Air Products

13.3.205

Date 8 May 1980

INTEROFFICE MEMORANDUM

Subject

To Distribution

(Location, Organization, or Department)

From M. R. Chmura

(Location, Organization, or Department)

Route

1. ~~E. J. Carey~~
2. ~~A. K. McMillan~~
3. ~~W. T. Decker~~
4. M. R. Chmura

I note none of you were on the Distribution of the attached article. I have contacted Earl Primeau and Larry Allen to make certain they and their staff have the article and are aware of its implications.

Calvert City has continuous O_2 analyzers and monitors pH also. Escambia monitors O_2 levels by periodic sampling. Larry Allen will investigate the desirability of continuous O_2 measurement. Both plants use inhibitors.

MRC

M. R. Chmura

MRC/na

Attachment

RECEIVED
MAY 08 1980

(320)

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Air Products

RE D
MAR .. .90
J. C. NOVAK

INTEROFFICE
MEMORANDUM

Date 27 March 1980

Subject Explosion in Hüls PVC Plant

To Distribution
(Location, Organization, or Department)

From N. Friis — Plastics Technology
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Please find attached a report on the vinyl peroxide explosion which occurred in Hüls PVC plant December, 1978. This report is a pre-print of a paper to be presented at the International PVC symposium in Cleveland.

N. Friis

NF/nb
Attachment

(320)

Vinyl Chloride Peroxide Exp[illegible] in a Vinyl[illegible]loride Recovery Plant

B. Terwiesch
Chemische Werke Hüls AG, D-4370 Marl

Best Regards
Archie Hamilton
March 18(1980)

Introduction

The formation of vinyl chloride peroxides and their effect on the polymerization of vinyl chloride has variously been reported [1-4]. However, little has so far become known on the safety aspects assosiated with the formation of vinyl chloride peroxides in VC/PVC production facilities [5]. The paper reports on an explosion in the vinyl chloride recovery plant of Chemische Werke HÜls AG which is thought to be due to a thermally induced decomposition of vinyl chloride peroxides.

Description of the Recovery Plant and the Explosion

Fig. 1 shows a simplified flow diagram of the plant erected in 1973 for a capacity of 100 MT of recovered VCM/day. The unconverted VC obtained in the gaseous state in various polymerization plants is accumulated in a gas holder, compressed to abt. 8 bar and 110°C in a two-stage screw compressor with intermediate cooling and then condensed at temperatures of abt. 30°C. Ammonia was added during condensation for corrosion control. The condensed VC was scrubbed with water and then recycled to the polymerization plant. The non-condensed gases were passed through a batch-type water-fed scrubbing tower and then passed to the VCM plant for further treatment.

On the day before the explosion the safety valve of the gas scrubber was found to have a leak. Following this, the scrubber was blocked off and vented, the gas being delivered unscrubbed via a by-pass. The bottom of the tower was heated by steam at 3 bar to prevent freezing. The temperatures so obtainable inside the tower ranged from abt. 20 to 40°C depending on conditions.

On the day of the explosion it was originally intended to purge with nitrogen and then drain the water. However, before this work could be undertaken a severe explosion occurred in the plant on the morning of the 29th December, 1978. Within a few seconds, the entire plant was on fire. The works fire brigade kept the fire from spreading to the surrounding plants and, apart from this, allowed some 10 MT of VCM contained in the plant at the time of explosion to burn off in a controlled manner. The facilities located upstream and downstream of the destroyed plant were blocked off immediately after the explosion, critical situations did not occur.

Assisted by the fact that the plant was operated under remote control the explosion caused no injuries. On the other hand, the material damage was considerable. As shown in Fig. 2, the outdoor part of the installation was completely destroyed. The total material damage was in the order of magnitude of 2 million DM.

Reconstruction of Cause of Explosion

Investigations initiated immediately after the explosion showed without doubt that the explosion had occurred in the residual gas scrubbing tower. Fig. 3 conveys an impression of the brisance of the explosion. The bottom of the tower made of 10 mm steel plate was torn off, the cylindrical portion torn and folded up, and the feet compressed with enormous force.

In seeking the cause of the explosion the following possibilities were discussed:

1. Gas explosion of a vinyl chloride/air mixture
2. Runaway vinyl chloride polymerization
3. Decomposition of vinyl chloride peroxide

After taking account of all factors, possibilities 1 and 2 were ruled out. In particular, they could not explain the great violence of the explosion. The only possible cause left was the decomposition of VC peroxides. However, initially it was not understandable in what manner sufficient amounts of VC peroxide could have got into the scrubbing tower and why they decomposed just at that time. A comprehensive investigation program was carried out to clear up these questions. Backed by the results of these investigations we now assume the following course of events:

Phase 1 — As a result of insufficient cooling in the condensers recondensation took place in the scrubbing tower with formation of a liquid VCM layer.

Phase 2 — The oxygen that had concentrated in the residual gases, possibly supported by further impurities present in the recovered VCM, gave rise to VC peroxides, which initially were dissolved in the liquid VCM.

Phase 3 — After venting of the scrubbing tower the peroxides insoluble in water precipitated and desposited as a tacky mass on the walls of the tower.

Phase 4 — The heat supplied to the tower to prevent freezing was sufficient to heat the contents to abt. 40°C. At this temperature slow decomposition of the VC peroxide set in. Poor thermal conduction in the lumps of peroxide caused build-up of heat leading to another rise in temperature and finally, at abt. 100°C, the explosion-like decomposition of the peroxide. Activation energy ≈ 25-35 kcal/mole

Consequences for the Operation of VCM/PVC Plants

In discussing the consequences to be drawn for the operation of VCM and PVC plants, a distinction should advisably be made between measures to be taken to avoid peroxide formation and measures to be taken to safely remove peroxides already formed.

From our investigations it has meanwhile become known that contrary to information from the literature [4] no special impurities are required for the formation of peroxides from liquid VCM of usual specification with atmospheric oxygen in the presence of an aqueous phase. Therefore the first and foremost precaution to prevent peroxide [redacted] strict check on and [redacted] concentration. In VCM recovery plants it is recommended to use continuously operating oxygen analyzers.

Besides oxygen concentrations [redacted] by the addition of suitable inhibitors it is possible to cut out peroxide formation to the greatest possible extent, if not entirely. Since oxygen cannot be completely excluded from VCM recovery plants, the use of [redacted]

The VC peroxides obtained by us were readily soluble and relatively stable in chlorinated hydrocarbons. In vinyl chloride they were found [redacted]. Today the occasional

formation of PVC especially in VCM recovery plants is looked upon by us as a consequence of intermediary formation of corresponding amounts of peroxides. In this manner VC peroxide can be removed safety. If, however, the peroxide has been precipitated from a solution, it is hard to handle. Water to some extent has a stabilizing effect, it is true, but even gram quantities of peroxide [redacted] first under water. Against [redacted] which is frequently used for flushing equipment, peroxides [redacted]. Decomposition finally brought about by hot caustic soda solution all the same can be taken to be of a thermal rather than hydrolytic nature. Accumulations of large amounts of peroxide involve the danger of explosion. Safe destruction of major amounts of peroxide is possible only in solution or in the presence of solubilizers, e.g., with alcoholic caustic soda solution.

