MONSANTO COMPANY
Texas City, Texas

November 17, 1966

cc: Jim Berry
J. B. Cook
J. A. Glass
F. E. Grissom
H. D. Grove
E. L. Haile
J. H. Ingram
W. R. Nisbet
G. T. Ryan
R. D. Sadow
T. E. Shirley
K. F. Webb
Central Files

Subject: Abatement of Smoke from the VCM Flare System

Ref.: 1. Memo, Ray Rosenberg to R. D. Sadow, July 27, 1966
2. EWO 840.22Z2610, Sept. 16, 1966
3. Quotations, M. L. Bottomley of John Zink Co. to G. H. Weekley, Jr., October 4, 1966

TO: Ray Rosenberg
E. R. Hendrick

2223

The VCM flare system consists of a group of three separate flares (12, 6, and 3-inch pipes). Typical compositions and rates for each flare are listed in Table I. All of these flares have been observed to give off black smoke on different occasions. In response to your request, we have studied past problems and experiences with abating smoke from these flares and similar flares at other locations to arrive at possible or potential abatement methods. From these, a method of abatement is selected and recommended for this system.

Past Experience

A. VCM Flare System

During earlier VCM plant operation, the main 12-inch flare burned all streams, including those now going to the 3 inch flare and the incinerator in Dept. 24. Steam was injected both into the piping (about 3-1/2 ft. from top) and later sparged from a ring into the flame front to control smoke. We are told that considerable corrosion occurred to the piping and adjacent hardware. Furthermore, the resultant corrosion products plugged the flame arrestors. These conditions were greatly reduced by taking steps to prevent water (vapor and condensate) from contacting and absorbing HCl both in the piping and from burning chlorinated hydrocarbons. One step discontinued the use of steam; the other step routed the wet regeneration gases (acetylene and methane) to the 3 inch flare. The literature reflects that some corrosion still occurred to the piping, but it was more external from contacting hot HCl combustion vapors. The stainless steel (304) tips were replaced about once every 1-2 years.

CBY 1002605

Sometime later, air was sparged from rings above the flares (into the flame front) to improve combustion to control smoke and disperse the HCl vapors. This proved to be a good way to abate smoke, especially in burning the soot-producting acetylene going to the 3-inch flare. However, air sparging was discontinued due to a shortage of plant air and difficulties in avoiding overheating of the rings and flare tips. Since then, a natural gas diluent has been successfully used, in place of air, to partially accomplish the same objectives. Black, sooty tails were observed on the flares only during upsets, start-ups, intermittent regenerations and purges, and tank overpressures when venting rates were relatively high; the most objectionable smoke-producing event being the burning of acetylene from the 3-inch flare during intermittent purging operations.

In 1965, a further improvement was made when an HCl smog abatement project routed the HCl stream and the continuous chlorinated hydrocarbon streams (22D4 overhead and 22T19 vent) from the 12-inch flare to the incinerator (24H1) in Dept. 24. This change left mainly the natural gas diluent and intermittent chlorinated hydrocarbons from upsets, tank overpressures, etc., going to this flare. However, we understand that some of the diverted gases have to be flared due to restrictions in this line.

The 6-inch flare was installed to handle waste gases from the oxidative chlorination unit (Dept. 26). This flare also burns small quantities of chlorinated hydrocarbons.

B. Springfield Plant

Our Springfield plant uses a John Zink smokeless flare tip for intermittent burning of chlorinated hydrocarbons. They use superheated steam (i.e., throttled from 140 to 30-20 psig) to eliminate smoke and prevent condensation. Corrosion still occurs to require replacement of the flare tip about once per year. Several different metals of construction for the tips, including Hastelloy B and 309 stainless steel, have been tried without marked reductions in corrosion.

Potential Abatement Methods

A. Previous Design by Plant Engineering Services

Previously, Plant Engineering Services had studied this problem and came up with a very thorough (and ultimate) design for abatement. This design precluded any corrosion from HCl or HCl-water

condensation by scrubbing out the chlorinated hydrocarbons in the process area. Then, the remaining gases were burned from multiple shielded, ground level burners to prevent smoke. This design was not approved for installation due to its high cost ($160,000).

B. Route Some of the Flared Gases to the Incinerator, 24H1

It was suggested that it might be desirable to route some of the flared gases to the incinerator via the existing line. However, this would not be possible since this would re-mix the HCl and wet streams to lead to pipe corrosion. Also, as previously stated, the existing line has not been able to handle all of the present gases; and the installation of an additional line would be too expensive. The installation of a large line to handle tank overpressures would overload the incinerator.

C. Air Rings

Based on past experience, the use of air rings would require rather precise definitions of air requirements in order to avoid overheating the rings and flare tips. Also, a costly compressor or blower would be required.

D. John Zink Smokeless Flare Tips

Use of John Zink smokeless flare tips is attractive in view of Monsanto's favorable experiences with these tips at Texas City, Chocolate Bayou, and Springfield. The main concern has been with the sparging of steam from nozzles into the flame front and its effect on HCl-water condensation and corrosion. We feel that this will not be a major problem because of the following:

1. The HCl and chlorinated hydrocarbons going to the flare system are much less than in the past when steam sparging was tried.

2. As previously stated, the Springfield plant does not have an HCl-water condensation problem due principally to the use of superheated steam in the sparge nozzles of their John Zink flare. As a result, their frequency of replacing flare tips has been slightly greater than that for our VCM flare system.

3. John Zink has a flare tip in similar service at a plant in the Houston area. They report that this installation has been very satisfactory.

CBY 1002607

Conclusions

1. From past experience, it is apparent that abatement of smoke from the VCM flare system is not a continuous problem but required mainly during upsets, start-ups, tank overpressures, intermittent regenerations and purges, etc., when relatively large volumes of gases are vented for short periods. In our opinion, this and other considerations places an obvious limitation on the money that can be justified for purchasing abatement equipment.

