

MEASUREMENT OF CHEMICAL REACTION RATE DATA FOR SIZING EMERGENCY RELIEF AND APPLICATIONS OF PRESSURE DEWAR CALORIMETRY IN THE FINE CHEMICALS INDUSTRY

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The sizing of emergency relief systems requires characterisation of the runaway reaction. This involves identification of the worst case condition and measurement of pressure, heat generation rates, and gas evolution whilst simulating these conditions at plant scale. Case studies are used to describe the types of worst case scenarios that can occur in batch reactions. The techniques for measuring reaction parameters are also described by examples. Secondary aspects in relief system design are discussed.

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INTRODUCTION

In the Fine Chemicals Manufacturing Industry there is a wide variation in both reaction types and chemistry. There are also many sources of pressure generation, arising from, for example, excess sparging, normal gas/vapour generation etc and chemical reaction resulting from a deviation in the normal process and runaway activity. This paper discusses the latter problem.

In exothermic reactions, the pressurisation hazard arises either from the generation of heat causing an increase in the system vapour pressure or from the generation of permanent (non-condensable) gas. Hybrid reactions can also occur where pressure generation is due to both gas and vapour.

Methods of dealing with the overpressurisation hazard can be preventative or protective.

Typical preventative measures include:-

- Limitation of the heating media (Use LP Steam for example in place of HP or IP Steam) If the exotherm onset temperature (measured in a manner which takes account of bulk factors) is inaccessible by either the maximum temperature of the heating medium and/or the normal reaction exotherm then the system is inherently safe.
- Control of addition times. There are a number of methods available some of which may require trip systems. For example, orifice plates (single or multiple) can be used to regulate the flow of material but there would normally be a requirement to register such items as protective devices. These may be required in addition to software controls.

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Many other such methods are available to regulate the process within safe boundaries.

The primary protective method used in the heavy chemicals industry where both process and plant are dedicated, is that of pressure relief. However, this is not true of the Fine Chemicals Industry where preventative measures are generally employed (Ref 33). Other methods which are available include:

- Reaction inhibition. This is a useful and effective technique for polymerisation processes where there is a long induction period of self heating before exotherm activity becomes uncontrollable. Obviously adequate mixing of the inhibitor with the monomers is essential.
- Quenching. This is effective where sufficient time is available to discharge the contents of a reactor into a dump tank containing, for example, water or dilute caustic etc. Alternatively, quenching may be effected in the reactor by addition of the quench material. Again efficient mixing is essential.
- Containment (within the reactor). A technique which precludes the need to consider additional vessels, piping or disposal requirements, but nevertheless requires equal pressure strength of plant/vessels subjected to the peak reactor pressure. An aspect which may easily be overlooked also, is that of cleanout. From experience, decomposition residues can be extremely difficult to remove and may contain highly toxic by-products. These secondary problems resulting in protracted shut down periods or replacement of vessels may outweigh the advantages conceived initially.

It is axiomatic that the reliability and integrity of the prescribed safety system needs to be considered and this includes examination of the pressure relief devices and the duties and conditions under which they will be required to operate.

WORST CASE DEFINITION

In the design/sizing of emergency relief systems for processes with the potential to runaway, it is imperative to identify the worst case conditions, having decided that pressure relief is the preferred option. Typical maloperations which may arise individually or simultaneously have been discussed previously (Ref 4). It is useful however to look at specific examples which have arisen in batch manufacture of Fine Chemicals.

EXAMPLE 1

The reaction stage for the manufacture of an Intermediate involved the addition of potassium hydroxide to a reaction vessel containing recovered solvent which itself, contained a recycled material. The third component, a low melting point hydroxyl benzene derivative, was charged subsequent to the caustic addition.

A relief condition arose when the batch was held for a prolonged period prior to adding the third component due to its solidification, resulting in the reaction of hydroxide with recycled material.

