

# Safe Formulation and Manufacture of Acrylic Resins

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*DuPont*

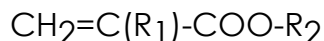
## ABSTRACT

Polymerization of acrylic resins is an inherently hazardous process, due to high heats of polymerization, the potential for uncontrolled runaway reactions, and the flammable and toxic properties of many materials. Following two process incidents in 1975, a comprehensive resin Reactor Safety program was implemented globally with the goal of achieving completely safe resin manufacturing. The purpose of this paper is to describe how resin formulation guidelines, safety screening procedures, and reactor design and operating standards help ensure safe formulation, scale-up, and manufacture of acrylic resins.

## INTRODUCTION

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

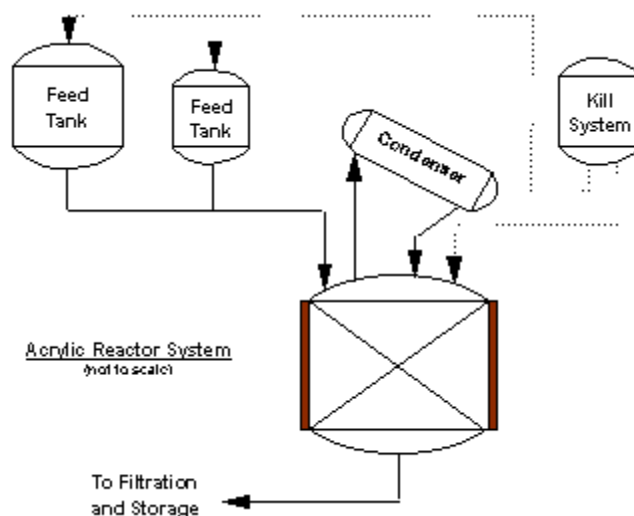
Acrylic monomers are esters of methacrylic and acrylic acids, which are characterized by the following structures, where R<sub>1</sub> is either H (acrylates) or CH<sub>3</sub> (methacrylates):



Acrylic monomers react to form high molecular weight acrylic resins via free radical polymerization [3]. Initiators, such as many organic peroxides, thermally decompose to form primary free radical fragments. These fragments 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), with every 10°C increase over the normal temperature approximately doubling the reaction rate. Free radical polymerization 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. A typical acrylic reactor system, consisting of reactor, feed tanks, condenser, and kill system is shown in Figure 1.

Failure to remove the reaction exotherm can lead to uncontrolled runaway reactions. Characterized by accelerating self-heating, runaway reactions generally result in rapid and sharp increases in reactor temperature and pressure. In severe cases, the reactor pressure rating can be exceeded, leading to catastrophic reactor failure and the possible release of toxic or flammable materials. Many conditions contribute to the occurrence of runaway reactions, including improper resin formulation, inadequate condenser design or operation, build-up of reactants due to processing problems, and mischarge of materials. Fortunately, these hazards can be minimized through safe resin formulation practices, reactor design and operating standards, and hazard screening procedures to match resin formulas with reactor capability.

Figure 1. Typical Acrylic Reactor System



## REACTOR SAFETY PROGRAM

In 1975, a runaway reaction occurred during the processing of an acrylic resin when a fouled reactor condenser was unable to remove the reaction exotherm. The contents of the reactor were ejected to a small catch tank, which overflowed, releasing hot resin and flammable vapors on the ground. The resulting vapor cloud ignited, seriously injuring one worker. This incident, closely followed by another serious process incident, led to the formation of a comprehensive resin Reactor Safety program with the goal of achieving completely safe resin manufacturing [4]. Reactor Safety has since been implemented worldwide at all DuPont Automotive resin manufacturing plants, with each plant subject to a uniform set of process safety standards. Resin process engineers at each plant, together with process safety, resin technology, and process control professionals, form a Reactor Safety Team, which develops and works on all program activities. With strong upper management commitment and support, Reactor Safety has worked to achieve process safety and resin manufacturing excellence for 20 years.