Literature Cited

/1/ G.A. Rasuwajew, K.S. Minsker, J. allgem. Chem. (Russ.) 28 (1958) 983

/2/ M. Lederer, Angew. Chem. 71 (1959) 162

/3/ J. Bauer, A. Sabel, Angew. Makromol.Chem. 47 (1976) 15

/4/ A.I. Kalinin et al, Chem. Industrie (1966) 1, 27

/5/ N.N., Case Histories af Accidents in the Chemical Industry, 3 (1970) 142

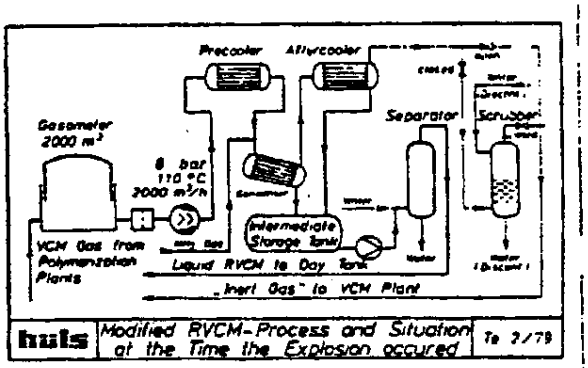

Fig. 1

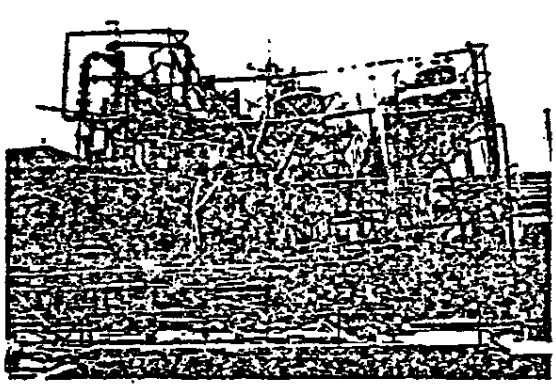

Fig. 2

Fig. 3

Air Products

Date 12 July 1982

INTEROFFICE
MEMORANDUM

Subject Vinyl Chloride Safety Meeting
VCM Exposure Risk Quantification

To A. J. Santay — Corporate Safety/Trexlertown
(Location, Organization, or Department)

From Howard L. Watson — Chemicals Manufacturing/Admin V
(Location, Organization, or Department)

cc: M. R. Chmura
R. E. Gadomski
F. J. Ryan

I have reviewed the Vinyl Chloride Exposure Risk Quantification study which was made in April, 1980 for the Trexlertown Emulsion Development Reactor Facility.

I understand that you are planning to present an abstract of the methods employed by Air Products in this study to the September 1982 meeting of the Vinyl Chloride Safety Committee.

My only concern was the use of the 3.5×10^{-5} criteria outside of Air Products. You indicated that all reference to this internal criteria would be removed. The entire page would not be submitted--merely an abstract.

I have no problem, then, with your plans to present the abstract in this manner.

Howard

Howard L. Watson

HLW:hes

(320)

R. W. Ormsby

AIR PRODUCTS & CHEMICALS, INC.

VINYL CHLORIDE EXPOSURE RISK QUANTIFICATION STUDY

TREXLERTOWN EMULSION DEVELOPMENT REACTOR FACILITY

Prepared by: L. C. Doelp
R. E. Linney
R. W. Noel
R. W. Ormsby

Issued: 1 April 1980

Distribution:
P. L. T. Brian
A. E. Cummins
P. Fong
A. Greene
J. R. Lovett
C. McKinley
D. J. Orr
J. B. Pfeiffer
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VINYL CHLORIDE EXPOSURE RISK
QUANTIFICATION STUDY

Table of Contents

1.0 Executive Summary

A risk quantification study was conducted for potential employee exposure to vinyl chloride monomer (VCM) on the Trexlertown site, based on a fault tree analysis for the proposed emulsion development reactor system.

Figures 1 and 2 show probability of exposure versus level of exposure curves for the three potential receptors chosen for this study. The risk of exceeding OSHA exposure criteria for each of the receptors is as follows:

	Frequency Rate, events/yr.
(1) Employees inside Allentown Labs Building	1.3×10^{-5}
(2) Employees walking between Allentown Labs and Trexlertown Lab #1	3.7×10^{-6}
(3) Employees inside main administration building	1.0×10^{-6}

It should be noted that OSHA criteria for VCM exposure are not normally applied to workers outside of the actual process area.

The probability of exceeding OSHA limits at any of the receptor locations is so low as to be acceptable, particularly since exposures at these levels have no known adverse effects on human health.

