



# LEARNING FROM INCIDENTS AWARENESS ALERT

For Industry-Wide Sharing

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## Explosions in SMPO Hydrogenation Unit

### Target audience for this alert

- Process Safety and Process Engineers
- Production staff in Refining/Chemical and hydrogenation processes

### What happened

On June 3rd 2014, a Styrene Monomer and Propylene Oxide (SMPO) unit was in the pre start-up phase after the scheduled shutdown and replacement of catalyst in the hydrogenation reactors. The reaction system contained two fixed-bed adiabatic, trickle-flow reactors. Operations were heating up the hydrogenation unit in preparation for the catalyst reduction step. The heat-up was performed by the circulation of Ethyl Benzene (EB) through the reaction system under a nitrogen blanket and continuous nitrogen purge. During this heat up, one hydrogenation reactor and an additional upstream separation vessel suddenly exploded. Two contractor workers, who were in the immediate process area, were injured with burns from hot catalyst particles. The explosion caused extensive damage requiring over a year to repair.



Figure 1 – Hydrogenator structure after the explosion.

### Why it happened

The incident investigation concluded that both the reactor and vessel had failed because of overpressure, resulting from unexpected exothermic reactions between Ethyl Benzene (EB) and copper chromite oxide catalyst which produced an excessive amount of gas.

Prior to the incident, it was generally believed that under inert nitrogen conditions EB would not react with the passivated catalyst. However, it was subsequently determined and proven in the laboratory that two exothermic reactions actually occurred during the heat up:

- EB reacted with active oxygen present in the catalyst (mainly but not limited to copper chromate  $\text{CuCr}^{\text{VI}}\text{O}_4$ ). The catalyst contained more copper chromate than the previous catalyst used at the site. The redox reaction started when the temperature exceeded approximately  $90^\circ\text{C}$ . The target temperature at the end of the heat up phase was  $130^\circ\text{C}$ , but due to the exothermic reaction the temperature increased further in local dry zones of the trickle bed reactors.
- Copper oxide ( $\text{Cu}^{\text{II}}\text{O}$ ) was reduced by EB when localized temperatures reached  $180^\circ\text{C}$ . This redox reaction generated large amounts of heat and gaseous molecules (such as  $\text{CO}_2$  and  $\text{H}_2\text{O}$ ) leading to the overpressure.

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The early heat generation by the EB-chromate reaction, in combination with reduced cooling capacity in localized dry zones created localized temperatures in the reactor bed, high enough to initiate the EB-copper oxide reaction. Contributing factors include:

Low nitrogen flow: In a trickle flow reactor, sufficient nitrogen flow is required to achieve a proper liquid distribution from the distribution trays to wet the catalyst in the catalyst bed. The actual nitrogen flow was lower than needed, which led to non optimum liquid distribution in both trickle bed reactors causing dry zones in the top part of the catalyst beds.

Low EB flow: The EB flow to the hydrogenator was, at times, lower than needed for proper wetting of the catalyst and the flow variations led to preferential or rivulet flow and stagnant wet zones in the trickle flow reactor catalyst bed. These conditions led to non optimal heat removal and as a consequence high localized temperatures

Increasing Pressure: About thirty minutes before the explosion, the vent gas valve on the second separator tripped closed on high level and stayed closed. The system pressure increased up to the nitrogen supply pressure and caused the nitrogen flow to the reactor to decrease. The increasing pressure reduced the evaporative cooling of the EB from the catalyst.

Reactive hazard understanding: A Reactive Hazard Assessment (RHA) had been conducted in 2011 for this section of the SMPO unit. The RHA was based on process development work, design knowledge, literature search and application of a tool that was developed and used for identifying unintended reactions. The RHA only identified the reactions with hydrogen during the reduction phase. The reactions of EB with the catalyst in the absence of hydrogen were not identified in the RHA. This, together with the previous operational reduction experiences, reinforced the belief that EB was an inert medium in combination with the catalyst.

### Lessons learned

- The passivated copper chromite hydrogenation catalyst contains bonded oxygen in the form of copper chromate and copper oxide prior to reduction. Where a hydrocarbon and oxidizing substance (i.e. both a "fuel" and reactive oxygen) are combined and in sufficient quantities, an exothermic reaction may occur and the only mitigation available may be the total amount of cooling provided.
- Heating up in EB, prior to the reduction step with hydrogen, was seen as normal and safe from a chemical reaction point of view. This influenced the choices made during the process design, process development work, the design of the trickle bed reactor, qualification of the catalyst and operational procedures.
- The purpose of a Reactive Hazard Assessment (RHA) is to identify consequences of the potential reactions, intended and unintended, between the components of the reaction streams. At the time of the Assessment, The composition of the reactants and the potential initiation temperatures were not understood adequately. Post incident investigation suggests that suitable analytical tools such as Thermogravimetric Analysis (TGA) may help to identify such exothermic reactions.
- A series of incremental and seemingly innocuous changes can allow unknown reactions to proceed and run out of control, resulting in a severe incident. Introduction of a new catalyst or catalyst supplier can introduce new components or changes even in small quantities of components that could lead to unidentified and unintended chemical reactions. The catalyst selection and subsequent change processes should address these with the focus on reactive hazards in both transient and steady state operations. Note that this may also apply to changes in process chemicals in other services (e.g. polymerization inhibitors, cleaning solutions, etc.).

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