

THE CONTROL OF RUNAWAY POLYMERISATION REACTIONS BY INHIBITION TECHNIQUES

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SUMMARY : The technique of reaction inhibition is a poorly researched topic. Other methods of runaway reaction control, namely inherent safety, process control, containment, reactor venting, crash cooling and drown-out, are well documented, established techniques that are regularly used for the protection against, or prevention of, runaway chemical reactions. Increasing environmental protection legislation will heighten the need to prevent loss of containment occurrences. This means that basis of safety such as reaction inhibition which provide total containment will become more widely used. This is particularly applicable to the polymerisation industry (the industry involved in the largest number of incidents reported in the period 1962 - 1984¹) where reactor venting is, almost exclusively, the sole basis of safety used industry-wide. Discussion is given of inhibition techniques, with particular attention paid to polymerisation reactions, and examples of successfully inhibited processes provided. It is interesting to note that even the Encyclopedia of Polymer Science and Technology² suggests :

"Their [inhibitors] technological importance is small, except as a means of stopping polymerisations at the completion of the desired conversion, and few studies have been reported."

(**KEYWORDS** : Inhibition, runaway, polymerisation, venting)

1. INTRODUCTION TO INHIBITION PROCESSES

Some reactions can be stopped, or the rate dramatically decreased by the addition of very small quantities of certain chemicals. These chemicals, termed inhibitors, can act in several ways :

- a. Stopping the reaction by deactivating a catalyst, e.g small quantities of sulphides can irreversibly deactivate platinum on carbon catalysts.
- b. Stopping a chain reaction by deactivating the active ends of the expanding chain and preventing further propagation.

- c. Stopping the reaction by providing an alternative reaction with one of the reactants that is not as energetic as the normal process.

2. POLYMERISATION INHIBITION

This paper outlines work undertaken on the inhibition of polymerisation processes. These types of processes are particularly suited for such studies, since :

- a. They were the major processing technique involved in reportable incidents in the period 1962 - 1984¹ accounting for 47.8% of incidents.
- b. By their nature, these reactions are chain branching reactions that can, in many cases, be inhibited by small quantities of certain chemicals.

There are two main routes by which macromolecules can be synthesised (each of which were involved in the reported incidents) :

CONDENSATION POLYMERISATION : A series of reactions that occur in which one reaction is essentially independent of the preceding one. Generally, units forming part of a chain need to have two functional units across which linking can occur. An example of this type of reaction (and the one attributable to a major portion of the reported incidents) is phenol formaldehyde resin formation.

ADDITION POLYMERISATION : A series of consecutive reactions in which units are added to a growing chain. The reactivity of the chain may be due to free radicals, cations or anions. A free radical is produced by the homolytic splitting of a chemical bond leading to the presence of an 'odd' (unpaired) electron. The polymerisation of all vinyl monomers is achieved by this route since the unsaturated bonds in vinyl monomers are particularly prone to attack by free radicals. This type of reaction is often referred to as a 'chain branching explosion'. There are three main stages of reaction (Figure 1) :

INITIATION : The reaction is initiated by forming free radicals in the monomer by thermally induced techniques or the addition of initiators which are split by small amounts of energy (UV light or relatively low temperatures (60 - 70°C)) to give free radicals. These radicals then add to monomer units giving monomer radicals.

PROPAGATION : The free radicals formed in the initial reaction add to other monomer units thus forming an expanding chain with the generation of a further radical. Chain lengths can be as high as 10,000 monomer units.

TERMINATION : The combination of two free radicals forms a stable molecule that can no longer propagate further reactions.

Free radical molecules are normally highly reactive species which react very rapidly, evolving much heat, once formed.

