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Monsanto Chemical Company
Texas City, Texas

September 3, 1959

To: W. R. Nisbet

cc: Plant Manager's Safety Board

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Subject: Process Spill, Department 3, August 31, 1959SUMMARY:

A liquid-vapor spill consisting primarily of anhydrous HCl, H₂, and light organics occurred from the department 3 catalyst manufacturing reactor (3V4) on August 31, 1959. An out-of-control reaction was the cause of the spill. The alarm was turned in at 9:05 AM, and the all-clear sounded at 9:27 AM. Catalyst manufacture in departments 2 and 3 was shut down for two hours. The spill had no effect on styrene production, and there was no equipment damage.

DESCRIPTION OF PROCESS AND EQUIPMENT:

Aluminum chloride catalyst used in the production of ethylbenzene is produced in the 3V4 reactor by reacting aluminum and anhydrous HCl in a liquid medium. The liquid medium is plant RM -- a mixture of catalyst complex and alkylated liquor. The aluminum chloride produced reacts immediately with the alkylated liquor to form additional catalyst complex. The heat of reaction is removed by circulating the reactor contents through an external cooler (see drawing attached). The circulating pump suction is

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taken from a nozzle near the top of the reactor to minimize the amount of aluminum in the circulating system. The catalyst product is withdrawn from this system, and the remainder of the cooled catalyst is returned to the reactor through a bottom nozzle. The RM balance is maintained by a continuous makeup of unfortified RM.

DISCUSSION:

At the end of shift 1, Sunday, August 30, a leak developed in the unfortified RM makeup line upstream of the reactor (3V4) inlet block valve. When attempts to stop the leak failed early on shift 2, the RM makeup line was blocked in, the aluminum feed was stopped and the HCl feed was reduced. Catalyst circulation from the reactor through the cooler back to the reactor was continued to consume the unreacted aluminum.

The 3V4 operator with the chief operator's approval, blocked in the HCl, and stopped circulation of the catalyst, within two hours of the time the aluminum feed to the reactor was stopped. According to both, the standard procedure of checking the catalyst from the reactor for aluminum was made, and no aluminum was noticed in the sample. They also observed, and charts confirm, that the temperature of the catalyst exiting the reactor prior to the time circulation was stopped was sufficiently low to indicate that the reaction had stopped.

Earlier in the week end, the belts on the catalyst building exhaust fan had failed. Following normal practice, these belts were not replaced during the week end, since the repair requires a shutdown. Whenever the fan is not in operation, HCl fumes accumulate in the catalyst building. These fumes were sufficiently bad on the shift 3 of August 30 that chemical cartridge masks were worn by the operators when entry into the building was necessary. At the start of shift 1, on August 31, the fumes in the catalyst building had worsened, and a dense fog of HCl had formed in the building.

First shift personnel and supervision determined that the source of the dense fumes was the reactor, 3V4. An attempt was made to stop the excessive volume of vapor from the 3V4 reactor by closing the off-gas valve on the common off-gas line between department 2 and 3 reactors. The vapor spill continued to increase and liquid began to spill over. The liquid spill was stopped by starting the pump from outside the catalyst building, and lowering the level in the reactor by pumping the catalyst through the catalyst complex line into department 3 alkylation. At the same time an attempt was made to circulate material through the system to remove the excessive heat with the 3E16 catalyst system exchanger. This was not successful as the

recycle inlet line was plugged near the reactor. At this time, 9:05 AM, as the reactor temperature continued to rise out of control, a spill alarm was turned in and fire water was used to cool the outside of the reactor and bring the vapor spill under control. At 9:27 AM, the all-clear was sounded, however, part of the fire crew was held on standby for another hour or longer. The 3V4 reactor vessel was then pumped out and further investigation revealed a small HCl leak into the reactor.

CAUSES:

The primary cause of the spill was that circulation of the reactor contents was stopped before all of the aluminum was consumed. The reaction continued throughout the night, and without cooling, gradually increased rate.

Secondary causes were:

- 1) Lack of forced ventilation in the building which prevented access to the building and corrective action to be taken by shift 1 personnel and supervision.
- 2) Lack of ability of shift 3 personnel to discover the source of the fume problem in the catalyst building.
- 3) A leak of HCl into the reactor through four block valves.
- 4) Lack of a temperature measuring element in the reactor which would have indicated the temperature buildup. The shift personnel observed no change in the temperature in the catalyst circulating line so assumed that no problem existed in the 3V4 system.

ACTION TAKEN OR TO BE TAKEN:

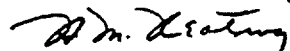
- 1) All operators and chief operators will be re-instructed in all phases of operation and shutdown of the catalyst manufacturing system. Operating procedures will be reviewed and altered as necessary.
- 2) Repairs to the exhaust fan will be made normally no later than the day following failure.
- 3) The block valves in the HCl line were replaced.
- 4) The following potential improvements will be investigated:
 - a) Addition of a temperature point inside the reactors.

- b) Provision of a steam turbine drive on the spare catalyst circulating pump to allow a safe shutdown of the reactors in event of an extended power failure.
 - c) Provision of cooling water distribution rings on each reactor.
5. Three faulty All-Purpose gas masks -- two on which straps broke, and one which failed with the clock in the 1/4 used position -- were turned over to the Safety Department for checking and followup.

The Safety Department also has Bell Telephone Company working on correcting the fire and spill alarm system. The alarm 2-3 was the third consecutive faulty signal from the styrene area.

RECOMMENDATIONS:

Periodic complete inspection of gas masks. It is understood that the Safety Department is well along on planning such inspections.


H. M. Keating

djl
Attachment

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EX

A

DRY BENZENE FROM

B

HCl FROM DEPT 22

→ FORTIFIED RM
TO DEPT 3 ALKYLATION

NE

COOLING TOWER
WATER

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