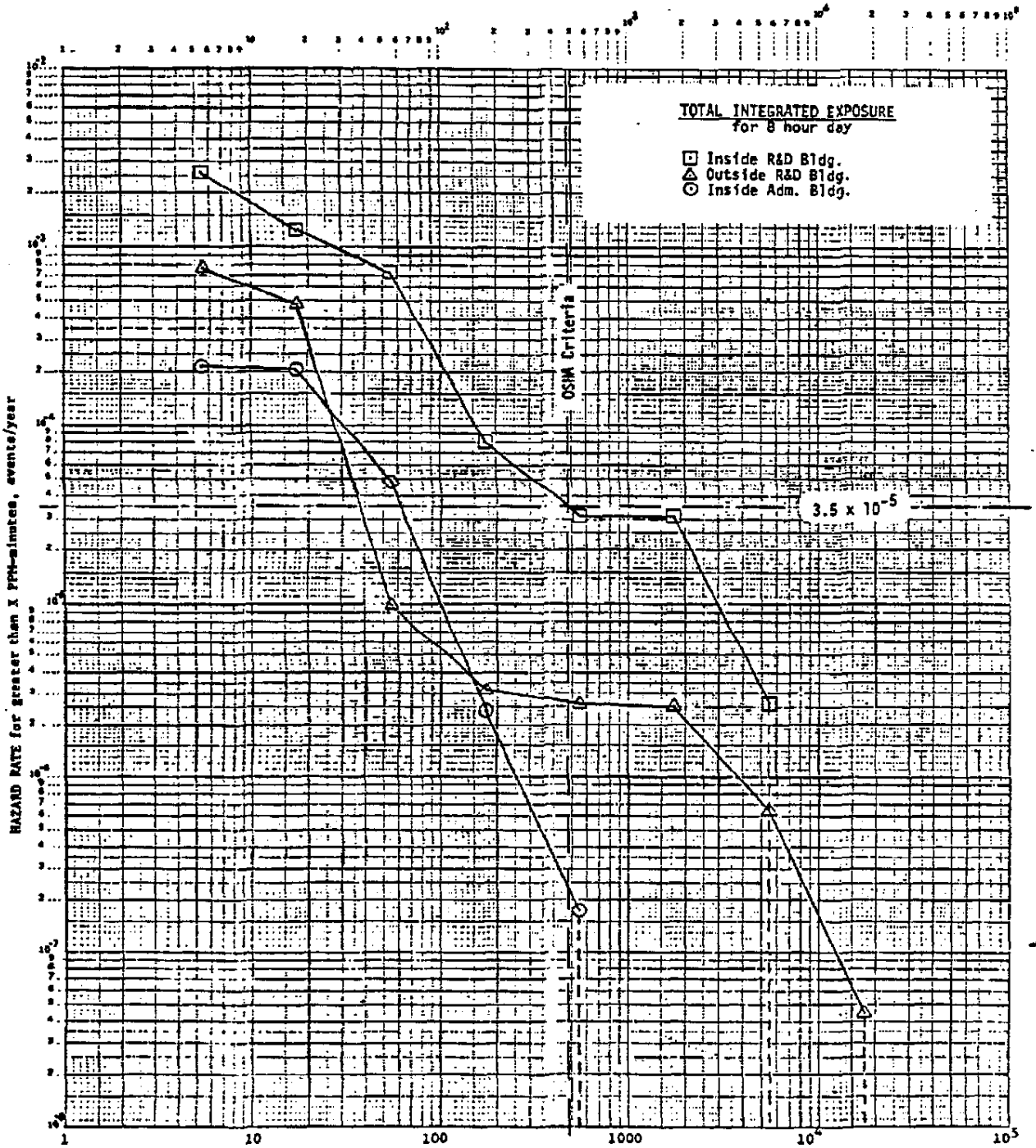
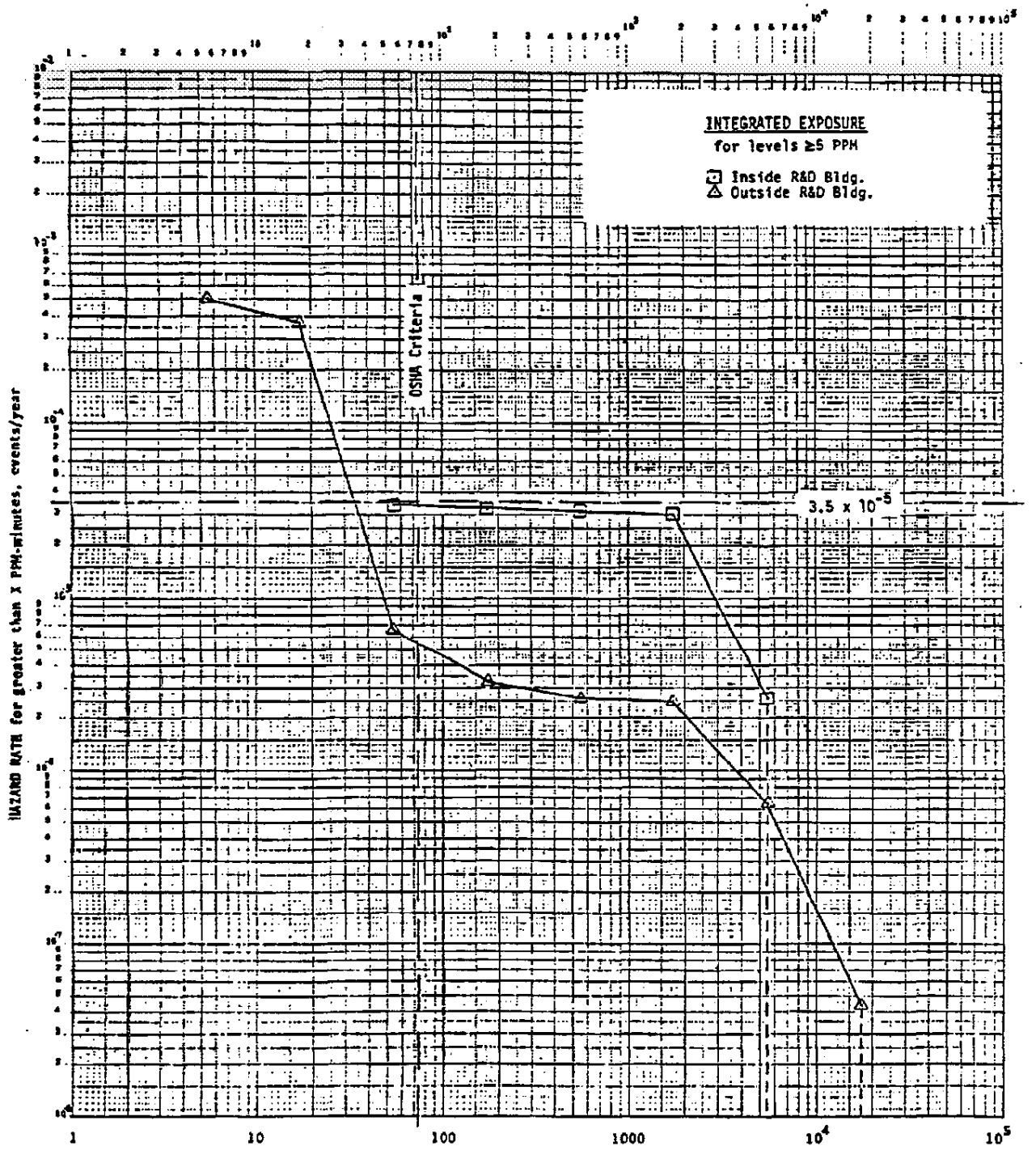


FIGURE I



X, VCM EXPOSURE, PPM-minutes

FIGURE 11

2.0 Process Recommendations

The following recommendations were identified during the fault tree analysis and must be implemented to achieve the calculated frequency rates for VCM exposure.

2.1 VCM Release from Cylinder in Storage

1. VCM cylinder size, type and connections should be standardized in order to facilitate a certification program to ensure reliability.

2. PCTD should become responsible for the inspection and certification program of VCM cylinders before the Trexlertown development reactor becomes operational. Procedures and policies should be prepared well in advance. The cylinders must be hydro tested every 5 years, per DOT regulations.

3. Sprinkler systems should be installed in all VCM cylinder storage areas to control fires and secondary releases from other cylinders.

4. Use fusible plugs instead of relief valves on each cylinder.

5. Institute controls for cylinder filling program as outlined in original CE. Proceed with approval of cylinder filling CE.

6. Ensure from procedures (cylinder filling CE) and cylinder design that overfill is not credible.

2.2 VCM Release from Cylinder in Process

7. All N_2 requirements for the VCM system should be dedicated.

2.3 Continuous VCM Release from Pump

8. High pressure hydraulic relief should be set as low as practical on the VCM delay feed pump.

9. Install automatic valve on discharge of VCM delay pump and interlock with the pump to ensure that VCM supply is shut when pump is off. This valve would then have to be opened before the pump would start.

10. Pulsations/vibrations caused by VCM delay pump should be checked at possible fracture points in the piping to determine if bracing is adequate. (Measurements will be made by Electro-Mechanical).

11. Chemical sealed pressure indicators should be used on all VCM feed lines.

12. Car seal priming valve on VCM pump closed.

13. Issue written permits for switching pump back to VCM service after being used for some other purpose.

14. Color code VCM pipelines.

2.4 Continuous VCM Release From Reactor

15. Install check valve in line between reactor shot pot and reactor.

16. Process piping changes should be logged and drawings kept current to facilitate safety hazards reviews. Process changes should be reviewed and a formal review held every two years. Inspection 1/yr

17. Reactor should be hydrostated prior to VCM series to ensure reliability of check valves as well as integrity of relief systems and vessel seals. Automatic vent on reactor must be tested during hydrostat.

2.5 Instantaneous VCM Release from Reactor

18. Install rupture disk under relief valve with a means to prevent pressure build-up between the two safety relief devices.

19. Relief valves and rupture disks should be inspected annually.

20. Consider installing block valves immediately down stream of all delay priming valves.

21. An approved back flow prevention system shall be installed to prevent emulsion from backing to potable/fire water supply system.

22. Develop fail-safe (open) operating mode for short stop addition valve. Install pressure gauge on short stop pot. Install three-way valve and recirculation line to short stop pot.

