosive violence.

Factors Affecting Polymerisation

Sunlight, pressure and most organic materials will not trigger polymerisation. Some polymerisation that occurs in the liquid can be reversible if the pH is adjusted quickly enough. Freezing will not separate the sulphuric acid out of the stabilised HCN.

Temperature

The thermodynamic critical temperature for HCN is 183 °C. That is the temperature at which the HCN cannot be liquefied at any pressure. HCN is unstable and will decompose violently if heated. The decomposition is also autocatalytic, so will occur at low temperatures if held beyond the induction time. The higher the temperature, the sooner polymerisation will occur.

Water Content

The presence of water in HCN increases the CN⁻ concentration, dilutes the sulphuric acid concentration, and doubles the polymerisation reaction rate. The amount of water present in HCN dictates the amount of acid required to prevent polymerisation. Low concentrations of water (0.1-0.2 wt. %) in HCN require sulphuric acid concentrations of 0.06-0.1 wt. %. Higher concentrations of water (up to 60 wt. %) in HCN require sulphuric acid concentrations of at least 0.25 wt. %. Too much water will result in HCN hydrolysis, but if the HCN/water mixture is properly stabilised, no polymerisation will occur. There is no hazard in adding water to HCN if it is properly stabilised, however if the acid stabiliser is depleted and if no more is added, then polymerisation proceeds at a rapid unchecked rate.

Water can be added to a vessel that is polymerizing to act as a heat sink. That means the addition of water to the vessel will cool the vessel and decrease the rate of polymerisation.

Container Effect

In a steel container, the metal of the container will eventually react with the sulphuric acid used for stabilising the HCN and the acid will be used up. Carbon steels are more reactive with sulphuric acid than stainless steels.

Cross Contamination

Cross contamination of HCN in storage tanks or in rails cars must be avoided. The consequences of cross contamination by amines or caustic are catastrophic. If cross contamination of a storage tank goes unchecked, polymerisation of the entire tank will occur. If the cross contamination were significant enough, the polymerisation could not be stopped by acid addition.

Historical Incidents Involving HCN Polymerisation

The HCN Safety Conference has compiled a list of all the major incidents to date (Clarke & McKinney 2013)⁶:

| | | | |
|---|---|---------------------------------|------|
| 1 | HCN Storage tank explosion | ICI (Cassel Works) | 1962 |
| 2 | Explosion due to hydrolysis by sulphuric acid | American Cyanamid (Fortier) | 1963 |
| 3 | Polymerisation of HCN/water soln | DSM (Geleen) | 1970 |
| 4 | Wrong mix due to passing HCN valve | Sterling Chemicals (Texas City) | 1993 |
| 5 | N5 100% tank polymerisation | Rohm & Haas (Deer Park) | 2000 |
| 6 | Explosion of laboratory HCN vaporiser | Monsanto (Texas City) | 1957 |
| 7 | HCN tank polymerisation | DuPont (Belle) | 1975 |
| 8 | Slop tank polymerisation | DuPont (Memphis) | 1984 |

The earliest of these incidents was in 1962 in the UK and involved a Syngenta legacy company. It occurred at the ICI Cassel Works in Billingham, in No 2 HCN storage tank.

The incident followed 2 weeks of problems with pumping from the tank, with poor stabilisation of the contents and mixing in of weak HCN.

Damage from the eventual explosive polymerisation indicated an explosion equivalent to 4.5 – 7.0 kg of TNT. Fortunately there were no injuries.

Table 2. Summary of Historical HCN Polymerisation Incidents



Fig 6. General View Looking North West

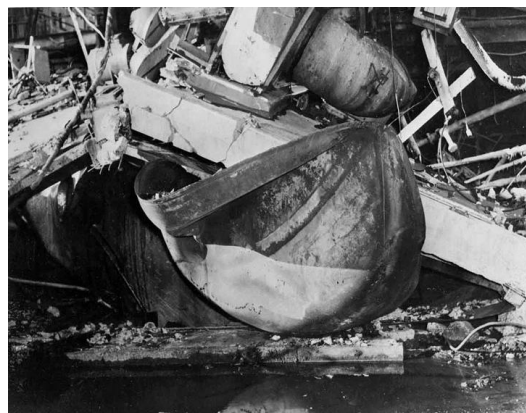


Fig 7. East End of No 2 HCN Storage Tank

Learning From Historical Incidents

Several good learning points were gained from investigation of this and some of the other incidents listed in the table. Including:

- Bulk HCN polymerization can have potentially catastrophic consequences
- There may be practical difficulties in pumping out product or maintaining circulation when polymer present.
- Water (and polymer) reduce HCN stability
- Adding more HCN to an unstable mixture is likely to just “add fuel to the fire”
- The bulk polymerization of 30% HCN solution can happen
- Adding sulphuric acid to a tank of polymerizing HCN is unlikely to work unless effective circulation (to cause mixing) can be established.

