# INVESTIGATION REPORT

**8/14/2012**
**Shell Oil Products US Martinez, California Refinery**
**Flexicoker Gas Plant Debutanizer Leak to Atmosphere**

## EXECUTIVE SUMMARY

This report documents the investigation team findings along with mitigation recommendations regarding a leak to atmosphere from the debutanizer column pressure safety valve (PSV) in Shell Oil Products US's Martinez, California Refinery (Shell) Flexicoker gas plant which occurred on August 14, 2012.

The material released from the PSV was a propane/butane mixture with mercaptan and H2S. The estimated quantity of hydrocarbon released was 7,700 lbs. The estimated quantity of mercaptan released was 6 lbs. The estimated quantity of H2S released was 24 lbs. The estimated quantity of sulfur dioxide (SO2) released from the flaring was 17 lbs.

The investigation process began the same day the incident occurred, 8/14/12, with the collection of data, witness interviews and the inspection of the PSV.

The investigation team included an experienced RCA facilitator/team leader, an operations representative from the Flexicoker unit, and a staff pressure equipment engineer. The team was chartered with identifying the mechanism(s) that led to the leak. This included identifying the functional causes of the leak and Human Factors, Latent Conditions or Management Systems as causal factors.

The investigation team concluded that the leak was caused by a deteriorated valve seat in the debutanizer column PSV. Although the seat was made of the same material which had been successfully used in this service in prior years, it deteriorated and began leaking just before the planned maintenance outage which was scheduled for the end of August, 2012. During the outage, the valve seat will be replaced with a seat made of an upgraded material which has an increased resistance to H2S in the debutanizer overhead vapor.

This report is based on information available to the team at the time of the investigation. The times and quantities referenced in this report are approximations only and are based on a variety of information sources. All times are reported in 24-hour format.

## DESCRIPTION OF THE FACILITY/EQUIPMENT INVOLVED IN THE INCIDENT

The leak to atmosphere took place through the Flexicoker gas plant debutanizer column PSV SVJ-197. SVJ-197 is located at the top of the debutanizer column and vents directly to the atmosphere through a standpipe attached to its exit. The standpipe has an attached acoustic sensor which transmits a signal to the gas plant board. The signal has an associated alarm which alerts the operator when there is a flow in the standpipe.

SVJ-197 is an Anderson-Greenwood series 200 pilot-operated relief valve. The set pressure of SVJ-197 is 220 psig, and at the time that the leak developed, the column was operating at 165-170 psig,

well below the set pressure. SVJ-197 is a pop action valve, meaning that it is designed to be leak tight to within +/- 5% or better of its set pressure. Figure 1 shows the main parts of the PSV.

Immediately after the leak, SVJ-197 was removed from the column and tested to see if it would relieve at the set pressure. On the test stand however, the valve was found to be leaking in the main seat area to the extent that a pressure test could not be performed. The valve was then carefully disassembled with observers from the investigation team present. Overall the following observations were made:

1. The tubing pieces which are necessary for communicating the process pressure to the top of the main seat or "dome" section as well as the pilot were found to be clear and tightly attached with no leaks.
2. The main valve seat, which was made of viton, was found to be significantly deteriorated. Its condition was such that it could not form a seal against the nozzle seat surface.
3. The pilot and main valve seat springs were found to be in acceptable condition, with no breakage or corrosion present.
4. The pilot piston and main piston o-rings were in acceptable condition.
5. The pilot piston and the main valve piston were found to be acceptably clean and there was no evidence of significant binding.
6. The filter between the tubing pieces from the process and the pilot had no liquid in it but it was slightly dirty. The amount of dirt would not have affected flow through the filter.