Major activities of the Reactor Safety program are listed in Table 1. Many of these activities are now part of plant process safety systems required to meet OSHA Process Safety Management (PSM) regulations [5], especially process technology, operating procedures, training, auditing, management of change, and incident investigation elements. Reactor Safety has long required a reactor design change authorization procedure, for example, that is now integrated with plant PSM management of change practices. Other Reactor Safety activities supplement PSM requirements. Reactor systems, for example, are audited using a specialized Reactor Safety checklist to evaluate resin manufacturing operations in addition to plant PSM audits and Process Hazards Analysis reviews. All current Reactor Safety design, training, and operating requirements are documented in Standards and Training Manuals, which are periodically updated as needed. These Reactor Safety requirements, in combination with a strong Process Safety Management program, contribute to safer resin manufacturing operations. Several of these practices, intended to achieve safe formulation, scale-up, and manufacture of acrylic resins, are discussed in more detail in the following sections.

## Resin Formulation

Early in the history of the Reactor Safety program, it was apparent that a group of guidelines aimed at assisting chemists and process engineers in developing safe resin formulas and achieving safe process scale-up was necessary. These guidelines were developed jointly by a committee of resin chemists, process engineers, and plant resin engineers with the purpose of promoting safe operation of pilot plant and commercial resin manufacturing

equipment, while at the same time allowing maximum flexibility in the use of commercial production equipment for making new resins. Each guideline includes explanatory material describing the reasoning behind the guideline to help ensure that all technical personnel involved in resin formulating, development, and scale-up understand key safety parameters related to resin manufacture. Guidelines have been developed for all resin formulas, not just acrylic resins, and have been continuously updated based on the introduction of new resin technologies and improved operating and technical experience. Potential benefits of following the resin design guidelines include fewer process incidents resulting from poor formulas, less scale-up effort, and better manufacturing consistency and resin quality.

Table 1. Major Reactor Safety Program Activities

<b>Activity</b>	<b>Description</b>
Standards Manual	Development of standards and best practices for reactor system design, resin formulating, product scale-up, and operating procedures.
Project Reviews	Extensive hazard review of all resin-related projects that could affect the safety of resin manufacturing, including Process Hazards Analysis.
Design Change Reviews	Review of all design changes to process equipment to ensure conformance with Reactor Safety standards and safe operating practices.
Audits	Use of a specialized checklist to evaluate conformance with Reactor Safety standards for equipment installation, training, and procedures.
Training Manual	A comprehensive training program with sections on resin chemistry, process hazards, and Reactor Safety standards, including specialized safety videos.
Resin Screening	Application of resin formulating and process safety guidelines to ensure the suitability of reactors for safe manufacture of new and modified resins.
Vapor Cloud Program	Prevention of flammable vapor cloud formation and ignition, including early detection, emergency ventilation, and emergency response.
Incident Investigation	Investigation of major process incidents to find root cause, identification of key learnings, and communication of findings to all resin plants.

Each guideline is designated as mandatory or advisory. Mandatory guidelines are critical to the safety of resin manufacturing and must be adhered to unless Reactor Safety has provided specific approval for deviation. Advisory guidelines are provided as important suggestions, which could enhance the safety of resin manufacturing, but are not required. Most of these guidelines are negotiable between formulators or engineers with Reactor Safety personnel, although process modifications, special operating procedures, or additional hazard testing may be required to ensure safe operations.

In general, most resin formulas can be made safely. Since process equipment capability sometimes varies significantly, proper matching of resin formulas with the appropriate manufacturing reactors is required, as discussed in more detail in the following section. Key resin formulating principles include:

- Safety is the responsibility of all persons involved in resin manufacture, including formulators, scale-up engineers, and operators. Taking risks involving safety can have devastating consequences due to the inherent hazards of the acrylic resin process.
- Any new process technology will be subject to intensive investigation of potential safety hazards prior to scale-up to pilot plant reactors.
- Pilot plant production of new resin formulas is required prior to plant production, based on formulas previously made in the laboratory.

