CHEMICALS PPG INDUSTRIES

INTEROFFICE / LAKE CHARLES

TO P/T Operating Personnel DATE October 25, 1979

FROM Arville Hoffpauir . SUBJECT

Startup of a Per-Tri reactor is critical from the standpoint of both safety and maximum tube life. Several things can occur if startups are rushed or for some other reasons done at other than a closely controlled condition. If organics is introduced too fast, you not only greatly increase the velocity causing excess catalyst carryover, but also increase the chances of having liquid entrainment into mixed feed headers and the heads on the tubes.

If O_2 is introduced too fast, you could have O_2 break through into the dome, causing a fire. Also, the temperature increase should be where it is easily controlled with dowtherm pressure where drastic changes will not have to be made to the reactor.

This new startup procedure should be followed closely and will work only with your cooperation.

cg

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PER-TRI REACTOR STARTUP

A. Organic vaporizer startup

1. Fill vaporizer with bleed valve open to insure all N_2 is bled from system. Bring level to 10-20 percent.

2. Start force recirculation pump. Check seal flush to pump.

3. Line up steam trap to pad and isolate from condensate header.

4. Start 500-1000 lbs/hr steam to vaporizer allowing it to heat up slowly.

5. When organics pressure reaches 25 psig, raise steam flow to 1260 lbs/hr.

6. When organics pressure reaches 35-40 psig, introduce organics into reactor using below procedure.

B. Reactor startup

1. Organic feed

   a. Slowly open organics valve to mixed feed header allowing vaporizer pressure to slowly drop to prevent shocking tubes and entraining liquid carryover from vaporizer.

   b. Slowly reduce N_2 to mixed feed header. (Do not cut N_2 completely out.)

   c. Monitor bed temperatures closely. As soon as an increase in temperature is noted, O_2 should be introduced into the reactor.

   d. Slowly increase steam flow until organics pressure lines out at 20-22 psig. At this time, N_2 can be removed from mixed feed header.

2. Oxygen feed

   a. After introduction of organics feed and an increase in bed temperature is noted, O_2 flow control valve should be open to introduce a minimum flow to the reactor. This is the critical stage of startup and should be monitored closely.

   b. Watch bed temperature and when the reaction has started, an increase in temperature will occur. At this time, raise O_2 flow to the reactor to 7500 SCFH stepwise and cut back N_2 proportionally.

   c. Watch bed temperature and when it reaches 700°F, O_2 flow and reactor pressure should be slowly increased to 15 lb. rates. This should be done slowly so that you are able to adjust dowtherm pressure to control bed temperature.

   d. When all N_2 is out of the reactor, flush water should be taken off primary, brine put on secondary, degasser lined up to DH feed tank, and vents put forward.

REACTOR PRE-STARTUP CHECK LIST

Reactor ______________
Date ______________

1. Reactor system leak check - Before charging catalyst. Put 35 psig nitrogen pressure on mixed feed headers, all organic feed lines, all O_2 feed lines, reactor vapor lines, primary and secondary condensers and drain lines, and degasser by isolating system and using fluidization nitrogen. Tape flanges and use LEC-TEC. Depressurize when finished.

Check/Done

- ______ 1. Cl_2 mix jet.
- ______ 2. Cl_2 orifice plate flanges.
- ______ 3. Mixed feed headers at bayonet flanges.
- ______ 4. Organic feed lines spool flanges underneath reactor.
- ______ 5. O_2 feed lines spool flanges underneath reactor. Remove tape when finished.
- ______ 6. Reactor head flanges (check by feeling for leaks with hands).
- ______ 7. Reactor head thermowell flanges.
- ______ 8. Catalyst addition ram valve flanges. Remove tape when finished.
- ______ 9. Catalyst blowdown ram valve flanges. Remove tape when finished.
- ______ 10. Reactor vapor line flanges. Remove tape when finished.
- ______ 11. Tant. tee by-pass flanges.
- ______ 12. Tant. tee bottom spool flanges.
- ______ 13. Degasser bottom spool flanges.
- ______ 14. Tant. tee inlet spools flanges. Remove tape when finished.
- ______ 15. Others:

2. Vaporizer system leak check - Before or after charging catalyst. Leak check vaporizer by closing organic block valve to reactor, completely isolate vaporizer, and pressurize it to 35 psig with nitrogen. Tape all flanges and check with Lec-Tec. Depressurize when finished.

- ______ 1. Float chamber flanges.
- ______ 2. Sight glass flanges.
- ______ 3. Uninsulated flanges on demistor block valves.
- ______ 4. Vaporizer manway.
- ______ 5. Reboiler flanges.
- ______ 6. F.C. pump suction ell and spool flanges.
- ______ 7. Organic vapor line block valve flanges.
- ______ 8. Organic flow orifice plate flanges.
- ______ 9. Others:

______ 3. Before catalyst is charged - Check for steam flange leaks by putting steam on Centrifix, ram valves, bayonets, superheater, steam tracing, steam heaters, and steam supply up to vaporizer steam FCV.

Check/Done

______ 4. This list is not to be taken as all inclusive. Therefore, make a walk-thru inspection of all systems and check that all piping flanges are made up, thermowells are in place, pressure gauges all in, and bleed valves closed.

______ 5. Anytime before startup: Stroke all automatic valves from their controllers.

______ 1. Both N_2 fluidization MLS valves.
______ 2. Cl_2 FCV.
______ 3. O_2 FCV.
______ 4. Steam and organics to vaporizer.
______ 5. Reactor PCV and vent MLS.
______ 6. Watch all Dowtherm valves run thru their motions.

______ 6. After leak check is complete, fill vaporizer with 300-400 gallons of organic feed. Then pad this out to the bottoms storage tank. After vaporizer is empty, refill it to operating level.

______ 7. Be sure an empty drum is under the catalyst blowdown catch pot.

PERNELL
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RX MAJOR OVERHAUL INSULATION LIST

1 – BTM OF RX (FEED PIPING AND HEADS).
2 – ORGANIC – CL_2 MIXING TEE.
3 – MIXED FEED HEADER BAYONETS.
4 – BOTH REACTOR RUPTURE DISK.
5 – REACTOR OUTLET VAPOR LINE FLANGE (TOP OF RX).
6 – REACTOR DOME THERMOWELL NOZZLES.
7 – TOP OF CENTRIFIX.
8 – CENTRIFIX.
9 – OUTLET OF CENTRIFIX.
10 – INLET TO PRIMARY TEES.
11 – OTHER
 1 – ______________________
 2 – ______________________
 3 – ______________________
 4 – ______________________

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THE ABOVE SHOULD BE DONE PRIOR TO REACTOR START-UP.