The hazards associated with polymerisation reactions have been minimised in recent years with a change in processing technique away from bulk processes to emulsion, solution or precipitation processes. These processes reduce the hazards since the active monomer is diluted into a solvent thus increasing the heat capacity of the system and lowering the adiabatic temperature rise. Other methods of controlling polymerisation processes are :

- Reactor venting methods (the most common of all techniques)
- Total process control (using controlled feeds) with cutout hardware.
- Controlling the reaction temperature by the controlled addition of initiator
- The use of low boiling solvents to remove heat by solvent reflux
- The addition of compounds that decompose endothermically at elevated temperatures and counter-balance the heat released by the reaction
- Other techniques universally available for runaway reaction control ie. dumping, crash cooling, quenching, containment, etc.

There are several disadvantages of using reactor venting that can be eliminated by the use of inhibition techniques :

- Loss of containment problems associated with venting can provide severe secondary discharge considerations associated with material flammability, toxicity and disposal.
- Solidification of polymerised material in cold vent piping may present a blockage risk.
- The environmental impact of monomer vapour release could be large (eg. vinyl chloride). Increasing environmental protection legislation could mean that extremely large fines may be imposed on a company for the uncontrolled venting of monomers.

The principle of reaction inhibition involves the termination of a radical to form a non-reactive species that does not propagate further reactions (or only propagates extremely slowly). Three types of compound can act as inhibitors :

- Stabilised free radicals which can react with radicals of the type present in polymerisation systems, but not with monomers. The most common substance in this class of compounds is diphenylpicrylhydrazyl ($C_6H_5)_2NNC_6H_2(NO_2)_3$.
- Substances that essentially act as transfer agents; the products of radical displacements are however so unreactive that they re-initiate very ineffectively.
- Substances to which primary or polymer radicals may become attached chemically giving new radicals which are relatively unreactive; processes of this type can be considered as copolymerisations of a special type.

Many types of inhibitors are available. Their existence was first discovered by Foord³ in 1940 and since then, many studies are reported for a wide variety of compounds that have inhibitory characteristics. The major types of chemicals that are currently used as inhibitors are :

- Quinone-based aromatic compounds (these require oxygen to become active).
- Nitro-compounds
- Some metal salts and complexes (although some of these also act as initiators).
- Nitrogen containing compounds (azo, diazo, nitroso, etc.)
- Sulphur containing compounds (mainly thiazine)

3. IDENTIFYING SUITABLE INHIBITORS

At present, inhibitors' main usage comes in the prevention of premature polymerisation during monomer storage. Part per million quantities of inhibitors are active in prolonging the storage life of a monomer for an indefinite period. Two of the most commonly used inhibitors have been investigated in methyl acrylate. The rate of polymerisation of this monomer is extremely rapid and the magnitude of the reaction is large ($\Delta H_r = -78.6 \text{ kJ.mol}^{-1}$)⁴. The polymerisation of this monomer in a Carius tube screening test⁵ is illustrated in Graph 1. Further isothermal screening tests were then performed to determine the relationships between :

- i. Temperature and induction period for uninhibited methyl acrylate
- ii. Inhibitor concentration and induction period for phenothiazine and *para*-methoxy phenol inhibitors in methyl acrylate under isothermal conditions.
- iii. The effect of normal contaminants (mild and stainless steel) on the induction period of methyl acrylate containing phenothiazine under isothermal conditions.
- iv. The effect of inert gas blanketing on the efficiency of phenothiazine and *para*-methoxy phenol inhibitors in methyl acrylate under isothermal conditions.

The results of these tests are illustrated on Graphs 2, 3 and 4. The mode of action of phenothiazine is indicated in Figure 2.

The selection of the most effective inhibitor and knowledge of the induction period given are of paramount importance in designing a system. The results of the screening tests conducted are consistent with traditional inhibitor theory. They illustrate that, even at elevated temperatures, small quantities of chemical inhibitors can markedly increase the induction period prior to rapid polymerisation. For methyl acrylate, it is clear that phenothiazine is a more efficient inhibitor than *para*-methoxy phenol (the commonly used storage inhibitor for vinyl monomers). The major reason for not employing phenothiazine for storage conditions is that the colour of the monomer tends to be adversely affected. Ferrous contamination slightly reduces the induction period but this effect would be expected to be more evident over extended test periods. The effect of inert gas is also likely to markedly effect the efficiency of storage inhibitors over extended periods.