Approximately 50 resin design guidelines are now documented, many based on common sense and many developed from operating experience and incidents. Several examples of guidelines for acrylic resins are provided in Table 2.

### Resin Screening

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. The safety screening of acrylic resins has a variety of goals, most achieved by use of computer models, others through the use of calorimetry. First, we seek to ensure that there will be no situations where chemical components of the process can react spontaneously and unexpectedly to create out-of-control situations and their accompanying hazards.

Table 2. Example Resin Design Guidelines

No.	Guideline	Explanation
1	Avoid charging of reactive mixtures to reactors prior to initial reactor heat-up.	Charge prior to heat-up does not allow proper condenser operation to be confirmed, possibly leading to a runaway.
2	Spread out addition of reactants to lower peak reaction exotherm.	Addition of reactants as feeds spreads the exotherm over a longer time period, reducing the peak exotherm.
3	Avoid use of initiators with slow decomposition rates at reaction temperature.	Slow initiator decomposition can allow unreacted monomer to build-up in the reactor, possibly leading to a high reaction exotherm and a runaway reaction.
4	Solvent reflux must be established prior to the start of feeds and maintained throughout the batch.	Reflux confirms proper condenser operation and minimizes the potential for accumulation of unreacted materials, which could lead to runaway reaction.
5	Solvent reflux must be established prior to the start of feeds and maintained throughout the batch.	Combination of unstable reactant mixtures, such as monomers and initiators, in feed tanks can lead to a runaway reaction, especially during operating delays.

Second, we seek to determine that the reactor system has adequate heat removal capability, to make certain that the polymerization will remain under control, provided a normal cooling medium supply is maintained. Third, we aim to ensure that the reactor system has the necessary emergency facilities to terminate or safely relieve a runaway reaction that might occur if normal cooling is not available to remove the heat of reaction. While it is recognized that this review may make formulating more difficult for resin chemists, these guidelines are considered an important requirement to help achieve resin process safety.

The concept of "resin safety screening" goes back to the start of the Reactor Safety program in 1975, when it was realized that very little was known about the hazards inherent in the production of the many acrylic resins then being manufactured. A computer kinetic model was developed for solution acrylic polymerization which has been continuously updated and improved [6]. Using this model, it is possible to quantify with a high degree of accuracy the hazards of acrylic polymerizations, by calculating the reaction exotherms under normal reaction conditions and by predicting the rate of heat release in simulated runaway conditions. Ultimately, by expanding the program and tying it to a reactor and feed tank data base, a procedure has been developed to relate the hazards of each acrylic process to the heat removal capability of specific process equipment and to the adequacy of the emergency relief system installed on that equipment.

As this process evolved further, resin safety screening was applied routinely to all production involving polymerization reactions in any resin area equipment. This procedure is mandatory, specifically stated as:

*No resin, intermediate or other product may be produced in resin manufacturing equipment unless written Reactor Safety approval has been received by the site.*

This evaluation involves review of formulas for compliance with resin design guidelines, computer simulation of formulas, and reaction calorimetry, as required. For this process to be effective, Reactor Safety personnel conducting this review must have good practical experience in resin chemistry, reactor operation, and hazards analysis.

**Heat Removal Adequacy.** The first stage of the computer screening process simulates a polymerization, as it would occur with normal cooling available, to determine the peak exotherm and the temperature at which the peak occurs. Using this data, the adequacy of condenser sizing is determined for processes run at the reflux temperature of process solvents. If the process is run at temperatures below solvent reflux, an evaluation is made to determine if the reactor jacket can be used successfully to maintain the required batch temperature and to control the reaction. The result is the calculation of a "condenser capability rating" (CCR), which is a measure of the ability of the reactor condenser to remove the peak reaction exotherm, as shown in Equation 1. The CCR is the heat transfer coefficient required for the condenser to achieve full condensation of solvent vapors at peak exotherm conditions, expressed as BTU/hr/ft<sup>2</sup>/°F.

