Process Safety of Polymer Resin Manufacturing: A 20-Year Perspective

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1. INTRODUCTION

The primary products of the worldwide Automotive Products (AP) business of the DuPont Company are automotive finishes. The backbone of these products are synthetic resins, includi1ng acrylics, epoxies, epoxy-esters, polyurethanes, alkyds, vinyl/acrylate latexes and polyesters. These resins are manufactured largely, to this day, in batch reactors with reflux cooling to remove any heat of reaction present. In 1975, two major process upsets in AP, closely following the Flixborough explosion, led to the formation of a program to upgrade the safety of resin manufacture. The "Reactor Safety" program continues to this day and this paper traces the 20-year history of that effort towards achieving continuous safe resin manufacture.

2. BACKGROUND

DuPont's emphasis on safety began in 1802 with the design and operation of the first black powder plants in Wilmington, Delaware. DuPont's commitment to process safety, begun by its founder, has continued to this day.

In 1965, a major incident at a DuPont plant led to a major corporate-wide assessment of the potential for explosion or major disaster in all manufacturing facilities handling flammable or reactive materials. All sites were required to take appropriate corrective action. This request represented the beginning of process safety management in DuPont.

The Flixborough disaster in 1974 [1] was followed by two much smaller, but similar, vapor cloud process incidents in AP in 1975. In the first, a runaway reaction occurred during processing of a highly exothermic batch of acrylic resin, when the reflux condenser, which was fouled, was unable to remove sufficient heat of reaction. The contents of the reactor were ejected into a small catch tank, which overflowed, discharging a mixture of hot resin and vapor on the ground. The resulting vapor cloud ignited and one worker was seriously burned.

The second incident was the result of the accidental introduction of a small amount of water under the surface of a thinning tank containing a large amount of hot alkyd resin solution. The water immediately flashed, causing the tank contents to erupt into the operating area through a pressure relief valve which was piped to discharge inside the building. A flammable vapor cloud filled the facility, but dispersed without igniting after electrical power to the entire plant was shut off. No serious injuries or equipment damage occurred.

3. EARLY PROGRAM HISTORY

3.1. Process Equipment Survey

Coming on the heels of Flixborough, and with the memory of the 1965 DuPont incident still fresh, the two incidents in our own plants highlighted our potential vulnerability to major injuries or loss of facilities due to improper equipment design or operation. The response of management was to set in motion a program to insure that process upsets of the magnitude of the 1975 incidents would never be repeated.

The initial question asked at that time was whether existing resin process equipment was adequately designed for the tasks to which it was being used. A survey of twelve resin-producing facilities worldwide was made by a team from the central DuPont Engineering Dept. and process engineers from AP. The initial management perception was that the equipment review and upgrade work would be a six month task for, at most, two people.

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It should be mentioned at this point that, due to the continuous evolution of paint technology over the preceding decades, some of the resin-making equipment in service in 1975 was not being used in the manner for which it had originally been designed. For example, some batch reactors being used for acrylic manufacture had originally been built for manufacture of less hazardous processes such as non-exothermic alkyd resin polymerization. Equipment design, particularly for resin reactors, was without any uniform basis due to the varied nature of the original manufacturing uses. The survey found that, in many cases, the equipment was likely not optimally suited to the current production tasks from a safety standpoint.

It was recognized, moreover, that not enough was known on the hazard potential of the resins currently being manufactured, and that the data for determining the sizing adequacy of emergency relief systems was not readily available. In many cases, the emergency discharges from process vessels had the potential for creating large vapor clouds at ground level, often within operating buildings. As a result, it was determined that, not only would a sustained technical effort be required to define and carry out needed upgrades, but that substantial capital expenditures would also be required. This was the task that was begun about 20 years ago and, to a large extent, is a work still in progress and continues to be modified to meet current needs.

3.2. Survey Recommendations

It became obvious from the initial survey that resin-related safety hazards needed to be better defined and quantified for each type of resin. It was clear that not all equipment could or should be used for all resin processes, but at that time, good standards did not exist by which to make these judgments. It was recommended that, after the initial hazard evaluation was completed, process equipment either be assigned to the specific tasks for which they were safely suited with no modification, or upgraded, if needed.

It was necessary to develop detailed design standards for safety features on resin process equipment and to apply these standards retroactively to existing equipment. Specific areas where standards needed development include:

- required pressure ratings of all process equipment
- size of vapor pipe from reactor to condenser
- surface area of primary condenser relative to maximum expected heat load
- specifications for feed tanks and other auxiliary tanks
- emergency relief systems
- vent configuration
- solids loading devices
- instrumentation and control systems
- materials of construction.