The primary cause of the exothermic behaviour was that the concentration of the reactive component in the recycled solvent had increased over a period of weeks to a level which was greater than expected and due to the delay in charging the low melting point solid, sufficient time elapsed for the side reaction to take place.

The example illustrates that two separately innocuous deviations can combine to produce a hazardous situation.

EXAMPLE 2

This process requires that methanol and acetic anhydride are run from feed vessels simultaneously in the ratio 4/1 through a static mixer into a larger mixer pot from which the mixture overflows into the reactor (see fig 1). The bottom run-off valve is opened to drain the mixer pot immediately after the addition is completed. The residence time in the mixer pot is under normal operation, no longer than 2-3 minutes.

By experiment the mixture was shown to react slowly at ambient temperature and under adiabatic conditions, to take several hours to reach the boil. Therefore if the operation is carried out as described with a short residence time, no chemical hazard would arise.

The plant in question however was computer controlled and loss of power could result in the valves closing, thus sealing the mixer pot and feed lines.

Although the 4/1 mixture would not have resulted in overpressurisation, it was feasible to feed at the stoichiometric ratio resulting in a temperature rise of 150 K and a final pressure of 200 psia, well in excess of the design pressure of the mixer pot.

Consideration of the calculated vent size and the tortuous path of the vent pipe needed for a safe discharge, led to the conclusion that emergency relief was not a feasible proposition and consequently, the mixer pot and isolating valves were removed to provide an unimpeded flow of mixed liquids to the reactor (see fig 3). This is ultimately a more satisfactory measure since it removes the source of the hazard. Again this is an example of overpressurisation arising from a combination of events.

Whilst it is rare for such a simple solution to be available, this example does show that the need for relief can sometimes be eliminated by appropriate changes in the design or operation of the plant.

EXPERIMENTATION

The testing procedure in the FCMO (ICI) has been discussed in detail previously (Refs 1,2). The basis of the procedure is to examine the thermal behaviour of the reaction on the small scale (10 g) prior to larger scale Dewar testing. This precludes the need for large amounts of sample which are

not always readily available particularly at the laboratory process stage. Use of small scale testing also reduces the potential hazard from, for example, material which decomposes at very high rates evolving copious amount of gas. Thus, the 10 g tube test is a useful and valuable screening tool.

It must be said that such small scale testing is not always possible particularly in cases where additions need to be made to the reaction vessel during the process. Larger test cells such as the adiabatic pressure Dewar apparatus need to be employed in this situation.

An essential feature of any test apparatus and test procedure is that it should be capable of simulating the upset condition on the plant scale in terms of the heat loss to the plant vessel, and heat loss to the surroundings and the mode and rate of addition of materials where applicable. The need for simulating low heat loss conditions is both well known and well documented and is achieved by testing under adiabatic conditions with a test cell of low thermal inertia. However, it is also important to simulate the feed rate and feed sequence as well as the point of addition within the vessel ie above or below the liquid surface.

Within the Fine Chemical Manufacturing Organisation of ICI the adiabatic pressure Dewar apparatus is used to measure emergency vent parameters such as flow regime characterisation within the vessel (ie single/two phase flow), reaction type classification and reaction rate parameters.

Characterisation of the relief condition in terms of pressure generated by permanent non-condensable gas as opposed to purely vapour pressure is important in the way that the size is determined. In the former case, the vent sizing is based on the peak plant scale gas generation rate unless it can be shown reliably that the reaction vessel will empty before the peak condition arises. Also, setting a low activation pressure for the relief device has little advantage other than that the loss of reaction mass through the vent in the early stages of the runaway may lead to a lower peak gas generation rate. However, in the latter situation, once the vent has opened, provided that it has been adequately sized sufficient latent heat can be dissipated to temper the reaction within safe limits. Thus in a vapour generating system there is a major benefit in selecting a low operating pressure for the relief device since control of reaction temperature is synonymous with control of pressure. This may also be true of some hybrid systems which generate both gas and vapour.