This learning helped to establish some “universal HCN handling rules” to avoid polymerisation:

Keep HCN Inhibited

100% HCN is normally inhibited with (ca. 500 ppm) H₂SO₄

- Other acids can be used, but must be compatible with materials of construction and may require different concentrations (phosphoric acid, acetic acid, SO₂ vapor)

Keep HCN Uncontaminated

- No Caustic / No Amines / No NH₃
- No cyanide polymer (contains NH₃)
- No water-based Fire Fighting Foam / No Water

Keep HCN Moving

- Avoid stagnant regions where impurities can concentrate
- Maintain mixing for homogeneous inhibitor distribution
- Maintain mixing for effective temperature control

Keep HCN Cold

- The rate of HCN polymerization increases when heated

Syngenta HCN Production and Shipping

On the Syngenta facility, onsite storage is provided by 3 large tanks (200 m³ each) and 4 railcars (70 m³ each), with 1 railcar maintained empty for emergencies – this can be used to transfer material suspected of starting to polymerise, so that it can be quenched more efficiently. The HCN in the storage tanks is kept acidified, cold and circulating to minimize the chance of polymerisation. HCN in storage tanks and in process vessels is sampled frequently to insure that adequate sulphuric acid exists to prevent polymerisation.

Consequences of polymerisation occurring in large storage tanks or a railcar would be catastrophic. The proximity of the storages to each other, the railcars and to the plant control room, makes the polymerisation scenario particularly serious.

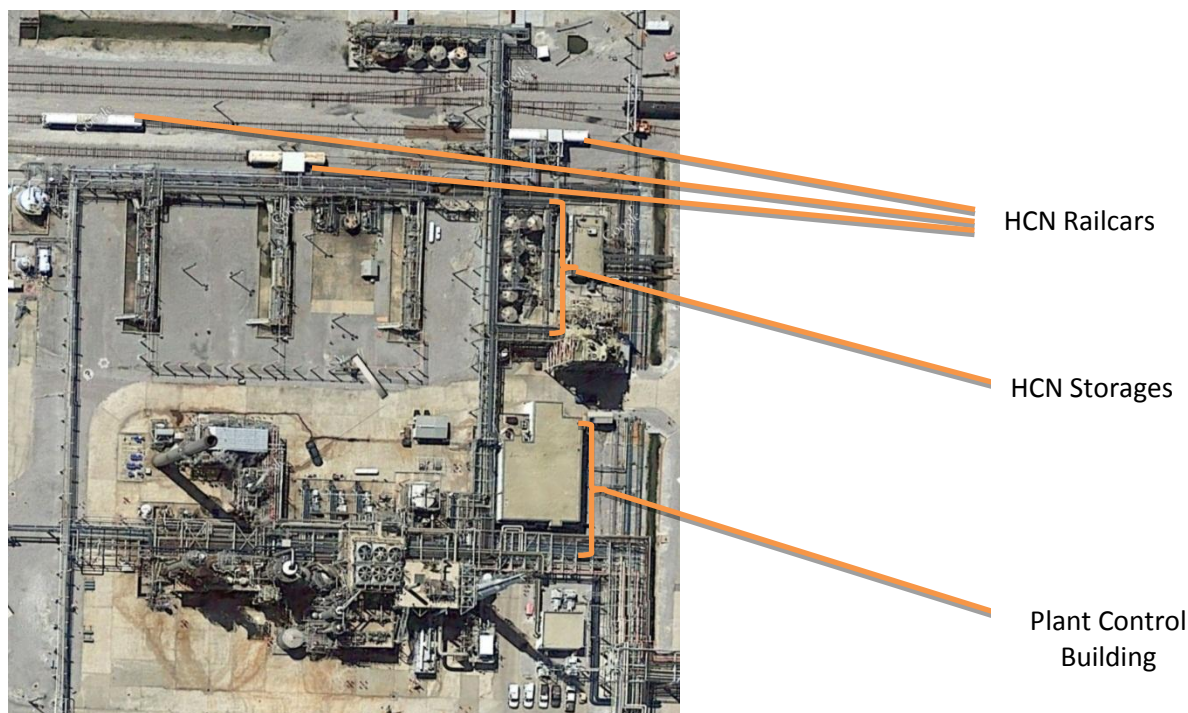


Fig 8. Syngenta HCN Facility

If an HCN rail car is loaded with high water or without stabiliser, the car would eventually polymerize and explode. The rail car pressure safety valve (PSV) is designed for protection against flame impingement only (HCN boiling) and will not handle a polymerisation event. Safety studies (see later) indicate that by the time the PSV lifts it will be a matter of minutes before the car explodes.

