CHARACTERIZATION AND SAFE HANDLING OF REACTIVE INITIATOR SOLUTIONS[1]

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The thermal stability of initiators used in free radical polymerizations has been well documented. Initiators are often used in solutions, with relatively long feed periods to help control the heat of polymerization. In some cases, the stability of the initiator solutions is limited, especially at higher concentrations, and runaway reactions can potentially be severe. This paper reviews the chemical reactivity of concentrated initiator solutions and considers PHA studies and feed tank design to help ensure safe handling and manufacture.

INTRODUCTION

DuPont has supplied specialized coatings to automotive manufacturers for over 75 years, beginning with the development of nitrocellulose-based coatings in the 1920's [1]. These coatings are used to protect against vehicle corrosion and to help improve vehicle appearance. Automotive coatings based on many synthetic polymer resins are now available. Acrylic polymers, in particular, have been used for many years due to their many outstanding properties, including chemical resistance, durability, clarity, film strength, and appearance [2].

Acrylic Polymerization

Acrylic polymers are based on esters of methacrylic and acrylic acids, which are characterized by the following structure, where R_1 is either H (acrylates) or CH_3 (methacrylates):

$$CH_2=C(R_1)\text{-}COO\text{-}R_2$$

Acrylic monomers react to form high molecular weight acrylic polymers via free radical polymerization [3]. Initiators, such as many organic peroxides, thermally decompose to form primary free radical fragments. The free radicals react with monomer molecules and quickly grow into long polymer chains. The rate of polymerization is very rapid at typical reaction temperatures (100-150°C) and is highly exothermic, with the heat of polymerization in the range of 50-75 kJ/mole of monomer. Solvents are normally used to transfer this heat through condenser cooling of solvent vapors. In addition, reactants are usually added to the reactor over extended periods to reduce the peak reaction exotherm for safer operation. The hazards

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associated with acrylic polymerization can be minimized through safe polymer formulation practices, reactor design and operating standards, and hazard screening procedures to match polymer formulas with reactor capability. A typical acrylic reactor system, consisting of reactor, feed tanks, condenser, prefilter tank, and shortstop system is shown in Figure 1.

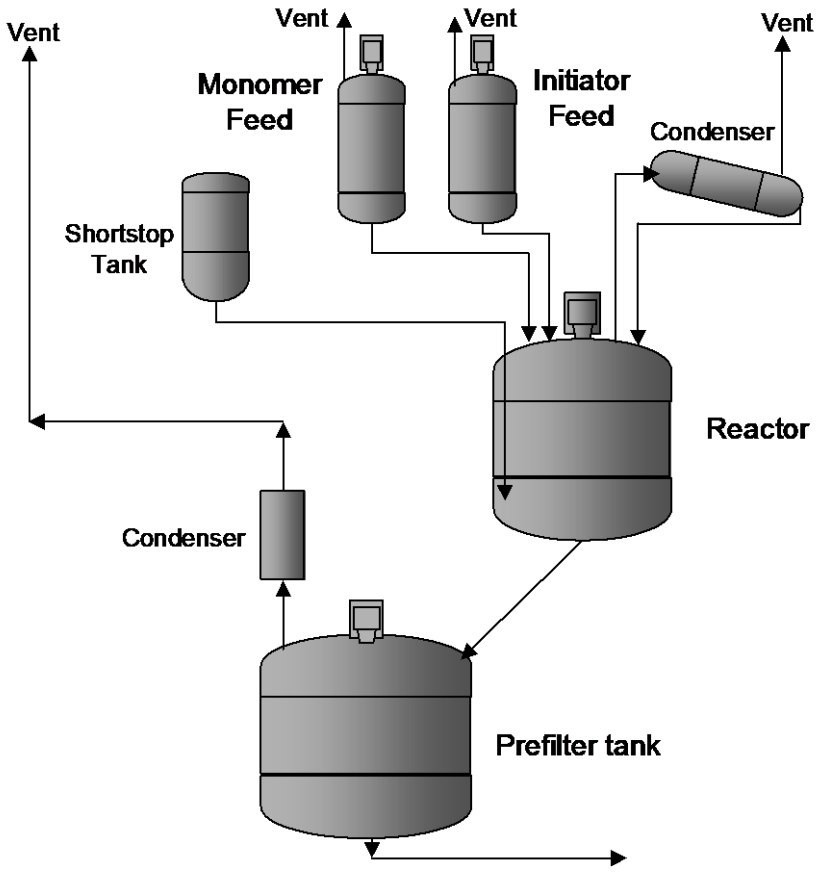

Figure 1. Typical Acrylic Polymerization Reactor System

Free Radical Initiators

Initiators commonly used to start acrylic polymerizations include organic peroxides and nitriles [3], which decompose thermally to form two free radical fragments and a gaseous byproduct such as carbon dioxide or nitrogen. For peroxides, the general reaction is:

$$R - O - O - CO - R' \rightarrow RO\cdot + R'\cdot + CO_2$$

Depending on side reactions and other conditions that affect initiator efficiency, each free radical can react with monomer to form polymer radicals that continue to react with monomer, forming long polymer chains. Each initiator has different thermal decomposition characteristics which determine its usefulness for polymerization and the specific requirements for safe handling and storage. The heat of reaction is typically 100-200 kj/mol. Several initiators are listed in Table 1.