$$CCR = \frac{0.6V_B\Delta H_R}{(T_M - T_W)A} \quad (1)$$

where  $\Delta H_R$  = Peak heat of reaction in BTU/min/100 gallons  
 $V_B$  = Maximum batch size in reactor in gallons  
 $T_M$  = Reflux temperature at peak exotherm in °F  
 $T_W$  = Local maximum cooling water temperature in °F  
 $A$  = Condenser area in ft<sup>2</sup>

It has been found for our equipment that a CCR greater than 50 will usually result in incomplete condensation of the vapor generated, creating a greater potential for a runaway reaction. These cases will not normally receive Reactor Safety approval. Reactions with a CCR between 30 and 50 are closely analyzed for other potential hazards. In some cases, reduced batch size or reformulation may be required to lower the CCR to a safer level.

**Emergency Relief Sizing.** Early in the development of the computer screening protocol, the decision was made that the screening process could not include the many possible combinations of loading and process errors that could occur. As a result, the worst case scenario for emergency relief sizing is defined as the worst runaway reaction resulting from simultaneous loss of condenser cooling and venting, assuming the reactor and its feed tanks are charged correctly, the reactor is operated at normal temperature, and the feeds are introduced at normal rates. After loss of cooling, it is further assumed that the ingredient feeds continue normally.

After completing the normal polymerization simulation to evaluate the adequacy of condenser cooling, the computer model automatically runs a series of adiabatic runaway simulations, where loss of cooling occurs at various times during the batch. Typically, these cases start at time 0 and continue at intervals of 10 minutes until the end of the batch. The purpose of this group of simulations is to find the time at which loss of cooling results in the runaway reaction that requires the largest emergency vent area. This then becomes the worst case runaway for the resin formula and reactor combination.

Figure 2 illustrates the simulated temperature profiles for loss of cooling at 0, 50 and 100 minutes after the start of a batch for a particular resin. Clearly, loss of cooling at the start of the batch (time 0) results in the highest exotherm and is thus the worst case. The pressure build-up for this case is shown in Figure 3. After loss of condenser cooling at time 0 minutes, the runaway reaction can generate a maximum pressure of over 350 psig. Since, in this case, this pressure is above the maximum allowable working pressure (MAWP) of the reactor system, adequate design of the emergency relief vent is critical to prevent possible rupture of the reactor system. A correctly sized rupture disc that bursts at 50 psig or similar relief pressure, therefore, will safely vent the reactor pressure, maintaining the pressure below the reactor MAWP of 150 psig.

Figure 2. Computer simulation showing temperature profiles for an acrylic runaway reaction due to loss of condenser cooling, starting at 0, 50, and 100 minutes after the start of the feeds.

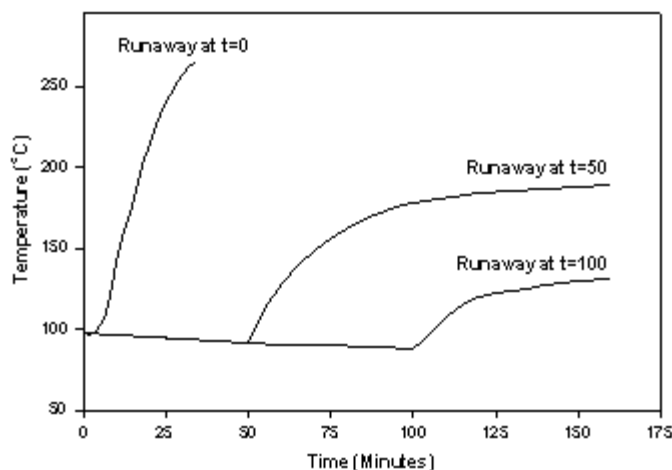
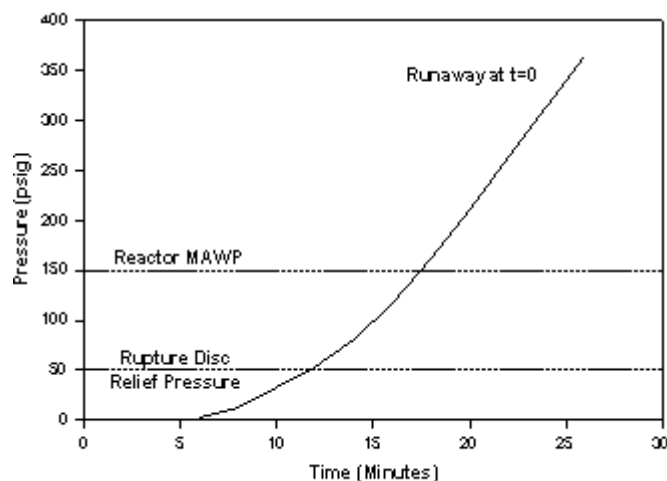