4. 'IN-SITU' REACTION INHIBITION

Most published literature on inhibitors relates to their use in preventing premature polymerisation during monomer storage. Virtually no data has been published on the use of inhibitors for quenching runaway reactions. Although the subject is complex and diverse, it is possible to design a safety system based on inhibition techniques. As with any other basis of safety, a systematic assessment of possible upset process conditions must be made such that the safety system is designed to cope with the worst case scenario. The nature of chain reactions is such that there are a wide range of contaminants capable of initiating the reaction at low concentrations (ie. peroxide formation in the monomer during storage, rust / iron from materials of vessel construction, acid or base contamination, inhibitor depletion during extended storage periods, etc.). All possible contaminants must be evaluated and considered during the experimental programme. One of the only items of published data on in-situ reaction inhibition relates to the quenching of a runaway acrylic acid polymerisation using a 10% volume of a 10% solution of copper (II) acetate⁶.

4.1 DATA COLLECTION FOR DESIGNING AN INHIBITION SYSTEM

As with all bases of safety, a thorough assessment procedure is required to evaluate the process and all conceivable maloperations. Once the worst case maloperation has been identified, an experimental programme of work should be undertaken to evaluate the characteristics of the process (ie temperature and pressure data) and the following tests performed to determine :

- a. The most suitable inhibitor (by performing screening tests with a set concentration of inhibitor in the monomer system under study at an isothermal temperature for a variety of inhibitors)
- b. The point during the runaway at which the inhibitor should be added. This point may be triggered by over temperature alarms, over pressure alarms or possibly by a viscosity alarm.
- c. The quantity of inhibitor to be added to quench the reaction and provide a sufficient induction period to allow cooling or emptying of the vessel contents before the inhibitor is consumed. It is recommended that sufficient inhibitor is added to provide a minimum induction period of 24 hours following the initial quench.
- d. The mode of inhibitor injection. If the reaction is rapid at the set point, the injection may need to be achieved by a suppression-type compressed gas system.
- e. The viscosity of the reacting system at the set-point in order to determine whether homogeneous inhibition in the vessel can be achieved. This may require an advanced dispersion system or may adequately be achieved by the reactor agitator (providing this is functioning at the set-point).

4.2 AN EXAMPLE OF IN-SITU REACTION INHIBITION

The styrene polymerisation process (initiated by 0.5 % wt/wt benzoyl peroxide) has been studied intensely as part of the DIERS round-robin tests⁷. Data for this reaction was collected from 19 different laboratories such that each piece of apparatus (mainly VSP apparatus), could be validated. Test data for the reaction gained using the Adiabatic Pressure Dewar Calorimeter system at Chilworth Technology is illustrated in Graph 5. The pressure Dewar apparatus⁵ is particularly well suited for such studies since :

- i. The sample size (800 g) is relatively large preventing problems associated with the addition of small quantities of reagents
- ii. The system is easily adaptable and can be connected to any number of addition devices
- iii. The low heat loss of the system allows direct simulation of plant scale heat loss conditions
- iv. The agitation system is reliable and robust

The styrene polymerisation reaction is also particularly well suited for such studies since :

- i. Much published work is available on the kinetics and mechanism of the reaction
- ii. Published work is also available on potential inhibitors for the polymerisation process

Data on potential inhibitors is available for many polymerisation systems and consultation of the literature to identify a suitable inhibitor will reduce the testing required in the selection process. For the purpose of inhibiting the styrene polymerisation, *tert*-butyl catechol (the standard storage inhibitor) has been used. The efficiency of this material as a storage inhibitor has previously been determined^{8,9}.

The Adiabatic Dewar apparatus was modified to include an inhibitor dispersion system (Figure 3). The inhibitor injection was triggered by a temperature alarm and used a compressed air hydraulic system to disperse the inhibitor throughout the sample. The first example of 'in-situ' inhibition (Graph 6) illustrates the effect of the addition of *tert*-butyl catechol (in a 5:1 molar ratio with the initial quantity of initiator present) at 130°C.