If an HCN rail car were being loaded at the same time from the same HCN storage tank that was undergoing polymerisation, the instantaneous heat of the polymerisation reaction would increase the temperature and pressure on the rail car making it difficult if not impossible to unload. The rail car would quickly heat up and explode when the HCN polymer began decomposing around 100 °C. The result would be devastating. The rail car would explode releasing 30 te of HCN. A vapour cloud explosion would occur almost simultaneously. The pressure surge from the car exploding would impact the HCN control building and production unit. The metal fragments from the rail car may penetrate the HCN storage tanks releasing more HCN to fuel a fire or increase the atmospheric concentration of HCN.

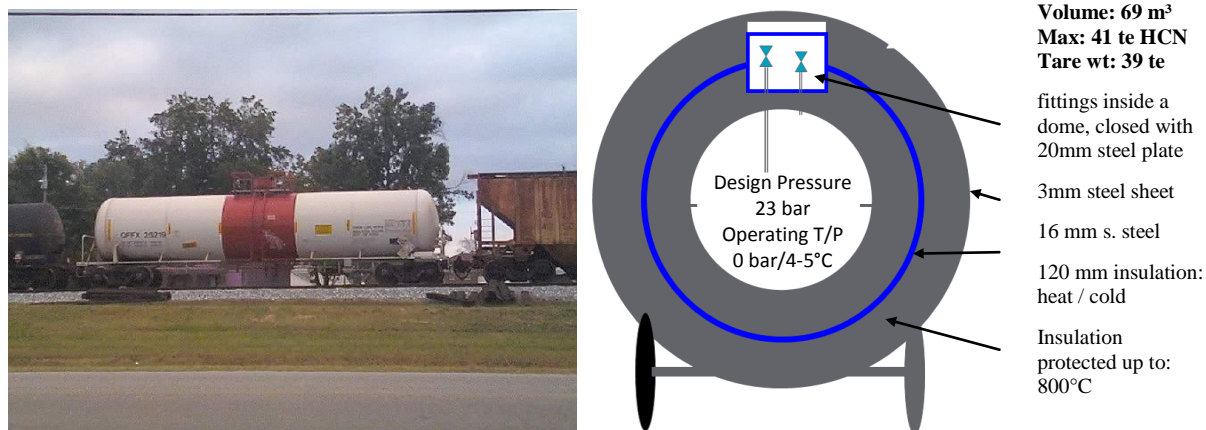


Fig 9. HCN Railcar

To maintain high levels of safety on the Syngenta HCN facility and transported railcars, the available safety data on HCN polymerisation is regularly reviewed at Syngenta, with company representatives from HCN production and HSE attending the annual HCN Safety Conference to keep abreast of current best practices. One concern that was raised by the HCN team was the issue of HCN storage/transportation in railcars. HCN can occasionally be held in railcars for a number of weeks and the team felt that the current available safety data did not provide enough definitive information on the safe hold time in this situation. The team were especially concerned in case a railcar became accidentally contaminated (e.g. with water) and was then held up for a significant length of time during shipment. The available safety data was therefore reviewed.

Historical Safety Data

The Fauske Study”

In the mid 1980’s a safety study was commissioned by some member companies of the HCN Safety Conference. Participating companies included American Cyanamid Co., BASF Chemical, Ltd. (U.K.), Ciba-Geigy Corp., Degussa Corp., E.I.DuPont de Nemours & Co., Imperial Chemical Industries (U.K.), Monsanto Corp., Rohm and Haas Co., W. R. Grace Co., and Sohio Chemical Co.

A series of “Thermal data and vent sizing tests” was carried out by Fauske and Associates in three phases between 1985 and 1988. This work is now referred to as the “Fauske Studies” (Fauske & Associates 1985-1988). Using the Vent Sizing Package (VSP) 43 tests were carried out. A number of “closed system” tests were performed to investigate the thermal characterisation of the runaway, whereas the bulk of the work was carried out in an “open system” to determine vent flow regime characteristics and also to investigate the feasibility of quenching using a various reagents.

A small number of “macro tests” were also carried out. The objective of these tests, carried out in 600 ml glass beakers, with pH and weight loss measurement, was to allow visual observation of the polymerisation, whilst testing the effect of various quench agents. From the VSP data the polymerization reaction runaway was characterised in terms of:

- Impact of different contaminants / concentrations
- Impact of starting temperatures
- Impact of water

Basic data was also obtained for vent sizing which indicated that the reaction exhibits two-phase flow characteristics at relief with a churn-turbulent flow regime. Most importantly the data indicated that the reaction is actually accelerating during the tempering period and mass loss reached a peak rate coincident with the second exotherm. This implied that it would be impossible to design a relief system that would cope with the final exotherm. As such quenching was recommended as a basis of safety and the use of SO₂ gas recommended to be one of the more effective methods.

