THE INVESTIGATION OF EMERGENCY PRESSURE RELIEF OF DECOMPOSING ORGANIC PEROXIDES

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MOTIVATION

Organic peroxides are a class of chemical compounds with some special properties. They are chemically unstable and have a high hazard potential. If a critical temperature is exceeded a self accelerating exothermic decomposition of the organic peroxide will be induced. One of the decomposition products in the gas phase is a certain amount of non-condensable carbon dioxide gas (CO_2). (The relief stream represents a so-called hybrid system. The gas phase contains the produced gas and vapour corresponding to the vapour pressure of the liquid phase.) Nevertheless the CO_2 is well soluble in the used solvent, the decomposition leads to an enormous pressure rise in closed containers.

To avoid the destruction of the transport or storage container caused by an intolerable pressure rise a well designed emergency pressure relief system is necessary.

PROBLEM

Normally with other substances after the bursting of the rupture disk at the pressure p_{set} and the following pressure relief the container is out of danger. But this is not necessarily true for decomposing organic peroxides. After the bursting of the rupture disk only a small amount of the peroxide is decomposed. Nevertheless when the relief orifice is open the increasing decomposition and gas production lead to a two-phase flow which causes a second pressure rise. Under certain circumstances the now reached pressure peak is higher than the first one and the container is in danger of bursting.

Up to now the second pressure peak can be determined only by trial and error methods. For a good design of an emergency pressure relief system a method for a better prediction of the second pressure peak is required.

METHODS

At first we have to find out the qualitative and later the quantitative influence of different influence parameters to the decomposition and the relief process. Therefore we carry out test series of pressure relief experiments with decomposing organic peroxide solutions. They are performed in a new developed testing apparatus called *STOP*[1] (Storage Vessel Test for Organic Peroxides). Briefly this apparatus is a scaled-down copy of a cylindrical transport tank for organic peroxides which is placed in a heating chamber. The tank container has an emergency pressure relief system on top. In comparison to the so called *10 litre test* recommended for such tests by the United Nations[2] the *STOP* has a volume of only approximately 1.9 litre. This makes the test series cheaper and less hazardous.

The measured parameters are the temperature at different places in the tank, the pressure in the tank and the amount of liquid phase that leaves the tank during the pressure relief period. A charting of the thermocouples placement in the tank can be seen in figure 1. With the thermocouples at different places, it is possible to follow the front of the exothermic decomposition through the container.

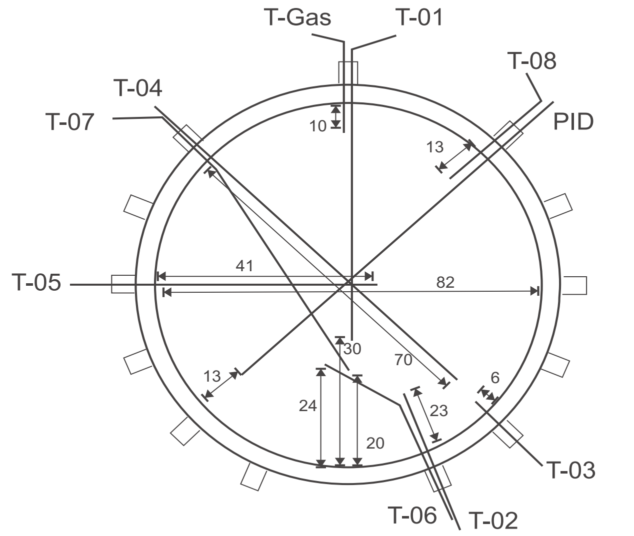

Figure 1: Placement of the thermocouples in STOP

The height of the above mentioned second pressure peak is a function of a number of parameters. For the following introduced experiments only two parameters are varied

- the relief diameter and
- the set pressure.

For different set pressures p_{set} corresponding rupture disks are used. The relief diameter can be varied by using orifice plates with diameters between 1 and 10 mm. The filling level and the concentration of the peroxide solution at the beginning of the experiments are constant.

EXAMPLES

The experiments have been carried out with the following constant parameters:

- Organic peroxide solution: Diisononanoylperoxide (INP); 30 Mass % in Isododecane
- Filling level of the tank: 90 Vol. %
- Temperature of the heating chamber: 120°C

Effect of relief diameter

In a first test series the relief diameter was varied. As can be expected the second pressure peak increases with decreasing relief diameter due to the increased pressure loss in the orifice.

Effect of set pressure

Now the set pressure p_{set} of the rupture disk was varied. The results of this test series were quit unexpected. The second pressure peak decreased with increasing p_{set}. The influence of both high and low response pressures of the rupture disk on the process of the decomposition can be seen in figures 2 and 3.

With respect to the temperatures in figure 2 it can be seen that the front of the reaction propagates more steady through the liquid. The decomposition is induced at the surface of the liquid and propagates through it to the bottom. Due to this the gas production rate is more steady, the liquid volume fraction in the relief flow and the pressure loss is low and the second pressure peak is low.

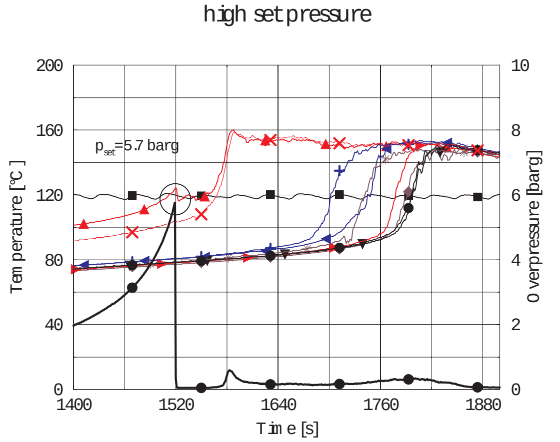

Figure 2: high p_{set}

On the other hand, the propagation of the decomposition in figure 3 occurs with a longer delay. But then the decomposition propagates much faster through the liquid. In this short time interval the gas production rate, and due to this the volume fraction of liquid in the relief flow, is higher. This leads to a second pressure peak which is much higher than p_{set}.

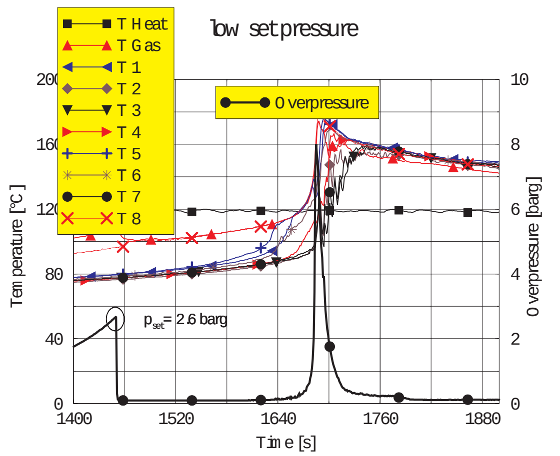

Figure 3: low p_{set}

CONCLUSIONS

For an explanation of this phenomenon the conditions of the system must be investigated at the moment when the rupture disk bursts. At this moment the differences between the two considered examples are the different amounts of CO_2 which is dissolved in the liquid and the slightly different temperatures T-Gas and T-8. The mechanisms by which these influencing variables causing the process flow have to be explored in the future.

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[1] Gmeinwieser, T.: Untersuchungen zur Auslegung von Notentspannungseinrichtungen für Lager- und Transportbehälter für organische Peroxide. Diss., Technische Universität Berlin, 2001.

[2] United Nations: Recommendations on the Transport of Dangerous Gods, Manual of Tests and Criteria. Second revised Edition, New York, 1995.