It may appear strange that these basic design details were lacking 20 years ago, but because of the manner in which the technology evolved, insufficient attention had been placed on the changing safety aspects of the newer types of resins.

It was recognized that multiple safety systems would be required on vessels where runaway potential was high, such as for acrylic reactors and feed tanks. The "layered" system envisioned at the time consisted of:

- high pressure alarms on reactors to warn of the start of a runaway
- high temperature alarms on feed tanks, particularly where mixed monomer/initiator feeds might be used
- shortstop (kill) systems for acrylics on both reactors and feed tanks
- adequate emergency relief systems connected to large catch tanks.

While now common, the use of concentrated inhibitor solutions (shortstop systems) to terminate out-of-control acrylic polymerizations was fairly new in the mid-1970's and was based on technology used earlier for deactivating monomers for disposal. Systems needed to be designed and installed to introduce inhibitor solution automatically in case of an incipient acrylic runaway. Manual addition bypasses were also provided.

One of the difficulties faced at the time (and still today) was that almost all of the resin reactors in the system were used to manufacture many types of resins, under widely differing operating conditions. In addition, the more sophisticated emergency relief sizing methods developed over the last decade, such as DIERS, were not available in the mid-1970's.

Virtually none of the reactor systems at the time had provisions to contain any material ejected from a reactor or feed tank in case of a runaway or similar process upset. The relief pipes were either vertical, terminating at the roof, or were horizontal and terminated within the process area. As the 1975 runaway reaction incident demonstrated, however, the worst case runaway would essentially empty the reactor and could lead to a flammable vapor cloud at ground level. It was thus necessary to design new catch tanks to contain essentially the entire liquid inventory of the vessel served, while simultaneously ejecting upward any vapor releases to minimize the possibility of a vapor cloud at ground level. Catch tanks had to be designed and installed for every resin manufacturing area.

It is clear from this list, summarized in Table 1, that the initial thrust of this program was primarily equipment-oriented. While operating standards, operator training and the like were recognized as an important part of the upgrade effort, this area was not given as much attention in the early years. One of the original recommendations, though, was to institute a system of periodic audits to assure proper implementation of the new safety standards. The audit program initiated at that time continues to this day and is one of the key elements of the current program.

Table 1. Initial Program Recommendations in 1975-76

- Better define resin-related process safety hazards
- Re-assign production based on process capability
- Develop detailed equipment design standards
- Upgrade process equipment
- "Layered" process safety systems
  - High pressure/temperature alarms
  - Shortstop systems
  - Emergency relief systems
- New catch tanks
- Periodic process safety audits

A final recommendation was that the program length be extended past the original six month time limit. No one realized at that time that it would be an active and important process safety activity twenty years later in 1995.

3.3. Program Implementation

Management supported the recommendations of the original study, although it is doubtful that anyone really knew the whole extent of what would be involved. Two senior engineers were initially assigned, one process and one mechanical. The upgrading of the resin manufacturing areas began early in 1976, in about the following order of priority:

Emergency Relief Systems - All vessels, including reactors, feed tanks, and thinning tanks were evaluated for adequacy of the emergency relief system. At the time, the work of the DIERS [2] organization was not available, and the new emergency vent sizes were calculated on the basis of vapor-only venting with a 100% safety factor added to the calculated area. At least 1/2 of all vessels were retrofitted with larger emergency relief systems.

Shortstop Systems - As indicated earlier, use of concentrated inhibitor solutions to terminate runaway acrylic reactions was a technique previously used, although not in an automatic actuation mode. Experimentation was necessary to establish the correct inhibitor and solvent, concentration of inhibitor, method of introduction, etc. Ultimately, all reactors and appropriate feed tanks were protected by shortstop systems that fired both manually and automatically, based on high pressure for reactors or high temperature for feed tanks.

Condenser and Reflux Systems - Existing reflux cooling systems were examined for adequacy in removing the heat of reaction of the most severe exothermic polymerizations envisioned for the reactor system, using a generous safety factor.

Catch Tanks - A catch tank was designed to hold the entire contents of the largest vessel in each reactor system. All emergency vents were connected to the catch tank. The tasks of the catch tank were:

- separate the emergency discharge into liquid and vapor phases
- contain the liquid portion of the discharge
- dissipate the vapor phase into the atmosphere in such a way that the potential of a vapor cloud reaching the ground is minimized
- provide a low oxygen atmosphere for the discharge to minimize the possibility of a fire.