As with acids, SO₂ neutralizes basic sites which are necessary for initiation and propagation - good mixing for complete contact is critical

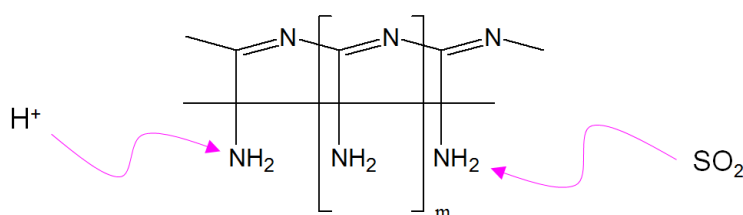


Fig 10. Mechanism of quenching

Limitations of the Fauske Data

The Fauske testing was primarily concerned with characterisation of the runaway, to determine rates of temperature/pressure rise and mass loss, principally to obtain data for relief vent sizing. It is known that HCN polymerisation is autocatalytic and therefore is subject to an induction or “incubation” time before it goes into exothermic runaway. At ambient temperatures, this induction time is very long, particularly for stabilised material. As such, each experiment was “initiated” in some way (either by contaminant or temperature) to keep the test length down to a manageable time (1-3 hrs).

This meant that the reaction runaway itself could be characterised easily and quickly, and the relative rates of reaction for various material qualities could be easily determined. This data provided valuable data about the reaction peak rates and relief condition and showed that under most circumstances, pressure relief would not be a feasible basis of safety for the runaway polymerisation. Alternative bases of safety were therefore recommended and adopted by manufacturers.

However, the work did not look at induction time to runaway. Therefore, whilst manufacturers were aware that they had to take drastic and immediate action should a runaway occur, they did not know for sure how much time they have (in storage or transport) before the runaway will start. This means that process operators are required to implement regular checks by sampling HCN storages and make a judgement on colour or pH to determine whether polymerisation has begun.

Some testing (DuPont 1965)⁷ had been carried out many years previously which gave some crude idea of induction times of stabilised HCN and material contaminated with water and base. However, all the data was obtained at elevated temperature and any predictions of induction time at ambient were extrapolations from, at best, 2 data points!

A summary of the data for “standard” DuPont product HCN (ca 0.2% H₂O, 0.08% H₂SO₄) is given below:

Table 3. Induction Time v Temperature

| Temp (°C) | Induction Time (hrs) |
|-----------|-------------------------|
| 150 | 11 |
| 95 | 408 |
| 40 | 45000 (extrapolated) |

The induction time at 40°C is estimated from an extrapolation of the data points at 95 and 150°C and equates to ca 5 years. This data seems to be accepted and is still quoted today. However, it is interesting that when shipping bulk HCN in railcars, DuPont recommend that the limit for storage in a railcar is 3 months – a very conservative safety margin compared to the safety data they produced themselves. It was decided to conduct a new safety study on HCN induction time.

HCN Induction Time – New Safety Study

The study was carried out at the Process Hazards Section laboratories at Syngenta Huddersfield manufacturing plant. The initial remit was to produce reliable induction time data for HCN:

- Pure material
- Stabilised with H₂SO₄
- Contaminated with water

PHS has a number of experimental techniques available for determination of thermal stability characteristics. The most suitable methods for determination of induction time are:

- DSC – small sample (5-10 mg), sealed crucibles – high pressure
- Phi Tec I – intermediate scale (1-5 g) – high pressure
- Carius Tube – intermediate scale (1-10 g) – high pressure
- Adiabatic Dewar – large scale (100 – 200 g) – atmospheric pressure
- Pressure Dewar – large scale (500 – 800 g) – high pressure

The preliminary study focussed on DSC and Phi Tec I, with a small number of Carius tubes for comparison

HCN Preparation:

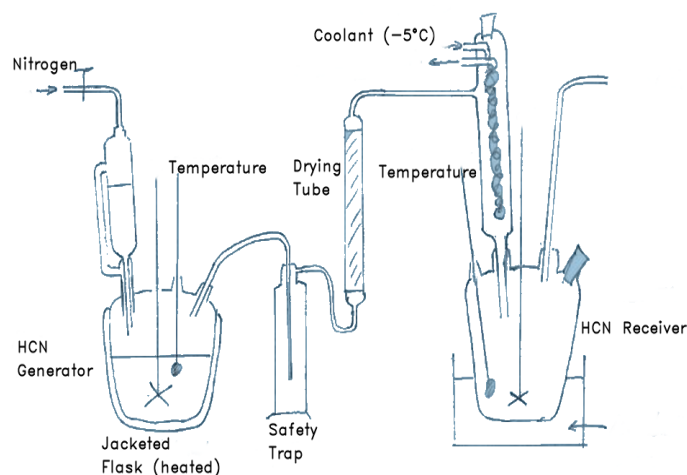


Fig 11. Laboratory Glassware set-up for HCN

For DSC and Phi Tec experiments, only small samples were required, therefore it was decided to synthesise the HCN for each test on demand in the laboratory rather than attempt to ship from a manufacturer or make larger quantities for storage. The advantage of this was that fresh HCN was used each time and there were no doubts about the provenance or thermal history of the samples used.

