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Risk Analysis in Transport and Storage of Monomers: An Accident Investigation

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Summary: In this work the analysis of an accident in transport of dangerous goods is proposed. The objective of this study is to contribute to the determination of the causes that brought about the self-polymerization of commercial divinylbenzene (DVB 63%) contained in an iso-container, in order to prevent this accident to happen in the future. Time and conditions during transport and storage of monomers (in particular the storage temperature) are very important factors, that affect the self-polymerization aptitude of these substances. 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. In particular one hypothesis has been investigated: probably the quantity of oxygen in the tanker was insufficient to activate properly the inhibition mechanism of TBC. From this consideration the self-polymerization of DVB and the inhibition mechanism of TBC have been studied as a function of temperature and monomer exposure to air. Different calorimetric techniques have been applied, in particular Differential Scanning Calorimetry and Adiabatic Calorimetry, to investigate the causes of the accident.

Keywords: adiabatic calorimetry; differential scanning calorimetry; inhibitors; mitigation system; runaway; storage and transport safety

Introduction

Divinylbenzene (DVB) is an aromatic monomer used principally for cross-linking styrene in the production of ion exchange resins.[1] Much of this production is located in Europe. The 23th August 2006, in the Scottish seaport of Grangemouth, divinylbenzene (DVB 63%) contained in a tanker (24000 litres) exposed to sunlight on the docks self-polymerized.[2,3] The tank fracture (Scheme 1), due to its displacement, caused the loss of very big amount of DVB, as white and dense plume of vapours.

The firemen sealed off the zone for a range of 500 metres. The residents were not evacuated but they were forced to stay home for 24 hours as a preventive measure because of the irritating characteristics for the skin and eyes of the substance. The seaport was idle for 36 hours, until the wind had completely dispersed the cloud of vapours. No injuries were reported.

From available data, came out that oxygen influences considerably the inhibition properties of TBC. Because of this reason, in this study attention has been paid to the effect of atmospheric oxygen exposure of DVB/TBC system and to the storage temperature.

Oxygen Role in Inhibition Mechanism: Thermo-Kinetic Considerations

Divinylbenzene is an aromatic hydrocarbon which may be regarded as a derivative of styrene; it can exist as three isomers. Com-

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Scheme 1.
The isotainer involved in the accident.

mercial DVB is a mixture of DVB isomers and ethylvinylbenzene (EVB) isomers, e.g. 63%-DVB contains 63% by weight of DVB and 37% of EVB. Some properties of 63%-DVB are summarized in Table 1.[5]

4-tert-Butylcatechol ($C_{10}H_{14}O_2$) is added at a level of 900–1200 ppm by weight to commercial DVD to act as an inhibitor to prevent the self-initiated autopolymerization of the material.

DVB polymerizes by a self-initiated radical chain mechanism.[1] Termination can be either by the reaction of two polymer radicals (by combination or by disproportion[6]) or by the action of the inhibitor. Initiation consists of two steps. In the first, two monomer molecules undergo a Diels-Alder reaction to give a dimer. The Diels-Alder reaction involves the reaction of a conjugated diene with an alkene to give a cyclohexene.[7] In DVB the monomers are acting both as a conjugated diene and as an alkene. The rate of initiation depends on the dimer concentration and this depends on both the thermodynamics and kinetics of the Diels-Alder reaction. Considerations about the equilibrium constant for the formation of divinylbenzene Diels-Alder dimers[8,9] and the kinetics of the initiation reaction indicate that because of the small standard enthalpy of reaction and the small equilibrium constant for the dimerization reaction, initiation steps will not contribute to any self-heating in the reacting system. Self-heating will be due to the exothermic polymer radical propagation.

Table 1.
Properties of 63%-DVB.

Divinylbenzene/%	*62–64*
Ethylvinylbenzene /%	34–37
Total polymerizables (DVB and EVB)/%	96 min
Low Boilers/%	0.5 max
Diethylbenzene/%	0.5 max
High Boilers (other than naphthalene)/%	1.0 max
Napthalene/ppm	1000 max
Polymer/ppm	10 max
p-t-butyl catachol/ppm	1000–1200
Specific gravity (25 °C)	0.915
Melting point/°C	−88
Boiling point/°C	195
Solubility in water/% (25 °C)	0.0052

The inhibition mechanism of TBC toward DVB is highly influenced by oxygen.[1] The first step of this mechanism is the reaction of a polymer radical with oxygen to form a polymer peroxy radical:

$$P\cdot + O_2 = PO_2\cdot$$

The second step is a transfer reaction of this radical with TBC and the extraction of the hydrogen atom from the phenol group para to the t-butyl group with the formation of a polymer peroxide and a TBC radical:

$$PO_2 + TBC \rightarrow PO_2H + TBC \cdot$$

The last step is the reaction of the TBC radical. This can be with a polymer, leading to termination of a second polymer chain.