The pressure Dewar apparatus linked to a containment pot is shown in Figure 3. Essentially, the apparatus comprises a thin walled stainless steel Dewar with internal volume 1000 ml. The reactor is fitted with a mechanical stirrer, bursting disc, thermocouple, pressure transducer via a grease link, electrical heater and provision for upto three feed pipes for remote addition of materials during the reaction. The Dewar vessel is sited in an oven to minimise heat losses to the surroundings. Also, the Dewar is operated with an 80% fill ratio to minimise thermal inertia effects (ie the test cell has a water equivalent of approx 60 g). The robust design enables flexibility in operation by allowing, for example, variation in agitator type, multi-temperature monitoring (upto 3 thermocouples internally) and bottom venting tests with viscous material where the flow might be expected to be laminar.

For open type tests when undertaking tempering experiments or reactions involving non-condensable gas, the Dewar is linked via a vent pipe of 1/16" - 1/4" to the containment cell. This is external to the oven and comprises a pressure transducer, mechanical stirrer, bursting disc and thermocouples.

For safety reasons both vessels and the oven are enclosed in a explosion proof cubicle. Control of temperature, pressure (valve sequence) and additions is achieved remotely by means of a micro-computer and where applicable, high pressure pumps.

ROUND ROBIN TEST DATA

The performance of the Dewar has been discussed previously (Reference 4) by comparison with data generated in the Fauske VSP apparatus.

However, in 1987, a formal Round Robin Testing Programme was initiated by the DIERS User Group for the VSP apparatus (Fike/Fauske) to investigate reproducibility of data. Companies with other test equipment (applicable to emergency vent design) were also invited to participate in the test programme, one of which was ICI FCMO. Details of the test conditions and results are given in Reference 5.

Phase I of the programme involved the study of two reacting systems - the polymerisation of styrene with 0.5% by weight benzoyl peroxide and the decomposition of 15% by weight di-tert-butyl peroxide in toluene (or benzene) solvent. Both reactions were tested in the closed system mode.

A comparison of test data was made between the VSP and the adiabatic pressure Dewar for the two reacting systems. The result from the Dewar are shown graphically in Figures 4 and 5 for styrene and di-tert-butyl peroxide respectively. The kinetics of both systems have been studied and the results showing the comparison with VSP data are plotted in Figures 6 and 7.

The rate constant was determined using the equation shown below:-

$$K = \frac{dT/dt}{T_{max}-T}$$

Both sets of data show good agreement with the VSP test results throughout the temperature ranges.

CASE HISTORIES

The following case histories have been chosen to illustrate the diversity of conditions encountered in the Fine Chemicals Industry, although the first is an example of a dedicated, continuous process rather than the more common batch multistage synthesis.

PROCESS A

Phosphorus pentasulphide is manufactured by reacting molten phosphorus with sulphur at approx 500°C. The process is continuous and is achieved by the controlled addition of both reactants to the base of the reactor via dip-pipes.

The phosphorus is stored under water to eliminate the possibility of reaction with air. However, in the event of a depleted feed of phosphorus, water could be fed to the molten material resulting in the generation of steam and hydrogen sulphide below the melt. Experimental work was undertaken therefore to quantify the relief requirements since in a sealed system such an occurrence would result in subjecting the plant to considerable overpressure.

Calculations indicated that relief from the reactor would be two phase, even if the system was a non-foamer. The data showed that the level swell in the reactor in the case of water ingress, would be 200-300% of the normal working level due to gas/vapour hold-up in the liquid and that this would cause molten P_2S_5 and gas to enter the relief vent.

The stainless steel pressure Dewar apparatus (see figure 3) was used to simulate the reactor. It was fitted with vapour and liquid thermocouples, a heater, pressure transducer, dip-pipe and vent pipe. The phosphorus pentasulphide charge was 500 g and the whole apparatus was sited in a cylindrical furnace.