It is clear that the reaction is inhibited severely by this relatively small injected quantity. The system is suitably non-viscous to allow homogeneous mixing of the inhibitor in a short period of time. It should be noted that the reaction is not stopped at this point but there are sufficient inhibitor radicals to mop up the monomer radicals. At this temperature however, further radicals are thermally

induced and the reaction slowly continues to exotherm. Providing the induction period is long enough, corrective measures should allow the reaction to be brought under control before it runs away for a second time. If the set point is low, this will prevent any pressurisation of the vessel, setting of the reaction mass and need to treat vented materials. A second example illustrates the effect of having the set point too high (Graph 7) - causing the induction period to be considerably shorter and the reaction to runaway for a second time (giving rise to vapour pressure hazards).

5. CONCLUSIONS

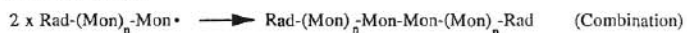
Polymerisation reactions can be inhibited, even under runaway conditions. The experimental strategy for evaluating a suitable system involves :

- a. Determining whether the reaction can be inhibited.
- b. Selecting a suitable inhibitor (either experimentally or from literature)
- c. Determining the required concentration of inhibitor to provide a sufficient induction period for plant personnel to take corrective action before the second runaway begins to occur. Also determining the optimum conditions for inhibition (set point of injection, stirring requirements etc.)
- d. Designing a suitable injection and mixing system to provide homogeneous inhibition. This includes evaluating whether viscosity increases make inhibition impossible.

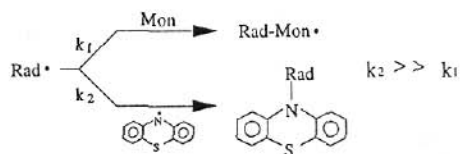
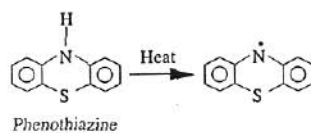
Inhibition systems could be employed in any situation where reactive monomers are stored or used (ie. in storage, road tankers, reaction vessels - for bulk, suspension or emulsion processes). With increasing pressure on companies to reduce environmental emissions, the technique of reaction inhibition (a total containment technique), provides one potential solution to the problem.

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Figure 1 : Free Radical Polymerisation**INITIATION STEPS****PROPAGATION STEPS****TERMINATION STEPS**

Disproportionation can also occur to giving saturated and unsaturated molecules

Figure 2 : Phenothiazine Inhibition

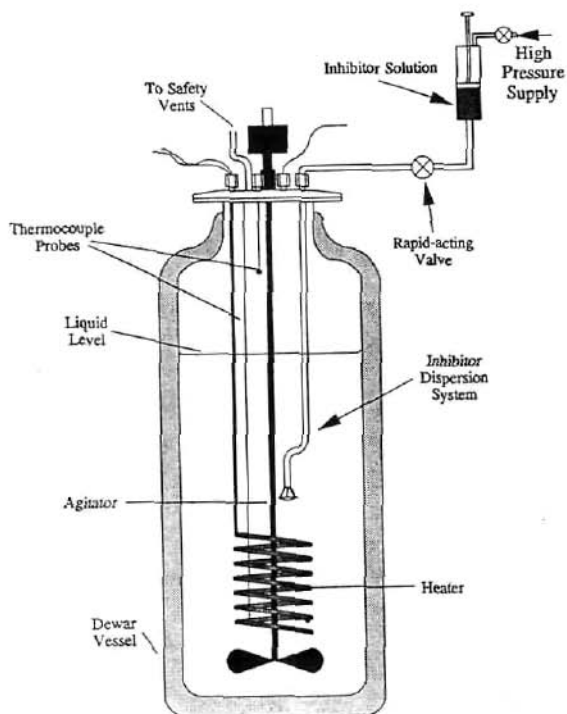
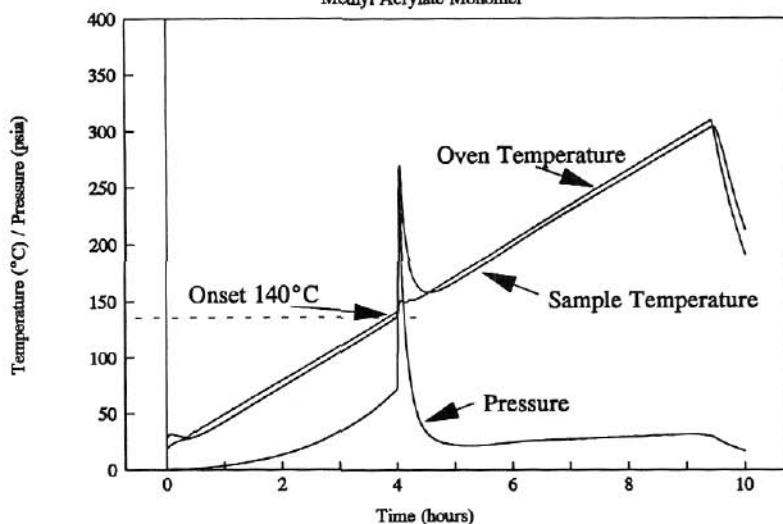