LCP 4610

Flanges to be Tightened after Reactor Startup

1. Both reactor rupture discs
2. Reactor outlet vapor line flange
3. Spool top of centrifix
4. Spool outlet of centrifix
5. Spools inlet to primary condenser tees.
6. Spools Btm of primary condenser tees
7. Other
    a. ______________________________
    b. ______________________________
    c. ______________________________
    d. ______________________________

The above should be done prior to increasing reactor rates.

NORMAL PER-TRI REACTOR SHUTDOWN

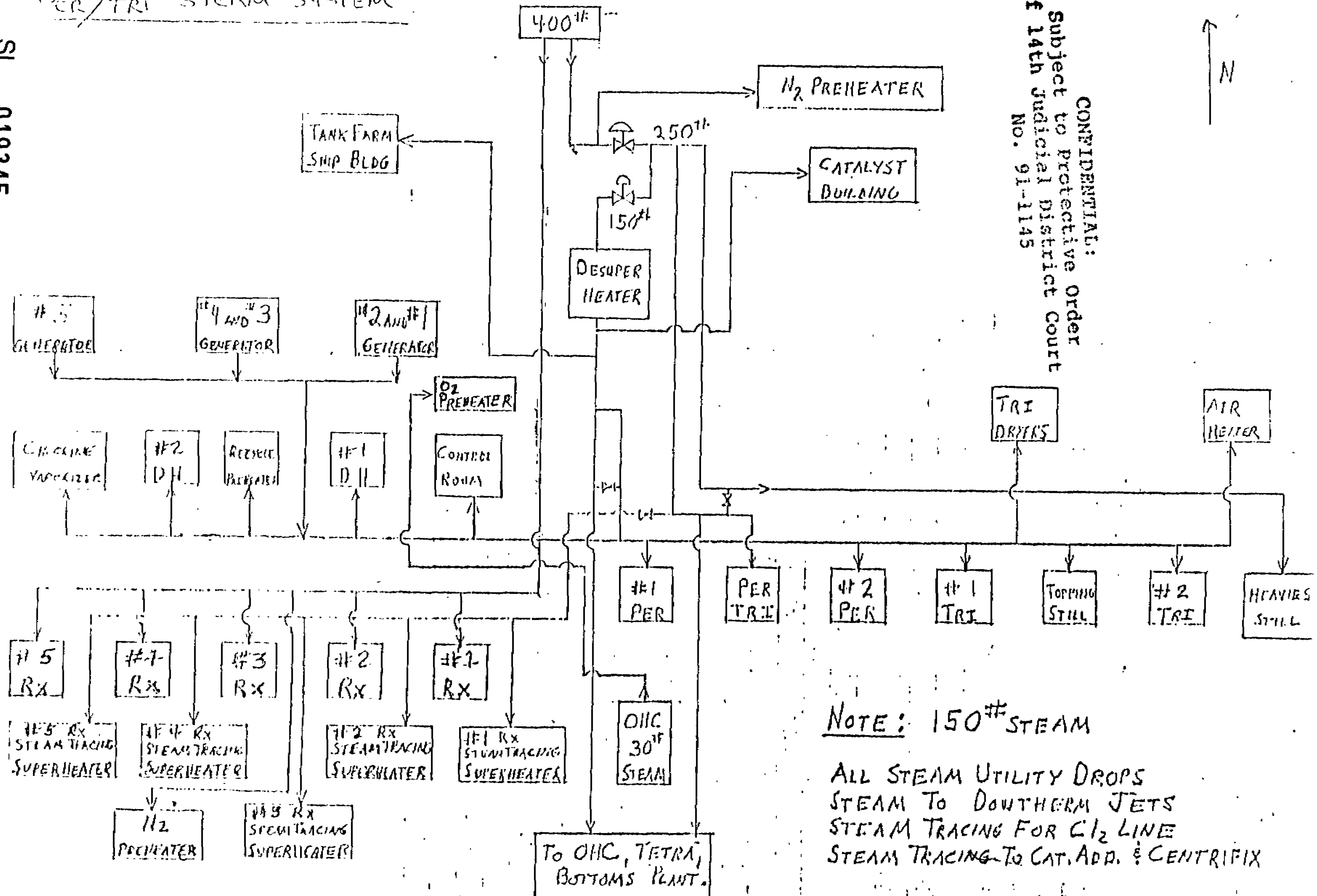
1. The reactor rates must be lowered to 15 psig using rate guide in SOP manual.
2. Stroke flush water MLS and solenoid valves.
3. Reactor vents lined up through startup header and degasser lined up to acid pit.
4. Brine to secondary condenser blocked.
5. Flush water put on primary condenser.
6. Nitrogen is slowly introduced into the "O" ring and oxygen feed slowly removed. When the nitrogen flow is at 9000 SCFH, oxygen should be blocked.
7. Nitrogen started into windbox. The flow should be brought up to 25,000 SCFH and the organics to the reactor blocked.
8. Both the above steps should be done by insuring extra nitrogen flow at all times to prevent defluidization.
9. After all feeds are blocked, call to have the pancake removed.
10. Pad out organic vaporizer to bottom storage tank.
11. After pancake is removed, open fluidization valve, close vent valves, and shut off flush water.
12. Block, tag, and drain reactor for necessary work to be done.

ABNORMAL REACTOR SHUTDOWNS

These shutdowns occur for various reasons and at these times the reactor will have to be put on nitrogen as quickly as possible.

The same steps that are taken in a normal shutdown will have to be taken only much faster. Therefore, the possibility of defluidization of the reactor is greater. Each operator involved in reactor shutdowns should know exactly what must be done to safely secure the reactor during any upset condition. Study and practice all emergency procedures.