Apparatus:

The experimentalist was equipped with normal lab protection: coat and light eye protection and work carried out in a standard fume hood using a personal HCN gas sensor:

A nitrogen supply with isolation valve was to flush apparatus (before & after)

200ml Jacketed flask for HCN generator with
Drying tube Position 3, filled with calcium chloride
Condenser Position 2, with circulating coolant at $-5-0^{\circ}\text{C}$.

Exhaust gas through a bubbler and into a scrubber filled with excess aq-NaOH operating at ambient temperature.
Hot air gun to gently warm the safety trap and drying tube at the beginning.

Preparation.

Apparatus flushed with nitrogen and scrubber started. The condenser and reactor pre-cooled to -5°C to 0°C . The safety trap and condenser warmed.

Reaction.

Aqueous sulphuric acid (50% w/w, 40g, 0.20mole) is charged to the reactor. A solution of NaCN (16.4g, 0.34 gmole) in water (40g) is prepared and charged to the pressure equalized dropping funnel. The reactor is heated to $40-45^{\circ}\text{C}$. The aqueous NaCN solution is slowly charged. The temperature in the reactor rises quite rapidly and is maintain at $70-80^{\circ}\text{C}$ by moderating the NaCN flow from the dropping funnel. HCN flows through the drying tube and condenses in the cold trap. At the end of addition the temperature in reactor is maintain at $80-90^{\circ}\text{C}$ and the aparatus flushed with nitrogen until no more HCN condenses out. Yield ca. 7g HCN (75%) . HCN samples are taken from the trap using a glass pipette and charged directly to the DSC crucible or Phi Tec bomb. The crucible/bomb is sealed in the same fume-cupboard before being transported to the test kit.

DSC Analysis

Background:

In a typical DSC a small sample of material is placed in a metal capsule (pan) and heated at a constant rate. Sensors detect any heat absorbed or evolved by the sample relative to an inert reference (empty pan).



Fig 12. High pressure DSC crucible

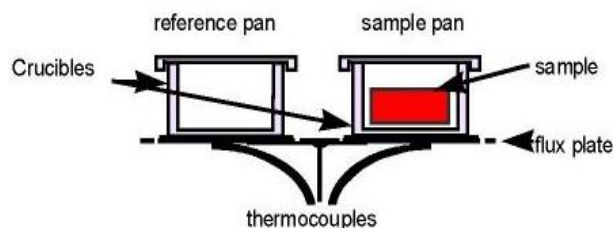


Fig 13. DSC schematic

Tests can be run under dynamic/ramped temperature profile or isothermally. In the case of HCN, we are looking at an autocatalytic decomposition rather than typical nth order. This type of decomposition shows clear characteristics in both dynamic and isothermal DSC tests.

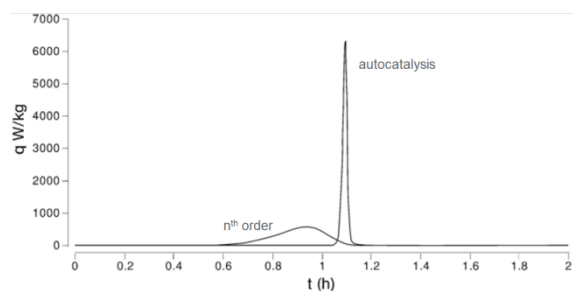


Fig 14. Dynamic DSC

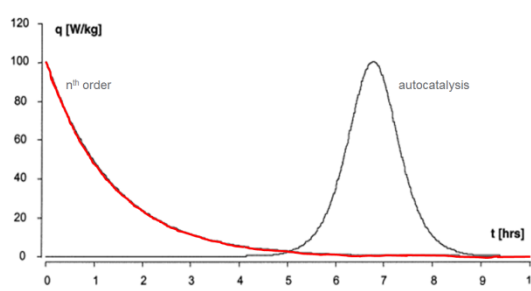


Fig 15. Isothermal DSC

In dynamic tests, autocatalysis is characterised by a sharp peak, with relatively large peak power output, the heat being released over a relatively small temperature range compared to nth order decompositions. In isothermal DSC gives very different traces for nth order and autocatalysis. Nth order decompositions start at an initial peak rate which decays over time. This initial peak rate is dependent on the isothermal test temperature, as is the proportion of decomposition that will occur. The whole decomposition may not occur if the temperature is low enough and some residual heat may be seen if a subsequent dynamic test is carried out.

Autocatalytic decompositions appear to nothing at first then occur, in full, after a certain incubation or induction time. The induction time is dependent on temperature and if it the time is determined at several temperatures, the data can be used to predict induction times at much lower temperature.

HCN Dynamic tests:

HCN was tested in both stainless steel high pressure crucibles. Normally, gold plated crucibles are used in DSC analysis to give an inert surface in contact with the sample and avoid catalysis. However, HCN is known to interact with gold – and as the railcars and storages used tend to be of steel construction, it was considered best to use the steel crucibles to simulate the storage MOC. Approximately 5 mg of HCN was used in each test.

