WV-01226 #171

MEMORANDUM

TRANSMITTED BY:
Mr. O.O. Gray 5319

INVESTIGATION INTO AN UNCONTROLLED REACTION IN A DPP STORAGE TANK

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Date: November 20, 1964

Approved by: E.P. Matzen

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PLAINTIFF'S EXHIBIT
UC-2408

SUMMARY

An uncontrolled reaction occurred in a storage tank of DPP. This report indicates the probable cause of the reaction, as determined during the investigation, the steps taken to prevent recurrence, and suggested improvements to the system that should be incorporated in the future or used in new facilities.

No personnel or equipment damage resulted from the reaction, indicating an adequate design of the venting devices of the tank.

INTRODUCTION

On August 30, 1964, an uncontrolled reaction occurred in the dipropionyl peroxide (DPP) concentrates storage tank. An investigation of the equipment, analysis of the decomposition products, and eye witness reports, indicate that the reaction was catalyzed by contaminants in the system. In particular, iron and graphite were present in sufficient quantities to trigger the reaction. The decomposition was almost complete. No personnel or equipment damage resulted due primarily to the adequate design of the venting devices of the tank.

Extensive use of gasket materials other than teflon was found, and materials other than specified 304 and 316 S.S. Garlock gaskets (graphite impregnated asbestos), Klingerite gaskets, and "Fel-Pro" gasket dope were found in several locations. Mild steel nuts were found in the tank on a clamping arrangement of internal spargers. 400 series stainless steel was used in several locations. Polyethylene was used for gasketing. Sand was found in the tank.

Further investigation pointed to several serious equipment design defects. Remote temperature recorders were of a narrow range and did not indicate above the normal operating range. Lighting in the area was poor. No method of dumping the tank contents from a remote station was provided, although requested. Several dead headers were found where there was no flow during normal operations. The types of pumps used for cooling circulation and DPP injection are not ideal as packing leakage is inevitable.

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DISCUSSION

On August 30, 1964, an uncontrolled reaction occurred in a DPP concentrates storage tank which contained 20 wt. percent DPP in a nonane type solvent. The attached schematic drawing, MFD-C-1575-A, shows the system layout. The sequence of events leading up to the incident are as follows:

a. Considerable difficulty was experience during August with the cooling system compressor. The difficulty was found to be entrainment of liquid propylene in the disengager. The system was shut down for installation of the larger disengager and repair of the compressor. Cooling water was being used in the heat exchanger for temperature control. The tank contained 6,000 lbs. of a 20 weight percent solution of DPP.

b. The tank temperature was 25 - 26° C during the day of August 30th. At 7:00 P.M., the temperature had risen to 30° C. The ambient temperature was 85° F (29.5° C). The cooler was backwashed to remove any blockage or fouling caused by dirt in the cooling water. The cooling water return (which was introduced to the cooler during the backwashing) was approximately 40° C.

c. A reaction (decomposition of DPP) was occurring in the storage tank due to the contaminants in the system. During the backwashing operation, the rate of decomposition was accelerated due to the elevated temperature. When normal cooling water flow was re-established, the reaction (decomposition) was out of control.

d. At 10:15 P.M., the vents on the tank started to relieve. The vents are set at 1.5 and 2 oz. of pressure. The sprinkler system on the tank was manually activated. Approximately 4,000 lbs. of material erupted through the vents. The discharge lasted approximately 60 seconds.

e. The temperature of the tank contents at 11:00 P.M., after 45 minutes of continuous water spray, was 50° C.

f. The area was neutralized with slaked lime in the event that any DPP was unreacted. Samples taken from around the tank after neutralization indicated 0 ppm DPP.

g. The remaining 2,000 lbs. of solution in the tank was dumped into slaked lime and samples retained for analysis.

The sample contained two layers. The bottom layer was approximately 5% of the total.

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DISCUSSION (Continued)

	Top Layer	Bottom Layer
Copper	Nil	Nil
Iron	3 ppm	28 ppm
Carbon	Nil	50 ppm
Ash(1)	22 ppm	286 ppm
Water(2)	0.14 %	10.7 %
IPA(3)	0.40 %	3.3 %
DPP	0.16 %	0.01%
Solvent(4)	99.3 %	86.0 %

(1) White silica sand used for sand blasting.
(2) Probably introduced by sprinkler.
(3) Used as flush when unloading carboys.
(4) Espesol 310A.

The carbon, ash, and iron concentration prompted a further investigation.

The system was dismantled and the following defects found:

1. All 2-inch V-588 valves had Garlock bonnet gaskets. Valves were tagged indicating Teflon packing.

2. All 3-inch V-588 valves had Garlock bonnet gaskets. Valves were tagged indicating Teflon packing.

3. Check valves had Neoprene swing check pin gaskets and Garlock bonnet gaskets.

4. Gauge glass valves had graphite impregnated stem packing and 400 series stainless steel ball checks. The balls were substituted when the supplier had no 304 stainless steel balls. Specification to the supplier requested Teflon packing.