PER/TRI STEAM SYSTEM



NOTE: 150# STEAM

ALL STEAM UTILITY DROPS
STEAM TO DOWTHERM JETS
STEAM TRACING FOR Cl_2 LINE
STEAM TRACING TO CAT. ADD. & CENTRIFIX

MONITORING OF PER-TRI FEED QUALITY

Since the quality of organic feed to Per-Tri is controlled by other operating units, it is critical that operators and lead operators closely monitor the sample analysis. The composition of the feed is the single most important factor in controlling ratios and conversions. The higher percentage of TCE in the feed the lighter the total feeds will be. The lighter the feeds, the lower the ratio.

Since PPG does purchase feed material from outside sources, there is a percentage of the material that we don't know the composition of. But there are some bad actors that we do know about and guidelines have been set up on acceptable quantities.

EDC	Less than 3%
Ferric Chloride ($FeCl_3$)	Less than 15 ppm
Water	Less than 50 ppm
Hexachloroethane	Less than 2%

A high EDC concentration will cause increased cracking and burning in the reactor. Since burning (pyrolysis) causes a direct loss of carbon, it is very undesirable. Also, when the EDC increases, other light materials also increase. These react the same as EDC so that the problem compounds.

Ferric chloride also increases cracking and burning at the higher pressures and temperatures. It also causes rapid fouling of the vaporizer reboiler. The 15 ppm limitation is because it concentrates in the vaporizer and causes fouling and plugging.

Water acts much the same as $FeCl_3$ as far as cracking. It also causes severe corrosion.

Hexachloroethane causes plugging in the feed piping and head. When hexachlor condenses from the vapor state, it goes to a solid form. The only way to remove it is to dissolve it in liquid organics.

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PER-TRI REACTOR CONTROL

There are several different types of chemical reactions taking place simultaneously in the Per-Tri reactors. In order to obtain the optimum yields and production rates, these reactions must be controlled. The intent of this scenario is to point out methods of desired reactor control.

One way to view reactions in the Per-Tri reactors is in zones. Shown below is a graph of the many reaction zones. These zones deal mostly with O_2 feed.

Zone 7 -	Denoted by reactor dome reactions or fires and possibly free Cl_2 in vent.
Zone 6 -	Denoted by high HCl-TPD in reactor vent, high % burning, and dark crudes.
Zone 5 -	Denoted by high HCl-TPD in reactor vent and high % burning.
Zone 4 -	Optimum zone denoted by lowest HCl-TPD in reactor vent possible with the % burning as low as possible.
Zone 3 -	Deacon reaction going but not optimum. Denoted by high HCl-TPD in reactor vent and low % burning.
Zone 2 -	Pyrolysis happening. Denoted by high HCl-TPD in reactor vent, low % burning, and dark crudes.
Zone 1 -	Some deacon reaction going. Denoted by high HCl-TPD in reactor vent and low % burning.

O_2 increases

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A reactor can run in any reaction zone except Zone 7. The reactor will not give optimum yields and produce maximum production rates in any zone other than Zone 4.

Listed below are conditions, results, etc., occurring in each reaction zone:

Zone 1

This is the first reaction zone during and after starting up a reactor. The deacon reaction will be going some but not very much. There will be high HCl-TPD in the reactor vent and the % burning will be low. This would indicate a need to increase O_2 feed flow. One word of caution... you should not make large O_2 feed flow increases because you could put enough O_2 feed into the reactor to go all the way to Zone 7 and not know it until there is a fire in the reactor.

Zone 2

Here is where pyrolysis will occur. Pyrolysis (chemical decomposition caused by heat) will occur before the desired control points (the lowest % burning possible that gives the lowest HCl-TPD in the reactor vent possible) are reached. This means the deacon reaction is not going all the way. High HCl-TPD, low % burning, and dark crudes will show up in this zone. You have to add enough O_2 feed to get past pyrolysis but do so in small increments while calculating % burning and HCl-TPD in the reactor vent. All O_2 feed adjustments should be based on % burning and HCl-TPD in the reactor vent. Tee plugging is experienced while in Zone 2.

Zone 3

At this point in the zoned reaction chain, you have the deacon reaction going but is not being driven to optimum. One nature of the deacon reaction is that the O_2 fed will go to the deacon reaction first until the deacon reaction has been driven as far as possible without increasing the % burning. High HCl-TPD in the reactor vent and low % burning will be present in Zone 3. Dark crudes will disappear when you reach this zone. Again, more O_2 feed is needed. You need to add O_2 in very small increments (say 200-300 SCFH) at this point. Again, all O_2 feed changes must be based on calculated % burning and calculated HCl-TPD in the reactor vent. Remember that you are very near optimum at this stage of the game.

Zone 4

We have reached the top of the mountain, Zone 4 is the optimum zone. Ideal control is when there is enough O_2 feed to drive the deacon reaction to the desired point while maintaining the burning reaction at the lowest possible. This means the hold point on O_2 feed is when the HCl-TPD in the reactor vent is as low as possible with the % burning as low as possible. Past this point, the % burning and the HCl-TPD in the reactor vent will both increase.

The actual control range, which is Zone 4, is not very wide. In comparison to most of the other reaction zones, it is very small. This means this is the hardest zone to stay in. This is why you need to make small O_2 feed adjustments--200 SCFH of O_2 addition or reduction can put you out of Zone 4.

Zone 5

You just went past the optimum. Too much O_2 feed caused you to go above the limits (optimum % burning and HCl-TPD in the reactor vent). Calculate % burning and HCl-TPD in the reactor vent. Study this data along with past data and decide on amount of O_2 feed reduction--keep it small.

Zone 6

You are headed toward an unsafe and uneconomical situation. Burning has increased way too much. Any additional O_2 feed will increase burning rapidly to the point where you have entered or could enter Zone 7. High % burning and high HCl-TPD in the reactor vent will show here. Back off O_2 feed and calculate % burning and HCl-TPD in the reactor vent at the lower O_2 feed rate. Always keep O_2 in reactor vent below 6%. Dark crudes will be present in Zone 6. Also tee plugging.

Zone 7

The reactor will probably be on fire at this point. There is the possibility that free Cl_2 will show in the reactor vent. Either lower O_2 feed and get the fire out or shut the reactor down--you may not have a choice because the fire may have destroyed the TFE expansion joints on the primary condenser piping or you may blow a reactor rupture disc.

All seven reaction zones have been defined but there are a few other things to keep in mind:

1. Study the composition of the organic feed. As the organic feeds heavy up, less O_2 feed is required. As the organic feeds lighten up, more O_2 feed is required.