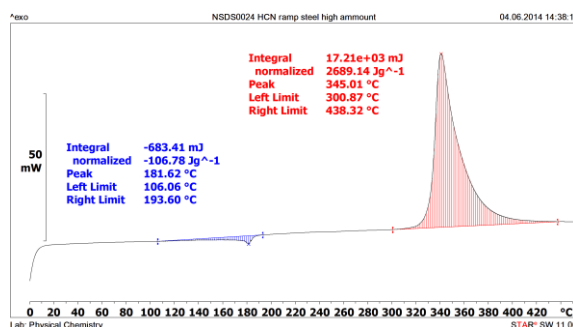


Fig 16. HCN dynamic DSC test

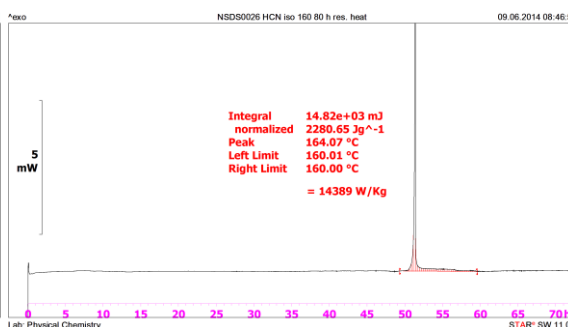


Fig 17. HCN isothermal test (160°C)

The dynamic trace shows clearly the characteristic sharp peak of an autocatalytic decomposition and the isothermal tests exhibit distinct induction times followed by rapid complete decomposition.

Isothermal tests were carried out in the range 220-140°C and the induction times summarised below:

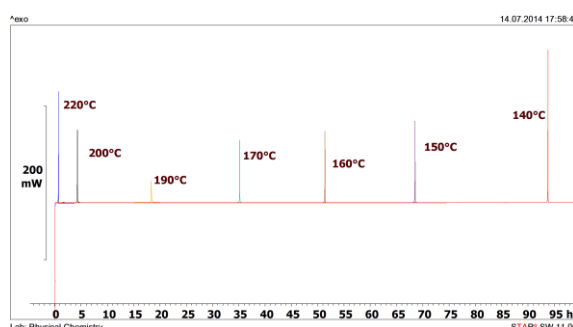


Fig 18. Overlay of the HCN isothermal traces

| Temperature (°C) | Induction Time (mins) |
|------------------|-----------------------|
| 220 | 24 |
| 200 | 235 |
| 190 | 1070 |
| 170 | 2065 |
| 160 | 3035 |
| 150 | 4079 |
| 140 | 5604 |

Table 4. Summary of the induction times

A plot of Ln (Induction time) v 1/Temperature (Kelvin) should give a straight line. However, a distinct deflection is noted which seems to coincide with the critical temperature of HCN:

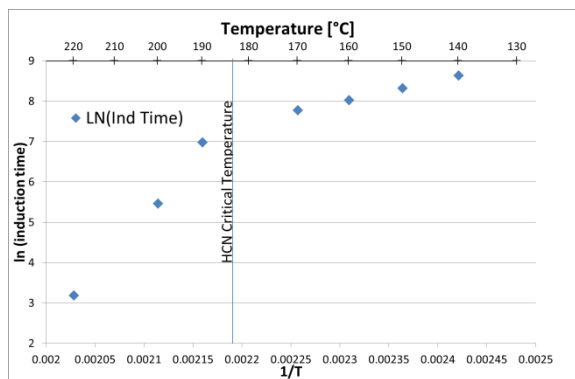


Fig 19. Logplot of HCN induction time

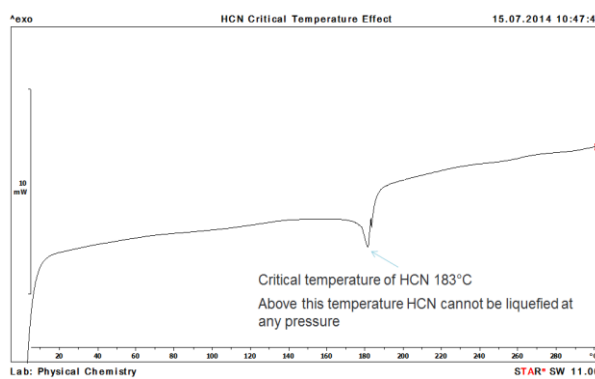


Fig 20. DSC of HCN indicating critical temperature effect.