$$P \cdot + TBC\cdot \rightarrow P{-}TBC$$

It has been reported [1] that the TBC radical can also react with oxygen, probably with the formation of a TBC peroxy radical, which could itself form a peroxide either by reaction with a polymer radical or with a TBC radical:

$$TBC \cdot + O_2 = TBC - O_2 \cdot$$

The new radical, depending on its reactivity may either terminate another radical or initiate polymerization either by addition of a monomer or by chain transfer to a monomer. There may also be homolysis of the peroxide O–O bond with the production of two radicals $PO\cdot$. These radicals may then react by terminating radicals or by acting as initiators for polymerization. At lower temperatures the peroxides would be expected to react more by chain transfer and the radical produced to terminate another radical. At higher temperatures homolysis of the O–O bond would be expected to predominate and the radicals formed to initiate polymerization. The peroxides may therefore pass from having an inhibiting effect at low temperatures to acting as initiators at higher temperatures.

Because of the possible reaction of the TBC radical with oxygen there may not be an exact stechiometric ratio between oxygen and TBC consumed.

Oxygen is present dissolved in the DVB and in the air in the container head space. The molar ratio (R) of available oxygen to TBC is an important factor in TBC inhibition. A concentration of 15 mg/l has been reported for oxygen dissolved in DVB at 25 °C.[1] For a TBC concentration of 1200 ppm R is ≈0.06. Fig. 1 shows how R varies with the fractional head space volume (fhsv) for air at 25 °C and atmospheric pressure. This calculation has been made using the perfect gas equation an oxygen mole fraction of 0.2.

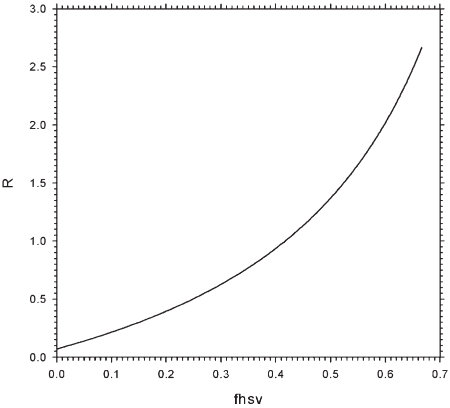

Figure 1.
R (the molar ratio of available oxygen to TBC) versus the fractional headspace volume (fhsv) at 25 °C.

So the inhibition mechanism discussed requires the formation of radicals, and therefore the rate of inhibition (v_{inhib}) cannot exceed the rate of initiation (v_I). Similarly the rate of termination (v_t) cannot exceed the rate of initiation. We will consider the induction period to be the time necessary to achieve the following condition

$$\Delta v = v_I - v_{inhib} - v_t > \Delta v_{critical} \quad (1)$$

where $v_{critical}$ is a condition that depends on the DSC instrument, the exothermicity of the reaction and the rate of the propagation reaction. Each DSC instrument has a certain maximum sensitivity. The greater the exothermicity of the reaction the easier it will be to detect the chemical heat flow. Finally the more propagation steps a radical undergoes before it is terminated, the easier it will be for the instrument to detect the heat changes due to the inhibition reaction.

Considering just the first two steps of inhibition mechanism, as inhibition takes place during the early part of the reaction, the contribution from the termination may be neglected. The two important differential equations then become

$$\frac{d[P\cdot]}{dt} = v_I - k_f[P\cdot][O_2] + k_r[PO_2\cdot] \quad (2)$$

$$\frac{d[PO_2\cdot]}{dt} = k_f[P\cdot][O_2] - (k_r + k[TBC])[PO_2\cdot] \tag{3}$$

with reaction rate constants k_f for the forward reaction and k_r for the reverse reaction of the first step and with a reaction rate constant k for the second.

Application of the steady state approximation to $PO_2\cdot$ gives

$$[PO_2\cdot] = \frac{k_f[P\cdot][O_2]}{(k_r + k[TBC])} \tag{4}$$

Substitution into Eqn. (2) gives

$$\frac{d[P\cdot]}{dt} = v_I - \frac{k_f k[P\cdot][O_2][TBC]}{(k_r + k[TBC])} \tag{5}$$

Two situations may be considered

(a) $k[TBC] \gg k_r$

$$\frac{d[P\cdot]}{dt} = v_I - k_f[P\cdot][O_2] \tag{6}$$

(b) $k_r \gg k[TBC]$

$$\frac{d[P\cdot]}{dt} = v_I - \frac{k_f k[P\cdot][O_2][TBC]}{k_r} \tag{7}$$

Remembering that the equilibrium constant for the formation of $[PO_2\cdot]$ is

$$K = \frac{k_f}{k_r} \tag{8}$$

$$\frac{d[P\cdot]}{dt} = v_i - kK[P\cdot][O_2][TBC] \tag{9}$$

In (a) soon after a $PO_2\cdot$ radical is formed it is removed by reaction with TBC. This would correspond closely to the usual view of an inhibitor if oxygen was regarded as the inhibitor. In (b) there is the possibility of some build up of $PO_2\cdot$ radicals.