## NARRATIVE TIMELINE

Incident Timeline:
The operation of the debutanizer column was stable until the moment the leak developed. The investigation team reviewed the process conditions in the column, and found no evidence of any unusual pressure or temperature variations prior to the leak. At 12:16 on August 14th, the acoustic sensor on the SVJ-197 standpipe went into alarm, indicating a flow from the PSV. Since the control panel indicated that the column was well below the set pressure of the PSV, the board operator requested that the outside operator verify the column pressure by reading the local pressure gauge on the column. This was done and the pressure was found to match the pressure indication on the control board. The outside operator also verified that the leak to atmosphere was occurring at this time. At 12:22, the board operator reduced the reboil steam going to the debutanizer in an attempt to reduce the pressure in the column and reseat the PSV. The pressure in the column only went down by about 5 psi from this move, so at 12:25, the column pressure was vented to the flare for a period of 2 minutes. The column pressure continued to decrease, but the acoustic sensor still indicated a flow out the PSV into the atmosphere. In the period between 12:35 and 12:47 additional steam reductions to the reboiler and diversions of debutanizer column tops to the flare were made to reduce the column pressure in an effort to reseat the PSV. By about 13:35, the column pressure had decreased to approximately 33 psig, and the leak had diminished, but it became clear that the PSV would not reseat. To completely stop the leak, a plan was then developed to safely block in the PSV. After consultation with Operations, Technical and HSE department personnel, emergency responders ascended the column and manually blocked in the PSV, stopping the leak to atmosphere at 14:25.

SVJ-197 Maintenance Timeline:
The investigation team reviewed the history of SVJ-197, with special attention to the "soft goods" materials used. The soft goods are the expendable parts of the valve (usually o-rings and valve seats) which must be replaced after each service run. The refinery has been using viton for the main valve seat in SVJ-197 for the majority of the service runs since the valve was first installed in 1984. When the valve was first installed in 1984, the main seat material was Buna-N. The recommendation to switch from Buna-N to viton for this service originated from a letter to the refinery from the valve servicer at the time, Brock Easly Co. in 1986. The typical run length for this valve has been three years, and in general the performance of viton has been satisfactory. At the conclusion of the 2003 to 2006 run, the PSV was inspected and although the main seat was described to be "battered" there were no indications of leaking while in service. The service reports indicated that the valve relieved about 7 psi below its set pressure, and that there was some leaking after it relieved, but after the soft goods were replaced and adjustments were made and the valve was returned to service in good working condition. At the end of the 2006-2009 run, inspection reports again indicated that the main seat was in battered condition, however there were no reports of leaking, so once again viton soft goods were installed for the 2009-2012 run.

## ROOT CAUSE INVESTIGATION METHODOLOGY

Shell Oil Products US, Martinez Refinery used a Cause and Effect Analysis method to conduct the Root Cause Analysis (RCA) investigation. This method includes features that 'test for cause' and examine data quality. In addition, the team used the Latent Conditions checklist[1] as an aid to the investigation.

The investigation team conducted interviews, reviewed documentation, witnessed the disassembly and inspection of the leaking PSV and visited the incident site as part of the investigation.

## INCIDENT INVESTIGATION TEAM FINDINGS

The investigation team considered possible causes of why the release of vapor could have occurred through SVJ-197. These are shown on a cause and effect diagram (Figure 1) prepared by the team. Based on the review of the process data and the post-incident inspection, the investigation team found that SVJ-197 was operating as designed until the leak in the main seat developed. The evidence indicated that the valve did not relieve below its set pressure, but rather that the main valve seat began to leak while the main valve piston was being held in its usual closed position by the pilot.

### Root Cause

The root cause of the leak was the deterioration of the viton main seat in SVJ-197. The deterioration was probably caused by the presence of H2S in the debutanizer overhead stream, which, over time caused a breakdown in the viton seat. The investigation team did not find any causes related to latent conditions for this incident (Table 1).

[1] Latent conditions are the hidden causes that may contribute to human errors. The Latent Conditions Checklist used is based upon the Contra Costa County Health Services Department Human Factors Program Guidance Document.