2. In order to control a reactor, you must look at the HCl in the reactor vent in lbs/hour or tons/day--not in % HCl in the reactor vent gas sample.

3. You must calculate % burning.

4. Each reactor will have to be compared to itself--not to the other reactors. This is because of different conditions on each reactor such as catalyst level, catalyst condition, heat transfer, etc.

5. Catalyst level and condition of catalyst must be maintained properly in order to run a reactor properly.

Attached are four graphs that show the results of O_2 feed decreases and increases.

Graph #1 points out what happens to the HCl-TPD in the reactor vent when you do not have enough O_2 feed--Graph #2 shows how the % burning moves without enough O_2 feed. Both graphs point out an optimum range of % burning vs. HCl-TPD in the reactor vent. These two graphs are based on actual O_2 feed decreases.

Graph #3 points out what happens to the HCl-TPD in the reactor vent when you have too much O_2 feed--Graph #4 shows how the % burning moves when too much O_2 is fed. Again, both of these graphs show an optimum range of % burning vs. HCl-TPD in the reactor vent. These graphs are based on actual O_2 feed increases.

Both cases--not enough O_2 feed or too much O_2 feed--show there is an optimum point to run a Per-Tri reactor. In the past, we have not really tried to control the chemical reactions in the Per-Tri reactors. If we are to get the best from the reactors, we have to control them. Control means to calculate % burning and HCl-TPD in the reactor vent, compare these two controls with previous calculated data, and make the changes on feeds, etc. to hold the reactions at optimum levels.

BURNING CALCULATIONS
(SHORT CUT METHOD)

VARIABLES NEEDED:

% CO IN VENT

% CO_2 IN VENT

VAPORIZER FEED RATE (gpm)

BLOWDOWN FLOW RATE (gpm)

% OF VENT FLOW (chart Reading)

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$$\% \text{ BURNING} = \frac{(\%CO + \%CO_2)(\% \text{ VENT FLOW})(0.06)}{\left[(\text{VAPORIZER FEED})(117) - (\text{BLOWDOWN FLOW})(99)\right]} \times 100$$

EXAMPLE:

VENT FLOW = 55%

% CO = 3.5 %

% CO_2 = 32 %

FEED = 20 gpm

BLOWDOWN = 3.5 gpm

$$\% \text{ BURNING} = \frac{(3.5+32)(55)(0.06)}{20(117) - 3.5(99)} \times 100$$

$$= 5.88\%$$

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HCl IN VENT

$$(\% HCl)(\% \text{ VENT FLOW})(0.002) = T/D \text{ HCl}$$

C. Vent and Crude Analysis

The sample analysis is very important in reactor operations. By watching the different components in the crude and vent, the reactor can be operated at the optimum. This will vary depending on the composition of the reactor feeds. A typical range for the different components are listed below.

Crude	
Per + Tri (conversion)	89-92%
TCE	.1%
Lights	5%
Heavies	6%
Vent	
HCl	50%
O_2	1-3%
N_2	Depends on dead tubes
CO	4-7%
CO_2	30-40%

D. Vaporizer Blowdowns

A blowdown stream is taken from the bottom of the organic vaporizer that should be maintained at approximately 10% of the vaporizer feed.

This stream is for two reasons, first to control the ferric chloride concentration and secondly to prevent heavy materials from concentrating in the vaporizer. Either of the above can cause plugging and fouling in the vaporizer and reboiler.

F. Reactor Catalyst Level

The reactor was designed to maintain a certain velocity (.55 ft/second) through the catalyst bed. If either the velocity or the amount of catalyst changes one or both of two things happen. First the reaction is not completed and there will be oxygen breakthrough in the reactor dome causing excess burning, and secondly the heat transfer area will be affected causing the vapor spaces to run hot. This can be monitored by watching the vapor space temperatures and by checking for dark crude.

Reactor Dowtherm Levels

A low Dowtherm level acts like a low catalyst level in that the vapor space temperatures will run hot and the crude will be dark. This is caused by loss of heat transfer area, and when the reactor vapors are not cooled properly, then burning increases with an increase in temperature.

Feed Piping and Checking Individual Tubes on Reactor Total

After the reactor has been dumped and the mixed feed header cleaned, the bayonets are reinstalled and a wash flange put on where the mixing tee normally goes. All organic valves to individual tubes should be closed except for tubes 1 and 3. A water hose is then attached to the wash flange and the mixed feed header filled. Then with water pressure on the feed piping to each tube is flushed.

Nitrogen is then put on the "O" ring and each rotometer is checked to be sure it is clear and working and that the O_2 piping to each tube is clear.

To complete work on each individual gauge, valve and tubing on the individual nitrogen system is checked and any bad ones tagged.

CHEMICALS INDUSTRIES

INTEROFFICE / LAKE CHARLES

TO Per-Tri Operators

DATE January 19, 1981

FROM Arville Hoffpauir

SUBJECT Reactor SOP

TUBE KILLING

This writeup is to present a few ground rules on when to take a tube out of service. It also discusses our philosophy on tube deactivation.

At all times we want the maximum production out of the reactors, but at the same time we want the equipment protected from damage. (The same holds for people, but this will only discuss equipment.) If at any time you feel that some piece of equipment is being damaged, immediately remove it from service. You are the people who will be most familiar with a certain problem and your judgment decision will be honored if you kill a tube. You will never be criticized for removing a tube, but if it is felt that the tube should have been left operating, we will discuss it with you so there will be no misunderstanding.

A dead tube representa 6.3 TPD of lost production. A reactor shut down for overhaul represents 240 to 250 tons of lost production. If killing a tube prevents a reactor overhaul, that dead tube would have to be unproductive for 40 days to make up for the overhaul. Therefore, you can see that dead tubes, on a production basis, are better than reactor overhauls.

There are many things that can cause a tube to act abnormally. I will present a few cases where a tube must be killed. There are other ways the tube can act, and in these situations you must use your own judgment on whether or not to let the tube operate. I will repeat again, you are operating the plant and you must make these decisions.

The three most common things that can happen to a tube are:

1. Bad thermocouple,
2. Plugged mixed feed orifice,
3. Plugged windbox.

In case (1), the temperature of the tube will go anywhere or just follow the tube in front of it. The ring and windbox pressure will be normal and show good bed fluidization. Here, get the thermocouple replaced.

