



**KOREA OCCUPATIONAL SAFETY & HEALTH AGENCY**

## **INVESTIGATION REPORT**

### **Explosion in BD Plant**



**Yeosoo, Korea**

**August, 2004**

#### **KEY ISSUES:**

- **Deviated operation from design condition**
- **Implementing MOC Strictly**

## **ABSTRACT**

This investigation report examines the reactor explosion incident that occurred on August 25, 2004 in a BD Plant, Yeosoo, Korea. The accident was occurred by the self-decomposition reaction of butadiene peroxide in the sulfur removal reactor. One operator was killed and one was critically injured. This report identifies the root and contributing causes of the accident and makes recommendations for control of hazardous routine maintenance, management of change.

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## 1.0 INTRODUCTION

On August, 2004, An explosion occurred in the BD plant in Yeosoo, Korea while workers were attempting to purge the sulfur removal reactor for the preparation of replacing of catalyst using steam. One operator was killed and one was critically injured.

After the plant was shutdown to replace packed catalyst in the reactor, the reactor was in by-pass operation.. First, C4 mixed oil component was drained from the reactor and the reactor was purged using N<sub>2</sub> to remove remained hydrocarbon. The reactor was exploded while providing steam to the reactor for additional purging.



**Fig. 1 Plant after Explosion**

## 1.1 Incident Description

- Date of accident : August 25, 2004
- Accident type : Fire and explosion
- Accident consequences :
  - o Injury : 1 operator
  - o Fatality : 1 worker
- Accident description

The exploded reactor(Sulfur Removal Reactor) was installed to remove sulfur acting as a catalyst poison in hydrogenation reactor at the BD plant. After the process was shutdown to replace catalyst that packed in the reactor because of deterioration of sulfur removal performance, the reactor was in by-pass operation. C4 mixed oil component was drained from the reactor and the reactor was purged using N2 to remove remained hydrocarbon. The reactor was exploded while providing steam to the reactor for additional purging for 5 hours.

### Accident Facility

- Accident process
  - Sulfur removal Reactor in the acetylene removal process at BD plant  
( Licencer : UOP )
- o Equipment specification
  - Sulfur Removal Reactor
    - . Capacity : 20.55 m<sup>3</sup>
    - . Diameter : 1,900mm
    - . Height : 6,600mm
    - . Design pressure : 12.5 kg/cm<sup>2</sup>G , Operating pressure : 6 kg/ cm<sup>2</sup>G
    - . Design temperature : 65 °C , operating temperature : 35 °C
    - . Material : A516-70
    - . RT test : 20%

## Work status

### o August 21st, 2004

- After inlet and outlet valves of the reactor were closed, the pressure of reactor was downed to atmospheric pressure opening flare valve(2”).
- C4 mixed oil component was drained from the reactor and the reactor was purged to remove remained hydrocarbon using N2 after the reactor was bypassed.
- Slipplates were inserted in the inlet and outlet piping, and the inlet of PSV ( Slipplate inserted position : Annex #3)

### o August 25, 2004

- 8:30 : After N2 purging for 5days, the result of released gas analysis identified 30ppm of hydrocarbon concentration.
- 11:30 : In order to remove hydrocarbon completely, Low pressure steam was provided through the vent valve in raw material feed line.( In early stage steam was provided as a small amount a little bit opening of steam valve)
- 14: 40 : providing steam of 147 C full opening of steam valve(3/4”)
- 16:59 : Fatality found that rubber hose releasing steam were fluctuated and directed injury to stop the hose fluctuation to close releasing valve(1”)
  - . After the hose fluctuating was stopped, at the moment the workers were about to moving the other place they heard odd sound from the reactor
  - . Just before the accident, they found that band winding insulation of the reactor was cut off and run to the reactor for emergency respond.
- 17:00 : Exploding the reactor, an operator were killed, the other one was critically injured. The debries of the reactor(200~300Kg) were flown to 200~300m.



**Fig. 2 Reactor Skirt after exploding**

## **2.0 SYSTEM ANALYSIS**

### **2.1 BD PROCESS**

The plant was built in 2003. The process was installed to remove sulfur acting as a catalyst poison in hydrogenation reactor at the BD plant.