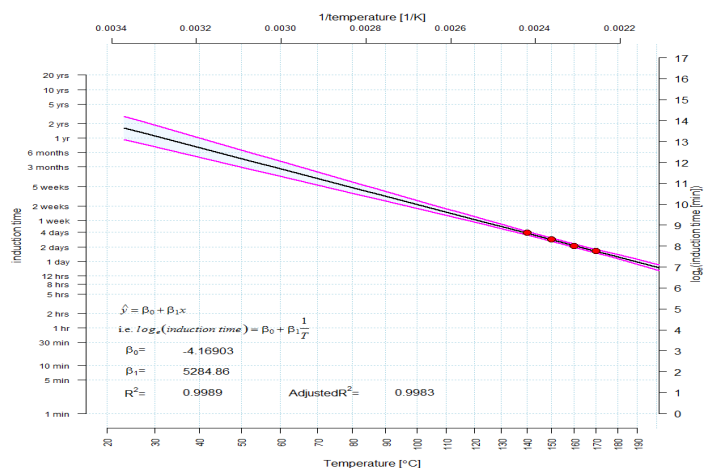


Fig 21. Prediction of HCN induction time

The induction times measured below the critical temperature were used to predict downwards to 40°C, with suitable uncertainty limits:

Extrapolated induction time at 40°C

4.5 – 12 months

Fig 22. Phi Tec I calorimeter

Phi Tec I Tests

The high vapour pressure of HCN was a limiting factor in both choice of experiments and bombs in the Phi Tec. Experiments were limited to isothermal tests as in ramped or adiabatic tests the pressure at onset (ca 300°C) is already very high (>100 bara). This is too high for glass bombs and would result in bursting of steel bombs due to additional pressure rise from the decomposition. Bursting metal bombs can cause significant damage to the Phi Tec internal components. For induction time determination from isothermal measurements, the temperatures used were much lower than the normal “onset”. However, glass tubes were used to allow for burst, without danger of damage to the kit. Glass was considered to be inert to HCN. Approximately 2-3 g of HCN was used for each test.



Phi Tec Isothermal Results

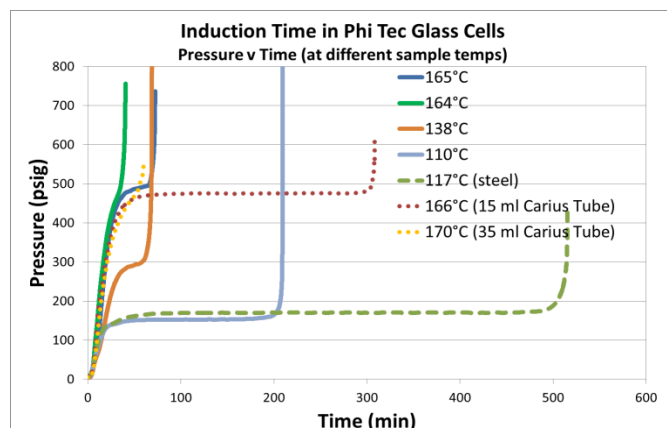


Fig 23. Phi Tec Isothermal Traces

Table 5. PhiTec HCN Induction Times

| Temperature (°C) | Induction Time (min) |
|------------------|----------------------|
| 110 | 209 |
| 117 ^a | 515 |
| 138 | 69 |
| 164 | 40 |
| 165 | 72 |
| 166 ^b | 308 |
| 170 ^c | 60 |

a – steel Phi Tec bomb; b, c – 15 ml, 35 ml Carius tubes

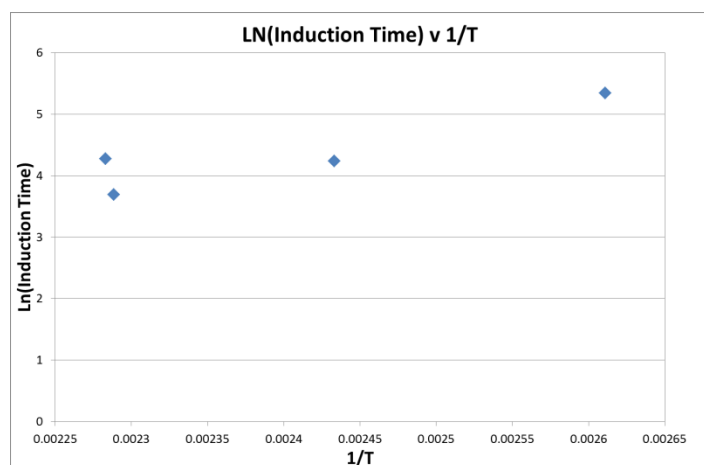


Fig 24. Logplot of Phi Tec HCN Induction Times

Induction times from the Phi Tec tests show markedly shorter induction times than measured in DSC and also greater inconsistency. Ignoring outlying points, the predicted induction time for 40°C is ca 3 days (c.f. 4-12 months in DSC). The initial suggestion for the difference was the tests cell material (glass v steel). However, a sample run in a steel Phi Tec bomb also gave a significantly shorter induction time than predicted from DSC (515 min c.f ca 11,000 min predicted).

Differences in volume to surface area ratio and/or ullage space were also considered. However, the inconsistent Carius tube results are not consistent with this theory.