23. Verify that automatic valve to receiver can maintain blowover rate.

2.6 Continuous VCM Release from Degasser

24. Degasser should be routinely hydrostated as often as the reactor to prove leakage integrity and relief system reliability.

25. Consider orifice on N_2 flow to degasser.

26. Install interlock on bottom valve of degasser with reactor transfer valve.

27. Consider installing block valves immediately downstream of all post-add priming valves.

2.7 Instantaneous VCM Release Degasser

28. Increase rating of rupture disk on degasser to pressure more near the vessel's certification of 300 psig.

2.8 Instantaneous VCM Release from Receiver

29. Eliminate or armor sight glass.

2.9 Continuous VCM Release from Incinerator

30. Reduce size of bleed valve between two block valves.

31. Detailed hazards review should be done on incinerator when new P&I's are available.

P&I drawings for the existing facility were used for the analysis. Although these were not in a final approved form, the team was able to identify the major causes for releases of VCM. A subsequent hazard review addressing other potential hazards in addition to VCM releases in the emulsion development system has been recommended when final drawings are available.

It was decided that the initial quantification for VCM releases would be done on the system as it now exists at Piscataway. However, recommendations which would affect release rates and the probability of releases were documented (see Section 2.0). The initial thrust was to determine where we are now and how this compared to a criterion so we could choose the most cost effective recommendations to meet that criterion.

As a criterion evolved and the air dispersion calculations improved in quality, a clearer picture evolved as to what recommendations had to be implemented. The final fault trees presented in the appendix assume the implementation of these recommendations.

3.2 Frequency of Releases

Once the fault trees were generated it became necessary to assign frequencies for each of the primary events. Some of these could be obtained directly from our APCI Failure Rate Data bank (e.g. check valve failure). However for other primary events it was necessary to rely on the experience of the people involved in emulsion processing to obtain frequency information (e.g., agitator seal failure). This understanding of the process was also critical for obtaining frequencies for operator errors (expressed as failures per demand) which required knowledge of the number of demands per year.

The blending of two disciplines - emulsion polymer expertise and hazard quantification expertise was crucial for accurate representation of each primary event.

3.3 Release Rates

The two major factors that influenced this parameter are the total quantity of VCM which can be released and the total time of the release. The quantity of VCM released for the major causes were determined from knowledge of the process. The time of these releases was also estimated based on experience and judgment. One other factor which was considered in the "release time" was whether the release was directly outside, such as a relief device operating, or whether the release occurred inside the process area, such as a spill. If the release did occur inside, the effect of room ventilation was taken into account when calculating the release rate.

Smaller causes such as leakage from valves, pump seals and connections were also estimated and used in the analysis. Although these sources did not contribute to significant VCM exposure levels outside the emulsion development reactor building, they could contribute to worker exposure within the building and some of the recommendations from the preliminary hazards review deal with this concern.

3.4 Overall Frequency Rates

Appendix B describes the calculation of frequency rates for the individual releases from all sources in the development reactor system. These calculations require the combination of dispersion models, probabilities of releases, magnitude of releases and wind direction data to generate probability of exposure versus level of exposure curves.

This data was used to determine the total probability of exceeding OSHA exposure limits at the following three receptors:

	Frequency Rate, event/yr
(1) Employees inside Allentown Labs Building	1.3×10^{-5}
(2) Employees walking between Allentown Labs and Trexlertown Labs #1	3.7×10^{-6}
(3) Employees inside main administration building	1.0×10^{-6}

3.5 Criteria

We are concerned with the potential exposure of Air Products employees at this site to vinyl chloride. Trexlertown is the company headquarters, with a large number of office workers and administrative employees. These people, for the most part, are not aware that a small quantity of vinyl chloride is used at this site and they have not been asked to accept any risk of exposure. Employees working in the PVC laboratory and the emulsion development reactor building, however, have been educated about vinyl chloride and have accepted some risk of exposure.

The only published cirteria for exposure to vinyl chloride are regulations generated by OSHA for workers in process areas. These regulations consist of the following:

(1) A worker shall not be exposed to greater than 1 ppm vinyl chloride averaged over 8 hour workday (the integrated exposure level would become 480 ppm minutes for a full workday).

(2) A worker shall not be exposed to greater than 5 ppm averaged over any 15 minute period (the integrated exposure level is 75 ppm minutes for this 15 minute period).

Noncompliance with these regulations could result in a citation from OSHA. These criteria provide a conservative limit for exposure of employees outside the process areas.

At present, there is no accepted APCI hazard rate goal for exposure to carcinogens. However, the total hazard rates for exceeding OSHA limits are below the existing rate goal for fatal events. Since VCM exposures at or below OSHA limits have no known adverse health effects, the calculated hazard rates for exposures caused by the Emulsion Development Reactor System should be considered acceptable.

APPENDIX

Appendix A

Dispersion Calculations

Continuous Release

The continuous point source equation is used as follows:

$$\frac{C}{C_o},\ ppm = \frac{10^6 D_x \dot{Q}_T}{2\pi U \sigma_y \sigma_z C_o} e^{-\frac{y^2}{2\sigma_y^2}} \left\{ e^{-\frac{(z-h)^2}{2\sigma_z^2}} + e^{-\frac{(z+h)^2}{2\sigma_z^2}} \right\} \quad (1)$$

$\dot{Q}_T$ = total gas release rate, kg|sec

$\dot{Q}_T = \dot{Q} + \dot{Q}_A$

$\dot{Q}$ = active gas release rate, kg|sec

$\dot{Q}_A$ = associated air rate, kg|sec

D = dilution factor

$$D = \frac{\dot{Q} MW_T}{\dot{Q}_T MW} \quad (2)$$

MW = molecular weight of active gas

MW_T = MW of total gas

$$MW_T = \frac{\dot{Q}_T}{\left(\frac{\dot{Q}}{MW} + \frac{\dot{Q}_A}{29}\right)} \quad (3)$$

C_o = density of release mixture

$$C_o = \frac{21.924 \times MW_T}{(460 + T^\circ F)}\ , kg|m^3 \quad (4)$$

z = height of receptor, m

h = height of source, m

x = distance from source, m

y = lateral distance from centerline of plume path, m

σy and σz are calculated from Pasquill-Gifford relationships using a virtual source, x_v

$$\sigma y = \sigma y(x + x_v), \text{ m} \tag{5}$$

$$\sigma z = \sigma z(x + x_v), \text{ m} \tag{6}$$

See Figure 1. An area is calculated such that at the source:

$$2y^*z^* \times U \times C_o = \dot{Q}_T \tag{7}$$

where y* and z* are defined as follows:

$$y^* \times 1 = \int_o^\infty \frac{C}{C_o} \Big|_{\substack{z=o \\ h=o}} dy = \frac{\dot{Q}_T}{\sqrt{2T_1}\sigma z C_o U} \tag{8}$$

$$z^* \times 1 = \int_o^\infty \frac{C}{C_o} \Big|_{\substack{y=o \\ h=o}} dz = \frac{\dot{Q}_T}{\sqrt{2T_1}\sigma z C_o U} \tag{9}$$

Substituting 8 and 9 in 7 gives:

$$\sigma y \sigma z = \frac{\dot{Q}_T}{\pi U C_o} = \sigma y(x_v)\sigma z(x_v) \tag{10}$$

U = wind velocity, m|sec

At x = o, an x_v is selected that satisfies Equation 10. This is equivalent to displacing the model source backward until at the real source the cloud area times the wind velocity is equal to the source rate. Equation 10 also satisfies the condition that the concentration at the real source is 100% of the emitted gas mixture. Equation 1, $C|C_o$, gives the concentration, ppm at any point downstream of the real origin. For an outside observer the exposure E_1 is given as:

Figure 1

Calculation of Virtual Distance

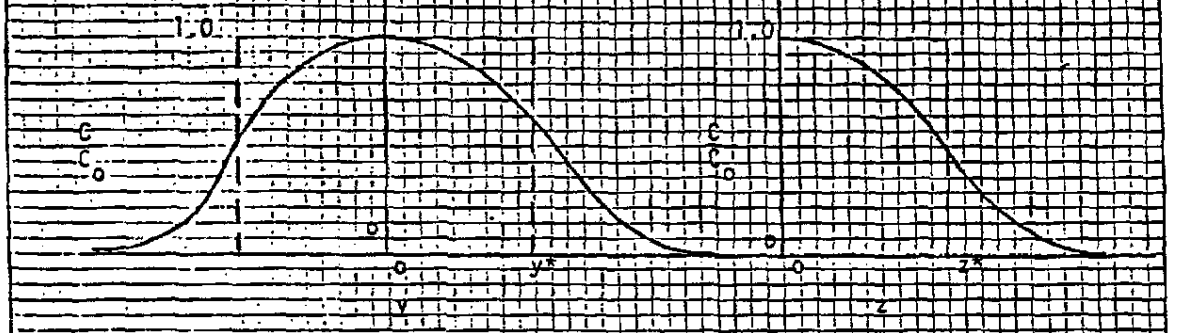
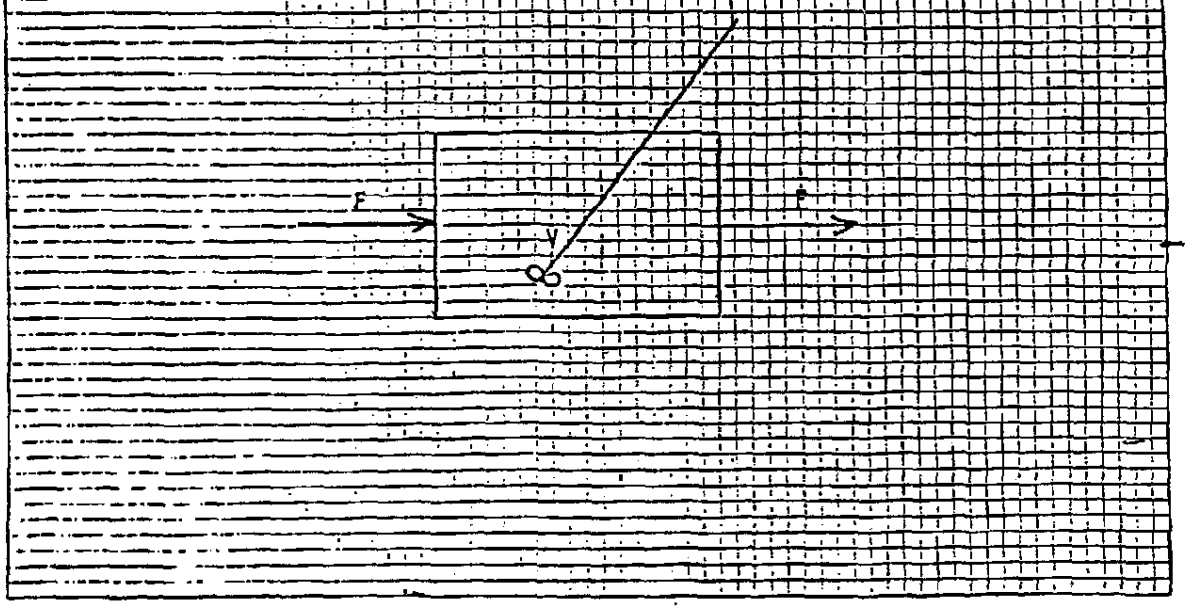


Figure 2

Exposure Inside a Building



$$E_1 = \frac{C}{C_o} \times T_1 \times \frac{1}{60}, \text{ ppm min} \qquad (11)$$

where:

$C|C_o$ = steady state conc, ppm

T_1 = duration of release, sec.

A similar exposure E_2 is obtained when $\frac{C}{C_o}$ is above a given threshold.

$$E_2 = \frac{C}{C_o} \times T_1 \times \frac{1}{60}, \text{ ppm min}$$

$$E_2 = E_1 \text{ if } \left(\frac{C}{C_o} - \frac{C^*}{C_o}\right) \geq o \qquad (12)$$

$$E_2 = o \text{ if} \left(\frac{C}{C_o} - \frac{C^*}{C_o}\right) > o \qquad (13)$$

$\frac{C^*}{C_o}$ = threshold ppm

Exposure inside a building is obtained by treating the building as a well mixed tank. See Figure 2. The exposure above zero is given as:

$$E_1 = \frac{1}{60} \times \frac{C}{C_o} \left\{ T_1 - \frac{V}{F} \left[e^{-\frac{F}{v}(T_2-T_1)} - e^{-\frac{E}{v}T_2} \right] \right\} \qquad (14)$$

E_1 = ppm min

$C|C_o$ = concentration at ventilation intake of building, ppm

T_1 = duration of release, sec but not greater than T_2

T_2 = duration of residence in building, sec

Concentration inside the building for the two time periods is given as follows:

$o < t < T_1$

$$\frac{C_B}{C_o} = \frac{C}{C_o} \left(1 - e^{-\frac{Ft}{v}}\right), \text{ ppm} \qquad (14\text{-A})$$

$T_1 < t < T_2$

$$\frac{C_B}{C_o} = \frac{C}{C_o} \quad e^{-\frac{Ft}{v}} \left(e^{\frac{Ft_1}{v}} - 1 \right), \text{ ppm} \tag{14-B}$$

The calculation of E_2 type exposure is illustrated in Figure 3. E_2 is the area under the curve between T_1^* and T_2^*. T_1 is the duration of the release. E_2 is given as:

$$E_2 = E_2^{1} + E_2^{11} \tag{15}$$

E_2^{1} = exposure from T_1^* to T_1

E_2^{11} = exposure from T_1 to T_2^*

$$E_2^{1} = \frac{C}{C_o} \left[\left(T_1 - T_1^* \right) + \frac{v}{F} \left\{ e^{\frac{-FT_1}{v}} \quad e^{\frac{-FT_1^*}{v}} \right\} \right] \tag{16}$$

$$E_2^{11} = \frac{v}{F} \frac{C}{C_o} \left(e^{\frac{FT_1}{v}} - 1 \right) \left\{ e^{-\frac{FT_1^*}{v}} - e^{-\frac{FT_2^*}{v}} \right\} \tag{17}$$

where

$$T_1^* = -\frac{v}{F} \ln \left(1 - \frac{C^*/C_o}{C/C_o} \right) \tag{18}$$

$$T_2^* = \frac{v}{F} \ln \left[\frac{C/C_o}{C^*/C_o} \left(e^{\frac{FT_1}{v}} - 1 \right) \right] \tag{19}$$

$\frac{C^*}{C_o}$ = threshold concentration, ppm

$\frac{C}{C_o}$ = concentration at vent intake, ppm

When a continuous release is made through a vertical vent, additional credit is given to the height of the release as well as dilution achieved by the vertical jet. A top hat, neutrally bouyant jet model is used. See Figure 4.

