

# LEARNING FROM ACCIDENTS: INVESTIGATION AND RISK ANALYSIS OF AN INCIDENT IN THE TRANSPORT AND STORAGE OF MONOMERS

Giuseppe Maschio <sup>a\*</sup>, Maria Francesca Milazzo <sup>b</sup>, Valeria Casson <sup>a</sup>

<sup>a</sup>Dipartimento di Principi e Impianti di Ingegneria Chimica “I. Sorgato”, Università di Padova  
Via F. Marzolo, 9 – 35131 Padova – ITALY.

<sup>b</sup>Dipartimento di Chimica Industriale e Ingegneria dei Materiali, Università di Messina  
Viale Ferdinando Stagno d'Alcontres, 31 (Villaggio S.Agata) – 98166 Messina – ITALY.

\* giuseppe.maschio@unipd.it

This work presents the analysis of an incident occurred during the transport of divinylbenzene (DVB); the event is investigated by means of experimental analysis and mathematical modelling. The objective of the experimental part is to contribute to the determination of the causes that brought about the self-polymerization of commercial divinylbenzene contained in an isothermal container. Time and conditions during transport/storage of monomers are important factors that affect the self-polymerization aptitude of these substances. The modelling of the incident has been made in order to point out the need of a detailed risk analysis to support emergency management in the transport of hazardous materials. The importance of risk analysis in the transport of dangerous goods has been evidenced by several studies in the last decade, these also showed that in some case the risk associated with the transport of hazardous substances could be comparable to those associated with chemical plants.

## 1. INTRODUCTION

During the past decade several studies have demonstrated that incidents related to the transportation of dangerous goods are comparable in number and magnitude to those occurring in chemical plants. This is evident considering that tankers for the transport of dangerous substances, even containing a smaller quantity than storage tanks, often crosses urban areas with high population density (see Egidi et al., 1995 and Milazzo et al., 2002). According to these considerations, it is obvious that the transport of dangerous substances can cause severe risk to human health and environment. For this reason, even without a specific legislation to control the risk associated with the transport of hazardous goods, methods and risk analysis tools have to be used in order to estimate risk indexes.

This paper focuses on an incident in the transport of divinylbenzene. A post-incident analysis has been executed to provide elements that contribute to the knowledge of the dangerousness of this substance. The objectives of this work are two: to contribute to the determination of the self-polymerization causes and to model the incidental scenarios due to the release of the divinylbenzene.

Firstly the event has been examined from the experimental point of view. In particular one hypothesis has been investigated such as the insufficient quantity of oxygen in the tanker to properly activate the inhibition mechanism. According to this consideration the influence of the exposure to air on the self-polymerization of the monomer and on the inhibition mechanism have been studied. To this purpose different calorimetric techniques have been applied, in particular the Differential Scanning Calorimetry and the Adiabatic Calorimetry.

Then a simulation of the event has been performed by means of mathematical models. Data processing provides a risk index, which allows drawing a risk map. Results point out the need of a detailed analysis of all potential scenarios associated to the transport of the substance in order to manage the emergency.

### **INCIDENT DESCRIPTION**

The incident investigated in this paper occurred in the Scottish seaport of Grangemouth. Divinylbenzene, contained in a 24000 L isothermal container, self-polymerized due to the sunlight exposure. A tank fracture, caused by its displacement, generated the loss of very large amount of DVB. Following the release of the substance a white and dense plume of vapours dispersed in the atmosphere. Figure 1 shows the location of the container.



*Fig. 1. Location of the container in the seaport of Grangemouth.*

The firemen sealed off the zone for a range of 500 m as shown in figure 2. The residents were not evacuated but they were forced to stay home for 24 hours as a preventive measure because of the irritating effects of the monomer for the skin and eyes. The seaport was idle for 36 hours, until the vapour was completely dispersed by the wind. No injuries were reported.



Fig. 2. Emergency zone (the ray of the circle is equal to 500 m).