FIGURE 3 : Pressure Dewar Calorimeter fitted with Inhibitor Dispersion System

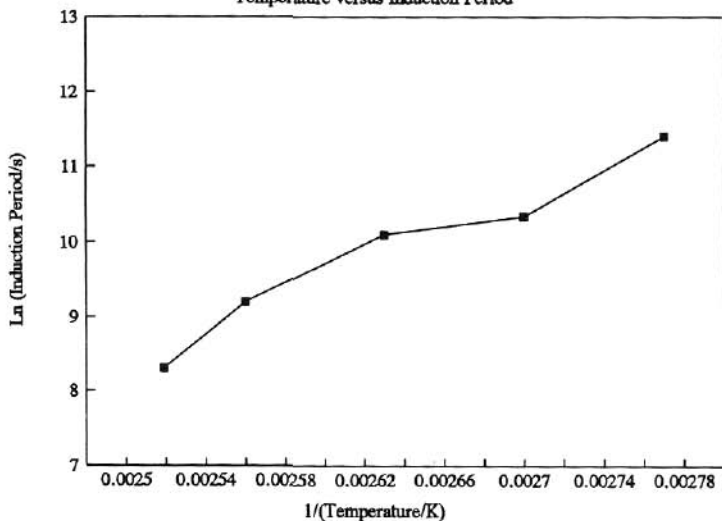
GRAPH 1 : CARIUS TUBE SCREENING TEST

Methyl Acrylate Monomer

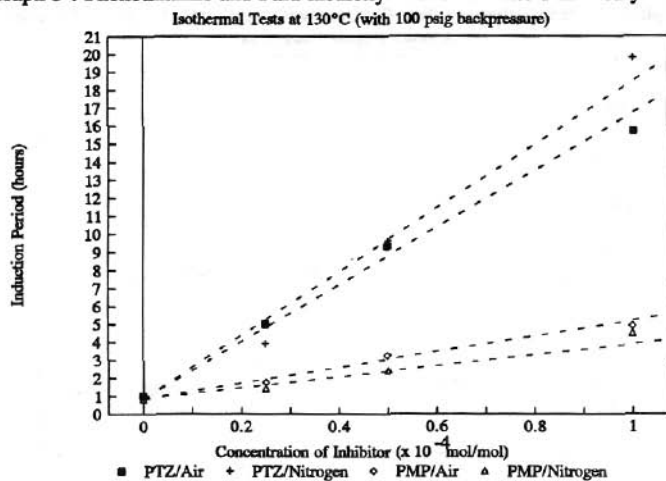


GRAPH 2 : MONOMER STABILITY (Methyl Acrylate)