All breathing vents were also routed to the catch tank, avoiding the need for flame arrestors for many separate lines.

Instrumentation - Instrumentation on reactors and feed tanks was upgraded to provide the following functions:

- warn of potential out-of-control situations
- provide information for corrective action
- record and retain process data for after-the-fact analysis of reactor incidents
- provide automatic controls and interlocks to reduce dependence on personnel in an emergency.

Increasingly, these tasks are now being overseen by process control computers.

At the start of this program, it was realized that little was known of the magnitude of the hazards associated with the exothermic reactions involved in resin manufacture, and that some reactors were possibly not suited to such production. It became apparent that a systematic approach to assuring resin process safety was needed, in combination with assuring that the process equipment had the safety features needed for the task. Thus was born "resin safety screening" which is still in place today. No resin, intermediate or product may be produced in resin equipment unless written reactor safety approval has been received by the site.

As the reactor safety program developed, a procedure was begun to audit the design and installation of equipment as the upgrading process progressed. This process was carried out by reactor safety personnel and focused initially on plant compliance with equipment design standards. Eventually, all aspects of resin production were included in the audit.

Implementation of the original reactor safety program world-wide took 7 years with millions of dollars of capital improvements. Details of the program in its current state are given in the next section.

4. CURRENT REACTOR SAFETY PROGRAM

The reactor safety program has continuously evolved since its beginnings in 1975-76. The program now includes a blend of engineering standards and administrative guidelines emphasizing three main elements with the goal of achieving and maintaining safe polymer resin manufacture:

- resin formulation and evaluation
- auditing and procedures.
- equipment design and operation

This section will briefly describe some of the key activities of the current reactor safety program in each of these areas.

4.1. RESIN SAFETY SCREENING

"Resin safety screening" is the process by which reactor safety personnel, through the application of safety and process guidelines, determine the suitability for production of all products manufactured in resin area process equipment. As mentioned previously, ***no resin, intermediate or other product may be produced in resin equipment unless written reactor safety approval has been received by the site***. Approval is provided for manufacture of specific batch sizes in specific resin area equipment. Development of the standards defining adequate safety for each type of process was begun in 1976 and continues today.

Reactors and auxiliary equipment must be equipped, as needed, with the following:

- automatic kill systems to terminate out-of-control acrylic reactions
- a condenser or jacket suitably sized to provide assurance that the process will remain under control under normal operating conditions through removal of heat of reaction
- emergency relief systems of a size adequate to provide satisfactory protection for the vessels in the event of a runaway reaction,
- an inerted catch tank to collect the liquid inventory from reactors and feed tanks in case of an emergency discharge
- loading devices for the introduction of solid raw materials into the reactor at temperatures above 80°C, which provide an adequate barrier to prevent eruptions from the reactor during loading
- sufficient instrumentation to permit operations to follow important process variables and provide enough information for corrective action under emergency conditions.

Specifics of the screening program for certain types of resins are given below.

Acrylics - In the early 1970's a computer model [3] was written to simulate the reaction kinetics of acrylic solution polymerization for use by resin formulators. This model was modified to provide assistance in determining the adequacy of the reactor system to handle a "worst case" runaway reaction and is now an integral part of the resin screening process. Specifically, the program calculates the thermal effect of total loss of reactor cooling at different times during the process to simulate different adiabatic runaway reactions. As the batch temperature increases due to continued heat of reaction, reactor pressure also increases, as shown in Figure 1. Pressure buildup may be gradual or very rapid, varying for each resin formula modeled. If the pressure exceeds the burst pressure of the rupture disc, a required relief area is calculated and compared with the actual relief area available. The maximum pressure that is reached when the batch loses cooling depends on the specifics of the feed schedule and polymerization rates and can occur either at the start of the feeds or ar some later time, as shown in Figure 2. The model also calculates a "condenser capability rating" (CCR), which is a measure of the ability of the condenser to carry away the peak heat load. The CCR is defined as:

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

where ΔH_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 ft²

Based on experience with our reactor systems, reactions carried out at reflux having a CCR greater than 50 will not receive reactor safety approval for production at maximum batch size. Reactions with a CCR between 20 and 50 are closely analyzed for other potential hazards. In some cases, reduced batch size may be required to lower the CCR to help ensure safe production.