Divinylbenzene is a flammable and toxic liquid and is stored in atmospheric tankers. According to its properties, the common equipment design and handling techniques for its hazardous class must be practiced to prevent conditions that can cause fire or explosion and/or the dispersion in the air.

DVB is an aromatic monomer used principally for cross-linking styrene in the production of ion exchange resins. To stabilize this monomer, usually 4-tert-Butylcatechol (TBC) is added at a level of 900-1200 ppm by weight to act as an inhibitor to prevent the self-initiated autopolymerization of the material. Available data showed that oxygen influences considerably the inhibition properties of TBC. Because of this observation, in this study, attention has been paid to the effect due to the atmospheric oxygen exposure on DVB/TBC system.

## 2. CALORIMETRIC ANALYSES

DVB polymerizes by a self-initiated radical chain mechanism. As the inhibition mechanism of TBC toward this monomer is highly influenced by oxygen (Casson and Maschio, 2010), in a container with air in the head space the rate of inhibition could become controlled by the rate at which oxygen is dissolving in the monomer. After the polymerization reaction is started, the inhibition reaction may go on but at a decreasing rate (because of the oxygen consumption, and this would be manifested in an apparent self-acceleration of the reaction).

To determine the oxygen influence on TBC inhibition mechanism, a sample of DVB has been stirred (500 rpm at 50°C) for different periods, ranging from 0 to 13 days, in order to create a deep contact between the sample and

the air. This modified sample has been tested in both scanning and isothermal experiments in a Differential Scanning Calorimeter. The aim of scanning tests is to determine the onset temperature of the reaction. Isothermal tests are useful to evaluate the heat produced by the polymerization, the conversion and the induction period as a function of the set temperature.

## 2.1 Experimental results

In figure 3 the results of the scanning tests ( $5^{\circ}\text{C}/\text{min}$  from  $30^{\circ}\text{C}$  to  $250^{\circ}\text{C}$ ) are reported, where the 0d curve refers to fresh DVB. From this graph it is possible to see that incrementing the contact period between air (oxygen) and DVB/TBC system, the polymerization starts at higher temperatures. A considerable difference can be observed after 1 week of air exposure: in particular the curve that refers to an air exposure of 13 days shows that the onset temperature changes from  $162^{\circ}\text{C}$  to  $178^{\circ}\text{C}$ .

Experimental profiles derived from isothermal tests (set temperature:  $130^{\circ}\text{C}$ ) are shown in figure 4. The 0d curve refers to fresh DVB, and the other to treated DVB as explained before, from 1 to 7 days.

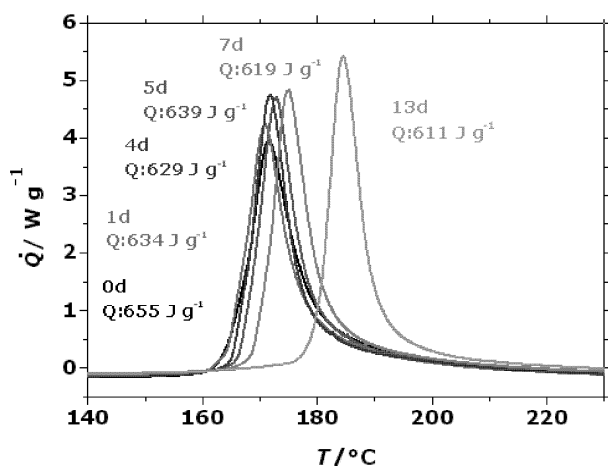


Fig. 3. DSC scanning tests: the effect of air exposure on DVB polymerization.