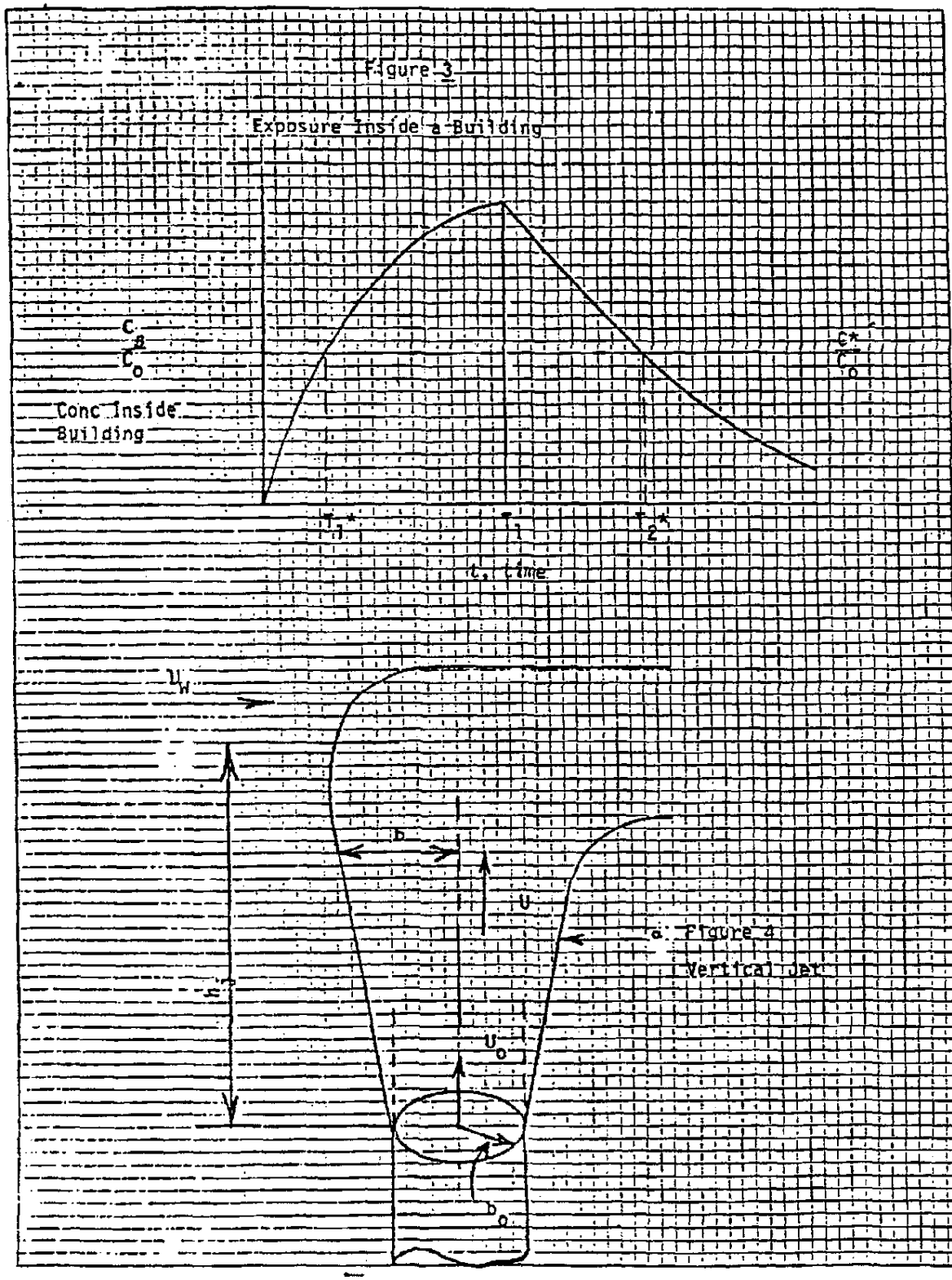


Figure 4
Vertical Jet

The model is based on conservation of mass and momentum. It is assumed that the jet will be turned down stream when the jet velocity slows down to the wind velocity. Dilution is achieved by air inspired into the jet, α. Equations for the effective jet height, h_j, and dilution are:

$$h_j = \frac{b_o}{2\alpha}\left(\frac{U_o}{U_w} - 1\right) \tag{20}$$

$$\text{Jet Dilution} = \frac{U_o}{U_w} = \frac{\text{mole|sec gas at } h_j}{\text{mole|sec gas at stack}} \tag{21}$$

b_o = radius of stack, m

U_o = velocity in stack, m|sec

U_w = wind velocity, m|sec

h_j = effective jet height above stack height, m

α = 0.11 - 0.13, dimensionless inspiration constant

h_j is added to the stack height, h_s, to get the total release height. The moles of air inspired are calculated from the jet dilution and added to the source rate of air, $\overset{\circ}{Q}_A$.

$$\overset{\circ}{Q}_{AT} = \overset{\circ}{Q}_A + \overset{\circ}{Q}_J \tag{22}$$

Instantaneous Release

The instantaneous point source equation is used as follows:

$$\frac{C}{C_o} = \frac{10^6 DQ_T}{(2\pi)^{3|2}\,\alpha x I \alpha y I \alpha z I C_o} e^{-\frac{(x-Ut)^2}{2\alpha x I^2}} e^{-\frac{y^2}{2\alpha y I^2}} \times \left\{\quad\right\}$$

$$\left\{\quad\right\} = \left\{ e^{-\frac{(z-h)^2}{2\alpha z I^2}} + e^{-\frac{(z+h)^2}{2\alpha z I^2}} \right\} \tag{23}$$

Q_T = total gas released, kg

$Q_T = Q + Q_A$

Q = active gas released, kg

Q_A = air released, kg

D = dilution factor

$$D = \frac{QMW_T}{Q_T MW} \tag{24}$$

MW = molecular weight of active gas

MW_T = MW of total gas

$$MW_T = \frac{Q_T}{\left(\frac{Q}{MW} + \frac{Q_A}{29}\right)} \tag{25}$$

σxI, σyI and σzI are calculated from Slade "Meteorology and Atomic Energy".

The initial cloud volume is $\frac{Q_T}{C_o}$, m^3.

This cloud is assumed to have the dimensions of half a spheroid:

$$x = 2.15\ \sigma xI \tag{26}$$

$$y = 2.15\ \sigma yI \tag{27}$$

$$z = 2.15\ \sigma zI \tag{28}$$

of volume:

$$\frac{Q_T}{C_o} = \frac{2\pi}{3} \times (2.15)^3\ \sigma xI \sigma yI \sigma zI \tag{29}$$

Equation 29 is used to estimate the virtual source distance as follows:

$$x_v = \left\{ \frac{3Q_T}{2\pi C_o (2.15)^3 a^2 c} \right\}^{\frac{1}{(2b+d)}} \tag{30}$$

where a, b, c and d are the coefficients given by Slade for the sigmas

$$\sigma xI = \sigma yI = a(x + x_v)^b \quad (31)$$

$$\sigma zI = c(x + x_v)^d \quad (32)$$

Equation 23 gives the concentration, ppm, at a point down stream at x, y and z. As the cloud passes by the concentration varies with time. The exposure, E_1, above zero is obtained by the integral:

$$E_1 = \int_{T_1}^{T_2} \frac{C}{C_o}\, dt \quad (33)$$

T_1 to T_2 is the time period it takes for the cloud to pass by.