Figure 3. Computer simulation showing pressure profile for runaway reaction starting at 0 minutes after the start of the feeds. The rupture disc burst pressure is 50 psig and the reactor MAWP is 150 psig.



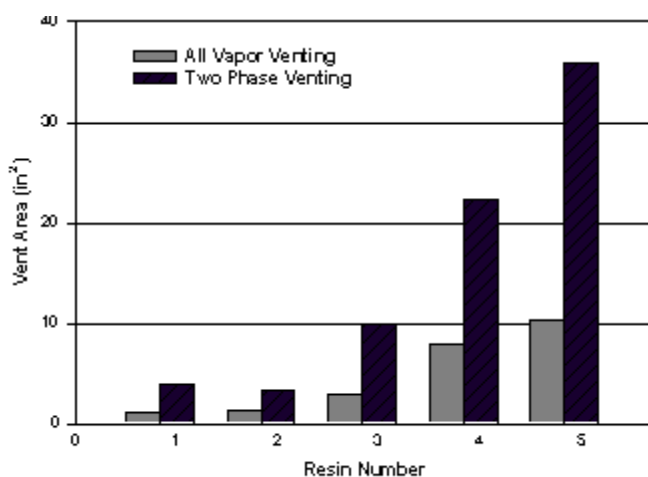
Initially, emergency relief sizing was based on all-vapor venting [7], with a 100% safety factor added to the calculated vent area to partially compensate for the potential of two-phase flow during the discharge. More recently, the Design Institute for Emergency Relief Systems (DIERS) has developed two-phase flow technology [8], which has become the recognized standard for the analysis of emergency vent sizing. This approach has been added to the computer screening model to calculate emergency vent areas for all simulated runaway reactions.

Acrylic solution polymerizations exhibit high vapor pressure, with tempered behavior on relief. In the DIERS calculation, zero disengagement of liquid and vapor in the vessel (homogeneous equilibrium venting) is conservatively assumed. The existing vent configuration (diameter, length and vertical height) is included in the data base for each reactor and feed tank. The computer model predicts the maximum pressure that will be reached in the reactor for a series of runaway reactions, as described earlier, and calculates the required emergency vent area to safely relieve the pressure, using a 20% overpressure allowance. The largest vent area required in this series of simulations is compared with the existing rupture disc vent area to determine if the resin can be safely made.

For many acrylic resin formulas, a relatively high rupture disc relief pressure allows the reaction to be essentially complete before venting occurs, resulting in a smaller required vent area. In some cases, the maximum pressure generated by the runaway reaction is less than the relief pressure, and venting is not required. In all cases, however, the rupture disc relief pressure is set well below the reactor MAWP to provide an additional safety margin. The computer model can also be used for emergency relief system design by determining the effect of different rupture disc relief pressures on emergency vent area requirements.

Figure 4 illustrates the required vent area for a series of 5 acrylic resins manufactured in a 2,500 gallon reactor, using either all-vapor or two-phase flow venting. In general, the DIERS vent areas are 2 to 4 times that for vapor-only venting, using the 20% overpressure criteria.

Figure 4. Emergency vent area required to safely vent a worst case runaway reaction for five acrylic resins in a 2500 gallon reactor, based on all vapor or two-phase design calculations.