Case (2) plugged mixed feed orifice - The temperature of the tube will fall, the oxygen ring pressure will be normal but the windbox pressure will be low.

The tube temperature drops because not enough organic is being fed to the tube and the oxygen is acting as a coolant. If you let this condition exist, a fire will develop in the dome of the reactor. The oxygen passes unreacted through the tube and builds up in the dome and vent system. High oxygen concentration in contact with reactor crude and catalyst fines is ideal for rapid oxidization. There is also a chance for an explosion in the dome under these conditions.

The action you would take would be:

1. Replace O_2 with N_2 to the ring of that tube.

2. Replace mixed feed with N_2 and close mixed feed valve to that tube. Add extra N_2 and build up pressure between windbox and closed valve. Then rapidly open the mixed feed valve and allow N_2 to flow backwards through valve to flush out the valve port. Repeat this procedure about three times. Then replace N_2 with mixed feed.

3. Put one-half the normal oxygen back in the tube, leave one-half N_2.

4. Check tube temperature. If it lines out below pack and mixed feed pressure is back to normal, remove all N_2 and bring O_2 back to normal. Keep a close watch on this tube. If it goes back into the pack and both pressures are normal, the tube is all right to operate.

5. If both pressures are normal, but the tube temperature remains below the pack, kill that tube.

Case (3) plugged windbox - A plugged windbox will make a tube run cold. A plugged windbox can be noted by high windbox pressure and low tube temperature.

The usual procedure for attempting to unplug the windbox is to blast the windbox with nitrogen. If the windbox cannot be unplugged, the tube must be killed. If allowed to operate, a fire will develop in the reactor dome. The possibility of severe clinker formation is good as the C/O_2 ratio will drop and excessive burning will take place. This also holds for plugged mixed feed orifice.

Unusual tube operation where a tube <u>must</u> be killed is as follows:

1. A tube will start going high and low temperature and oxygen adjustments do not affect the tube's temperature.

2. A tube cools off and oxygen increases do not heat up the tube.

3. A tube goes hot and oxygen cuts do not cool off the tube.

4. A tube cools off a few degrees and the oxygen ring pressure drops.

5. Any other condition where you think a tube needs to be removed from service.

Normally, 1, 2, and 3 can be attributed to clinker formation, No. 4 would indicate the riser has severed, and the primary reaction zone has been displaced a few inches from the thermocouple.

To sum it all - When in doubt about a tube, kill it.

TUBE OPERATION AND KILLING

This writeup is to present a few ground rules on when to take a tube out of service, saving tube, and recovery of dead tubes.

At all times we want the maximum production out of the reactors, but at the same time we want the equipment protected from damage. The same holds for people. If at any time you feel that some piece of equipment is being damaged or people are in danger, immediately remove it from service. You are the people who will be most familiar with a certain problem and your judgment decision will be honored if you kill a tube. You will never be criticized for removing a tube, especially if every attempt has been made to keep operating. If it is felt that the tube should have been left in service, we will discuss it so that there will be no misunderstanding. An attempt to recover a tube is no indication that it should have been left on line. Conditions when tube is killed and when trying to revive can be completely different.

At maximum rates, a dead tube represents 6.6 TPD of lost production. You can see the importance of trying to keep a tube operating. The other side of the coin is a reactor outage costs 5.2 T/Hr of production. A complete overhaul takes at least 36 hours or a loss of 190 tons of production. A "mere" rupture disc blowing will cause a minimum shutdown of eight hours or 42 tons. A tube can be unproductive for a month before it makes up for a total reactor outage. If you consider that a few tubes can be replaced faster than all 19, you can see that a dead tube is a lot better than reactor outage due to damage.

The following is an outline the rest of writeup:

1. Items to check which should indicate if tube must be killed immediately or attempt to save.

2. Possible things wrong and procedure for trying to keep operating.

3. Recovery procedure on dead tubes.

We cannot possibly list every symptom problem or situation that may occur. You must use your own judgment, and, we repeat, you are operating the plant and you must make these decisions.

To sum it all up, out goal is to try every method of keeping a tube operating if the situation allows. When in doubt about a tube--kill it.

I. Checking Procedures on Errant Tubes

The majority of the time the first indication of problems on a tube will be a change in temperature. This can be heating up or cooling off. You should form the habit of watching every tube temperature punch once. The possibility of a bad thermocouple exists and one tube following another. This can cause serious problems which could be corrected beforehand. Finding a tube heating up or cooling off early enhances the saving procedure.

Other indications of possible problems may be change of windbox and O-ring pressure, and rotameter positions. When causes the above will be discussed in Section II.

The checks below apply when a tube is gradually heating up and not when it jumps to 900 F in two punches, which calls for immediate deactivation, unless you know it is thermocouple. Usually, a tube does not cool off drastically enough to necessiate immediate killing, but caution should be exercised. A tube at 600 F or below can cause fire in dome if adding oxygen or just working with. A tube this cold should be killed.

Checks:

A. Check reactor vapor space temperature on L & N and vapor temperature to primary on IBM. Any sharp increase, kill bad tube.

B. Check reactor pressure--any increase, kill bad tube.

C. Check color of reactor crude--if black and shocking or cutting back on oxygen does not help, kill bad tube.

D. Check percent of oxygen flow on rotameter.

E. Replace thermocouple if checks do not show extreme conditions.

F. Shock windbox and watch the rotameter bob. If it is driven down, we are losing fluidization.

G. Shock O-ring.

H. Check motion of rotameter bob and pressure gauges; if they are moving, the tube is still capable of being recovered.

The reason for killing a tube should be stated in log book so it can be determined if tube can be tried with recovery procedure and how much effort should be made. Results of checks should be noted, i.e., rotameter driven down when shock windbox, changed thermocouple, etc.

II. <u>Causes of Bad Tubes, Indications, and Correction</u>

Tubes may have to be killed for mechanical reasons. (1) Thermowell leaks--this will be found when have to replace thermocouple or noticing organics dripping on pad under reactor. (2) Flange leaks on piping or heads. If we can not tighten up, the guilty tube must be killed. (3) Thermocouple failure--heat will cause failure of wire and you will get erratic temperatures or follow tube in front of it. The checks will lead you to bad thermocouple. Change and the tube should be operable without killing.