5. The spargers in the tank were held together by stainless steel U bolts on a stainless steel angle iron. The nuts on the bolts were mild steel. These were installed by the contractor.

6. The rupture disc assembly on the heat exchanger was installed by Process Safety using a Klingerite gasket.

7. The circulating pump shaft had a small Klingerite washer and colloidal copper gasket dope was used on the casing gasket. This pump was checked and reassembled by the Maintenance Department.

8. The tank head gasket was Garlock covered with polyethylene. The polyethylene was cracked.

9. The tank contained several pounds of white silica sand of the type used for sandblasting.

10. The majority of the ½" and 1" valve seats and gates were magnetic as were all 2" and 3" valve bodies. These all contained rust. The valves are 316 cast S.S.

11. One line in which no DPP circulation occurs could not be flushed or drained.

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DISCUSSION (Continued)

Dr. Magli of Lucidol was contacted with regard to the effect of iron and carbon on the rates of decomposition of DPP. Their studies indicated an increase in the decomposition rate of 10 to 65 percent at 30° C. with the addition of various iron compounds. A control sample lost 3.6% DPP concentration in one week. A sample with iron octenate lost 5.9% DPP concentration in one week under similar conditions.

S.A.D.T. (Self Accelerating Decomposition Temperature) studies indicated that at 32° C. the decomposition was not self-sustaining, but at 38° C. it was. Hence 32° C. is the maximum temperature to which DPP solutions should be subjected, and not 38° C. as previously indicated.

Mr. J.O. McGrew of Union Carbide Chemicals Company in South Charleston was contacted concerning this experience in a similar incident. Their problem was primarily lack of circulation of the solution in the tank. The reaction occurred at the top of the tank at elevated temperatures, yet the temperature in the bottom of the tank was normal. Mr. McGrew recommended:

a. Good circulation of the solution to ensure good mixing and temperature control.

b. Good temperature monitoring.

c. A method of dumping the solution from a remote station.

Mr. C.P. Dillon of Union Carbide Chemicals Company, was contacted concerning the cleanup of the system, and the materials of construction. He recommended the use of sulphamic acid for removing rust and scale. Types 304 and 316 S.S. are suitable materials of construction for peroxides. Magnetic 316 S.S. (cast) was not the source of iron in the system in Mr. Dillon's opinion. Passivation with 20% nitric acid was recommended. This is specified by the U.S. Navy in hydrogen peroxide handling equipment.

RECOMMENDATIONS

It is recommended that:

1. The DPP system be reassembled with close inspection to ensure all materials meet specifications. All rust should be removed with sulphamic acid, and the system passivated with 20% nitric acid. Following passivation, the system should be flushed with isopropanol, and determinations made before and after of the iron, carbon and copper content of the isopropanol. After the results of these evaluations, the system may be used for bulk DPP storage.

2. A monthly analysis be made of the DPP solution to determine the normal level of contaminants. Any wide fluctuation from this "base" level should be investigated.

3. Bulk storage of DPP be at a temperature not exceeding 20° C. nor at a temperature below -10° C. Optimum storage conditions are 0 - 10° C.

4. The following design changes be made to the existing system before reuse:

   a. A dump motor valve be installed on the concentrated DPP storage tank with a remote station for activation.

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RECOMMENDATIONS (Continued)

4. b. A thermocouple be inserted in the base of each storage tank. The span should be -25° C. to +100° C. so that temperatures other than those of normal operation be recorded. A second thermocouple be installed at a position such that the temperature in the centre of the tank be measured.

   c. The existing temperature transmitter ranges all be set at -10° C. to +15° C, and the high and low temperature alarms be set at -5° C. and +15° C.

   d. Dial thermometers on each heat exchanger have ranges of -25° C. to +100° C. minimum.

   e. One "dial leg" be valved off and a flush line installed so that following use, the DPP may be flushed from the line.

5. The following changes in the area be considered:

   a. Providing a second remote station for dumping the tank contents. The one station may be inaccessible depending upon wind direction.

   b. Improvement of lighting at the heat exchangers.

   c. Replacement of the centrifugal circulating pumps with canned pumps to prevent large spillages as would occur should a seal fail.

   d. Replacement of the high pressure injection pumps with diaphragm pumps to eliminate leakage.

6. Equipment materials be rigidly checked by:

   a. The Design Engineering or Works Engineering personnel specifying the equipment.

   b. The Operating personnel:

      This may in some cases dictate continuous field supervision, particularly when materials are critical.

      It is further emphasized that when special material specifications are required that the Maintenance Department be provided with these specifications, and reminded of same when working on equipment. Such reminders could be given on the Hazardous Work Permits.