Electrical power was applied to both the internal coil and the furnace to raise the sample to a temperature of 500°C. At this temperature, water was pumped into the reaction melt via a dip-pipe, simulating the plant feed rate. To overcome the risk of hydrogen sulphide emission to atmosphere, the experiment was conducted in a 40 m³ Fire Trial Enclosure which was ventilated to atmosphere via an After-burner.

In direct scaling tests, it is essential to ensure that non-equilibrium effects on the small scale do not occur. Work carried out by the Design Institute for Emergency Relief Systems (DIERS) has shown that a vent pipe not less than 100 mm long is needed to overcome this problem. Consequently, a vent pipe of 110 mm in length was used for all of the tests.

Violent gas evolution with entrained droplets, commenced immediately following the addition of water with little reduction in temperature (see Figure 8). After approximately 5 seconds the discharge spontaneously ignited forming a plume about 60 cm in length. A dense white cloud of decomposition products formed with burning liquid droplets falling to the floor in a large area surrounding the apparatus. A fire also started at the top of the small scale reactor as burning material accumulate on the fibre insulation.

The test described does not simulate plant superficial gas velocities because the interfacial area between the liquid and vapour in small scale vessels is generally too large in proportion to the large scale reactor. Therefore, the degree of swelling and liquid discharge on the small scale is considerably less than would occur on the plant scale. Further tests were carried out to simulate full scale swell conditions by increasing the feed rate of the water to give the same superficial gas velocity as plant scale, albeit with an increased gas generation rate. The effects were similar to those described above.

All of the tests were examined in detail from a video recording of the experiments.

The minimum vent requirement was calculated to be 7211 mm^2 . This is applicable to a two-phase discharge and limits the pressure in the reactor to an acceptable level. However, there are a number of secondary effects which need to be given consideration.

In the relief situation, when the device has activated, the ejection of burning fragments and a stabilised flame 5-15 m in height would give rise to secondary fires and thermal radiation hazards in neighbouring plant. Operatives working in the vicinity of the plant would also be at risk from falling molten and burning material.

Secondly, toxic effects need to be considered. Experiments on the small scale showed that spontaneous ignition of the discharge although likely, is unpredictable and depends on the steam content of the emission. In the event of ignition, the combustion products would contain mainly SO_2 . If ignition does not occur, the discharge would consist of hydrogen sulphide which in addition to being extremely toxic, has a very low odour threshold value (<0.005 ppm for 100% recognition). It is feasible to limit the duration of the emission however by provision of a shut-off valve on the feed supply to the reactor. This could be activated by the operation of the relief device.

Thirdly, there exists a risk of solidification in the vent pipe caused by molten material entrained in the gas. Although the risk of blockage is low during the release, if the discharge was intermittent and the relief system called upon a second time, deposits in the downstream pipework may cause a serious flow restriction. It would be essential therefore to trace heat the discharge pipework and components (flanges, bursting disc etc), to prevent overpressurisation of the reactor caused by deposition in the discharge pipe.

It is common practice to provide a catchpot system for emergency vents to safely contain the emitted material and reduce the environmental hazard. In this case however, it is considered that the safe discharge of emitted material was not practicable since a dump tank would need to be nitrogen blanketed to prevent autoignition, heated to prevent solidification and blockages, vented to relieve the permanent gas produced and connected to a scrubber to remove $\text{SO}_2/\text{H}_2\text{S}$.

In this instance, the only reliable means of ensuring safety was to use a high integrity trip system.

PROCESS B

Polymer A is produced by an emulsion polymerisation process on the 8000 Kg scale. The process involves the addition of two chemically different initiators and an emulsifying agent to the monomers at controlled rates and at various stages of the reaction.

For emergency vent design, it is necessary to identify the worst case upset condition in terms of subjecting the reaction vessel and interconnected equipment to overpressure.