2. In view of the preceding considerations, we feel that it is more desirable to abate smoke with the relatively inexpensive John Zink smokeless flare tips. Later, if some unforeseen trouble should be encountered with the steam sparging, a less condensible mixture of steam and air could be substituted by using a jet compressor in place of the control valve, as shown in Figure 1. This revision would be relatively inexpensive and easy to make but requires extensive testing.

Recommendations

1. It is recommended that John Zink smokeless flare tips be installed on each of the three flares (see Figure 1). These tips will each consist of three feet of main piping, steam nozzles, ring and piping and pilots (1 per flare). These will be fabricated of Hastelloy C and solution annealed as per Corrosion's recommendations. Corrosion desires the mill test reports and furnace charts for this operation. In addition, each tip will be fastened to the existing pipe with 150 lbs. carbon steel split Van Stone flanges. John Zink has quoted a price of $5,935 for this equipment (less steam throttling equipment, ratio controllers, and installation).

2. Steam for the sparge nozzles should be obtained by reducing from 600 psig to 200 psig across a control valve to achieve the necessary superheat. Plant Engineering should design for trottling a maximum of about 3,000 lbs/hr (normal operation would use an average of about 300 lbs/hr). To avoid losing this superheat, the steam piping should be insulated to the top of the flare. Additionally, John Zink "flow sensors" should be installed on each pipe so that the steam is automatically ratioed to the flow of waste gases and natural gas diluent. Production should maintain good natural gas diluent rates so that this ratio controller will automatically ensure that steam is always flowing and the flare tips are hot.

CBY 1002608

3. The waste gas line from VCM to the incinerator should be debottlenecked so that all of the gases can be burned. We feel that this is a relatively minor operation of removing restrictions (weaker check valve, bigger orifice and control valve) at the incinerator end of the line. PT and E will more accurately define this problem.

We have recommended equipment which should eliminate smoke nearly 100% of the time. However, there is some question in our minds as to whether the emission characteristics of this flare warrant the level of expenditure anticipated. Mr. J. H. Ingram of Plant Engineering Services has proposed a cheaper approach of installing only one John Zink tip on the 3-inch flare, since this flare appears to be the most objectionable smoke producer and does not burn chlorinated hydrocarbons or vent HCl. It should be noted that this approach would not eliminate the need from eventually replacing the other flare tips (corrosion), which is a sizeable part of the equipment cost of the recommended course. To get a better comparison, we have asked Plant Engineering to prepare two separate cost estimates for these two approaches. Upon receipt of these estimates, we will review them with you to determine which one, if any, should be pursued to a conclusion.

George H. Weekley, Jr.

GHW:eh

Encls.

CBY 1002609

TABLE 1

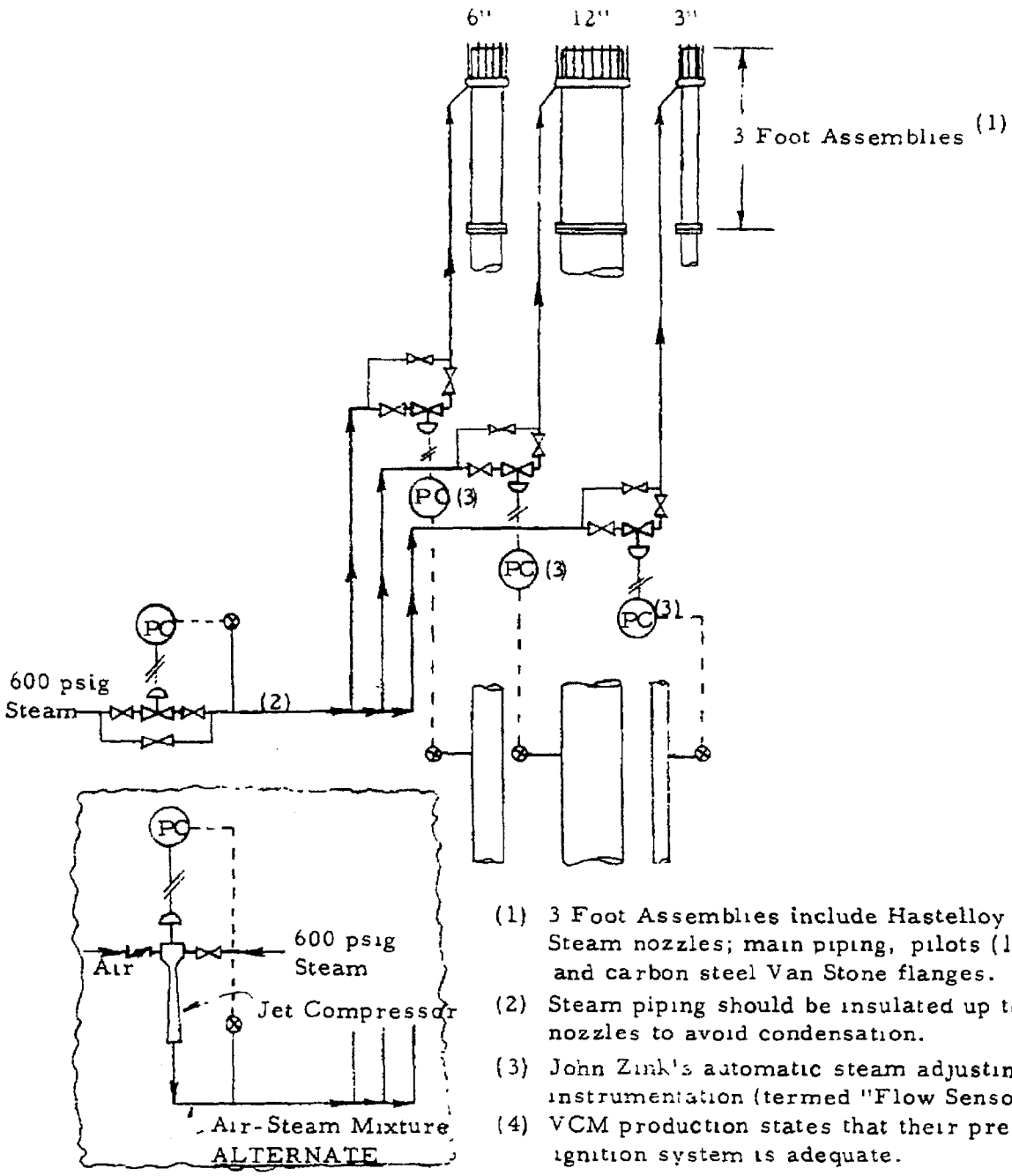
FLOW RATES FOR THE VCM FLARE SYSTEM
(Lbs/Hr)