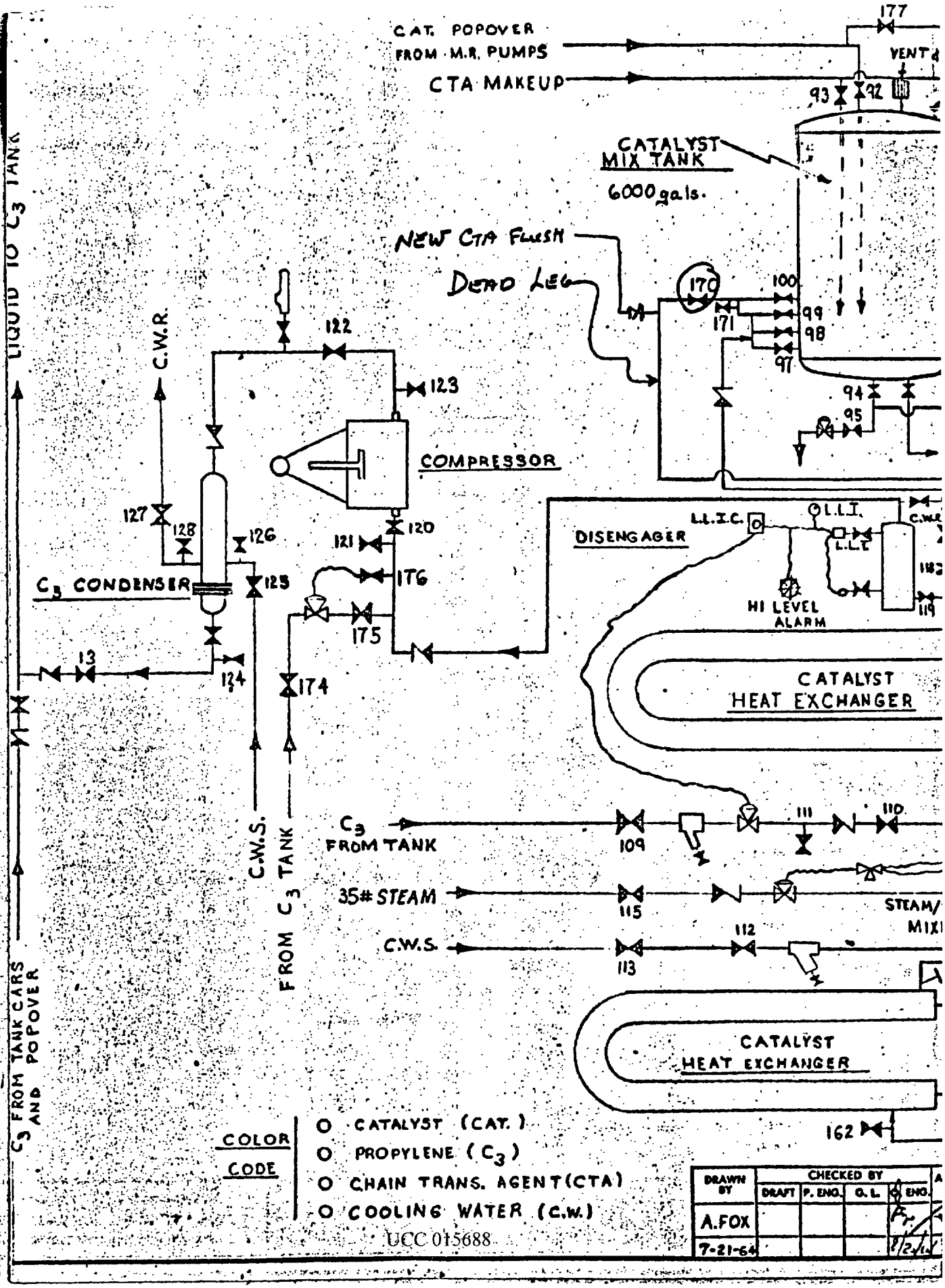
ACKNOWLEDGMENTS

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/bn
Attachment

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CAT. POPOVER FROM M.R. PUMPS
CTA MAKEUP
177
VENT
93
92
CATALYST MIX TANK
6000 gals.
NEW CTA FLUSH
DEAD LEG
170
171
100
99
98
97
94
95
LIQUID TO C_3 TANK
C.W.R.
122
123
COMPRESSOR
127
128
126
121
120
C_3 CONDENSER
125
176
175
DISENGAGER
L.L.I.C.
L.L.I.
HI LEVEL ALARM
119
13
124
174
CATALYST HEAT EXCHANGER
C_3 FROM TANK
109
111
110
35# STEAM
115
STEAM/
C.W.S.
112
113
CATALYST HEAT EXCHANGER
162
C_3 FROM TANK CARS AND POPOVER
C.W.S.
FROM C_3 TANK
COLOR CODE
CATALYST (CAT.)
PROPYLENE (C_3)
CHAIN TRANS. AGENT (CTA)
COOLING WATER (C.W.)
DRAWN BY
CHECKED BY
DRAFT
P. ENG.
G. L.
ENG.
A.FOX
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