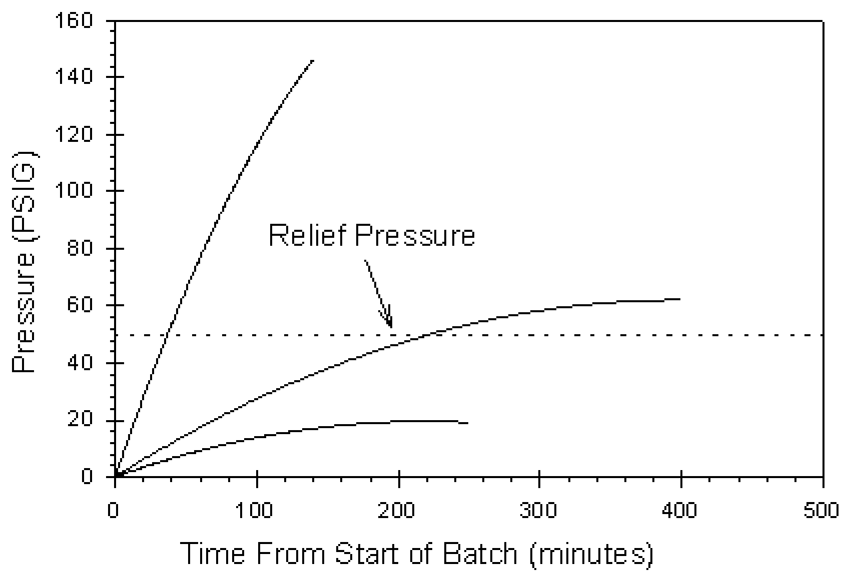

Figure 1. Computer simulation showing reactor pressure buildup during an acrylic runaway polymerization for three different acrylic resins. Upon loss of cooling at time 0, batch temperature increases, raising the reactor pressure until all reactants are depleted. If the pressure exceeds the rupture disc relief pressure, the reactor will vent to a catch tank.

The computer model is augmented by calorimetry when computer simulation programs are not available, to determine the stability of reaction mixtures, or to permit experimental emergency relief sizing using DIERS methodology. In general, good agreement is obtained between the model prediction and experimental calorimetric data. Experimental data and computer results for an initiated methyl methacrylate solution are shown in Figure 3.

Alkyds and Polyesters - Since alkyd and polyester polymerizations are endothermic, they do not have the runaway potential of acrylic reactions. The greatest potential hazard occurs during loading of solid ingredients, which constitutes a substantial fraction of the total manufacturing cycle time. Accidental introduction of moisture in raw materials into a hot reaction mass can generate superheated steam, which can be ejected with solvent vapors out of an open manhole or loading port possibly forming a vapor cloud in the operating area. Loading of solid ingredients into a reactor whose contents are above 80°C therefore requires a fully-enclosed solids loading system, such as a screw feeder or star valve. In some cases, special handling below 80°C may also be required.

Other Polymers - Other types of polymers made in resin reactors include polyurethanes, epoxies, and vinyl/acrylate latex resins. Special resin screening guidelines are also available for manufacture each of these polymers, but will not be discussed here due to space limitations.

A key principle of the resin safety screening activity is that each resin formula must be carefully evaluated in each candidate reactor system available to optimally match the requirements of the resin process with the capability of the reactor system. As resin technology changes, new screening guidelines must be carefully developed, and in some cases, reactor systems must be upgraded to make newer resins more safely. A set of resin design guidelines detailing essential principles of safe resin manufacture has been prepared for resin formulators to help assure that safety is designed into new products as they are being developed. Use of these guidelines has proven instrumental in minimizing non-approval of new products due to safety concerns and also in providing early warning that reactor system upgrades may be required.