	12 Inch Flare		6 Inch Flare		3 Inch Flare	
	Total Rate	Composition	Total Rate	Composition	Total Rate	Composition
Normal Firing Rate:						
Continuous:	Natural Gas Diluent		250	Methane 164 Acetylene 30 EDC 17 Ethane 11 CO 7 Ethyl Chloride 6 A 5 Propane 3 Oxygen 3 N_2 2 CO_2 2 250	Natural Gas Diluent	
Intermittent:	2500 (6 hrs. twice/wk.)	Methane -2500	4000 (1 1/2 hrs. at Start-up)	Methane-4000	200 (15-20 Min. every 12 hrs.)	Methane-100 C_2H_2 -100 200
	2500 (4 hrs. twice/wk.)	Methane -1875 Hydrogen- 625 2500				
Abnormal Firing Rate:						
Intermittent:	>2000 (upsets, tank over-pressures, etc.)	Chlorinated Hydrocarbons	-------	--------	--------	-------

CBY 1002610

RSV0032831

FIGURE 1 - PROPOSED JOHN ZINK TIPS FOR THE VCM FLARE



(1) 3 Foot Assemblies include Hastelloy C Steam nozzles; main piping, pilots (1 per flare) and carbon steel Van Stone flanges.

(2) Steam piping should be insulated up to steam nozzles to avoid condensation.

(3) John Zink's automatic steam adjusting instrumentation (termed "Flow Sensors")

(4) VCM production states that their present ignition system is adequate.

CBY 1002611

MONSANTO COMPANY

Location : Texas City, Texas

cc: ~~J. A. Glass~~
W. H. Slager
K. F. Webb
G. H. Weekley

Date : July 27, 1966

2273

Subject : VCM Flare System

To : R. D. Sadow

The VCM flare stack contains three separate flare lines for burning vent gases from the VCM area. 22A1's and 22R4's are purged through the 3" line. Department 26 uses the 6" line. The 12" line is the main flare and handles unit upsets, equipment purging prior to maintenance, Department 22 RV's and some of Department 23 RV's.

The VCM flare system normally burns leaving a black sooty trail which can easily be seen from the ground. The quantity of soot that is made varies with operations or problems in the area. The sooty flare is considered objectionable.

You are well aware of the emphasis now being placed on reducing atmospheric pollution originating within Monsanto property limits. I, therefore, request that a study be made to divert, reduce, or discharge the materials going to the flare in such a manner as to eliminate the VCM flare as a source of continuous atmospheric pollution.

R. Rosenberg

R. Rosenberg

mg

CBY 1002612

~~JDS~~/C.F.

MONSANTO COMPANY
Texas City, Texas

cc: W. H. Slager
A. J. Romeril
R. F. Kaeble
E. D. Moore
~~B. H. Hartzog~~
T. E. Shirley

Date : July 14, 1964

2273

To : J. B. Cook

FILE COPY

Subject: Smokeless Flare for Department 22

As you know, there is increasing emphasis on reduction of air pollution from the plant. We now have EWO's for revising the 3" C_2H_2 flare from VCM, and for diverting the normal vents from 22D4 and 22T19 to the Department 24 stack. These projects should reduce smoke and smog from normal vent streams.

There is still a possibility of formation of large quantities of smoke should a relief valve vent to the flare. This happened recently when the VCM spheres were overpressured. We must have a flare system which will provide clean burning for this eventuality.

Because of the HCl generation when most VCM streams are burned, steam injection is on undesirable method of smoke reduction. ~~We have had an~~ air "ring" at the top of the main flare which could be turned on manually to reduce smoke. I feel air is probably the best material to reduce smoke from our flare. This system, however, had two disadvantages: 1) air demand can be very high, and 2) it is not automatic. An air ring or air nozzles at the flare tip supplied by a stationary air compressor with automatic starting is just one system that might be installed for our flare. There are probably other systems that could be devised. (There might be air compressors soon to be salvaged in Department 1 that might be suitable).

The attached EWO is to cover the engineering for this job.

J. W. Kongable 7-14.

J. W. Kongable

/jb

CBY 1002613

RSV0032834

CBY/KBB

Houston Central Files -

cc: J. M. Chamberlin
E. R. Hendrick/Hutchins
J. P. Hickman
H. M. Keating
V. L. Linton
J. G. McQuarrie
W. R. Nisbet
M. L. Owens
G. E. Pratt
G. D. Rucker
W. H. Slager
W. F. Zimmermann

MONSANTO CHEMICAL COMPANY

Texas City, Texas

April 12, 1961

227-3

FILE COPY

To: J. W. Kongable

Subject: Soot from VCM Flare at 1500 on April 10, 1961

JR

The Occurrence

A dense black smoke plume from the VCM flare was observed between 1500 and 1530 on April 10. The wind was straight out of the southeast. The plume was clearly visible overhead all the way across the city. Although casual observations at the foot of the flare and across the city did not reveal any soot falling out, had weather conditions been different, soot fall-out might have been serious. No complaints have been received about this incident. However, everyone in Texas City could see that Monsanto was again putting soot into the atmosphere.