Generally, small scale screening tests are carried out to investigate the sensitivity of the normal reaction profile to various credible maloperations, as discussed earlier. However, due to the relatively

small quantities of material involved, a direct simulation of the process (and maloperations) was not possible on the small (10-50 g) scale. Adiabatic pressure Dewar (1000 ml) techniques were therefore employed throughout the investigation.

The test apparatus (see Figure 3) comprised a 1000 ml stainless steel pressure Dewar fitted with stirrer, thermocouples (2), internal heater, pressure transducer and liquid feed ports (2).

The Dewar vessel was enclosed in an oven which was set to run adiabatically thus ensuring minimal heat loss to the surroundings, simulating the large scale plant condition.

The first reaction to be run in the test was the 'normal process'. Data from this experiment is used as the basis for evaluating the various deviations resulting from maloperation. Some of the upset conditions considered were:

- i) Maximum possible feed rate of initiators (1 and/or 2).
- ii) Overcharging initiator(s).
- iii) Increase in strength of initiator solution(s).
- iv) Reduced water charge.
- v) Omitting water charge.

The results from the pressure Dewar experiments showed that the effect of increasing the concentration of the second initiator solution was to increase the peak power output from 42 W/Kg to 1137 W/Kg. This increased further by reducing the water charge to 10%, giving a peak value of 1582 W/Kg. Both tests were carried out with a higher initiator addition rate than the 'normal' process.

It was evident from all of the tests that the predominant effect on the reaction rate and pressure generation was that of increasing the strength of the second initiator to form a saturated solution. However, the effect of reducing the water charge was not insignificant in increasing the peak pressure from 170 psia to 281 psia.

It is worthwhile making the point here, that changing the concentration of a volatile reagent may be potentially hazardous in terms of pressure generation even though the change may result in a slower rate of reaction.

The peak pressures referred to above apply to the polymerisation reaction and occur concurrently with the peak exotherm temperature. However in the final test (see Figure 9) the experiment was allowed to proceed beyond the first exotherm peak to examine any after effects. A second self-heating stage occurred which became rapid after a further 35 minutes. This was attributed to the decomposition of the 'polymer' resulting in the generation of non-condensable gas, from an effectively solid residue.

Exothermic runaway caused by an increase in the concentration of the second initiating solution would not have resulted in overpressurisation of

the autoclave. However, the capacity of the relief system did need to be considered for the decomposition stage since the total quantity of non-condensable gas would have caused overpressurisation because of the relatively small ullage space in the reactor.

In this instance, the proposed vent size provided more than adequate relief capacity to prevent overpressurisation. In practice, the rapid pressurisation due to the polymerisation exotherm per se, could have been contained by using a high relief device set pressure. This is an interesting anomaly since generally it is prudent to set the relief device operating pressure as low as practicable for emergency relief cases.

DISCHARGE CONSIDERATIONS

The examples discussed in the previous section illustrate two extremes in discharge conditions, from a simple gas phase release at high pressure to an extremely hazardous and environmentally unacceptable emission. However, most relief events in the Fine Chemicals Industry fall between the two extremes, but often resulting in the loss of significant quantities of material even with non-foamy systems due to vapour or gas hold up within the bulk liquid. In cases where the system is inherently surface active, disengagement does not occur and the reactor, once vented, can empty completely. Knock-out and scrubbing facilities therefore are an essential consideration in the design of the relief system.

The use of proprietary equipment such as cyclones, separators etc may not be entirely practical since they are generally designed to operate under specific conditions of known flow velocity, temperature, pressure, composition etc. In the case of emergency relief however, such conditions are not always totally predictable and the design of a suitable discharge system which covers a wide range of operating conditions is both difficult to engineer and almost certainly uneconomic.

In the FCMO of ICI, one method which has been used for the disposal of offensive and odorous material is that of incineration. This utilises existing plant and facilities but does require the provision of a suitably designed explosion protective system to ensure safe operation.

In general however, the lack of adequate means of disposal and the secondary measures needed to effect a safe discharge often preclude the use of emergency venting as a safety measure.