The two most important thermal properties of initiators are the self-accelerating decomposition temperature (SADT) and the half-life. The SADT is the lowest temperature at which self-accelerating thermal decomposition may occur for the initiator in its largest-size shipping container. In the United States, for example, SADT provides data on commercial packages with a capacity of 225 liters. SADT is defined as the minimum temperature at which a specific package will exhibit a 6°C or more temperature rise above the thermostat within a period of seven days or less. The SADT therefore determines the safe handling and storage requirements for the initiator, such as ambient or refrigerated storage. The half-life is the time required for one-half of the initiator to decompose at a specific temperature and is a measure of how rapidly the initiator reacts when heated. The half-life therefore determines the usefulness of the initiator at the desired polymerization temperature along with other factors.

Name	Abbreviation	SADT (°C)
2,2'-azobis(methylbutyronitile)	AMBN	50
cumene hydroperoxide	CHP	82
di-t-butyl peroxide	DTBP	80
t-butyl peroxy acetate	TBPA	74
t-butyl peroctoate	TBPO	42
t-butylperoxypivalate	TBPP	29

Table 1. Common Free Radical Initiators

Reactor Safety Program

Given the potential hazards of acrylic and other industrial polymerizations, a comprehensive polymer Reactor Safety program has been implemented worldwide at all DuPont coatings polymer plants, with the goal of achieving completely safe polymer manufacturing [4]. One of the key activities of the Reactor Safety program is the mandatory, routine safety screening of all acrylic resin manufacturing formulas, prior to releasing these formulas for production in plant equipment [5]. Safety screening of acrylic resins includes checking the formula for inherent safety considerations, computer simulation to evaluate reaction exotherm and runaway reaction emergency vent sizing, and reaction calorimetry, as required. In all cases, no products may be produced in resin manufacturing equipment unless Reactor Safety professionals have conducted the required safety screening and issued written approval for manufacture.

HAZARDS OF INITIATOR SOLUTIONS

As discussed previously, monomer and initiator are generally added to a polymerization reactor slowly over an extended time to limit the peak reaction exotherm and help ensure safe operation. Separate monomer and initiator feeds are used, and feed times in semi-batch processes typically vary from one to ten hours [3]. Initiator feeds can contain pure initiator, or more often, mixtures of initiator and solvent. The solvent is required to dissolve solid initiators and also helps with control of feed rates when small amounts of initiator are used. Initiator feed solutions therefore usually range from 10 to 100% concentration, depending on the initiator and the polymer formula requirements.

The thermal stability of initiator solutions at the feed temperature, typically near ambient temperature, is determined by the type of initiator and the amount of dilution. Warnings, such as the following, can be found in vendor literature [6]:

> *More concentrated solutions (10% or higher), which are sometimes used to feed initiators into a process, can present a hazard if heated or exposed to hot surfaces. The heat liberated on decomposition… can further raise the temperature of the solution which, under some conditions of solvent, concentration and heat loss or cooling, can become self-heating; runaway reaction can occur.*

Clearly, the thermal stability of the initiator solution must be much greater than the required feed time, including the possibility for any extended delays due to mechanical or other operating problems. This is especially important if the solvent must be heated to higher temperatures in order to completely dissolve solid initiators. Higher concentration initiator feed solutions, depending on the thermal decomposition characteristics of the initiator at the feed temperature, can present high risk for a facility and must be carefully evaluated to ensure safe processing. In some cases, cooling capability and other equipment must be installed on feed vessels to maintain safe processing temperatures. In all cases, emergency relief requirements must be carefully evaluated to protect against runaway reactions, which can very rapidly increase vessel temperature and pressure due to initiator decomposition and release of gaseous byproducts. Some approaches for evaluating the stability of concentrated initiator solutions are discussed in the following sections.

Thermal Stability

While not recommended for rigorous analysis and design due to simplifying assumptions, the following equation based on an energy balance [7] can be used to illustrate the thermal stability of initiator feed solutions at different concentrations and temperatures:

$$T_{ad} - T_o = \Delta H_r \, I_o \, [1 - \exp(-k_d \, t)] \, / \, (m \, c_p) \qquad (1)$$

where $T_{ad} - T_o$ is the adiabatic temperature rise, ΔH_r is the heat of decomposition for the initiator, I_o is the initial initiator weight, k_d is the decomposition rate constant for the initiator, m is the total weight of the solution, and c_p is the heat capacity of the solution. This equation can be programmed in a spreadsheet to determine how solution temperature varies with time under adiabatic conditions. The decomposition rate constant can be determined using half-life data available from most initiator vendors, and the heat of decomposition is available for some initiators or can be estimated. More rigorous analysis would consider heat losses and other factors that would affect the overall temperature rise [7]. In all cases, an effective process safety management program, including process hazard analysis, would be required to ensure the safety of the process [8,9].