The Cause

The cause of this incident was an operator error. A VCM rundown tank was overfilled and blew its relief valve into the flare line.

Harold Oltmann

H. D. Oltmann

do

CBY 1002614

RSV0032835

MONSANTO CHEMICAL COMPANY

FROM: Texas City

AT: December 22, 1960

SUBJECT: VCM Flare Corrosion

REFERENCE: Memo PDM to ETM 11-22-60 and Memo ETM to LBE 11-29-60

cc: A.W.A. Coaker, Spgfld.
C. B. Hammond, Spgfld.
P. D. Montgomery
Central Files

TO: E. T. Molyneux
Springfield

At Texas City the VCM flare system has experienced corrosion, but the corrosion has been reduced considerably through several changes in the system. We believe now the corrosion is within the limits of that expected for the corrosive gases it handles. Several changes have been made from the original flare system.

The original system had one header line that handled the relief valve exhaust, tail gas, regeneration gases, and miscellaneous blowdowns. This gave severe acid corrosion internally in the larger head piping, flare sump, and flare tip. We believe the corrosion was caused from the acid formed by the HCl containing tail gas and the wet regeneration gases. A second smaller flare line was installed to handle the wet regeneration gases and wet miscellaneous blowdowns. Since this change was made in 1956, the flare tip has not been replaced, and corrosion to the piping has been more on the external surface from the atmosphere than internal.

The tail gases are burned continually in the flare. They consist primarily of acetylene, HCl, and dichloroethane. VCM is burned intermittently and only as an emergency measure to relieve pressure. A flow of fuel gas (methane) is also burned in the flare continually to maintain enough heat to disperse the HCl and prevent air pollution.

Steam has not been used on the flare flame in the four years I know of. It has been unnecessary because the black smoke problems have been very minor. Apparently, fuel gas has reduced our problem with incomplete combustion. Actually, the steam sparge and steam piping were removed at the last shutdown in October. We get atmospheric corrosion in the area just below the flare tip, and the smaller steam piping is particularly susceptible.

The flare tip is fabricated from 304 stainless steel without Hastelloy trim. I am unable to identify it as a Zink flare. It was redesigned when it was replaced in 1956.

CBY 1002615

RSV0032836

We have used linings in the sump section at the base of the flare stack -- first, with Ebonite rubber lining for protection against acid accumulation, and more recently it was lined with 'Duro' acid proof brick. The dichloroethane atmosphere attacks the rubber. We have experienced acid conditions of the dichloroethane condensated and accumulated in the sump, possibly from the slight wet condition of the fuel gas entering the flare at the base.

If we have had internal burning inside the flare, it has gone unnoticed and has not been a problem to our knowledge.

I hope these comments will help you with your flare problem; but, if you need additional information from us, please write.

hl

L. B. Bullock

CBY 1002616

RSV0032837

From MONSANTO CHEM. AL COMPANY

IN 10 AM 22395

At Springfield, Massachusetts

Date November 29, 1960

cc Mr. A.W.M. Coaker
Mr. C. B. Hammond
Mr. P. D. Montgomery - Texas City

To Mr. L. B. Bullock Reference

At Texas City Subject VCM FLARE CORROSION

Recently I contacted our Bill Coaker, Research Department here at Springfield, with regards to what happens chemically when VCM vapors are burned at the top of our VCM flare. This was an attempt to find out what causes the severe corrosion problem that we experience. I understand Bill called Phil Montgomery who, in turn, contacted you.

Since you may have some technology that would help us, here is a brief description of our system and the trouble we experience.

We have a flare stack which is used to burn off process gas, specifically vinyl chloride monomer vapors (CH_2CHCL). This stack stands 120 feet in the air. The top twelve feet of the stack consists of a removable 24-inch diameter cylindrical flare which is fitted with three city gas burners (to ignite the vinyl chloride monomer vapors), and a steam sparge for injecting steam just over the top of the 24-inch shell (to afford complete combustion). This upper 12 feet is a patented field flare manufactured by the John Zink Company of Tulsa, Oklahoma.

When the VCM vapors reach the top of the flare, they are ignited and would normally burn with a heavy black smoke. The injection of steam, however, adds sufficient O_2 to allow the carbon present to burn to CO and CO_2. Unfortunately, we believe that HCL is formed as a result of steam injection and we strongly suspect HCL is formed initially as part of the VCM, is heated up, polymerizes, degrades and releases HCL vapors. We have no idea what concentrations of HCL acid exist.

The flame temperature based on visual observation of flame color ranges between 1800°F and 2100°F. We believe internal burning occurs inside the flare when the venting rate is low. There have been visual observations at night which show the 24-inch shell to glow cherry red for the top four or five feet. This places the metal temperature around 1400°F.

CBY 1002617

The operation of the flare follows no set pattern except when the operators observe that VCM is burning--they turn on the steam sparge. After the burning has ceased, they turn off the steam sparge. There is always a small bleed of steam to keep the lines hot and to prevent freezing in the winter. The flare may burn for several days or just for an hour. The temperature extremes, therefore, can be severe and occur over a short period of time, particularly in the winter.

At present, we are using 309 stainless steel as the 24-inch diameter shell material. This shell (1/4-inch thick) has a life of about ten months and fails by corrosion on the upper five feet, approximately. Samples show that gross intergranular corrosion occurs on the inside of the shell accompanied by grain dropping and possibly chromium impoverishment.

The outside surface reveals pits and some intergranular corrosion. Stress corrosion cracking is prominent. There is one school of thought that believes the greatest contributor to the problem is the presence of chloride in the aqueous solution in contact with the flare at certain times when the flare is not operating or when rainy weather conditions exist. Admittedly, 309 stainless steel is poor for HCL service but does have high temperature resistant properties.