CONCLUSIONS

- (a) In the Fine Chemical Manufacturing Industry, there exists a wide range in reaction chemistry and process operations. This involves the use of multiproduct, non-dedicated plant units to meet the rapidly changing demands of the market.
- (b) Emergency relief is only one course of action in achieving safety. Often preventative measures can be used which preclude the need for consideration of secondary treatment and disposal of vented material.

- (c) Unique and novel techniques sometimes need to be developed for the evaluation of process hazards on the small scale.
- (d) Large scale (1000 ml) test equipment has certain advantages in as much as the process can be simulated more closely in terms of quantities, concentrations, feed rates etc. Such tests cannot however be run in isolation, smaller scale screening experiments are needed to identify reacting systems which decompose explosively prior to larger scale evaluations.
- (e) The calculation of relief size is only one aspect of relief system design. There is a continuing and increasing need to consider secondary effects such as flammability (and the risk of UVCE's), pollution (in both the long and short term) and by no means least adverse publicity.

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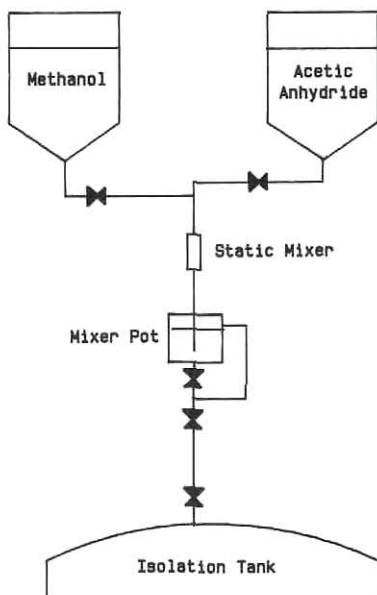