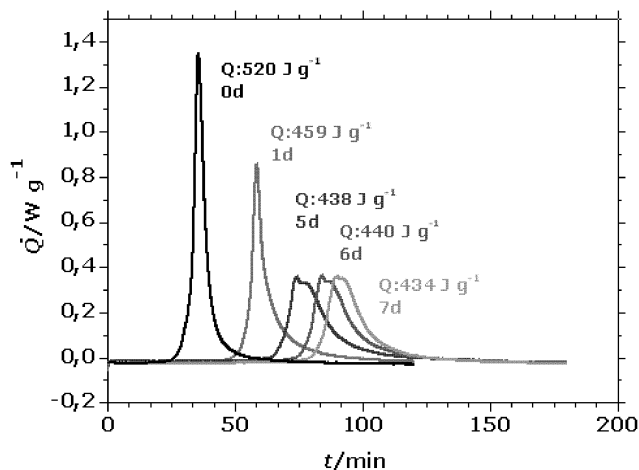


Fig. 4. DSC  $130^{\circ}\text{C}$  isothermal tests: the effect air exposure on DVB polymerization.



These data show that induction period increases for longer air exposures, confirming the role of the oxygen in TBC inhibition mechanism. Passing from shorter to longer air exposures also the shape of the peaks changes, getting lower and rounded, and the heat evolved by the reaction decreases. So oxygen carries out two actions in this process: it promotes TBC inhibition mechanism incrementing induction period but it also oxidize DVB, making the monomer inactive to polymerization (deduced by a lower heat evolved during reaction and a lower reaction rate).

These results are confirmed by the adiabatic calorimetric tests carried out in the PhiTecII calorimeter. In this case DVB is tested in two different chemical atmospheres: air and nitrogen. In figure 5 the experimental profiles of temperature and pressure versus time are shown for the air pressurized test.

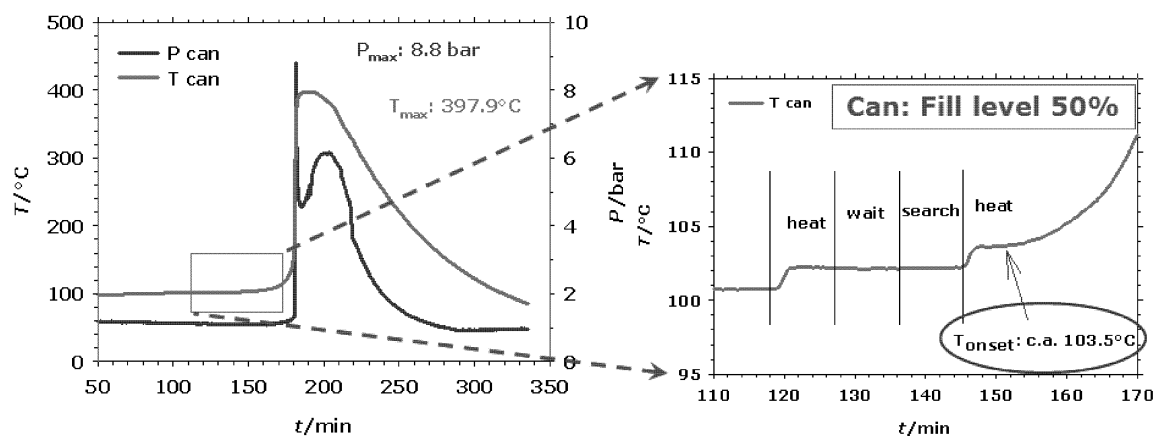


Fig. 5. Adiabatic test of DVB in air.

The inhibiting effect of the oxygen on the auto polymerization reaction is evident by comparing the results with another adiabatic test carried out in a nitrogen atmosphere. In Table 1 the results of these two tests are compared.

Table 1: Adiabatic tests: comparison between air and nitrogen atmosphere.

DVB [g]	atmosphere	$T_{\text{onset}}$ [°C]	$T_{\text{max}}$ [°C]	$\Delta T_{\text{ad}}$ [°C]	$P_{\text{max}}$ [bar]
50.38	air	103.5	397.9	294.4	8.8
50.35	N <sub>2</sub>	87.7	394.5	306.0	7.4

The detected onset temperature decreases of 16°C from air to nitrogen condition test, while  $\Delta T_{\text{ad}}$  increases of 11.6°C, as a prove of the inadequacy inhibition of TBC toward DVB in lack of oxygen.