Both Eqns (6) and (9) show that the rate of inhibition depends on the concentration of oxygen dissolved in the DVB. In a container with no head space, inhibition will cease shortly before all the oxygen is consumed, meaning that only a fraction of ≈ 0.06 of the TBC has reacted. In a container with air in the head space a situation may be reached where the rate of inhibition becomes controlled by the rate at which oxygen is dissolving. After the reaction has started the inhibition reaction may go on but at an ever decreasing rate, and this would be manifested in an apparent self-acceleration of the reaction.

Experimental Part

The aims of the laboratory tests are the comprehension of the role of the storage temperature in the auto-polymerization of DVB and of the role of the oxygen in the TBC inhibition mechanism toward this monomer, in order to validate the hypothesis done.

The first part of the experimental runs have been carried out in a Differential Scanning Calorimeter (DSC): both isothermal (in order to evaluate the heat produced by the polymerization, the conversion and the induction period as a function of the set temperature) and scanning tests (5 °C/min from 30 °C to 250 °C, whose objective is to determine the onset temperature of the reaction) have been run. In all DSC tests a mass of 20 μg of DVB at room temperature has been processed in aluminium pressured cans.

Figure 2 shows the results of a scanning test on DVB: the detected onset temperature for this reaction is 16 °C and the maximum value of the temperature reached is 173.7 °C

In Figure 3 the heat fluxes evolved during the polymerization are reported for all the isothermal tests done. It is possible to

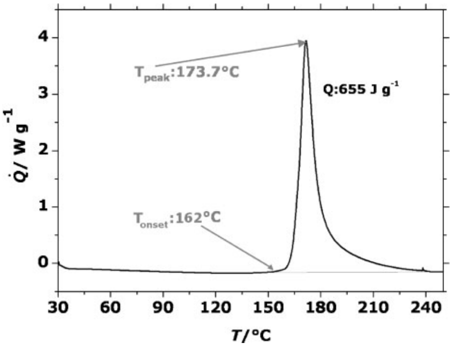

Figure 2.
DVB scanning test (5 °C/min): the onset and the peak temperature detected.

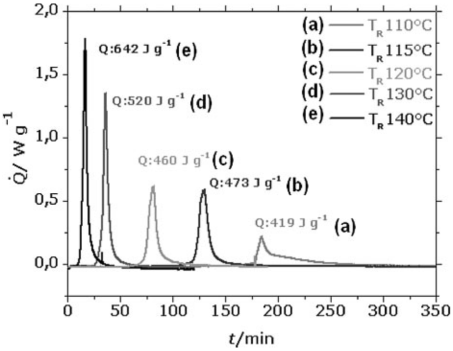

Figure 3.
DSC isothermal tests: the effect of temperature on auto-polymerization of DVB.

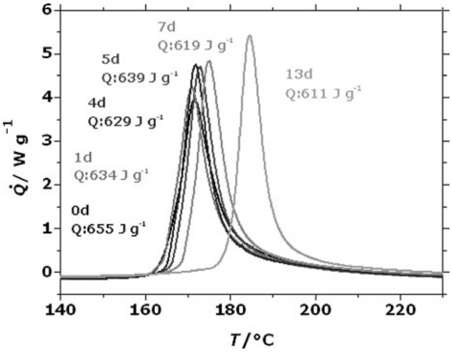

Figure 4.
DSC scanning tests (5 °C/min): the effect of air exposure on DVB polymerization.

observe that the reaction rate increases and the induction period decreases when the set temperature changes from 110 °C to 140 °C: in the first experiment the temperature peak is reached after 175 minutes from test beginning and it gradually slides to 10 minutes in the last isothermal run. Incrementing the set temperature, also the height and the shape of the temperature peaks change: they become higher and sharper, indicating a more hazardous behaviour of the monomer at higher temperatures. The heat evolved by the polymerization also increases with temperature; it could be due to:

- At lower temperatures the viscosity of the reacting mass increases, so the final conversion decreases (because of the reduced mobility of the propagating chains) leading to a reduction of the total heat evolved.
- During the induction period, for tests run at temperatures below 140 °C, in presence of air and peroxides, DVB can be oxidized to epoxides,[10] which are less reactive toward polymerization.