Figure 2 shows a typical result using Equation (1) for solutions of AMBN (see Table 1) in solvent. For a 20% solution at 37.8°C (100°F), the temperature rise is very slow, increasing less than 5°C over 48 hours. For the same period, the temperature rise is about 10°C and over 25°C for 30% and 40% solutions, respectively. The rate of temperature increase for the 40% solution is also rising very quickly as the temperature approaches 65.5°C (150°F), indicating self-

accelerating reaction behavior. While the temperature increase during a feed process of up to 10 hours at 37.8°C is small, any production problems which would delay more concentrated initiator feeds for extended periods would require careful monitoring of the feed tank temperature. Figure 2 also shows the temperature rise for a 40% solution at 43.3°C (110°F). In this case, the temperature increases fairly rapidly, rising to 65.5°C in about 18 hours. Using the time required for the solution temperature to rise to 65.5°C to approximate the time to thermal runaway, the effect of different initiator concentrations and initial feed temperatures can be estimated, as shown in Figure 3. In this figure, the time to runaway is shown for 20%, 30%, and 40% AMBN mixtures. Similarly, Figure 4 shows the time to runaway for several initiators at a 40% concentration. If the feed vessel temperature is too high in many cases, due to process conditions, preheating to help dissolve initiator, or a hot day, careful monitoring of the temperature would be required, and cooling capability or other process safeguards may be required to provide an adequate margin of safety.

Calorimetry

Reaction calorimetry is recommended for measuring the thermal stability of reactive materials when data for detailed hazard analysis and design, including emergency vent sizing, is required [7]. Figure 5, for example, shows the temperature results of a Reactive System Screening Tool (RSST®) calorimeter test for a 47% solution of AMBN in toluene, using a 0.5°C/min. heatup rate and a pad pressure of 100 psi to prevent solvent boiling. Figure 5a shows the reaction starts around 65-70°C, with the temperature rising to about 220°C in a short time. The maximum rate of temperature increase exceeds 3000°C/min., as shown in Figure 5b, indicating that a very strong runaway reaction can occur for this solution. The maximum rate of temperature rise for different concentrations of two initiators is shown in Figure 6. Significantly higher maximum temperature rates occur at higher initiator concentrations, with rates exceeding 3000°C/minute.

Due to the increasing temperature and to the release of gaseous byproducts released during initiator decomposition, vessel pressure can also rise rapidly. Figure 7, for example, shows the pressure results for the 47% AMBN in toluene RSST test. As shown in Figure 7a, the pressure rises very rapidly from about 120 psi to over 180 psi in just a few minutes. The maximum rate of pressure increase, as shown in Figure 7b, is over 2000 psi/min, again indicating a very strong runaway reaction. Unless the feed vessel is adequately protected for pressure relief, a catastrophic process incident could occur. The maximum rate of pressure rise for different