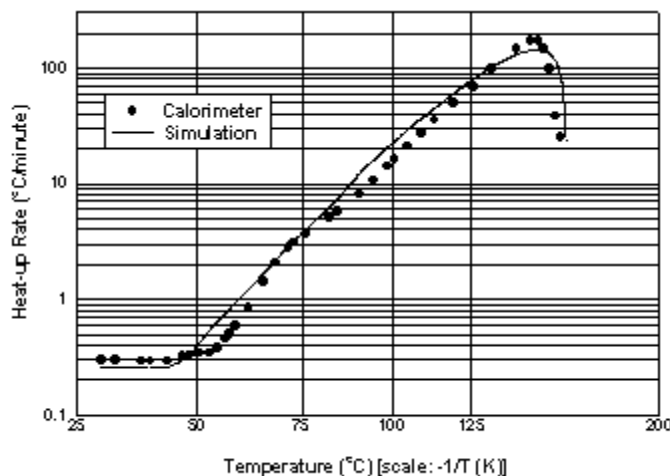


**Calorimetry.** Calorimetry is used as needed to supplement the computer screening model, particularly when kinetic data are not available for new monomers or other reactants. When the reaction kinetics are well known, good agreement is typically obtained between the computer model prediction and the experimental calorimetric data, as shown in Figure 5. In these cases, the computer model is used in an adiabatic heat-up mode to duplicate the experimental conditions used by the particular calorimeter in the tests. Calorimetry is also useful for determining the long-term stability of reaction feed solutions, such as mixtures of monomers and initiators, where computer modeling is limited, due to, for example, the presence of inhibitors in the monomers.

### Reactor Design

Many factors are involved in the proper design of acrylic reactor systems, including pressure vessel codes, proper materials of construction, etc. In addition, reactor process safety is based on a layering of safety equipment to provide early detection and control of runaway reactions. Each component of the emergency system is intended to operate independently if earlier stages are not fully successful in terminating a potentially hazardous condition. In most cases, sufficient time is available for responding to and controlling the early stages of a runaway reaction. Since very rapid pressure build-up is possible during a runaway reaction, however, the final component in the emergency response is critical and must be designed so that it will operate successfully if all other emergency equipment fails. Essential features of this layering approach are discussed below.

Figure 5. Self-heat rate for an initiated methyl methacrylate solution, showing the comparison between calorimetric data and computer simulation.



**Reactor Condenser Design.** As discussed previously, the reaction exotherm must be removed either by condenser cooling of solvent reflux or by reactor jacket cooling. These systems must be adequately sized to assure that the process will remain under control during normal operating conditions, therefore preventing the start of a runaway reaction. If, however, the reaction exotherm exceeds the available cooling capacity, due to poor design, mischarge, or other causes, pressure will begin to build in the reactor. Initial reactor venting occurs at a slightly elevated pressure, as hot process vapors are forced through the vapor or reflux return lines to the condenser vent, which is connected to a catch tank. Since the condenser vent, designed to maintain atmospheric pressure and vent non-condensable gases, is usually quite small, pressure may continue to increase in the reactor due to continued reaction.

**Process Instrumentation and Alarms.** Process instrumentation is designed to monitor key process variables, such as reactor temperature, pressure, and condenser operation. If abnormal conditions are detected, alarms sound to provide early warning, allowing time for either operator or process computer response to bring the reactor back into a normal condition. Corrective action may include providing additional cooling, adding solvent to reduce batch temperature, or stopping the addition of reactant feeds. Instrumentation also provides process data for incident investigation of all abnormal process events.

**Kill (Shortstop) Systems.** If operator or process computer action is not sufficient to bring the reactor back to a normal condition, the next stage of emergency response is the automatic activation of a kill system safety interlock. The kill system operates automatically at a specified pressure to add a concentrated inhibitor solution to the reactor to terminate continued free radical polymerization, effectively stopping further reaction. Selection of the optimum inhibitor and solvent, solution concentration, and the method of addition to the reactor is critical and must be specific to the reactants used in the process. Manual activation of the kill system is an option always available to operators, at their discretion, if the early stages of a runaway reaction are detected.

