Chemical Reactive Hazards			
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CONTROL OF ACRYLONITRILE POLYMERISATION DURING STORAGE

by R Rowlands

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Summary

This DIN has been produced in direction response to an FCG request. It provides information to inspectors on acrylonitrile, its safe storage and precautions to control unwanted polymerisation. In particular, it explains the involvement of oxygen as a polymerisation inhibitor and the role of nitrogen blanketing.

This DIN updated DIN 5007 issued in April 1996, which should now be cancelled.

Q1: What are the properties of acrylonitrile?

A: Acrylonitrile (AN) is the nitrile of acrylic acid: CH_2 = CH-CN, also named vinyl cyanide or cyanoethylene. As the names indicate, it is chemically related to vinyl and acrylic monomers.

It is a liquid, boiling at 77.3^{O}C, freezing at -83.5^{O}C. Water is also slightly soluble in AN - 3% at 20^{o}C. It is a versatile chemical intermediate used to make synthetic fibres, rubber and plastics by reaction with other monomers.

Q2: What hazards does it present?

It is toxic, highly flammable and can undergo exothermic polymerisation reactions:

• flash point	-1^{O}C	(closed cup)
• flammable limits	2.8 to 28.0	(vol % in air at 25^{O}C)
• autoignition temperatures	481^{O}C	
• heat of polymerisation	17.3 kcal/mol	

Stored under air, the vapour would be in the flammable range at temperatures from 0 - 29^{O}C.

Q3: What is the risk of polymerisation in storage?

A: AN is reported to be more thermally stable then related monomers - acrylic acid and acrylates - under normal storage and handling. However, as normally supplied, it is stabilised by inhibitors and manufacturers advise against keeping unstabilised material. Factors which can consume and inhibitors and initiate polymersiation include:

- exposure to heat and UV light;
- contact with strong acids and alkalis;
- contact with free radical catalysts such as peroxides.

Q4: What are the main methods to prevent polymerisation?
A: These include:

- Limit the time AN is kept before use;

  e.g by good stock management, minimising the quantity held, and using material on a first in, first out basis. Available guidance (1) recommends that storage times of more than 4 to 6 months are avoided.

- Control purity and avoid contamination of AN;

  e.g by ensuring that material adheres to specification and does not contact incompatible chemicals. Particular care is required if AN is returned from process to storage.

- Control the temperature at which it is stored;

storage temperatures below 30^{O}C are recommended.

- Monitor stored material;

  e.g by sampling regularly and testing for signs of polymerisation, such as:

  - development of haze or colour

  - an increase in pH

  - an abnormal temperature increase (may not be apparent until it is too late)

  - a drop in inhibitor levels.

- Maintain the levels of inhibitors:

  and do not store or transport uninhibited AN.

- Ensure storage and handling equipment is of adequate design;

  e.g by avoiding dead legs where material may accumulate.

- Adopt procedures for abnormal operations and emergencies;

  e.g including what to do if monitoring shows evidence of polymerisation.

A recently reported near-miss incident illustrates some of the principles of safe monomer handling - see reference 3.

Q5: What polymerisation inhibitors are used with AN?
A: Two inhibitor systems are commonly used. Either:

- MEHQ (Monomethyl Ether Hydroquinone) in the range 30 - 50 ppm plus 0.25 - 0.5% water; or

- Ammonia at 30 - 55 ppm plus 0.25 - 0.5% water.

The storage stability of the ammonia system is reported (1) to be lower than the MEHQ system: 6 months maximum as against 12 months maximum.

Q6: How do inhibitors work?
A: Water inhibits ionic polymerisation of AN, as do low levels of ammonia. MEHQ inhibits free radical polymerisation and requires trace amounts of dissolved oxygen (DO_2) to be effective (2). Heat, UV light and chemical initiators are all potential sources of free radicals in AN. Research by BP Chemicals (BPC - the main supplier in the UK) indicates that oxygen reacts rapidly with free radicals to form peroxy radicals, which are then deactivated by MEHQ.

Q7: What levels of DO_2 are required for effective inhibition?
A: Research has shown that trace amounts are sufficient. The mechanism for inhibition indicates that an amount equimolar to MEHQ would be required - 10 ppm DO_2 is equimolar with 40 ppm MEHQ. An equimolar ratio of DO_2 to MEHQ is the minimum suggested level.
Q8: Are there any problems in ensuring adequate levels of DO_2?
A: Oxygen is soluble to about 80 - 90 ppm in AN under ambient conditions and DO_2 levels are likely to be maintained when AN is stored under air. There are two concerns:

i) Unlike other inhibitors in AN, DO_2 levels are not routinely measured.

ii) AN may be stored, and possibly transported, under an inert - usually nitrogen - atmosphere to prevent the formation of a flammable mixture.

Q9: What is the effect of storage under nitrogen?
A: To move outside the flammable region, oxygen levels in the vapour space above AN have to be reduced to less than about 9.5% and purging of oxygen to below 8% is recommended (2). Rigorous exclusion of oxygen is discouraged because the inhibitor system may become less effective. DO_2 levels are reasonably well maintained when AN saturated with air is stored under a 95% nitrogen/5% oxygen atmosphere.

Q10: What steps can be taken to maintain DO_2 levels of AN kept under nitrogen?
A: Options that can be considered include:

- ensure incoming material contains DO_2, preferably close to saturation e.g. because previous handling has taken place under air;
- maintain around 5% oxygen in the vapour space;
- avoid handling which may bubble nitrogen through liquid AN;
- if DO_2 levels are, or are likely to be, depleted, bubble air through AN. Advice on measuring DO_2 levels may be obtained from the supplier.

Q11: What corrective measures can be adopted if AN shows signs of polymerisation?
A: Immediate action as follows is recommended:

- if pH>7.3, acidify to pH<7.0 by adding a 1:2 mixture of acetic acid: AN;
- add inhibitor using a 4% solution of hydroquinone (HQ) in AN to achieve an HQ level of 100 ppm;
- add water to inhibit polymerisation and to dilute the AN;

- apply external cooling to the AN container;
- relieve pressure in the container through an adequate vent system and inhibit the condensed AN vapour;
- once AN is stabilised against further polymerisation, remove it for disposal or reprocessing but continue to monitor for signs of renewed polymerisation.

References

1. CEFIC, 1995, *Guidelines for the distribution of acrylonitrile*, Acrylonitrile CEFIC Sector Group, Brussels.
2. BP Chemicals, 1995, *Acrylonitrile Safe Storage and Handling Guide*, BP Chemicals, London
3. Anon, 1995, Monomer stability near-miss, *Loss Prevention Bulletin* No. 122, 18.