Errant temperatures are basically due to improper C/O_2 ratio which may be due to the following.

A. Plugged mixed feed orifice in the mixed feed pipe.

B. Plugged windbox.

C. Improper oxygen flow.

D. Loss of fluidization.

(A) Plugged mixed feed orifice - This is a rare problem but can be caused by cracking and/or buildup on orifice plate. The temperature of the tube will fall, the oxygen ring pressure will be normal, but the windbox pressure will be low. To safe the tube, you must shock with nitrogen through the individual feed line. If this does not improve situation immediately, kill the tube.

(B) Plugged windbox - A plugged windbox will make a tube run cold and can be noted by a high windbox pressure. The tube temperature drops because not enough organics is being fed to the tube and the oxygen is acting as a coolant. If you let this condition exist, a fire will develop in the dome of the reactor. The oxygen passes through the tube and builds up in the dome. High oxygen concentration in contact with reactor crude and catalyst fines is ideal for burning. There is also a chance for an explosion in the dome. Notice that adding oxygen to a tube with plugged windbox can contribute to an already serious situation. The same thing is true with plugged orifice. Therefore, before adding oxygen be sure you do not have a plugged windbox and/or orifice.

The usual procedure for attempting to unplug the windbox is to blast the windbox with nitrogen. If the windbox cannot be unplugged, the tube must be killed. The tube may be attempted to be revived later by recovery procedure. If allowed to operate, a fire may develop in the dome and possibility of severe clinker formation is good.

(C) Improper oxygen flow - The temperature may go up or down depending on whether it is too much or too little. With people in the area, it will happen that block valves will be moved by accident. A simple check of flow will correct this.

Plugging of oxygen risers will be indicated by higher pressure, low flow, and low temperatures. Shocking of oxygen risers may unplug. The tube will cool off a few degrees and oxygen ring pressure falls off. The opposite on temperature can occur since there would be less pressure drop across ring and excess oxygen going to tube may cause burning and high temperature. Upon determining this as a cause of erratic operations, it is a <u>must</u> kill. Be sure to record that this is reason for killing as we do not want to try and recover.

Plugging of O-ring will be indicated by higher pressures, low flow, and low temperatures. Shcoking of O-ring may unplug.

(D) Loss of fluidization - Caused by windbox plugging, vaporizer boilup drop off, improper velocities, bad catalyst distribution. Tube will get warm depending on degree of fluidization. Check pressure gauges. What happens when shock windbox? Immediate shocking is proper corrective procedure for one tube. Lower pressure on reactor and increase boilup if this situation is affecting entire reactor.

III. <u>Recovery of Dead Tubes</u>

The attempts to recover a tube will probably be done on or after day shift after supervision has reviewed the characteristics of the tube, production demands, and maintenance required done. Instructions will be given when to do it.

The following will be the procedure:

A. Have thermocouples changed.

B. Have pressure gauges changed.

C. Bring reactor to atmospheric rates.

D. Shock dead tubes checking pressures to make sure you have fluidization.

E. Add chlorine to reactor - at least 3000 SCFH total.

F. Replace nitrogen to windbox with mixed feed. The temperature should come up to 600°F. A low temperature is a bad omen and should be considered when tube does not perform normally after oxygen is added and there is doubt as whether to kill or run.

G. Add one-half normal oxygen, leave one-half N_2.

H. As tube comes up to pack consistently, add oxygen and take out nitrogen.

I. Observe closely.

EMERGENCY PROCEDURES FOR POWER FAILURE

Reactor Operator

A. Switch control room to N_2, open doors (if necessary).

B. Immediately put all reactors on nitrogen.

C. Secure reactors.

Lead Operator (Subject to L.O. judgment and circumstances)

A. Check well water booster pumps. If not on, block discharge valves and open up fire water.

B. Block reactor feeds.

C. Check vent header rupture disc. If blown, isolate blown disc and insure the spare disc is unblocked.

D. Secure plant.

C Operator

A. Block discharge of condensate feed pumps.

B. Open bypass valves as necessary at metering stations.

C. Block reactor feeds.

D. Secure plant.

Auxiliary Operator

A. Help lead operator get fire water on to flush water system.

B. Help as lead operator sees fit.

_________ 1. Have pancakes removed on all reactors.

_________ 2. Block O_2 PCV.

_________ 3. Steam to O_2 and organic preheaters.

_________ 4. Block recycle tank LCV.

_________ 5. Block discharge valves on CTW pumps.

_________ 6. Block steam PCV's if necessary

CONDITIONS AND PROCEDURES IN EMERGENCIES INVOLVING UTILITY AND FEED LOSSES

Unusual or unexpected operating problems in the Per-Tri Plant have developed in the past, and, of course, will occur in the future. Each emergency situation such as a loss of one of the utilities or reactor feeds allows us a better knowledge of operations through experience. To summarize some of the previous problems, and consider other possible emergencies, this report is being compiled. Prior thought to loss of feeds or utilities, or other adverse conditions may avoid major damages or a disaster within the plant. Additions and corrections to the following discussions by any of the Per-Tri personnel are encouraged. This information should be kept up to date and should be especially beneficial for personnel newly assigned to the Per-Tri Plant.

Abstract

Conditions and operating procedures are discussed in this report for the following utility and feed losses:

1. Loss of O_2
2. Loss of N_2
3. Loss of both O_2 and N_2
4. Loss of instrument air
5. Loss of Cl_2
6. Power loss to the Per-Tri Plant
7. Power loss to the organics area (includes air compressors)
8. Power loss to include Liquefaction and the alternate emergency lighting power source
9. Loss of normal and alternate emergency lighting power

10. Loss of 400 lb steam

11. Loss of well water

Discussion

1. O_2 Loss

A loss of O_2 has occurred on one occasion in the past and organic vapors backing into the O_2 feed lines resulted in explosions which broke a number of rotameters on 3 of the 4 reactors.

Plant B has 2 sources of O_2 feed. Liquid Air is the primary source with approximately 125 lbs of pressure on their pipeline. Big Three Ind., the other source, has approximately 550 lbs of pressure on their pipeline.

A set amount is flow controlled from Liquid Air and the remaining pressure or flow is made up by Big Three. In the event we lose Liquid Air oxygen flow we would have no trouble making up the difference with Big Three, but if Big Three were to lose flow, Liquid Air could not maintain enough flow to operate all the reactors requiring O_2 in Plant B. Rates would have to be cut back to prevent shutdowns.