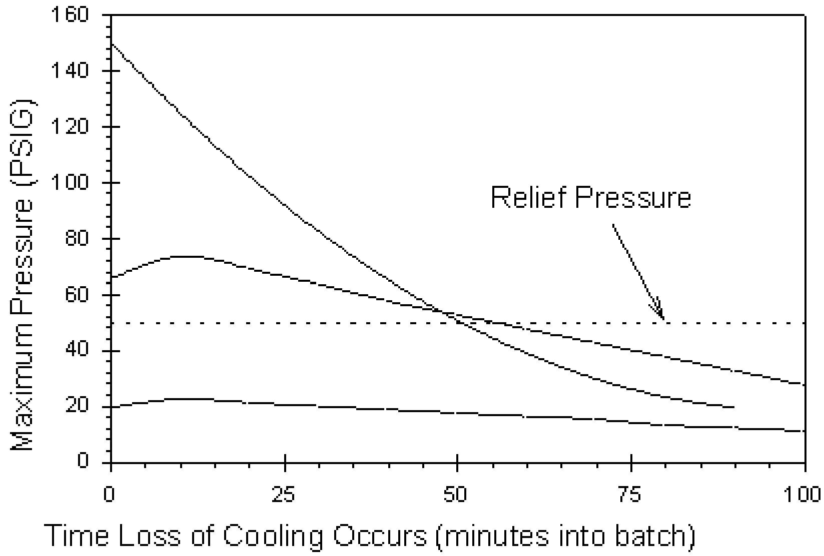

Figure 2. Computer simulation showing the maximum pressure reached during a runaway reaction for three different acrylic polymerizations. The maximum pressure is dependent on the time at which total loss of reactor cooling occurs, varying with differing feed schedules and reactant conversions. The maximum pressure shown at time 0 corresponds to the maximum pressures obtained in Figure 1.

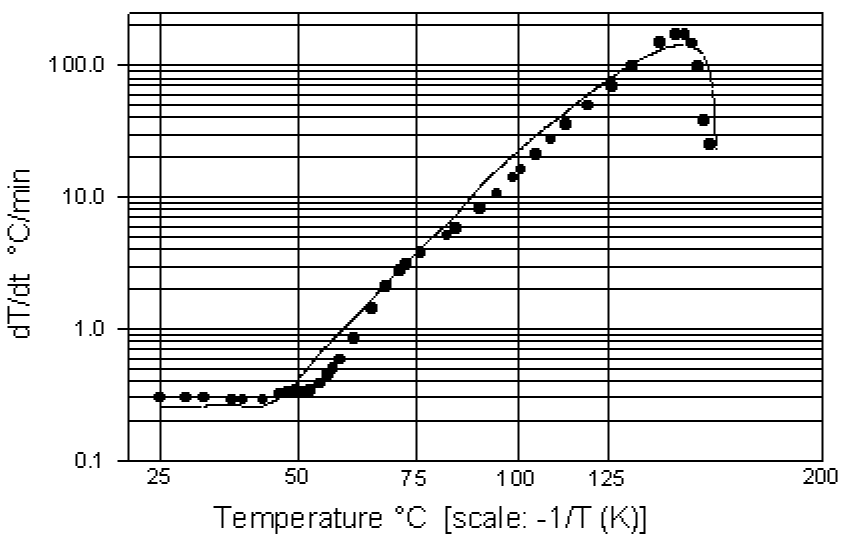

Figure 3. Self-heat rate for an initiated methyl methacrylate solution showing comparison between calorimetric data (•) and computer simulation (—).

4.2. Auditing and Procedures

One important change during the last 10 years has been increased involvement of plant personnel world-wide in the reactor safety activity. All plants are treated equally, despite differences in language and culture. Resin area engineers at each plant site are now representatives on a "reactor safety team". Every member of this group is in touch through electronic mail with his or her colleagues on any and all matters of safety in resin production. Ideas are exchanged freely, and many new ideas for safer operation that have come out of one plant have been adapted at other sites. This group and reactor safety professionals meet at least once per year at one of the plant sites to help drive continuous improvement of the program.

Training activities have also taken on an increasing importance over the last few years, particularly in more formal training activities in connection with OSHA PSM [4] requirements. Some of the plants have taken the initiative and sharing between sites, where possible, has been encouraged. Several training videos on vapor clouds, initiator handling, and other safety-related topics have also been produced.

In 1991, we published a reactor safety standards manual for company use. This is a complete compendium of all current resin manufacturing design and operating standards, which are continuously updated and amended as needed. Several copies are available at each site and are used routinely as reference documents. An important part of this manual is a section on resin formulating and scale-up guidelines, as mentioned earlier. These are intended to assist chemists and engineers in developing safe resin formulas and achieving safe process scale-up.

The standards manual contains considerable information on equipment design requirements. As an added check, however, any change in resin equipment must be submitted to reactor safety for approval before the change can be made. In practice, this is most often a process of discussion and occasionally negotiation between reactor safety personnel and the plant professional. The process of approval is called a design change authorization (DCA) and is now also part of the OSHA PSM Management of Change procedure.