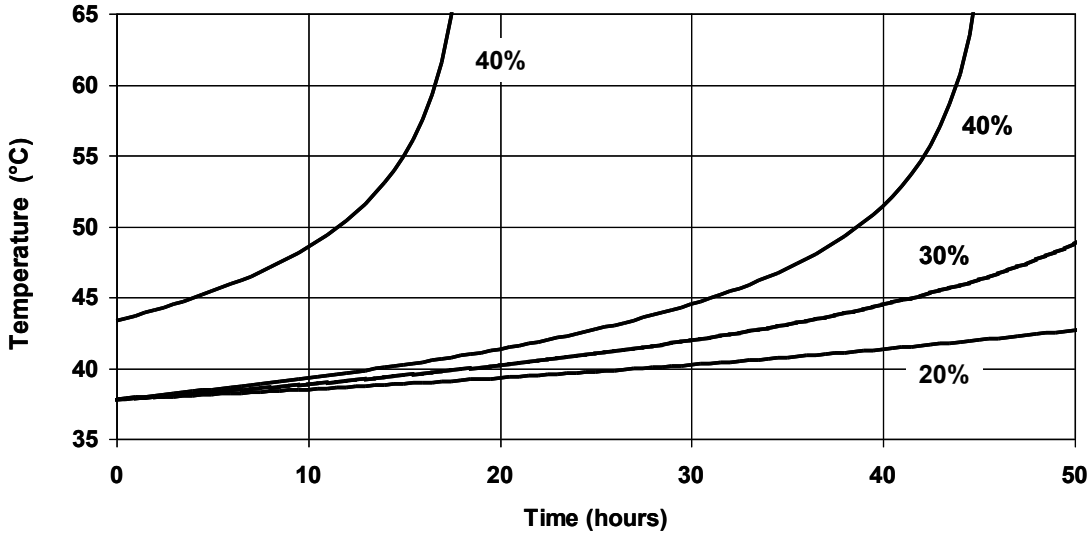

Figure 2. Calculated Thermal Stability of AMBN Solutions

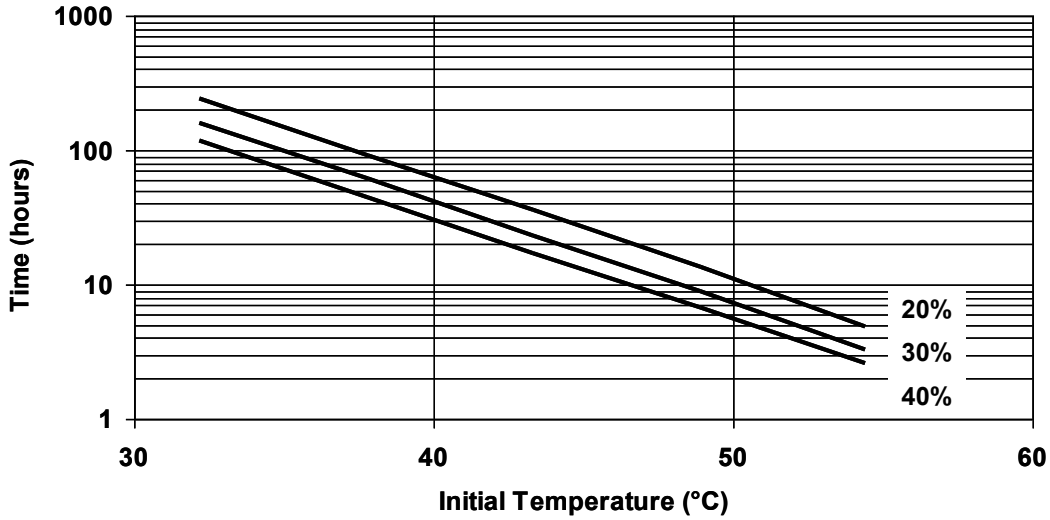

Figure 3. Calculated Thermal Stability of AMBN Solutions (time to runaway at 65.5°C)

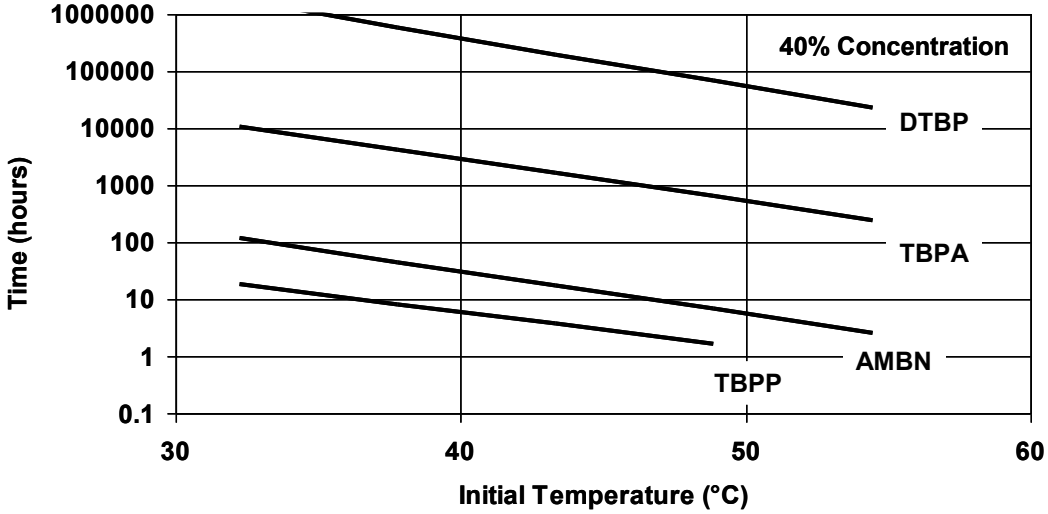

Figure 4. Calculated Thermal Stability of Initiator Solutions (time to runaway at 65.5°C)

concentrations for several initiators is shown in Figure 8. As expected, significantly higher maximum pressure rates occur at higher initiator concentrations, with rates exceeding 5000 psi/minute.

Using calorimetric data and two-phase flow (DIERS) analysis [10,11], it is possible to evaluate the emergency vent requirements for feed vessels. Figure 9 shows, as an example, the emergency vent sizing requirements [12] for a specific 800-gallon feed vessel at different AMBN concentrations. In this case, the feed vessel would require at least a 6-foot diameter emergency vent in order to safely use 40% initiator solutions. This results from the thermal stability of the high concentration initiator solution and the rapid temperature and pressure increase possible during thermal runaway. Since the emergency vent size is too large to be practical for a small feed vessel, either reformulation of the polymer process is required or additional hazards analysis is needed to ensure a safe process. Some feed tank design considerations for safe operation of initiator vessels containing concentrated initiator solutions are discussed in the following section.