For your information, Hastelloy B material, or equivalent, is currently being used for several of the parts on the flare and the following comments apply.

Flare tip (material similar to H. B per J. Zink Co.)	This is a 24-inch diameter casting welded on the top of the 24-inch diameter 309 stainless steel shell. It shows warpage, cracking and is badly corroded after ten months' service.
Steam tips and orifices (tips are H. B and orifices are of material similar to H. B per J. Zink Company)	There are 26 of these consisting of 1/2-inch H. B pipe with a cast orifice projecting upward from a common ring. The ring is located about one-foot below the flare tip on the outside. The orifice elevation is just about even with the top of the flare tip. These parts stand up well, probably for two reasons: (1) they are cooled by the steam, and (2) they are located away from the immediate area of combustion.

CBY 1002618

Gasburner shroud and tip (material similar to H. B per J. Zink Co.)

There are three of these castings located 120 degrees apart, and the tips are about even with the flare tip (about same elevation and position as steam nozzles). These parts hold up well, also.

We understand, through various conversations that people here have had with Texas City personnel, that you have at least one flare stack that has the John Zink flare. We believe this flare stack has the steam sparge feature and is used to burn off VCM vapors. This is probably the flare with a 309s.s. shell and Hastelloy B trim. Perhaps it would be well to explain if these statements are correct.

Here are a few specific questions if you do have a flare stack that burns off VCM vapors and uses a Zink flare.

a. Do you burn VCM vapors continually or intermittently?

b. Is a steam sparge used? If so, is it on all the time?

c. What is shell material of Zink flare?

d. Do you experience corrosion on upper portion of the flare shell?

e. How often do you repair or replace the shell portion of the Zink flare?

f. Have you ever tried refractory linings or center steam sparge in the Zink flare?

g. Have you experienced internal burning in the Zink flare; that is, does the flare glow red?

We would appreciate an answer to the above questions and any comments which you may feel are pertinent to our problem.

F. T. Molyneux

F. T. Molyneux

/d

CBY 1002619

Texas City, Texas

November 22, 1960

A. W. M. Coaker-Spfld.
L. B. Bullock

VCM Flare Corrosion

Frederick T. Molyneux
Springfield

Bill Coaker called yesterday with some questions concerning your corrosion problem with the VCM flare. I've talked to Burnie Bullock, our Divisional Engineering VCM man. We're not sure we understand your entire problem, but I will relay some comments.

We run HCl-containing streams through a separate flare line. Dry VCM gives a minimum of corrosion. We've never had a "black smoke" problem from the VCM flare. We add natural gas to the flare to create more of an upward thermal draft, to get the HCl to higher altitude and disperse it better.

We use a commercial stainless steel burner tip. Burnie doesn't know which stainless, but we could find out if its important to you.

We don't know the flame temperature. It could be calculated.

As I said above, we don't fully understand your problem--whether you're sucking HCl back into the flare line, or whether you're running wet HCl-containing streams to the flare. If it's the latter, you're in trouble. If you'd like to discuss the situation, I'd suggest you get in touch with L. B. Bullock personally. Burnie doesn't claim to be a flare expert, but he's lived with the VCM plant for a long time and maybe could be of further help.

P. D. Montgomery

PDM:pf

CBY 1002620

RSV0032841

Springfield, Massachusetts

November 29, 1960

Mr. A.W.M. Coaker
Mr. C. B. Hammond
Mr. P. D. Montgomery - Texas City

Mr. L. B. Bullock

Texas City

VCM FLARE CORROSION

2223

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CBY 1002621

RSV0032842

The operation of the flare follows no set pattern except when the operators observe that VCM is burning--they turn on the steam sparge. After the burning has ceased, they turn off the steam sparge. There is always a small bleed of steam to keep the lines hot and to prevent freezing in the winter. The flare may burn for several days or just for an hour. The temperature extremes, therefore, can be severe and occur over a short period of time, particularly in the winter.

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CBY 1002622

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F. T. Molyneux

/d

CBY 1002623

Texas City, Texas

November 22, 1960

A. W. M. Coaker-Spfld.
L. B. Bullock

VCM Flare Corrosion

22 Z3

Frederick T. Molyneux
Springfield

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P. D. Montgomery

PDM:pf

CBY 1002624

Printed File

2225

MONSANTO CHEMICAL COMPANY
TEXAS CITY, TEXAS

March 31, 1959

To: E. M. Jones
O. C. Jones

cc: J. S. Putnam
H. K. Eckert
~~W. B. Alexander~~/J. M. ~~Chamberlin~~
S. L. Hunter/R. J. Schatz
J. V. Waggoner
H. M. Walker
A. E. Withrow
J. P. Hickman

Reference: JSP to EMJ-OCJ, March 31, 1959

Subject: VCM Flare

As Mr. Putnam's letter states, there is little doubt but that the oxidative chlorination unit flare discharges gases which result in a vapor trail over Texas City when the wind direction is from the southeast to southwest quadrant. This condition has existed since department 26 was put in operation in September, 1958, but has become most noticeable during the past two months when the on-stream time has increased significantly.

Field construction work on the installation of the recycle compressor started last week. This installation is scheduled for completion by April 15, and is presently on schedule.

The operation of department 26 is now necessary in order to keep VCM in operation, since acid inventory is at maximum. When acetylene again becomes available, oxidative can be shut down. It is planned to shut oxidative down anyway on April 6, in order to change out the reactor porous plates and make the recycle tie-ins.

It is suggested that department 26 be operated until April 6 and then remain down until the recycle system is ready to operate, about April 15.