## 2.2 Considerations

The shapes of the isothermal test DSC curves show that the final conversion decreases as the oxygen exposure increases. This observation is important in order to estimate how much DVB was released in the atmosphere during the incident in Grangemouth. As the polymerization proceeds, the viscosity of the reacting system increases and this in some way must reduce the rate of initiation to such an extent that polymerization effectively ceases.

The quantity of dissolved oxygen is fundamental for the stability of the monomer. The inhibiting effect of the oxygen on the auto polymerization reaction is evident by comparing the results with another adiabatic test carried out in a nitrogen atmosphere.

### 3. SIMULATIONS

In the second part of the work the event has been modelled using specific simulation models. Firstly the event tree related to the release of the divinylbenzene has been constructed in order to identify the potential incidental scenarios. The event tree technique has also allowed the determination of the frequencies associated with each scenario. On the basis of knowledge of the storage conditions and the physical-chemical properties of the substance (Weast, 1985) the event tree of figure 5 has been obtained.

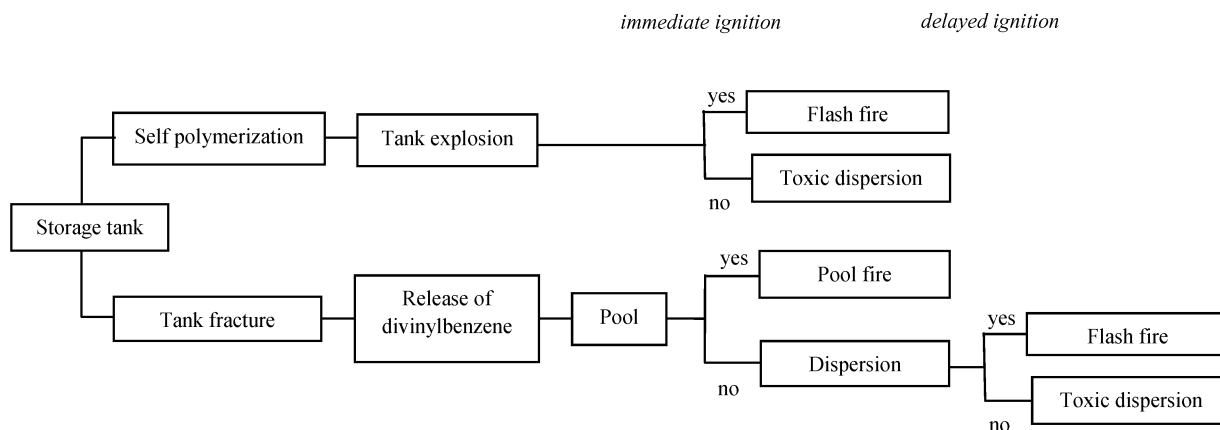


Fig. 6. Event tree.

According to the event tree, an explosion could occur following the self-polymerization, this is due to the exothermic reaction. In the case of the release of liquid, a pool is generated; if an immediate ignition occurs, a pool fire could be triggered. In absence of immediate ignition the substance evaporates and a toxic and flammable cloud diffuses in the atmosphere. The cloud could give a flash fire (or an explosion if the concentration of DVB is comprise in the explosiveness limits) or a dispersion of toxic vapours, depending on whether a delayed ignition will occur.

In the case of the Grangemouth incident, the catastrophic explosion of the tank did not occur but, as confirmed by the experimental results, the heating of the mass due to the self polymerization caused the vaporization of a portion of monomer that was released in the atmosphere because of the fracture on the container due to its displacement.

After the calculation of the amount of DVB in the cloud, the consequence estimation of the toxic dispersion has been executed using the mathematical models of the TNO (Yellow Book, 1997). Dispersions are affected by weather conditions, in this study the worst weather situations has been selected, named F2, which refer to the stability class F with wind speed of 2 m/s.

Then, using Probit functions, the *probability of damage* has been calculated and expressed as a function of the *dose*, which represents the entity of the consequence of a certain scenario. Finally the risk index has been obtained by multiplying the probability of damage and the frequency of the release. Frequency data was available in the HSE report.