Feed Tank Design Considerations

Safe process design and operation for concentrated initiator solutions requires a comprehensive PSM program [8] and, in many cases, a specialized technology-based process safety effort such as the Reactor Safety program described in Section 1.3. PHAs [9] must be conducted that evaluate the specific polymer process requirements and the thermal characteristics of the initiator solutions being considered, in order to develop appropriate process safeguards and risk management plans. Hazards analysis should normally include calorimetric test data and consider both routine and emergency conditions. Some examples are provided below, which should not be considered as sufficient in themselves to ensure process safety, but rather illustrate some of the factors that PHA teams would include in more detailed reviews as part of their PSM efforts.

Process Hazards Analysis

Several PHAs have been conducted for concentrated initiator solutions, using whatif/checklist, HAZOP, and other methodologies to help ensure safe feed vessel design and operation. Since the major focus for these systems relates to high temperature or to production delays that can result in extended times for the initiator solution in the feed vessel, HAZOP results can be very helpful. Some of the factors identified in the HAZOP that can lead to high temperature in the feed vessel, for example, include:

- Initiator decomposition
- Agitation (heat or mechanical friction)
- Too much electrical heat (if used to help dissolve solid initiator)
- High solvent temperature (if preheated to help dissolve solid initiator)

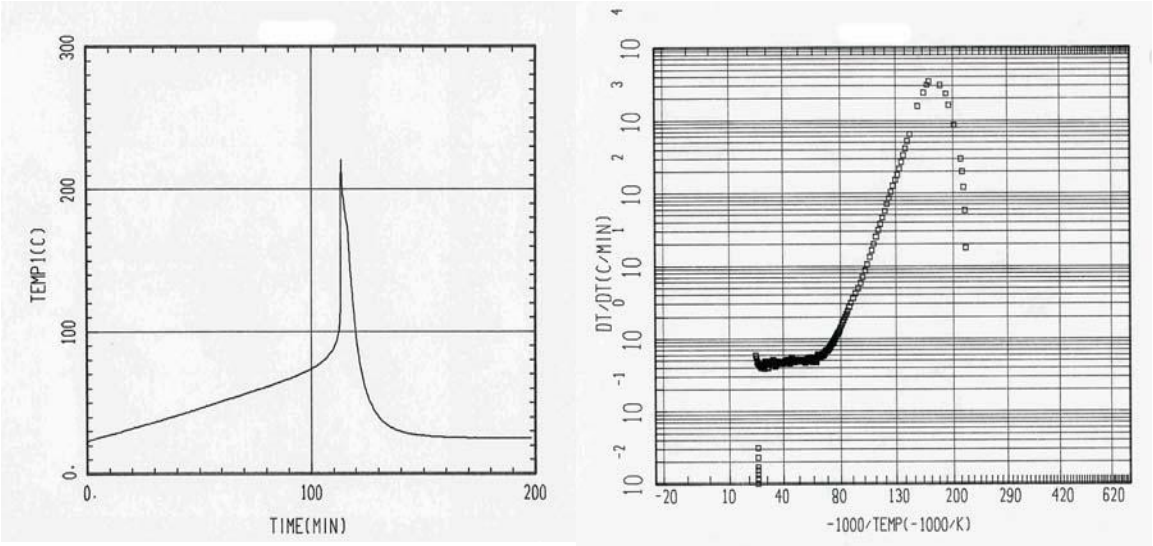

Figure 5. RSST Calorimeter Result for 47% AMBN in Toluene, (a) Temperature, (b) Rate of Temperature Increase