When an O_2 loss is indicated downstream of the Plant B metering station, open both N_2 block valves and put N_2 to the O-ring. Then begin shutting down the reactors. If the O_2 reaches zero before N_2 can be admitted, the O_2 feed flow control valves should be closed to prevent organic vapors—O_2 mixtures from reacting in the feed lines. Particular attention should be given to ensure that proper fluidization (N_2 flow) is attained during shutdown.

Emergency Procedures

Loss Upstream of Metering Station

a. If liquid Air O_2 is lost, loss must be made up with Big Three pressure.

b. If Big Three O_2 is lost, loss must be compensated for by cutting back the rates on all area reactors using O_2.

Loss Dowtherm of Metering Station

a. Admit N_2 into the O_2 feed header as soon as possible.

b. Close the O_2 automatic valve when the flow reaches zero.

c. Shut down and fluidize reactors.

The O Contract

First 120 tons from Liquid Air

Next 57 tons from Big Three

Next 60 tons from Liquid Air

All the rest from Big Three

2. N_2 Loss

N_2 entering Plant B is provided by two sources. Big Three is the primary cource with a pipeline pressure of 375 lbs. The second or supplementary source is Liquid Air with a pipeline pressure of 125 lbs. Both pipelines are connected at the metering station where there is the ability to both regulate and monitor N_2 flow.

The N_2 contract

First 70 tons from Big Three

Next 120 tons from Liquid Air

All the rest from Big Three

The N_2 is then reduced and regulated at 96 lbs inside the plant. As it enters Per-Tri, it devides into two streams at the rack north of the control room. The smallest of the two lines is for field instrumentation only, while the large line provides N_2 for reactor fluidization when needed, pads for tanks and condensors, utility drops, and for the Dowtherm pressure system.

If N_2 loss occurred upstream of the metering station by one of the suppliers, then the plant pressure would have to be maintained solely by the other. Both N_2 suppliers have the pipeline capacity to supply N_2 to Plant B under normal circumstances.

In the event of a loss of N_2 down stream of the metering station, nothing could be done except shut down and dump the reactors. All field instrumentation is on N_2 and at present time not capable of being switched to instrument air.

It is important that plant pressure should be maintained at 96 lbs at all times.

Emergency Procedures

Upstream of metering station (loss)

a. Immediate action should be taken to place the surviving supplier on line totally.

b. Isolation of defective pipeline.

c. Notify both suppliers.

Downstream of Metering Station (Loss)

a. Immediate shutdown

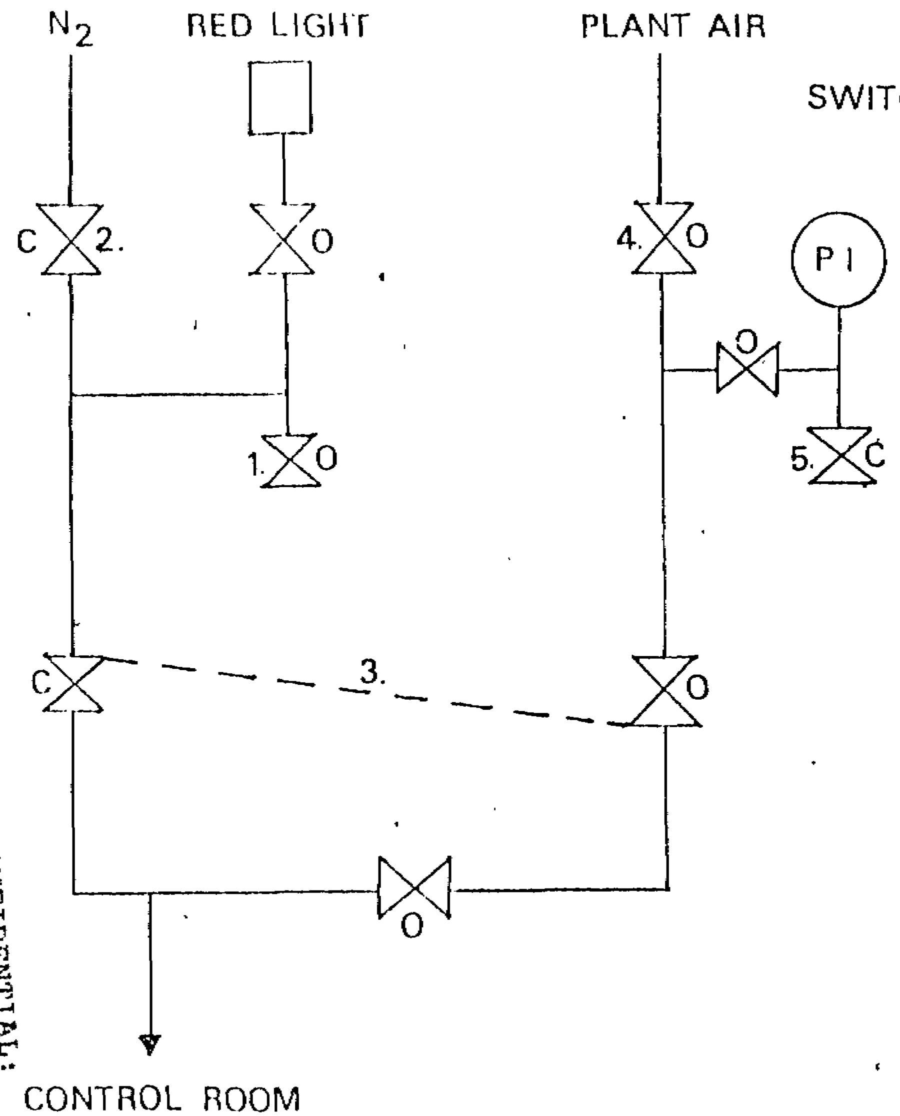
b. Block both N_2 sources

c. Notify suppliers

3. Loss of N_2 and O_2

Total loss of N_2 and O_2 would cause a total shutdown of all reactors. This would cause all reactors to be dumped also.