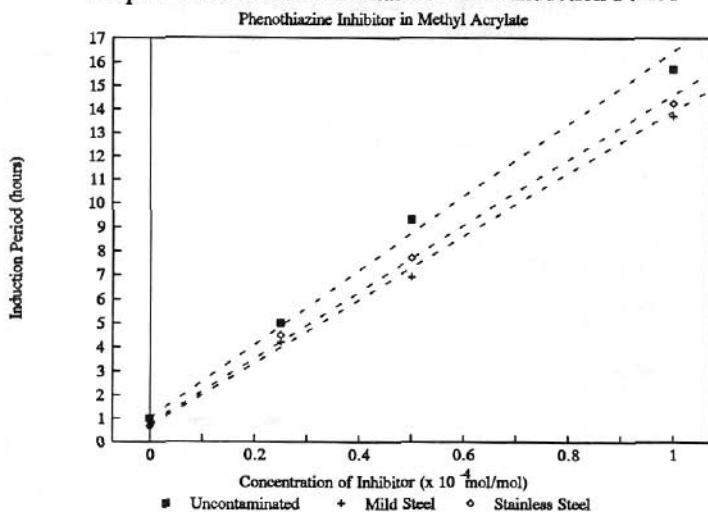
Temperature versus Induction Period

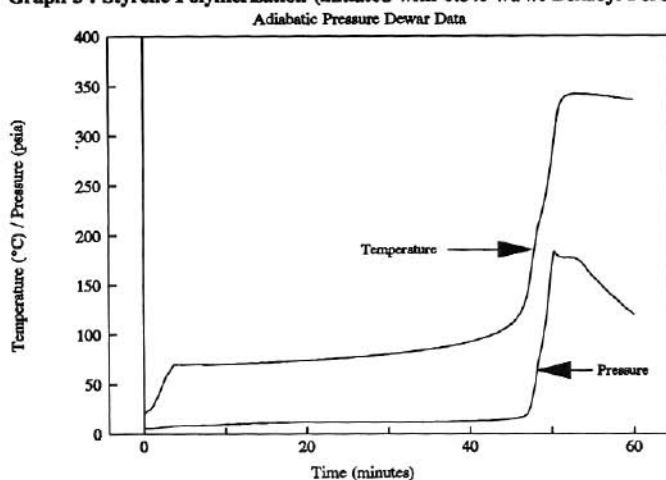
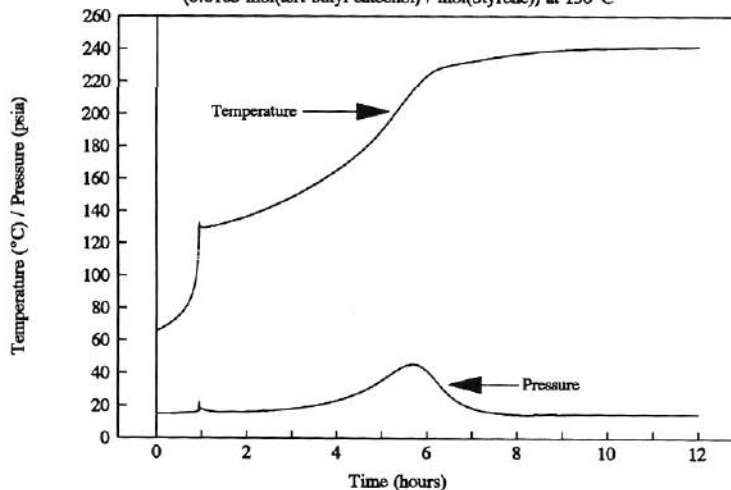


Graph 3 : Phenthiazine and Para-methoxy Phenol Inhibitors in Methyl Acrylate



Graph 4 : The Effect of Contaminants on Induction Period



Graph 5 : Styrene Polymerisation (Initiated with 0.5% wt/wt Benzoyl Peroxide)**Graph 6 : An Inhibited Styrene Polymerisation**(0.0105 mol(*tert*-butyl catechol) / mol(Styrene)) at 130°C

Graph 7 : An Inhibited Styrene Polymerisation(0.0105 mol(*tert*-butylcatechol) / mol(*Styrene*)) at 160°C