FIGURE 1. EXISTING PLANT LAYOUT

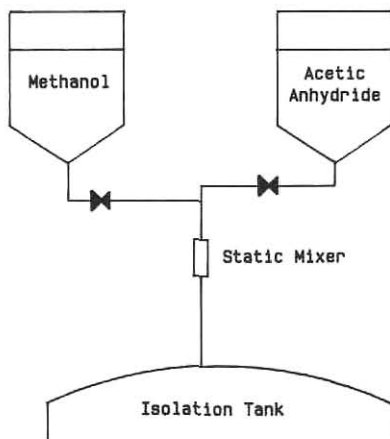


FIGURE 2. REVISED PLANT LAYOUT

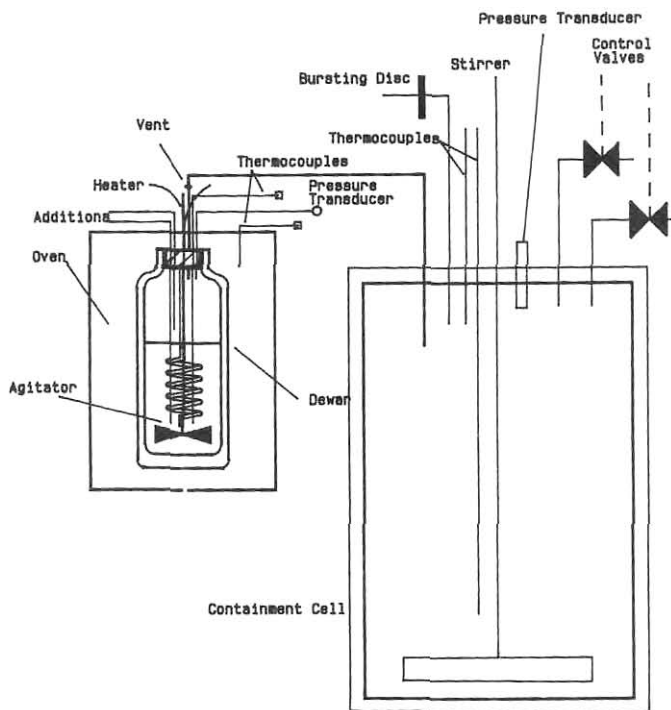


FIGURE 3. PRESSURE DEWAR AND CONTAINMENT APPARATUS

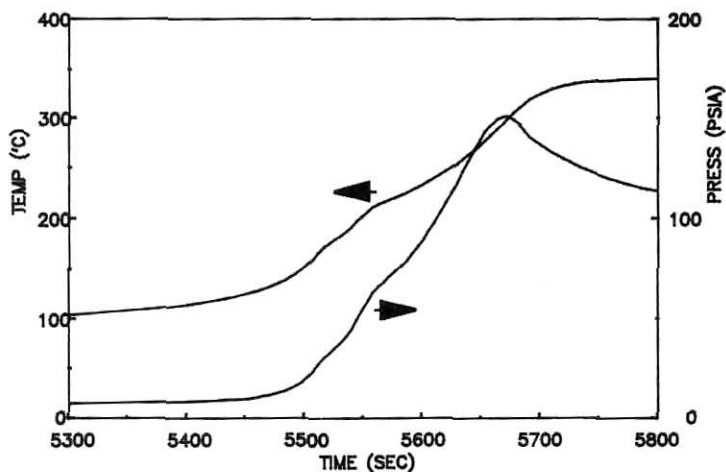


FIGURE 4. STYRENE + 0.5%wt BENZOYL PEROXIDE

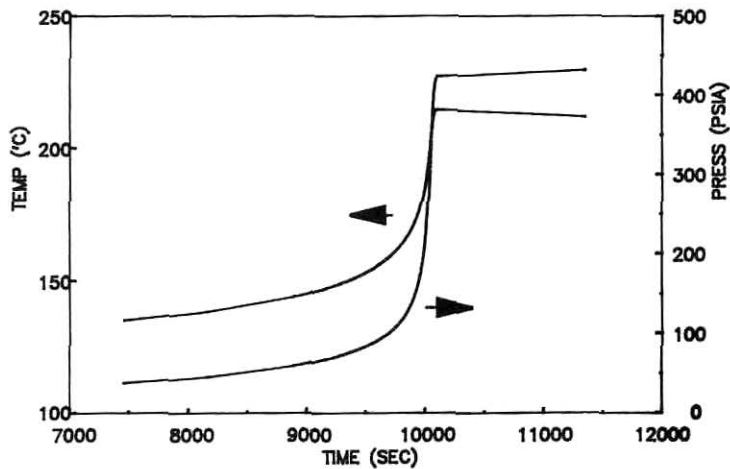


FIGURE 5. 15%wt DTBP IN TOLUENE