□ Property of Butadiene

Formular	M.W.	Boiling point( )	Flash point( )	Autoignition( )	Explosion limit
$\text{CH}_2(\text{CH})_2\text{CH}_2$	54	-4	- 21.7	429	2~11.5%

## [Annex #3] Sulfur Removal Reactor Outline



### **3.0 INCIDENT ANALYSIS**

#### **1. Causes in causing object**

##### **Self decomposition reaction of butadiene poly-peroxide**

Is assumed that Butadiene poly-peroxide of unstable state had accumulated inside reactor was self decomposition reaction caused by temperature of steam(147 °C) that is supplied for hydrocarbon exclusion(Item 4 : Physical and chemical special quality reference of butadiene poly-peroxide that is conclusion accident material)

##### **A. Cause material**

Butadiene(raw material) is produced unstable butadiene poly-peroxide in very small amount(PPM unit) of oxygen , air, ferrite oxide contacted condition in more than 35 °C

This accident process is assumed that butadiene poly-peroxide is produced because there is pre-heater. It heat butadiene(raw material) in steam condensate of 100 °C in reactor front(Usually, it is created at butadiene process)

Butadiene poly-peroxide kind created in pre-heater is accumulated on catalytic bed or catalyst upper part of reactor

\* By other butadiene creation conclusion, do to discharge C4 mixing oil that include inside reactor, and then supply nitrogen and removes remaining hydrocarbon, it can create butadiene poly-peroxide because very small amount of oxygen included in nitrogen reacts with butadiene but oxygen content among nitrogen is low, possibility is rare.

(Was confirmed that oxygen of plant itself analysis result and among nitrogen, 1PPM was contained, internal temperature was atmosphere temperature at purge)

## B. Ignition-source

Because butadiene poly-peroxide is unstable, is fired naturally causing own cracking reaction without separate way ignition-source in case of temperature is high.

## C. Oxygen

Oxygen is not one of element that is certainly necessary in explosion, but butadiene poly-peroxide kind assumed to accident occurrence major cause substance includes oxygen to itself and explosion by reaction is possible because do own.

## 2. Direct causes in work

### Operation that deviate design condition

Design temperature of reactor 65°C but they execute hydrocarbon exclusion work too long ours using steam of 147°C which have high temperature more than 2 times, conclusion that internal temperature of reactor was 147°C such as more than steam temperature (Appending data #5)

\* Hydrocarbon exclusion work by nitrogen is in contents presenting in UOP that is process patent system construction, but there is no reference about hydrocarbon exclusion work by steam of high temperature

Work using steam of high temperature after inquire only in reactor catalyst manufacturing company without doing question about steam use availability to UOP that is process patent system construction to remove remaining hydrocarbon of reactor

## 3. Assuming explosion circumstance

Is assumed that reactor pressure explodes zooming at maximum activation step while own cracking reaction by steam of high temperature that accumulative butadiene poly-peroxide is supplied explosion 2 hours ago on catalytic bed is proceeded.

\* According to DCS recording paper, temperature rise is gone gently before explosion 1 minute. Explosion 1 minute ago that the dissolution reaction rate soars and reactor internal temperature sharply exceeds more than supplied steam temperature. It agree very with conclusion explosion circumstance (Appending data #5)

## **Other possible causes**

### **1. Explosion of copper acetyl ride**

About 0.8% acetylene ingredient (Methyl acetylene, Vinyl acetylene etc.) that is flowed in during raw material react with copper (it included some in catalyst constituent) under water existence, while have formed acetylride and is accumulated, possibility to explode by temperature of steam at steam purge was latent

Copper acetyl ride material is explosive material, and when explode, temperature rise by own cracking reaction with butadiene poly-peroxide does not occur continuously and explode at the moment. Explosion possibility by copper acetylride material is assumed that is less seeing as temperature rise curved line of collected temperature recording paper.

### **2. Water vapor explosion**

A large amount of water is supplied through hose connection mistake in process that raise temperature of sulfur removal reactor, water vapor explosion can occur by much heat accumulated on catalytic bed. But, catalytic bed temperature of explosion verge is 162°C, and pressure of steam that can happen is about 6.7kg/cm<sup>2</sup>, and explosion possibility by this is rare because this pressure is been short on reactor design pressure 12.5 kg/cm<sup>2</sup>.

### **3. Explosion of air mixed hydrocarbon**

In process that raise temperature of sulfur removal reactor, after form hydrocarbon and hazardous atmospheres attaching on catalytic bed by much air inflow. May it explode by sudden oxidation reaction by catalyst. Usually, about when explode after hydrocarbon gas is mixed with air 9-10 times of first pressure of pressure rise happen. But, this time, possibility is

rare because do not get to burst pressure that consider factor of safety of reactor.

#### 4. Explosion by absurd mixing of C4 oil

In process that raise temperature of sulfur removal reactor. C4 oil, process material, is flowed in through absurd piping system and Pressure can be risen liquid C4 oil causes change of phase. But, C4 mixing oil's mixing is impossible because blind plate was inserted in inflow possibility region.