SWITCHING CONTROL ROOM INSTRUMENTS TO N_2



1. CLOSE VALVE 1.
2. OPEN VALVE 2. (YOU WILL GET RED LIGHT)
3. OPEN N_2 VALVE ; CLOSE AIR VALVE 3.
4. CLOSE VALVE 4.
5. OPEN VALVE 5.
6. OPEN CONTROL ROOM DOORS.

Emergency Procedure

Control Room	Field
a. Close the O_2 automatic valves.	a. Block off organic vapor lines from all vaporizers.
b. Close steam automatic valves	b. Block steam valves to the organic vaporizers.
c. Release reactor pressure	

4. Loss of Instrument Air

This will affect control room instrumentation and pressurization. The control room is pressurized with air to keep air that is contaminated in the atmosphere out of the control room air.

The control room is equipped with a switching station just outside the east door. At this station, the control room air can be switched to N_2. The control room doors must be opened to protect from over exposure to N_2.

Emergency Procedure

a. Switch from air to N_2 (outside east door)

b. Block open control room doors.

5. Loss of Cl_2

This is not a critical feed loss since the reactors are presently being operated without Cl_2. The potential hazard would be a leak or break to the atmosphere. In the event of a break or loss of line pressure, the Cl_2 auto feed flow control valves must be closed immediately to prevent organics backing up in the line. Then appropriate action would be to isolate the leak or break. Make appropriate feed cuts on reactors.

Emergency Procedures

a. Close Cl_2 automatic valves

b. Isolate leak or break

c. Notify supplier (Liquefaction)

d. Notify other on line users (EDC, Tetra, and Tri-Ethane II)

6. Loss of Power to the Per-Tri Plant (air supply not affected)

The emergency lighting and instrument power system should switch automatically to the alternate power source from the cylinder loading building bus: control room lighting, plant instrumentation, and much of the process area lighting would remain in service.

Critical flow losses would be cooling water, condensate feed for the steam drums, and all still flows. High pressure well H_2O to the reactor primary condensers is on emergency power, but an effort should be made to ensure that the power has been switched and the pump is on. Steam flows to the stills should be shut off at the panel board since pressures will quickly develop without condenser water. Except for the DH still, gradually decrease the steam flows to zero during an approximate two minute time interval. This will allow time for the safety relief valve to relieve the sudden pressure in the line which blew a steam line gasket during a previous still shutdown. The steam drums will not boil dry for at least five minutes at full rates. Therefore, adequate time should be available for putting the reactors on N_2. If a steam drum would happen to boil or drain empty, safety valves on each reactor dowtherm vapor line should relieve the sudden pressure buildup. A large O_2 cut initially would lower reactor temperatures and allow a dowtherm pressure increase to slow boiling in the steam drum. The discharge valves on the condensate feed pumps should be closed to prevent the steam drums from draining back into the condensate storage tank.

In the event of a temporary power failure, quick and immediate action by the personnel turning on all pumps should ensure continuous operation of the plant. If performed quickly enough, all product should stay in spec.

Emergency Procedures

Control Room

a. Shut off steam to the DH stills

b. Gradually shut off steam to the other stills during a time period of about 2 minutes.

c. Immediately reduce rates to approximate atmospheric, or until N_2 can be substituted for the flows. Make a large initial O_2 cut and maintain a small flow with a high dowtherm pressure.

Field

a. Close valves at the condensate pump discharge.

b. Drain the DH still to the sewer to minimize reboiler corrosion.

c. ISOLATE REACTOR FEEDS AS SOON AS POSSIBLE.

7. Power Loss to the Organics Area (includes air compressors)

Emergency Procedures

Control Room

a. Switch control room from air to N_2 outside east door.

b. Block open control room doors.

c. Follow the above power loss procedures.

Field

a. Follow the above power loss procedure.

8. Power Loss (includes Liquefaction and the alternate emergency lighting power source)

In addition to the previously mentioned critical flow losses of cooling water, condensate to the steam drums, and all still flows, there would be no lighting, temperature readings, or still panel board controls, and the Cl_2 flow would drop to zero. However, we would have use of all pneumatic instruments since all field instruments are on N_2 and control room instruments can be switched to N_2 as discussed previously. Shut down.

Emergency Procedures

Control Room

a. Switch control room to N_2, open door.

b. Shut off steam to DH stills.

- charge due to Fail H_2O condition

c. Dump reactor as soon as possible due to no flush water.

d. Close Cl_2 automatic valve.

Field

a. Close valves at the condensate pump discharge.

b. Block off liquid Cl_2 line to vaporizer.

c. Drain the DH stills to the sewer.

D - ISOLATE R FEEDS AS SOON AS POSSIBLE

9. Loss of Normal and Alternate Emergency Lighting Power

This is an unlikely problem but has happened in the past. The Per-Tri and heavies still temperature control valves would fail closed on a power loss to the board so it would necessitate a shut down. Both Tri stills and both Per still would have to be put on total reflux. The topping still would have to be shut down.

In the case of the reactors if you would lose the well water booster pumps, you would have to shut down as soon as possible and dump the reactors. Without well water booster pumps you couldn't keep the primary condensers cool enough to fluidize the reactors.

10. Loss of 400 lb Steam

Loss of 400 lb steam is not as critical now as it was in the past. We now have two powerhouses producing steam. Powerhouse A sends P/T 400 lb steam. Powerhouse C sends P/T 175 lb steam. The 400 lb steam header is sent directly to the reactors as 400 lb steam, and the 400 lb header is also reduced to 250 lbs. The 175 lb header is reduced to 150 lbs. All headers are tied into each other. The 175 lb header can be equalized with the 250 lb and the reactors at reduced rates can run on 250 lb steam if time permits. If not, reactors will have to be shut down and restarted.

11. Well Water Loss

The main concern with a loss of well water is the cooling tower. Well water is used to makeup water to maintain a constant level. Fire water can be used for short periods, if necessary to maintain a water level above the pump suction. In case of a well water loss put the stills on recycle because of the neutralization systems. Loss of well water would also mean that the flush water to the primary condensers would also be lost. In the event of a reactor shutdown, it would have to be dumped instead of fluidized.

Conclusion and Recommendations

Since an emergency shutdown is inevitable sometime in the future, we have at our disposal many means by which we can shut down without injury to personnel or to equipment. The quicker and safer the response to an emergency the more profits that are gained. It is recommended that all personnel be familiar and follow these procedures for safe and profitable operation of the Per-Tri unit.