The most likely explanation for the reduced induction time in Phi Tec bombs (and Carius tubes) could be a combination of 2 factors. During the preparation stage of HCN, as the generation rate is quite slow, the time required to generate 2-3 g for the Phi Tec tests was significantly longer (hours) than that required to generate a small amount for DSC. It is thought the HCN could have deteriorated slightly during this time.

Another factor is the construction of the Phi Te bombs and Carius tubes. To enable pressure measurements, the bombs/tubes are constructed with a metal stem, attached to the glass with a special glass/metal seal. The stem is constructed from steel with a relatively high nickel content. When charging the cells, the HCN comes into contact with the stem, which may result in contamination and cause some catalytic deterioration of the HCN. This may explain why the longest induction time was recorded in the all steel Phi Tec bomb, although it was still shorter than determined in DSC, possibly due to the reasons stated above. A DSC was carried out with fresh HCN containing a small amount of the Fe/Ni neck from a Phi Tec bomb and compared to uncontaminated material:

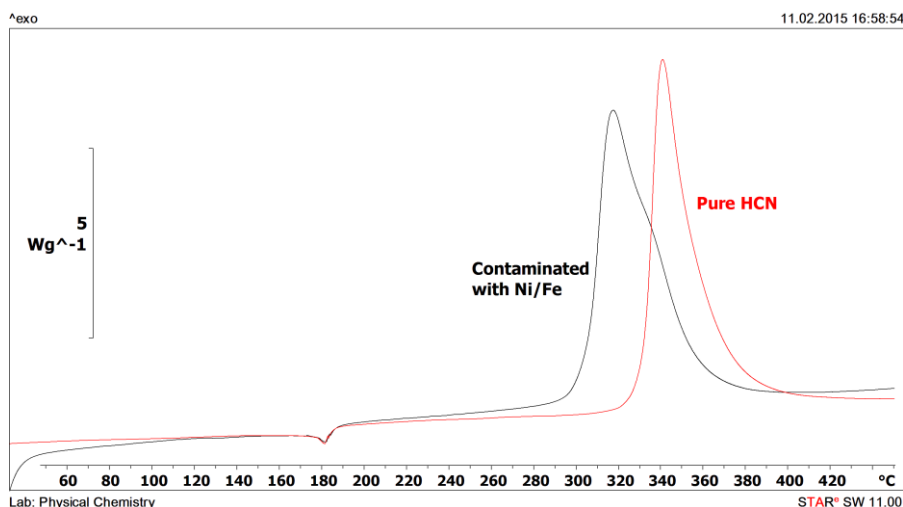


Fig 25. Effect of HCN Contaminated with Fe/Ni alloy

The contaminated sample showed a significant effect on the HCN decomposition exotherm, with reduced onset and peak temperatures and broadening of the peak. This suggests that the metal has had some catalytic effect on the decomposition and would most likely cause reduction of induction time as seen in the Phi Tec tests.

Summary of DSC and Phi Tec Testing

DSC analysis of pure unstabilised HCN showed that the decomposition is autocatalytic. In dynamic tests the decompositions onset occurred from ca 300°C. Isothermal testing showed a distinct induction time to decomposition which displayed a good correlation with temperature. Extrapolating the high temperature data it was possible to predict an induction time 4.5 – 12 months at 40°C. This compares to 5 years previously estimated for stabilised HCN. This also gives some justification to DuPont's 90 days limit for storage in a railcar, which allows an appropriate safety margin even in case stabiliser addition has been omitted.

Induction times measured in Phi Tec (and Carius tube) tests in both glass and steel were significantly shorter and more inconsistent than in DSC. There may be a number of reasons for this discrepancy, but further work would be required to prove the exact cause and allow us to determine if this is a feasible test method for measuring HCN thermal stability.

Summary and Conclusions

HCN is a very important precursor to many processes in the chemical industry. Its toxicity and reaction hazards mean manufacturers must continually strive to keep abreast of best practices to ensure HCN can be synthesised, stored and transported safely. The HCN Industry Safety Conference provides a valuable forum for people in the HCN industry to come together and share knowledge, helping to maintain the high safety standards required.

The 1980's Fauske Study into the HCN polymerisation reaction hazards, commissioned by the HCN Safety Conference member companies, was a comprehensive piece of work which provided valuable information on the appropriate basis of safety in case of uncontrolled runaway polymerisation, which is useful to HCN facilities even today.

Current safety data on induction time to HCN polymerisation is sketchy and inconsistent, however, we have shown in this paper that current procedures employed for storage and transportation of stabilised HCN allow a conservative safety margin for allowable storage time. We have shown that for unstabilised HCN, the induction time in steel containers is approximately 4.5-12 months at 40°C. Although time did not allow for investigation of stabilised HCN in this study, a review of all the current available safety data leads us to the conclusion that the induction time of stabilised HCN would be orders of magnitude greater than this. The current "recommendation" to limit storage of stabilised HCN in railcars to 90 days is in our view more than adequate.

Further work is ongoing to generate additional data on HCN polymerisation, including the effects of contaminants e.g. water.

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