In order to determine the oxygen influence on TBC inhibition mechanism, a sample of DVB has been stirred (500 rpm, 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 Figure 4 the results of the scanning tests (5 °C/min from 30 °C to 250 °C) are reported, where the 0d curve refers to fresh DVB. From this graph it's 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 °C to 178 °C.

Experimental profiles derived from isothermal tests (set temperature: 130 °C) are shown in Fig. 5. The 0d curve refers to fresh DVB, and the other to treated DVB as explained before, for 1 to 7 days.

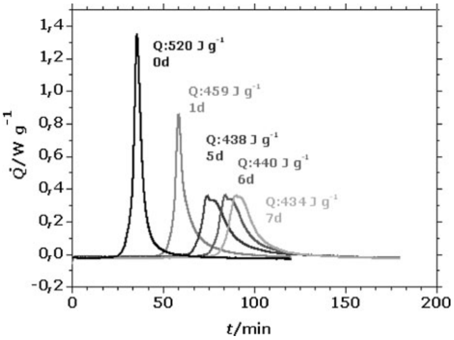

Figure 5.
DSC 130 °C isothermal tests: the effect air exposure on DVB polymerization.

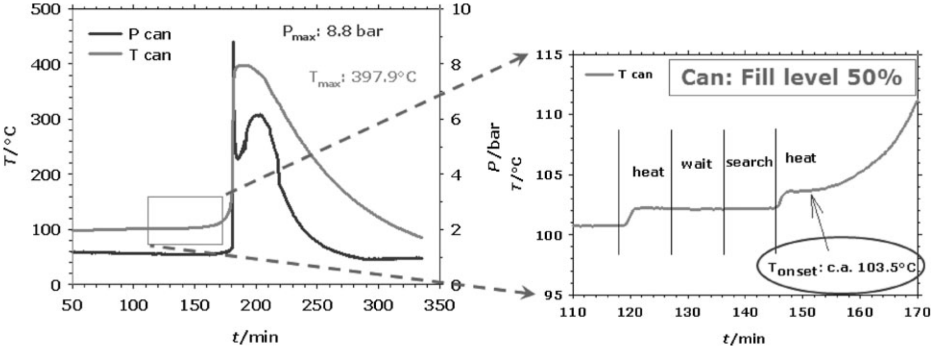

Figure 6.
Adiabatic test of DVB in air.

Table 2.
Adiabatic tests: comparison between air and nitrogen atmosphere.

DVB [g]	*atmosphere*	*Tonset [°C]*	*Tmax [°C]*	*ΔTad [°C]*	*Pmax [bar]*
50.38	air	103.5	397.9	294.4	8.8
50.35	N_2	87.7	394.5	306.0	7.4

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: these facts sustain the hypothesis of the DVB oxidation to epoxide. 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).

In the experimental runs, the second step is represented by adiabatic calorimetry tests, carried out in the Phi Tec II apparatus of HEL Ltd. In this case DVB is tested in *heat wait and search* mode (3 steps, step time = 27 minutes and $\Delta T_{step} = 1\,°C$) in two different chemical atmospheres (air and nitrogen). In Figure 6 the experimental profiles of temperature and pressure versus time are shown for the air pressurized test.

Because of the instrument sensibility, the detection of the onset temperature is more precise and conservative respect to the DSC runs: a value of 103.5 °C has been found; whereas because of its adiabaticity the temperature peak value is 397.9 °C, with an adiabatic temperature increment (ΔT_{ad}) of 294.4 °C. Pressure rises until 7.4 bar, with a maximum value of 8.8 bar.

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 2 the results of these two tests are compared.

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

Conclusion

In conclusion, the aims of this paper are the comprehension of the role of the storage temperature in the auto-polymerization of DVB and of the role of the oxygen in the TBC inhibition mechanism toward this monomer, in order to validate the hypothesis done.

The shapes of the isothermal test DSC curves on fresh DVB can be explained using the mechanism for radical polymerization, self-acceleration phenomena are accounted for by the gel effect. The final conversion decreases as the reaction temperature decreases. This observation is important in order to estimate how much DVB was released to the atmosphere in the Grangemouth incident. 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 isothermal tests show that the final conversion varies approximately linearly with the reaction time and that the induction period varies logarithmically with the reaction time.

The quantity of dissolved oxygen is fundamental for the stability of the monomer.

Because of the low concentration of TBC and oxygen we must conclude that the probability of forming a peroxy radical in an encounter of a radical with an oxygen molecule is greater than that for a propagation reaction when a radical encounters a monomer.

The increase in the induction period for DVB stirred in presence of air must be due to an increase in the quantity of inhibitor and we must conclude that there is some partial oxidation reaction which is contributing to this.

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