H. M. Keating

djl

CBY 1002625

RSV0032846

From MONSANTO CHI ICAL COMPANY

At Texas City, Texas

Date March 5, 1957

W. E. Alexander
H. K. Eckert

To Seaton Hunter

Reference

At Texas City, Texas

Subject VCM FLARE REVISIONS

Clyde Cunel WO 2273

Confirming our conversation, I have asked the Engineering Department to drop all work on the appropriation request for revisions to this flare to stop carryover, based on the premise that it would cost at least $45,000. This is too expensive.

Unless a less expensive method of guaranteeing no misting from this flare is developed, we will have to depend on good operations and dispersing the mist by the flame. I understand dispersement by flame is not good when our humidity is above 90%; there is a question of how good or how bad it would be under these conditions. Experience is the only thing that will give us this information. It is my understanding only one minor upset has been experienced since the major one last July (1956).

I believe our best policy is to proceed along these lines.

/e.vo

J. S. Putnam

CBY 1002626

IN 10

FILE COPY

Job File
Dept 22
Staff 2223

cc: W. E. Alexander, R. D. Dunlop, R. L. Heider, S. L. Hunter, W. H. Lane, J. R. Mares, H. E. Morris, C. T. Murray, R. G. Powell, R. W. Rotzler, Tom Ryan, H. G. Schleicher, F. A. Sherwood, W. H. Stanton

MONSANTO CHEMICAL COMPANY
Texas City, Texas
October 23, 1952

To: Mr. H. K. Eckert

At: Texas City

Subject: Report on Explosion at the Bottom of Flare 2243

Summary

An explosion occurred at the bottom of flare 2243. This flare serves Departments 22 and 23. The explosion is believed to have been caused by the reaction of ethylene with either chlorine or air in a dead space at the bottom of the flare.

Description

Department 23 manufactures ethylene dichloride by reacting ethylene with chlorine. The reaction is rapid and one of the problems is removing the heat of reaction to prevent a violent reaction. Ordinarily the ethylene feed to the reactor is kept in excess of the chlorine feed so that very little chlorine will pass through the reactor. The excess ethylene in the reactor effluent is (1) cooled to remove EDC, (2) scrubbed with caustic to remove chlorine, and (3) sent to the flare. The flare, 2343, is also used to burn gases used to purge the EDC crackers.

There was an explosion at the base of flare 2243 at 0245 October 12. Below is a chronological list of the events which preceded the explosion.

Oct. 9, 1000 to 1400. VCM diluted with natural gas was flared.

Oct. 10,0000 to 0230. The EDC reactor was being put on stream and the reactor effluent was being flared without being scrubbed with caustic. A faulty control valve on the chlorine feed was giving a large excess of chlorine at times. The flame at the top of the flare disappeared and the flare stack started to glow below the flame arrestor.

Oct. 10, 0230. The flame arrestor blew off.

Oct. 10, The flame arrestor was repaired.

CBY 1002627

RSV0032848

Oct. 11, 0200 to 0600. Natural gas was sent to the flare while purging an EDC cracker prior to putting the cracker on stream. The flare operated satisfactorily during this period.

Oct. 12, 0100. Lines were being tested prior to putting the EDC reactor on stream. The by-pass on the ethylene feed was cracked to allow an estimated 100 pounds/hr to pass through the reactor, caustic scrubber, and the atmospheric vent on top of the caustic scrubber. This is a very rough estimate of the ethylene flow since there is no flow meter on the by-pass. The chlorine feed line was tested up to the reactor. It was observed that when the section of line just ahead of the reactor was blocked in, it did not hold pressure.

Oct. 12, 0230. The atmospheric vent on top of the caustic scrubber was closed and the effluent gas from the scrubber was sent to flare. It was observed that there was no apparent burning at the top of the flare between 0230 and 0245. Messrs. Hutchinson and Cutcher reported this fact independent of one another.

Oct. 12, 0245. The plate at the base of the flare was blown off. Mr. Roscoe Wiley was standing in the road near Department 3 facing the flare. He reports that there was a flame which ran up the outside of the flare stack and then back down. A second or two later he heard the detonation.

The plate at the base of the flare was blown off with considerable force. The ladder up the flare was sheared in two and the plate crashed into the back of the foam house. The point of impact on the concrete wall indicated that the plate was traveling about horizontally. Considerable concrete was knocked from the wall by the plate, but no serious damage was sustained. Considerable damage to property would probably have occurred had the plate not been stopped by a concrete wall.

RSV0032849

Comments

Three possible causes of the accident have been suggested:

(1) The explosion was due to the spontaneous reaction of chlorine and ethylene.

(2) The explosion was caused by a mixture of air and ethylene at the bottom of the flare.

(3) The explosion was caused by peroxides collected at the bottom of the flare prior to the first explosion.

The arguments for the reaction of ethylene and chlorine are as follows:

(1) Chlorine was known to be in the flare line prior to the first explosion.

(2) There is a large dead space at the bottom of the flare in which heavy chlorine gas could pocket.

(3) If the flow rate of ethylene through the reactor was close to the estimated flow of 100 to 200 pounds per hour, the ethylene would have reached the flare about the time of the explosion. (It would have taken about 15 minutes to purge the flare line of methane that it contained.)

This theory does not explain why a visible flame did not rise from the flare as soon as ethylene was turned into the far end of the flare line. A small amount of condensate drained from the bottom of the flare after the explosion did not smell of free chlorine.

The arguments for an explosion between air and ethylene are that air could have been left in bottom of the flare after the first explosion. The mixture of air and ethylene could have been set off by a spark or flash-back.

The argument for a peroxide explosion is that oxygen and EDC will form peroxides in the presence of an alkaline solution. When the EDC reactor was operated in September, for about a week a small amount of air was bled into the reactor to inhibit the formation of substitution products. During this same period EDC was carried over into the bottom of the flare.

The three theories on the explosion have one contributing factor in common: the dead space at the bottom of the flare. The fact that the plate at the bottom of the flare was blown

off while the fins on the flame arrestor were undamaged make it fairly certain that the explosion occurred at the bottom of the flare and not in the flare line.