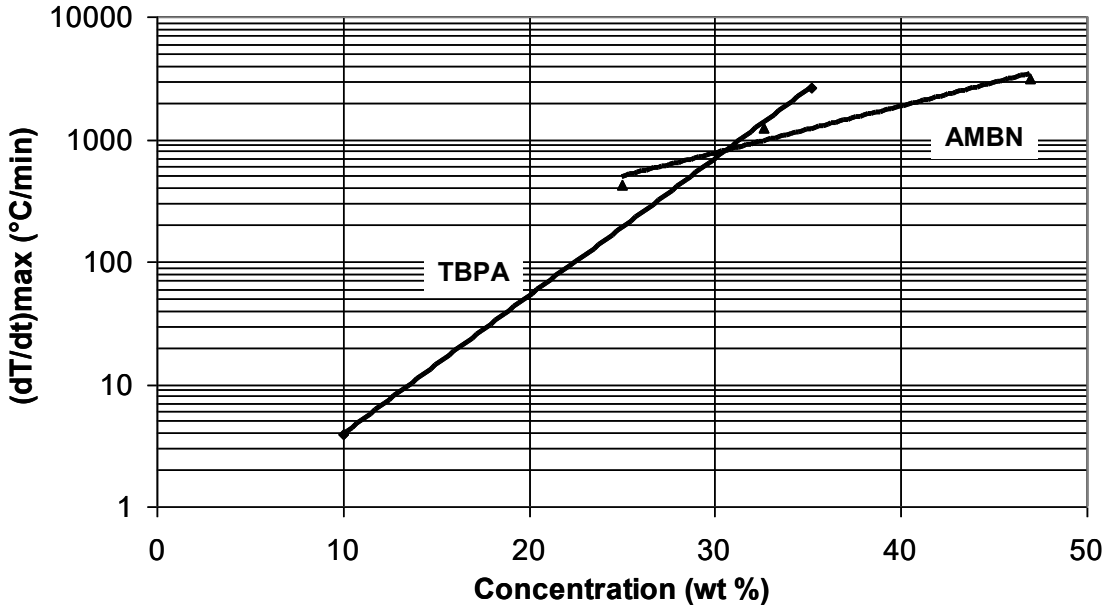

Figure 6. RSST Calorimeter Results for Initiator Solutions – Maximum Temperature Rate

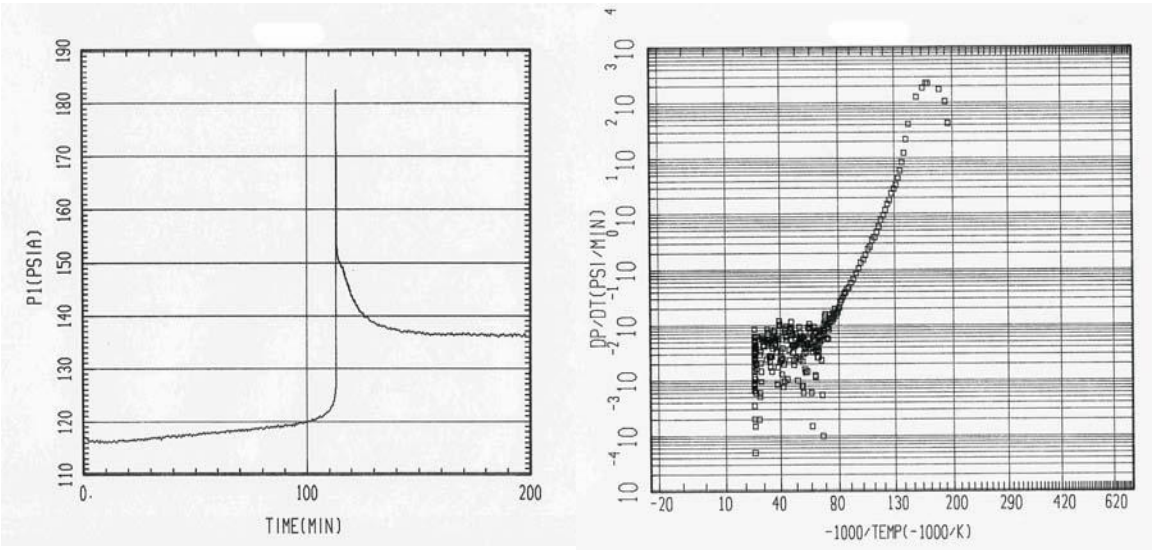

Figure 7. RSST Calorimeter Result for 47% AMBN in Toluene, (a) Pressure, (b) Rate of Pressure Increase

- Pump overheating
- High ambient or facility temperature
- Mischarge or contamination of initiator or solvent
- External fire.

Similarly, some of the factors that can lead to production delays include:

- Mechanical failure of the feed system (e.g., pump failure)
- Reactor not available to start the feeds

- Electrical outage or loss of other utilities
- Computer system failure
- Plugged feed line
- Safety interlock activated
- Raw material inventory shortage.

In particular, the external fire case is important, as it can result in much higher temperatures in the feed vessel than normally expected, leading to possible thermal runaway in shorter times.

Some Design Options

Several initiator feed vessel safeguards can be identified using PHAs to protect against high vessel temperature or extended production delays. Some examples include

Cooling – The feed vessel temperature can be maintained by circulating the initiator solution through a heat exchanger, by jacket cooling, or by internal cooling coils.

Transfer – The contents of the feed vessel can be automatically transferred to a larger tank, via bottom venting [13] for example, or fed more quickly to the reactor. In this case, the status of the receiving tank or reactor must be carefully evaluated to ensure that the transferred feed solution would not create a hazard in the new location.

Dilution – The feed solution can be automatically diluted to a lower concentration mixture that has smaller emergency vent requirements. Significant cooling may also result, depending on the amount of solvent added for dilution.