One section of the standards manual is a reactor safety self-audit checklist. This is a series of about 100 safety questions in several areas of resin operations. Every 12-18 months, each plant is expected to carry out a self-audit of the manufacturing area using the checklist as a basis. The audit team is made up of operators, mechanics, and the plant reactor safety professional. These self-audits are augmented by regularly scheduled audits by reactor safety personnel at each site world-wide approximately every 3 years. A typical self-audit question is shown in Table 2.

All safety incidents at every plant site are given wide circulation, and each plant is required to determine if the particular incident necessitates a change in procedure or practice at their own site. Sharing of process incident information between different DuPont business units is also common.

Table 2. Typical Reactor Safety Self-Audit Question

<u>Question</u> The identification tags on rupture discs should have the disc data on the downstream side of the disc. When you are looking at the rupture disc identification data, you should be looking toward the vessel the disc is protecting. Is this requirement being met?

Yes (acceptable)	No (not acceptable)	N/A (not applicable)

<u>Comment</u> The identification on the tag is ALWAYS on the downstream side of the disc. If the identification is not on the downstream of the rupture disc, the disc is installed upside down, which may prevent it from bursting at its rated burst pressure. Note that a rupture disc installed upside down in a safety head must be replaced by a new disc, because it has been irreversibly damaged.

4.3. Equipment Design and Operation

Equipment design standards and guidelines, as mentioned previously, are incorporated into the reactor safety standards manual available to all the plants. Many of these design concepts directly result from the process equipment survey conducted in 1975-76, which was discussed in an earlier section. These standards are updated as needed to reflect current resin technology and equipment requirements.

A major program during the last decade has been the vapor cloud prevention and mitigation effort. In 1989 and early 1990, several vapor cloud releases occurred inside resin production areas. Any one of these could have caused a serious incident, but fortunately none of the vapor clouds ignited. These incidents led to a vigorous attack on this problem. The result was a multi-pronged program of prevention and mitigation having the following major components:

- pressure leak testing of resin systems after maintenance activity or before each batch
- hydrocarbon sensors located throughout resin areas
- emergency ventilation
- area and plant evacuation procedures.

These changes and a greatly heightened awareness of the hazards of vapor clouds on the part of all resin area personnel have led to a dramatic improvement in our performance in this area. Over the last several years no vapor releases of any kind have occurred in resin production areas.

5. SUMMARY

A summary of the current reactor safety program is provided in Table 3. Activity in each of these areas is not a guarantee of safe polymer resin manufacture. Each type of polymer resin chemistry and the capability of specific processing equipment must always be carefully evaluated by experienced safety professionals on a case-by-case basis. When combined with a strong process safety management program and strong upper level management support, however, these activities can contribute to a safer resin manufacturing operation.

New developments, including two-phase venting methodology, environmental concerns, increasing use of sophisticated computer control of resin manufacture, and the role of reactor safety as a part of process safety management must also be considered. Current trends in the automotive paint business have also increased the challenges for the safety professional. Government regulations and market pressures for lower hydrocarbon emissions during paint application are leading to higher solids and lower solvent levels, increasing monomer and initiator concentrations and peak exotherms in acrylic resins. New types of resin chemistry are being introduced at an increasingly rapid rate, and the pressure to commercialize these products quickly is high. New and exotic ingredients are increasingly common. What started out as a six technical man-month effort has now passed forty technical man-years and is still going due to these types of continuing challenges.

The time, effort and money has paid off. As a result of this program and the dedicated work of many people, no resin area process-related injuries and no loss of resin manufacturing facilities have occurred in the last twenty years. Currently, uniform safety standards are applied across-the-board world-wide, and we are very active in meeting regulatory process safety management requirements. There is a greater appreciation of resin manufacturing safety at all levels in our plants, and most importantly, there is a sense of continuity in the effort and a knowledge that management continues to commit the resources to do the job. Over the years we have seen a steady evolution of responsibility from a centralized organization to the plant professionals. We are confident that the next twenty years will prove equally injury-free with continued effort and dedication.

Table 3. Current Status of Reactor Safety Program

- Resin Safety Screening
- Reactor Safety Team
- Training Activities
- Standards Manual
    - Design Standards
    - Operating Standards
    - Resin Formulating Guidelines
- Design Change Authorizations
- Audits
    - External
    - Self-audits
- Incident Investigations
- Vapor Cloud Program
- New Resin Chemistries

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