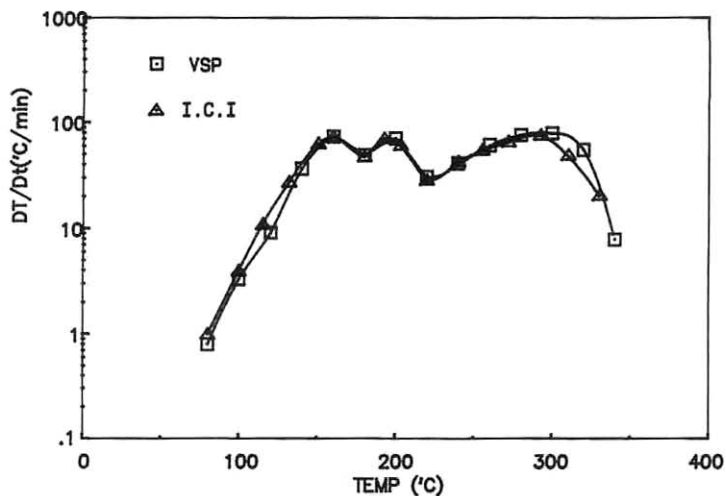


FIGURE 6. COMPARISON OF SELF HEAT RATES FOR
STYRENE + 0.5%wt BENZOYL PEROXIDE

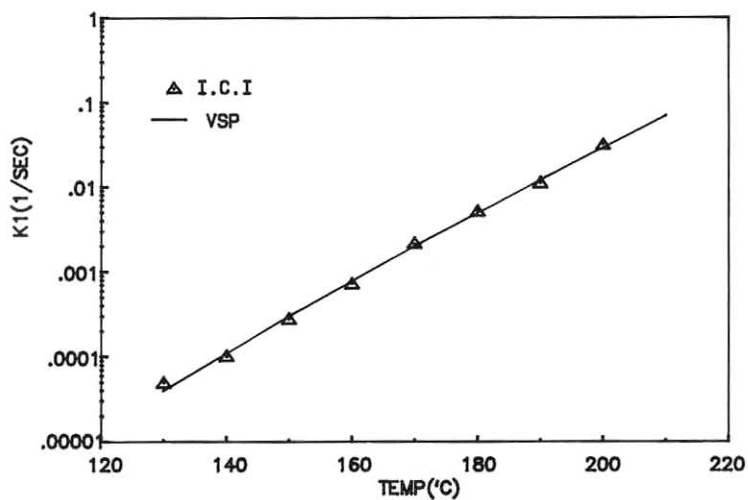


FIGURE 7. COMPARISON OF RATE DATA FOR 15%wt DTBP IN TOLUENE

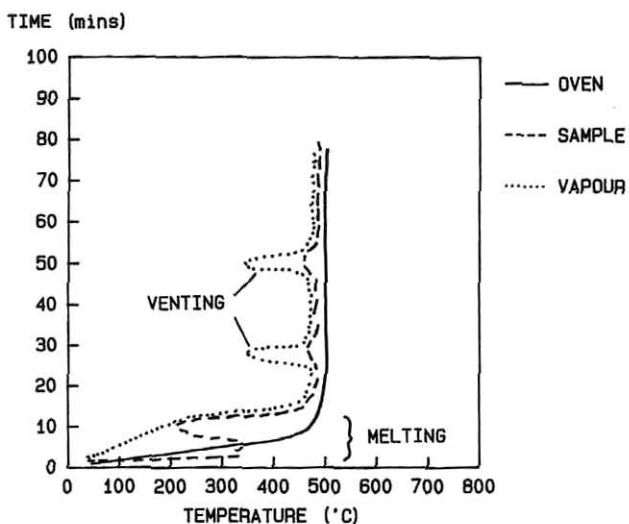


FIGURE 8. P2S5 TIME/TEMPERATURE PROFILE

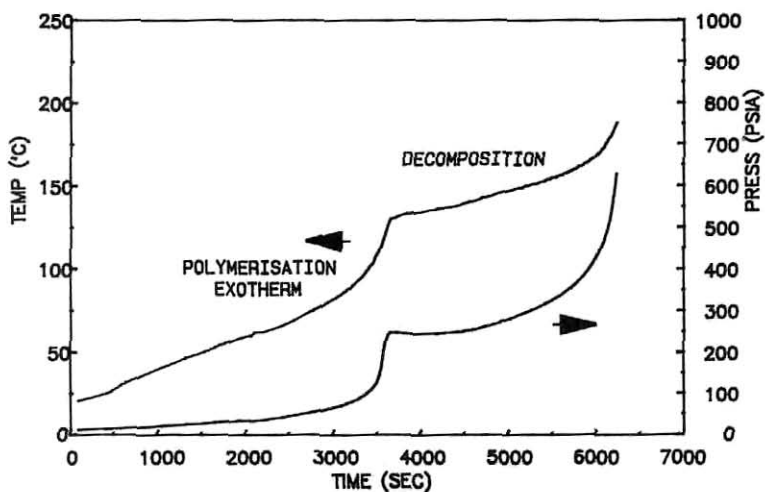


FIGURE 9. EMULSION POLYMERISATION REACTION