#### 3.1 Results

Figure 7 shows the results of consequence assessment. Since immediate toxicity data of DVB are not available in literature, the iso-consequence curve has been drawn on the base of the TLV-TWA (threshold limit value -time weighted average) representing the average exposure on the basis of 8h/day or 40h/week work schedule.



Fig. 7. Iso-consequence curve for the release of DVB (the ray of the circle is equal to 460 m).

Using the TLV-TWA (10 ppm) the consequence evaluation is extremely conservative; however results show that the emergency area coincides with the area evacuated by firemen.

The risk results have been shown using Cartesian graphs showing the dependence of the risk index ( $R$ , logarithmic scale) by the distance ( $d$ ) from the point where the event is initiated. In figures 8 and 9 the distance  $d$  represents, respectively, the downwind and crosswind directions. It is possible to note that the curves are not well defined near to the point of release due to the complexity of the consequence modelling in proximity to the source.

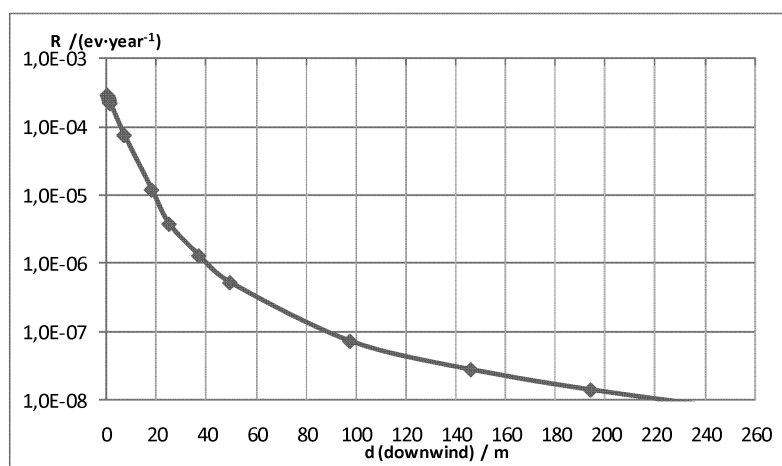


Fig. 8. Risk vs. downwind distance for a toxic dispersion of divinylbenzene (meteorological condition F2).

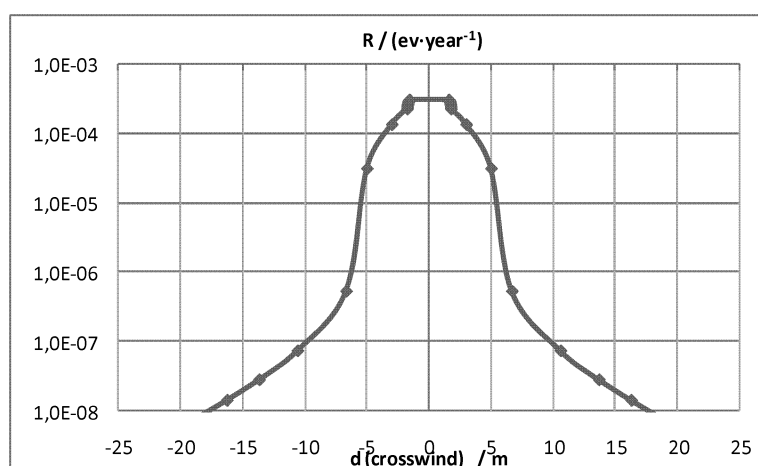


Fig. 9. Risk vs. crosswind distance for a toxic dispersion of divinylbenzene (meteorological condition F2).

The iso-risk mapping is shown in figure 10; the iso-risk curve has been drawn according to the most restrictive threshold limit of risk acceptability ( $10^{-8}$  event/year).



Fig. 10. Iso-risk curve for the release of DVB (the ray of the circle is equal to 220 m).

### 3.2 Considerations

The modelling provides results that in this paper are shown using two approaches: the consequence approach and the risk approach.