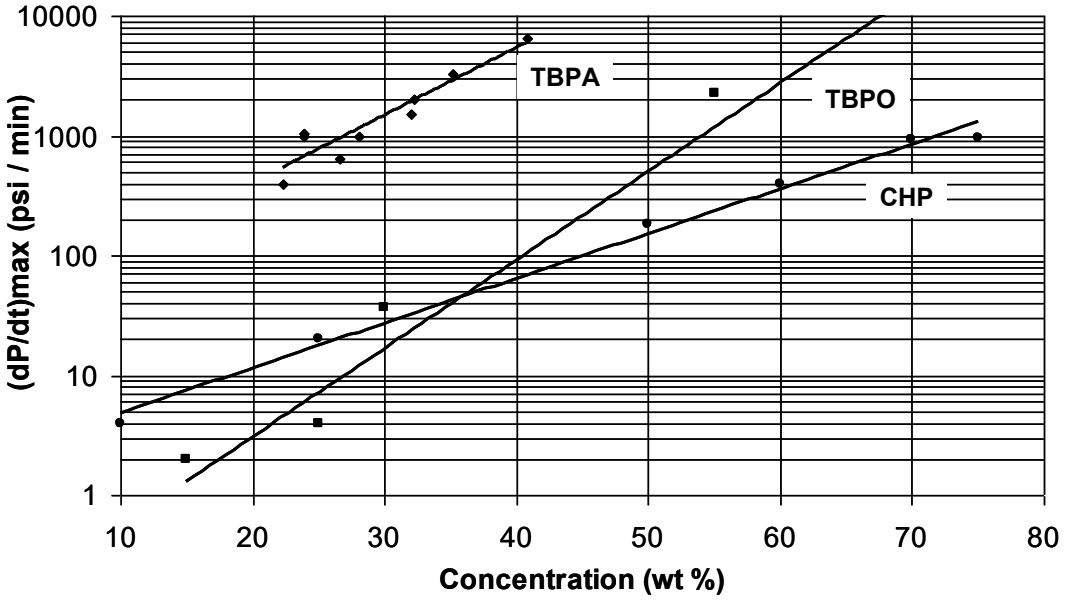

Figure 8. RSST Calorimeter Results for Initiator Solutions – Maximum Pressure Rate

More than one of these approaches, in addition to proper emergency vent sizing, may be needed to ensure safe processing based on the specific initiator solutions required for the process. In addition, minimal instrumentation requirements include:

- Redundant, independent temperature measurement
- High temperature and high-high temperature alarms

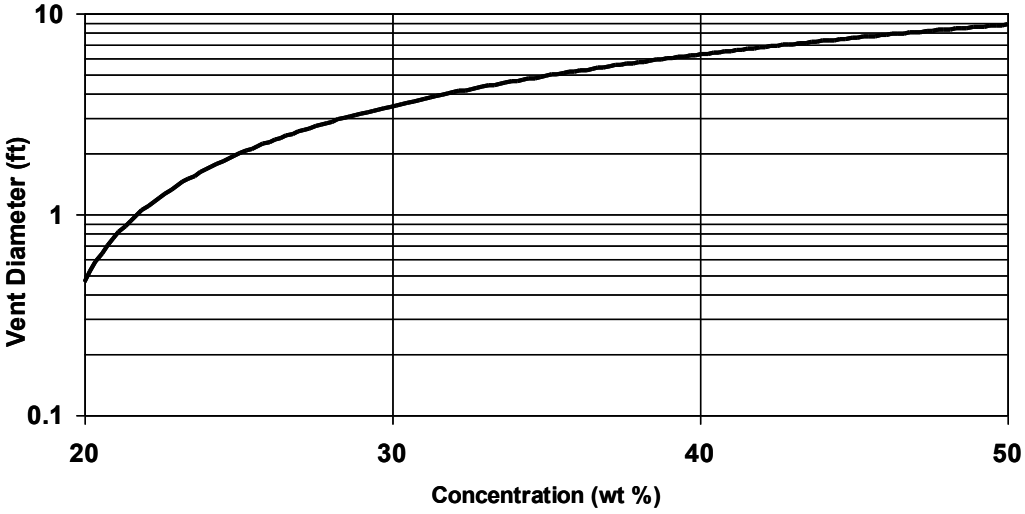

Figure 9. Example Emergency Vent Requirements for 800-gallon Feed Vessel (AMBN)

Example Design

An acrylic polymer formulation required use of a 40% initiator solution, with an impractical large emergency vent requirement for an existing initiator feed vessel, similar to the example discussed in Section 2.2. The feed vessel would also need capability for dissolving solid initiator, including preheating solvent prior to initiator addition and limited heating of the solution after addition in order to account for the large temperature drop resulting from the heat of dissolution. Some of the primary safeguards installed on the initiator vessel, based on PHAs and calorimetric testing, included:

- Pressure-rated vessel, with largest practical vent size connected to a properly-designed and inerted catch tank with an elevated stack
- Redundant, independent temperature measurement and alarms
- High tank level and weight alarms and interlocks
- External heat exchanger for preheating solvent prior to initiator addition and electrical tape on the vessel for slow heating after initiator addition, with temperature instrumentation and alarms, loss of agitation alarm, and procedures to ensure that initiator is properly dissolved
- Cooling of the feed vessel via circulation through an external heat exchanger
- Capability to feed the initiator solution to the reactor more quickly under an emergency procedure designed to ensure that runaway reaction in the reactor wouldn't result

- Automatic, independent interlock for transfer of the feed solution to a "quench" vessel containing sufficient solvent to dilute the solution to a maximum of 20% initiator, with an adequately-sized emergency vent connected to the catch tank.