#### 5. Defect of quality of the reactor material

Can consider explosion by topical defect of manufacture or increase of tension strength by temperature rise, but reactor was operated by 6.0kg/cm<sup>2</sup> in process that is driven for 1 year, and it was higher than pressure 3.5kg/cm<sup>2</sup> of steam that is supplied at steam purge, it is no possibility to be exploded by manufacture defect

#### 10. Lessons from this accident and reoccurrence preventive measures of the same kind calamity

##### Prohibition of steam purge

Clarify in technology standard and driving procedure lest should do steam purge about region that formation of butadiene poly-peroxide is expected, and executes education about danger about relevant workpeople.

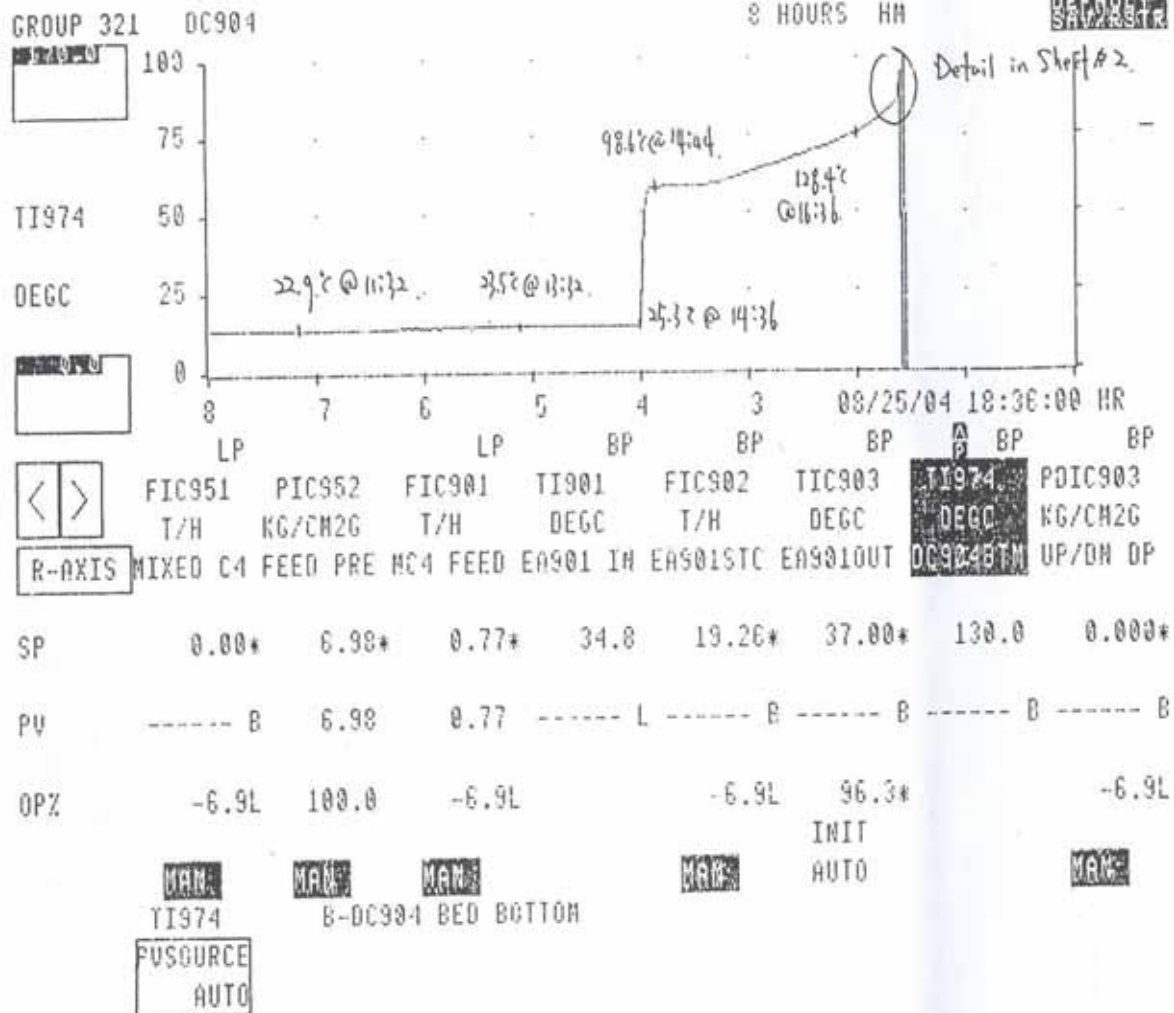
##### Heat source alteration of pre-heater

Change heat source of pre-heater low than steam condensate temperature, must minimize butadiene peroxide creation.