The consequence approach (deterministic approach) is based on the evaluation of the extent of the incident without quantifying its likelihood. It is based on the identification of the worst scenario, thus if there are enough measures to protect the population from the worst incident, enough protection will also be provided for any incident. The iso-consequence curves are drawn by estimating the distance where the physical magnitude (describing the consequences) reaches a threshold value corresponding to the beginning of the undesired effect (fatality).

The purpose of the risk approach (probabilistic approach) is not only to evaluate the severity of the potential incident, but also to estimate the likelihood of its occurrence. In general, the method uses more sophisticated tools and is more complete than the consequence approach. However, it is more complicated, time-consuming and expensive. It is based on the definition of a level of risk above which no person is permitted to be exposed.

Concerning the incident examined in this paper, in figures 7 and 10 the circles corresponding, respectively, to the iso-consequence curve (for a concentration of 10 ppm) and the iso-risk contour (for a risk levels equal to  $10^{-8}$ ), are presented. The application of the consequence approach results in establishing a control zone of 460 m from

the parking area of the tank, while the application of the risk approach results in a control zone of 220 m. There is a significant difference between the zones calculated by the two approaches.

Some considerations can be done about this observation. Applying the consequence approach, the worst scenario is associated to weather condition F2 (in the case of toxic dispersion). Taking into consideration the fact that in the D stability class is the most frequent, it is obvious anyway that this class is considered as relatively bad according to the consequence approach. Applying the risk approach, some uncertainties are introduced about the frequencies selected, but the protection must be increased for the stability class D because also the risk level increases due to the higher likelihood. This means that the extension of the zone delimited by the risk contour could be comparable with those delineated by the iso-consequence curve.

#### **4. CONCLUSIONS AND REMARKS**

The integrated approach between the experimental analysis and the modelling of the incident of Grangemouth give interesting contributions related to the knowledge of the causes of the release of the DVB and about its impact on the territory.

The experimental results showed the importance on the transport and storage conditions: an insufficient quantity of oxygen available in the system (due for example to an overfilling of the tank that reduces the free head space volume) can make inhibition mechanism inadequate. Also storage temperature is a fundamental parameter in case of polymeric materials: particular attention to self-polymerization onset temperature has to be paid.

The simulation of the dispersion of the cloud of DVB has permitted a comparison between the consequence approach and the risk approach for the emergency management. Both the approaches can be used and provides useful information during the emergency situation.

#### **5. REFERENCES**

- Bowden M. J., 1979, *Macromolecules. An introduction to polymer science*. Eds. Bovey F.A. and Winslow F.H., Academic Press, Inc., New York.
- Casson V., Maschio G., 2011. Risk analysis in transport and storage of monomer: an accident investigation. *Macromolecular Symposia* (in press).
- HSE, Health and Safety Executive, 2010. Failure Rate and Event Data for use within Land Use Planning Risk Assessments. Report.
- Egidi D., Foraboschi F.P., Spadoni G. and Amendola A., 1995. The ARIPAR project: analysis of the major accident risks connected with industrial and transportation activities in the Ravenna area. *Reliability Eng. & Systems Safety*, 49, 75-79.
- Milazzo M.F., Lisi R., Maschio G., Antonioni G., Bonvicini S. and Spadoni G., 2002. HazMat transport through Messina town; from risk analysis suggestions for improving territorial safety. *Journal of Loss Prevention in the Process Industries*, 15, 347-356.
- Morrison R.T., Boyd R.N., 1997, *Chimica Organica*, Casa Editrice Ambrosiana.
- Van den Bosh C.J.H., Weterings R.A.P.M., 1997. *Methods for the Calculation of Physical Effects* (TNO Yellow Book). Committee for the Prevention of Disasters, The Hague.
- Weast R.C., 1985. *Handbook of Chemistry & Physics* (65<sup>th</sup> edition). CRC Press Inc.

#### **ACKNOWLEDGEMENTS**

The financial support of the University of Padova is gratefully acknowledged.