## Recommendations

As a material viton has good resistance against almost all of the compounds in the debutanizer overhead stream. However it does not have optimal resistance against H2S, which is present in the system. The following recommendations were made by the investigation team to address the cause of this incident and prevent future incidents.

| Recommendation | Responsible Manager or Individual | Estimated Completion |
|---|---|---|
| 1. For SJV-197, install a new soft goods kit including a main seat with increased H2S resistance during the August 2012 Flexicoker Turnaround | Operations Central Pressure Equipment Engineer | November 1, 2012 |
| 2. Review chemical resistance of soft goods for all PSVs relieving to the atmosphere. Verify that the chemical resistance of the soft goods are optimal for the service. | Pressure Equipment Integrity Department Manager | June 30, 2013 |
| | | |

## Attachments

Figure 1: Schematic Diagram—Anderson Greenwood Series 200 PSV
Figure 2: Cause and Effect Diagram

Figure 1: Anderson Greenwood Series 200 Pop Action PSV.

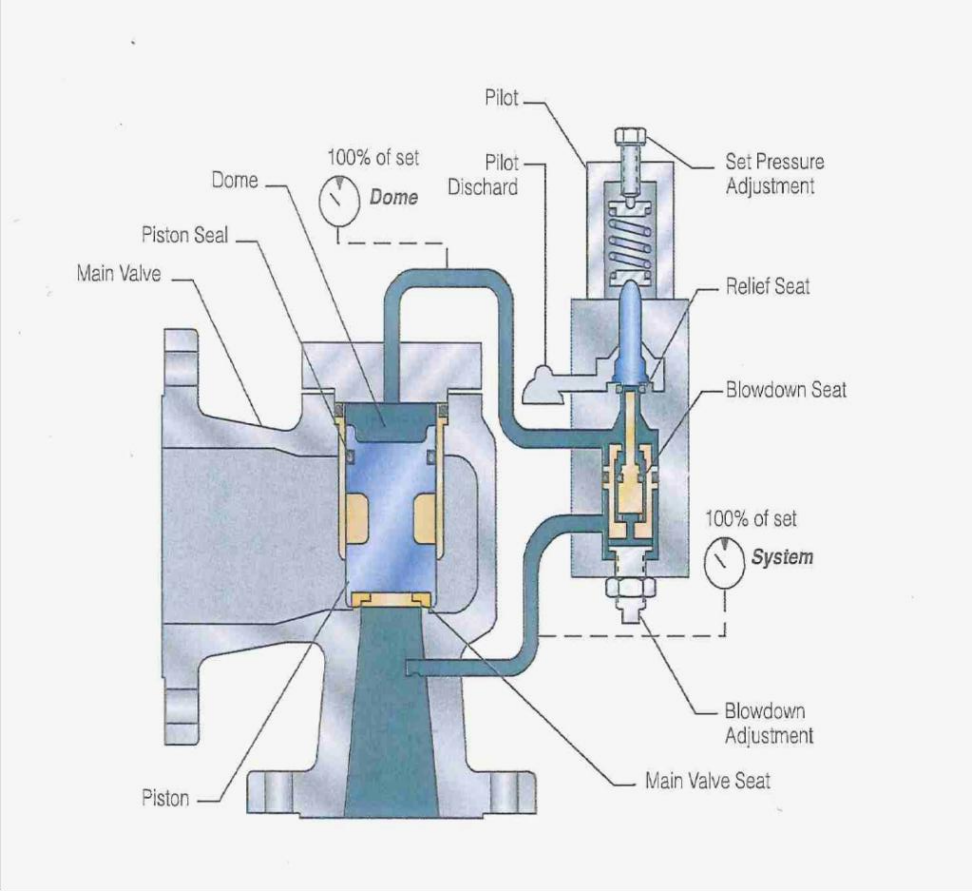

Figure 2: Flexicoker Gas Plant Debutanizer Leak to Atmosphere Cause and Effect Diagram
Incident Date 8/14/2012