##### Education enforcement about creation condition and danger of butadiene poly-peroxide

Educate to official and workpeople about creation condition of butadiene poly-peroxide and danger.

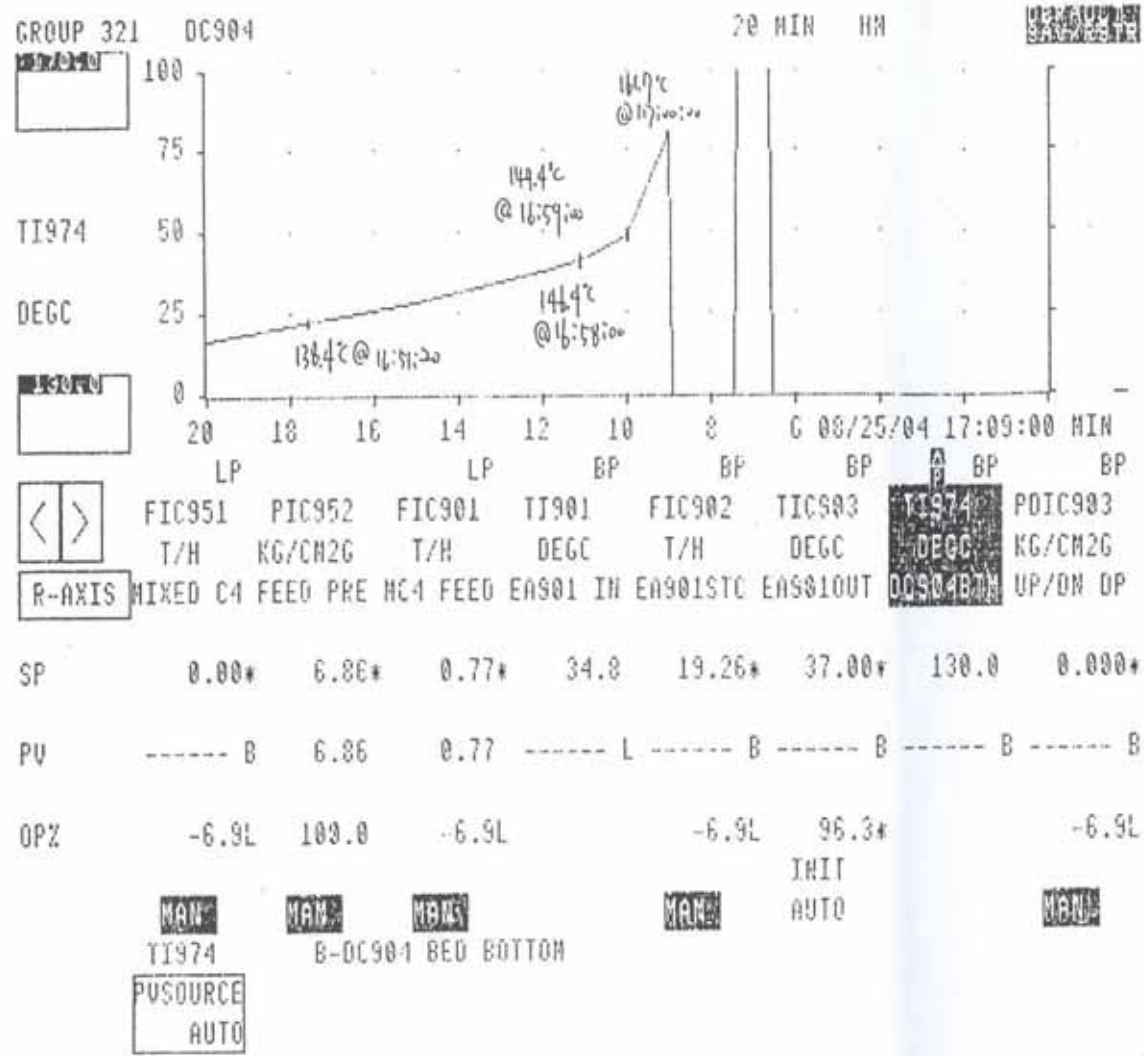
26 Aug 04 00:42:20 4



Temperature trend of the sulfur removal reactor

#2

26 Aug 04 00:37:00 4



Detailed temperature trend of the sulfur removal reactor before exploding