Recommendations

Since the cause of the explosion cannot be definitely determined without repeating the explosion, it is imperative to eliminate all possible causes of the explosion. Steps are being taken to eliminate the dead spot at the bottom of the flare, to prevent chlorine from getting into the flare line, and to prevent oxygen from getting in the flare line. The following specific changes were agreed upon in a joint meeting of personnel from Production, Process Design, and Engineering:

(1) A natural gas purge be installed at the bottom of the flare to eliminate any dead space.

(2) Decrease the liquid load on the caustic scrubber (23K1) so that it will handle the high ethylene rates obtained in starting up the EDC reactor. This will eliminate the necessity of by-passing the caustic scrubber during start-up and reduce the possibility of getting chlorine into the flare header.

(3) Increase the strength of caustic in 23K1 so that its capacity to remove chlorine will be increased.

(4) Install a separate scrubber for venting chlorine tank cars. Originally 23K1 was to be used for this service.

(5) Remove the by-pass around 23K1 so that there will be no chance of gas being sent to flare without first being caustic scrubbed.

The committee also recommends that the flare system be rechecked for dead spaces and that the flare problem be reviewed each time a new stream is added to the flare header.

HAZARD INVESTIGATION COMMITTEE

G. H. Lovett
Paul Malone
W. C. Fuller
T. B. McQuarrie

GHL:gh

CBY 1002630

extra

cc: W. E. Alexander
B. H. Hartzog
W. H. Lane
H. E. Morris
H. G. Schleicher
R. L. Seikel
J. H. Worth

Gilt Glare
Dept 22

MONSANTO CHEMICAL COMPANY
Texas City, Texas

July 31, 1951

To: Mr. R. G. Powell

C_2H_4 = 29
C_2H_6 = 30

At: Texas City

Subj: Design of Vent System for Depts. 21, 22, and 23

I During normal operations, two vapor streams are continually discharged to the atmosphere. The first stream is from Department 22 and consists of 70% inerts, 23% C_2H_2, 2% VCM and 5% EDC; the quantity is 3.5 cfm. The second stream is from Department 23 and consits of 80% ethylene-ethane, 2% DCE , and 18% inerts; the quantity if about 50 cfm. Gases exhausted are light and should readily mix with the air and rise so no fire hazard due to settling should be encountered. Also, no toxic problem exists from these vapors; therefore, it is felt that these streams can be exhausted directly to the atmosphere without flaring.

22D4

? Air = 28

? No?

II During an emergency shut down due to power failure, the following conditions would prevail in the columns in Department 22:

22D4

This column would drain quite readily as it is packed. The oil would be taken to 22T11.

✓ Steam pump

22D5

The hold-up on the trays would be about 5,000 lbs. However, it is noted that the richest VCM-EDC mixture in the column is about 20 mol. percent VCM. The vapor pressure above a 20-80 VCM-EDC mixture is about 20 psia at 100°F; the column is designed for 45 psia. It thus appears that as the liquid on the trays heats up, the HCl held in solution will be stripped out. Possibly 500 lbs. of HCl will be exhausted to the HCl Absorber (21D2) over a period of time of say 10-hours. Some

21 D2 with
wood steam spare

CBY 1002631

RSV0032852

Outside 10 hrs – pump to T11

if 22T... pump has steam spare steam cold lean oil may be added to D4 to absorb the VCM

VCM will be taken with the HCl and this will exhaust from the top of 21D2 if unabsorbed; however, this amount should be small and will not constitute a fire or toxic hazard.

Steam spare in 22D2 (P-)

No purge needed

22D6

Again the richest VCM-EDC mixture is about 20 mole percent VCM. Only small amounts of VCM would be stripped out as the liquid on the trays heated up. HCl would be stripped out but, if vented to 22D5, would end up in 21D2.

use to T11 or pump lean oil to D5 to absorb VCM.

22D7

Steam driven pumps?

Here the hold-up of fairly pure VCM (rectifying section) is about 2,000 lbs. It is suggested that we take the exhaust from this column to 22D5. If we circulate oil over 22D5, the VCM will be absorbed.

Is new pipe to D5 needed

22D8,9,10 & 11

Relieve vacuum? Steam Purge? or plant purge?

These columns contain EDC which at 100°F has a vapor pressure of only 3 psia; therefore, in case of shut-down, these columns would cool and actually pull a vacuum rather than develop a pressure.

add N (dry) to break vacuum?

From the above, it appears that we should make provisions to circulate water in 21D2 and lean oil in 22D5 during a shut-down occasioned by power failure. Vapors from 22D6 and 22D7 will be vented to 22D5. Vapors from 22D5 will be vented to 21D2 and any off-gas from this column will be vented to the atmosphere. Provisions should also be made to vent the VCM Reactor Condenser (22E11) to 22D5.

Cooling water to D5 desirable

In case of a fire in the area the relief valves would pop and organics such as VCM and EDC would be vented. HCl would also be vented if the capacity of 21D2 were exceeded. The toxic limits of EDC and VCM are of interest, as are the inflammable limits in air. These properties are listed below; benzene is included for comparison:

	Bz	VCM	1-1DCE	1-2DCE
Toxicity (Max. Safe Air Conc. for Extended periods)	About 30 ppm	500 ppm	100 ppm	75 ppm
Explosive Limits	1.5-8%	4-21.7%	?	6.2-15.9%
Boiling Point	80°C	13.9°C	57.25°C	83.5°C
Molecular Weight	78	62.5	99	99
Air approx	28	25	28	28

EB

104

CBY 1002632

What about our own open fires

It can be seen that the materials handled are not very toxic in nature but do have low flammable limits and are heavy gases. The possibility of these gases settling and catching fire in another area does exist, although this possibility is minimized as the vents will be well elevated and the normal wind velocity is high, which makes for good dispersion.