Many additional safeguards, including vessel inerting, vessel load cells, alternate loading equipment, additional interlocks, etc., have also been installed to ensure safe operation. A simplified schematic of the feed vessel system is shown in Figure 10.

Since the emergency vent requirements of the 40% initiator solution are very large, and the feed tank is not large enough for internal dilution, the quench tank provides the ability to automatically dilute the feed solution to a safe concentration. The quench tank is a pressure-rated vessel designed to receive the contents of the initiator feed vessel in an emergency, primarily high temperature in the feed vessel, and is equipped with temperature, pressure, and level instrumentation. The quench tank contains enough compatible solvent to cool and dilute the feed solution to a maximum of 20% initiator, which can be safely vented to a catch tank if reaction continues after dilution. The contents of the feed vessel can be transferred to the quench tank in three ways:

- A high integrity, independent interlock transfers the feed solution automatically when a preset temperature in the feed vessel is reached
- A valve in the transfer line is opened manually by an operator
- A fusible link in the transfer line is broken, in case of fire.

The multiple modes of operation are expected to provide high reliability.

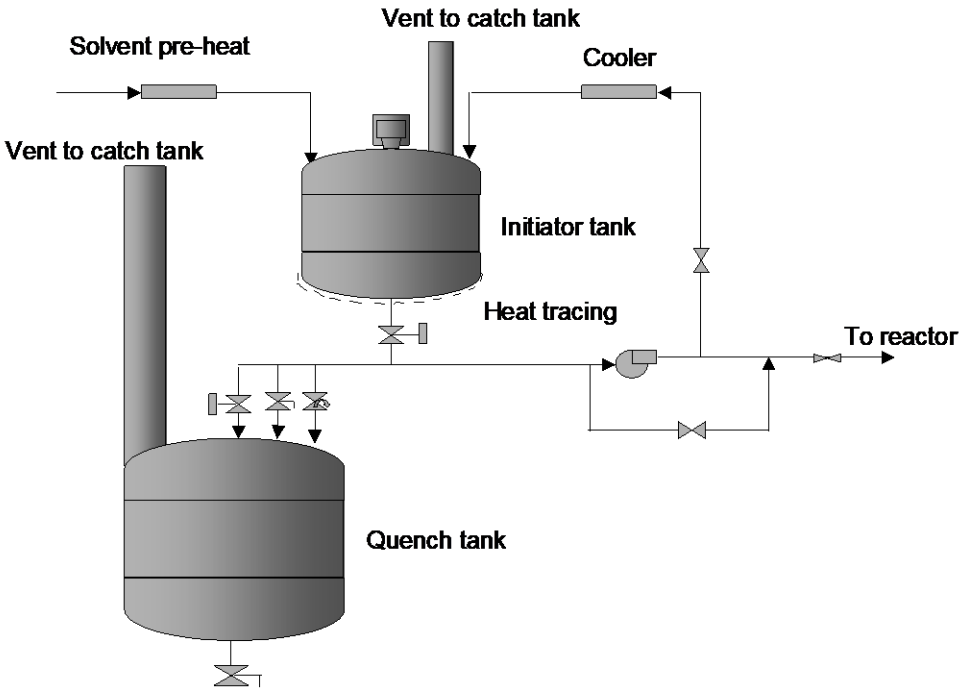

Figure 10. Simplified Schematic of Initiator and Quench Vessels

Summary

Initiator feed solutions are often used in acrylic polymerizations to reduce peak reaction exotherms, to dissolve solid initiators, and to provide good feed rate control. Many initiator solutions, though, can be hazardous as well, especially at higher initiator concentrations, depending on the thermal behavior of the initiator. While the hazards of initiators are generally well understood and managed, the hazards of concentrated initiator solutions are not as well characterized. In all cases, the thermal stability of the initiator feed solution must be much greater than the required feed time, providing a suitable safety margin to account for possible operating delays. The hazards of these solutions can be studied using simple equations and measured using calorimetric analysis to establish the thermal stability and runaway reaction behavior. Since the maximum rates of temperature and pressure rise can exceed several thousand °C/min or psi/min, runaway reactions can be very strong and emergency vent requirements can be very large. Data can be used by PHA teams, as part of a comprehensive PSM program, to design and operate safe feed vessel processes, both preventing and safely mitigating potential hazards.

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