**Emergency Relief Systems.** If the kill system does not stop the runaway reaction and pressure build-up continues in the reactor, a properly designed emergency relief system is essential to prevent the pressure from exceeding the reactor MAWP. This typically requires rupture disc sizing based on DIERS technology to account for two-phase flow, as discussed previously.

**Catch Tanks.** Both the reactor condenser vent and emergency relief vent are connected to a catch tank, designed to collect emergency releases from the reactor. Sized to hold the entire contents of the reactor, the catch tank contains the liquid portion of the emergency discharge, while simultaneously venting vapors high into the air to minimize the potential for the formation of a vapor cloud at ground level. The catch tank is also inerted to provide a

low oxygen atmosphere to prevent possible ignition of flammable materials. Special catch tank design may be necessary if highly toxic materials may also be present.

**Feed tanks.** Layered emergency systems are also required for feed tanks that may contain potentially reactive mixtures, such as monomer and/or initiator solutions. Since these mixtures are typically fed into the reactor near ambient temperature, pressure build-up does not provide adequate warning of the early stages of a potential runaway reaction. Feed tank temperature is therefore used to monitor for signs of reaction, trigger process alarms, and activate kill system addition. Since the initial reaction rate at ambient temperature is usually low, sufficient time is generally available for emergency operator response. Feed tank runaways, however, can often be very severe if not detected early due to the high concentration of reactants. Adequate design of the emergency relief system is therefore essential.

### **Operating Procedures**

Proper operating and maintenance procedures for reactor systems are critical for achieving and maintaining safe resin manufacture. Specific to the design of the reactor and its resin manufacturing task, these procedures must be well thought out and provide for both normal and emergency operating conditions. Examples of important procedures include handling and loading of hazardous materials, vessel inerting and grounding, reactor heating and processing, pressure integrity testing, instrument calibration, personal protective equipment, equipment testing and inspection, and emergency response and evacuation. Operator training on these procedures, in particular, is essential to preventing and properly responding to abnormal conditions that can lead to potentially catastrophic consequences.

Procedures for preventing and responding to flammable vapor clouds are very important [9]. The release of a flammable vapor cloud, due to a breach in the integrity of the reactor system during normal or emergency operating conditions, is very serious. Prevention of vapor cloud formation is the highest priority and can normally be achieved by following proper design and operating procedures, including electrical equipment standards and pressure integrity testing following maintenance work or before each batch. Early detection of vapor clouds is possible through use of hydrocarbon sensors in key operating locations. Hydrocarbon sensors can initiate warning alarms, system shutdown, and emergency ventilation. Emergency procedures to quickly evacuate and protect personnel are also essential. Similar emergency procedures may be required for detecting and evacuating in the event of toxic material releases.

### **SUMMARY**

Acrylic resins provide many desirable properties, finding application in automotive coatings and many other industries. Acrylic resin polymerization, however, is a highly hazardous process, with high reaction exotherms and the potential for uncontrolled runaway reactions. In addition, many reactants are flammable and, in some cases, also toxic. Since its beginning in 1975, the Reactor Safety program has worked to minimize these hazards, with the goal of completely safe resin manufacture. Through the development of specific resin formulation, reactor design, operating procedure, and hazards analysis practices, Reactor Safety has achieved an outstanding record of no significant process-related injuries and no loss of resin manufacturing facilities for over twenty years. With upper management support, and in combination with a strong PSM program, Reactor Safety will continue to work to achieve safe resin manufacturing, with the goal of zero significant process incidents and injuries, for many years to come.

### **ACKNOWLEDGMENTS**

The authors would like to acknowledge the contributions of many DuPont employees who have participated on the Reactor Safety Team and contributed to its success over the last 20 years, especially Dr. Frank G. Klein (retired).

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