Steam snuffers desired!

The opinion of people receiving copies of this letter is solicited. The writer's opinion is that a flare for the area is not required. Facilities should be provided to assure the operation of 21D2 and 22D5 during shut-downs occasioned by power failures. The following general rules will be used in determining venting requirements:

steam driven spare?

(1) Streams containing HCl should be vented to 21D2.

(2) Dry Streams containing VCM should be vented to 21D5. 22D5

(3) Streams containing EDC should be vented to atmosphere. ?

A detailed diagram of relief points, valve settings and points of discharge is attached. Common vent headers can be used where convenient. Atmospheric discharge points should be elevated above the highest point in the structure in the immediate vicinity, and should be protected by flame arrestors.

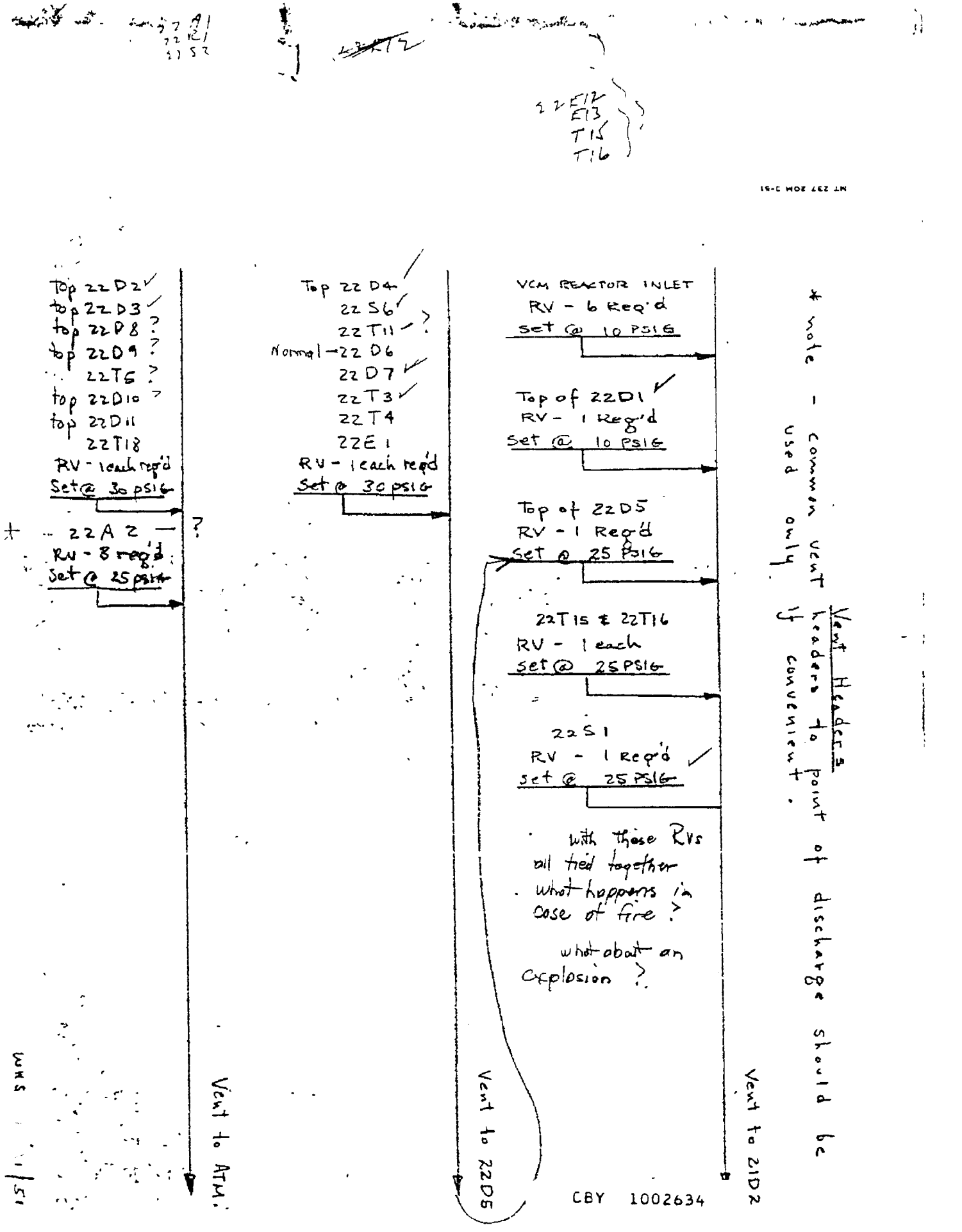
+ steam snuffer!

Walter H. Stanton

Walter H. Stanton

WHS:mlr
Enc.

RSV0032854


Top 22D2
top 22D3
top 22D8 ?
top 22D9 ?
22T5 ?
top 22D10 ?
top 22D11
22T18
RV - 1 each req'd
Set @ 30 PSIG
22A2 ?
RV - 8 req'd
Set @ 25 PSIG
Vent to ATM.
Top 22D4
22S6
22T11 ?
Normal - 22D6
22D7
22T3
22T4
22E1
RV - 1 each req'd
Set @ 30 PSIG
VCM REACTOR INLET
RV - 6 Req'd
set @ 10 PSIG
Top of 22D1
RV - 1 Req'd
Set @ 10 PSIG
Top of 22D5
RV - 1 Req'd
Set @ 25 PSIG
22T15 & 22T16
RV - 1 each
set @ 25 PSIG
22S1
RV - 1 Req'd
set @ 25 PSIG
with these RVs all tied together what happens in case of fire ?
what about an explosion ?
Vent to 22D5
Vent to 21D2
* Note - common vent headers to point of discharge should be used only if convenient.
CBY 1002634

RSV0032855