$$T_1 = \frac{x + 4\sigma xI}{U} \quad (34)$$

$$T_2 = \frac{x - 4\sigma xI}{U} \quad (35)$$

Combining Equations 23, 33, 34 and 35 gives:

$$E_1 = \frac{\sqrt{2\pi}\sigma xI\, J}{U} \times \frac{1}{60}, \text{ ppm min} \quad (36)$$

$$J = \frac{10^6 DQ_T\, e^{-\frac{y^2}{yI^2}}}{(2\pi)^{3/2}\sigma xI\sigma yI\sigma zI C_o} \left\{ e^{-\frac{(z-h)^2}{2\sigma zI^2}} + e^{-\frac{(z+h)^2}{2\sigma zI^2}} \right\} \text{ ppm} \quad (37)$$

J is the maximum concentration, ppm, experienced as the cloud passes by. The E_2 type exposure is given as:

$$E_2 = \int_{T_1^*}^{T_2^*} \frac{C}{C_o}\, dt \quad (38)$$

Where T_1^* to T_2^* is the time period for when the concentration is greater than the threshold, $\frac{C^*}{C_o}$.

$$E_2 = \frac{\sqrt{2\pi}\sigma x I\ J}{60U}\ \text{erf}\ \tau,\ \text{ppm min} \tag{39}$$

$$\text{Where:}\quad \tau = \sqrt{\ln \frac{J}{C^* C_o}} \tag{40}$$

The exposure in a building is obtained using an approximation. It is assumed that the cloud passes the intake vent in such a short period that during this time no active gas is discharged from the building. The amount of active gas taken in is:

$$Q_B = \int_{T_1}^{T_2} \frac{CF}{C_o}\ dt \tag{41}$$

The initial concentration in the building is:

$$\frac{C_{Bo}}{C_o} = \frac{Q_B}{V} \int_{T_1}^{T_2} \frac{C}{C_o}\ dt = \frac{\sqrt{2\pi} F\sigma x I J}{VU} \tag{42}$$

Where J is given by Equation 37. The concentration will then decline as follows:

$$\frac{C_B}{C_o} = \frac{C_{Bo}}{C}\ e^{-\frac{Ft}{V}} \tag{43}$$

The exposure above zero is given as:

$$E_1 = \frac{\sqrt{2\pi}\sigma x I J}{U} \left\{ 1 - e^{-\frac{FT}{V}} \times \frac{1}{60},\ \text{ppm min} \right\} \tag{44}$$

T_2 is the duration of residence in the building.

The amount of active gas taken in above the threshold concentration is:

$$Q_B = \int_{T_1^*}^{T_2^*} \frac{C}{C_o} F\ dt \tag{45}$$

The initial concentration is:

$$\frac{C_{Bo}}{C_o} = \frac{\sqrt{2\pi F_\sigma x I J}}{vU} \text{ erf } \tau \qquad (46)$$

Exposure inside the building continues until, T*, when the concentration falls below $\frac{C^*}{C_o}$.

$$T^* = -\frac{v}{F} \ln\left(\frac{C^*}{C_o} + \frac{C_{Bo}}{C_o}\right) \qquad (47)$$

The exposure E_2 is given as:

$$E_2 = \frac{\sqrt{2\pi\sigma x I J}}{U} \text{ erf } \tau \left\{1 - e^{-\frac{FT^*}{v}}\right\} \qquad (48)$$

Where $$\tau = \sqrt{\ln \frac{J}{C^* | C_o}} \qquad (49)$$

Appendix B

Frequency Rate Calculations

Probability of Occurrance, $\bar{P}_{occurance}$

Probability of occurance for each spill scenario was calculated using techniques described in the APCI Process Hazards Analysis Seminar notes. Failure rates were taken from industry sources and from operating experience at Piscataway. The rates used represent the concensus of the fault tree team.

Individual Probabilities, $\bar{P}$

The probability for each unique set of conditions (i.e., weather conditions, fan operation) was calculated by multiplying the probabilities for each condition.

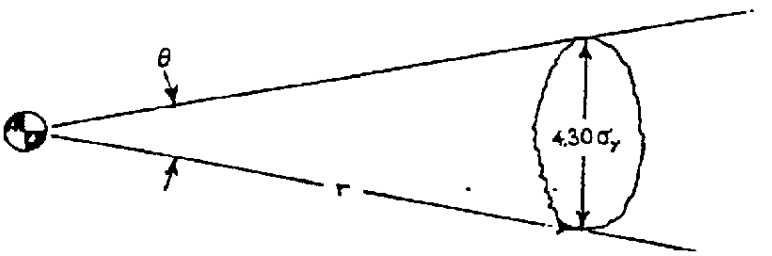
$$\bar{P} = (\bar{P}_{wind}) \ (\bar{P}_{weather}) \ (\bar{P}_{fan}) \ (\bar{P}_{occurance})$$

Frequency Rate, events/year

Because the probability of occurance was calculated based on a year's time and the $\bar{P}$'s are small, the frequency rate is approximately equal to $\bar{P}$/year.

Dispersion Angle of VCM Cloud,

Cloud width at radius r is $4.30\,\sigma_y\big|_r$



$$\theta = 2 \arcsin\left(\frac{2.15\,\sigma_y}{r}\right)$$

Probability of Wind being in Vent's Direction, $\overline{P}_{wind}$

The source is 32° NE at 38.1m

From National Weather Service Data, the fractional time the wind is 32° NE $\pm$ 45° is:

0.002336/degree of inclusion

therefore

$$\overline{P}_{wind} = 0.002336\,\theta = 0.004672 \arcsin\left(\frac{2.15\,\sigma_y}{r}\right)$$

Probability of Weather Stabilities, $\overline{P}_{weather}$

The weather conditions have been modeled by these six conditions:

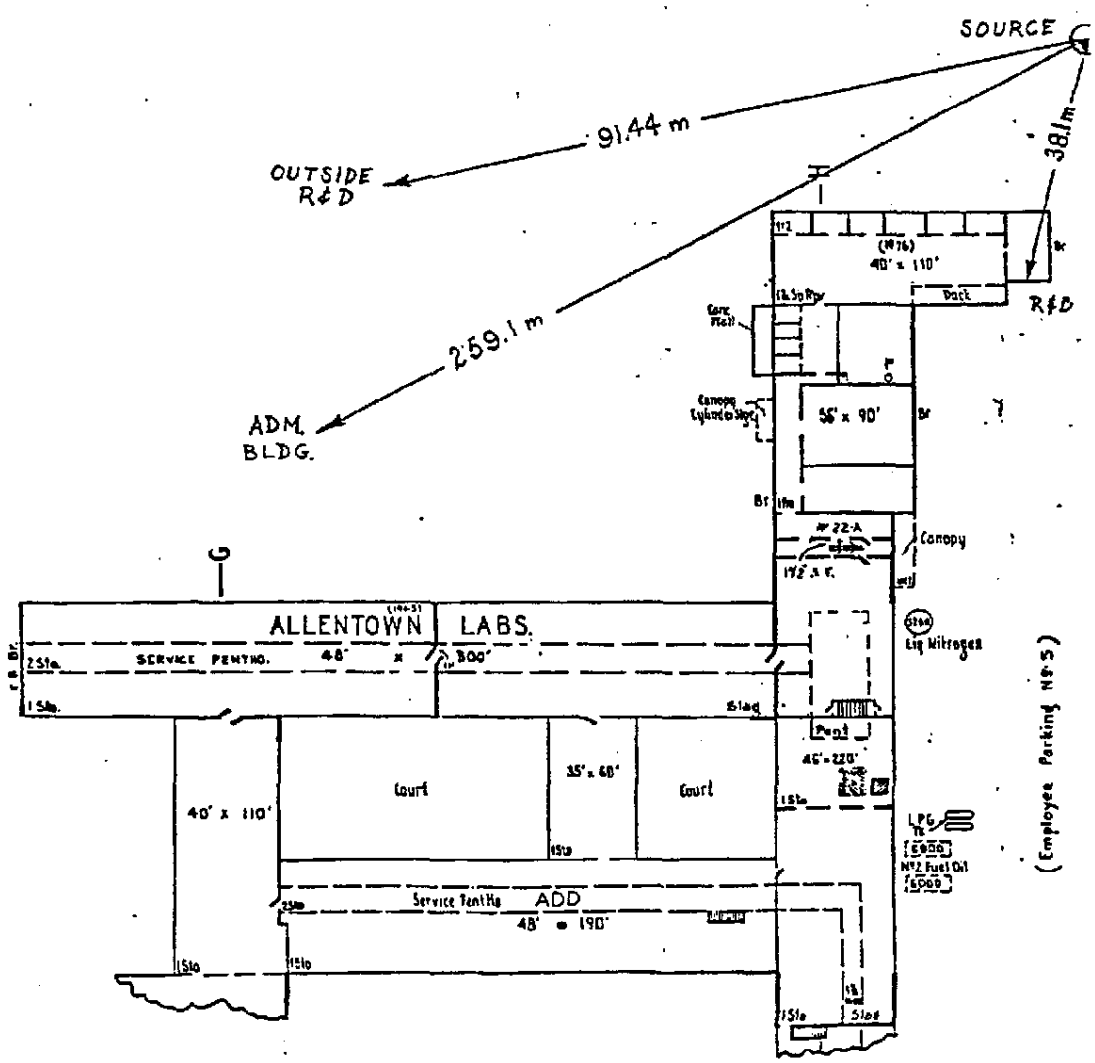
Stability Class	Wind Speed	$\overline{P}_{weather}$
F	1.544	0.03
D	1.544	0.06
B	1.544	0.01
F	3.4	0.27
D	3.3	0.54
B	3.9	0.09

Probability of Fan Speeds, $\overline{P}_{fan}$

The receptor has two air turnover rates. The lower rate occurs approximately 90% of the time while the high rate (100% turnover) occurs the remaining 10% of the time. These rates are independent of the emulsions development operations and are therefore considered to be random. Because different receptor fan rates had little effect on the longer releases, these probabilities were only considered for shorter releases.

When the hypothesized releases occur inside the process room, the room ventilation system was also taken into account. The process room's dual capacity fans should switch to high turnover if there is a spill. The probability of the system operating successfully is 98%.

SOURCE AND RECEPTOR LOCATIONS

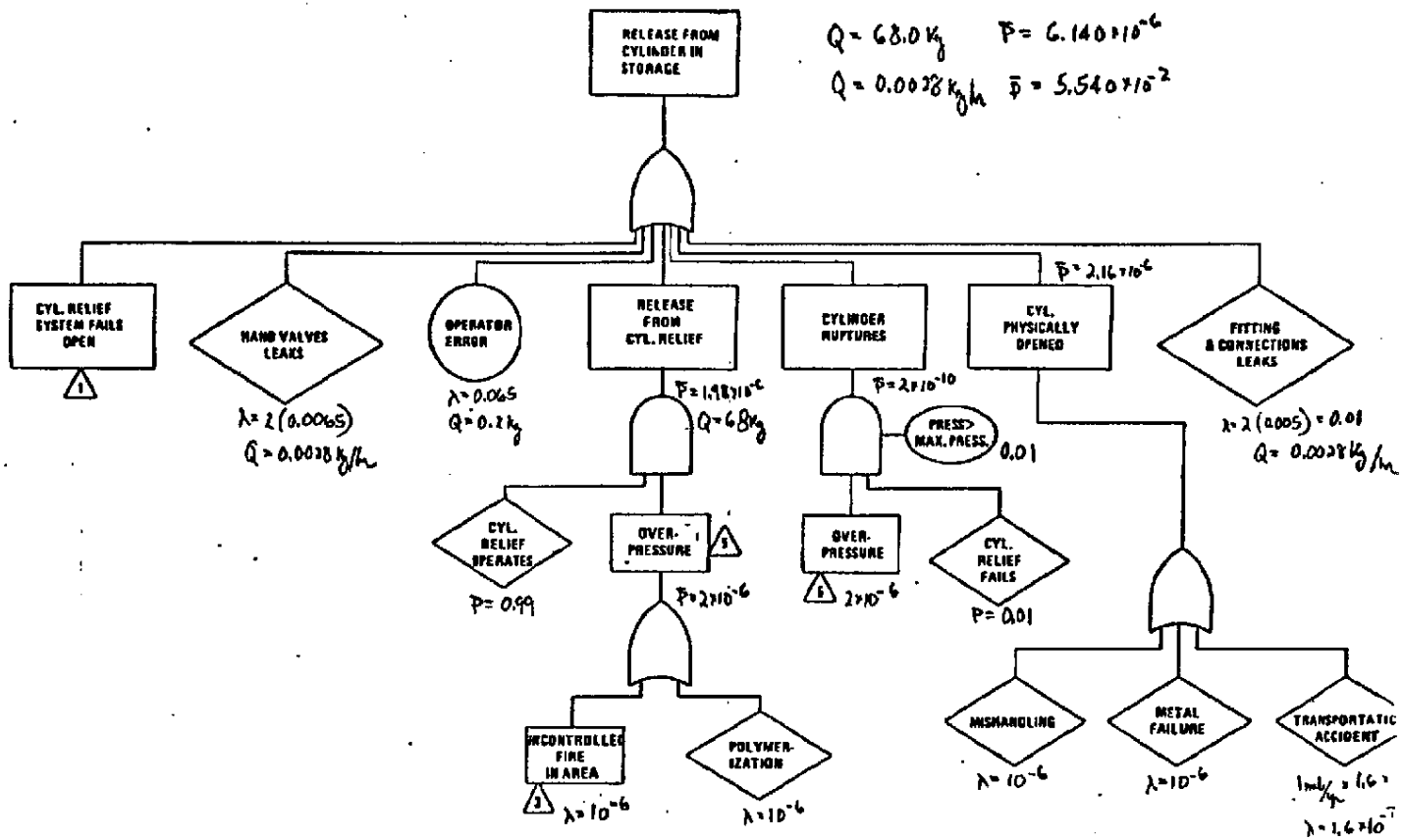


ELENCY RATES FOR CHA VIOLATION

	@ Outside R&D
[illegible]	4.835×10^{-9}
[illegible]	1.864×10^{-9}
[illegible]	1.097×10^{-8}
[illegible]	4.132×10^{-8}
[illegible]	1.633×10^{-8}
[illegible]	4.430×10^{-8}
[illegible]	2.062×10^{-7}
[illegible]	7.296×10^{-8}
[illegible]	3.987×10^{-7}
[illegible]	1.856×10^{-6}
[illegible]	6.567×10^{-7}
[illegible]	9.382×10^{-9}
[illegible]	3.498×10^{-9}
[illegible]	3.722×10^{-6}

Appendix C

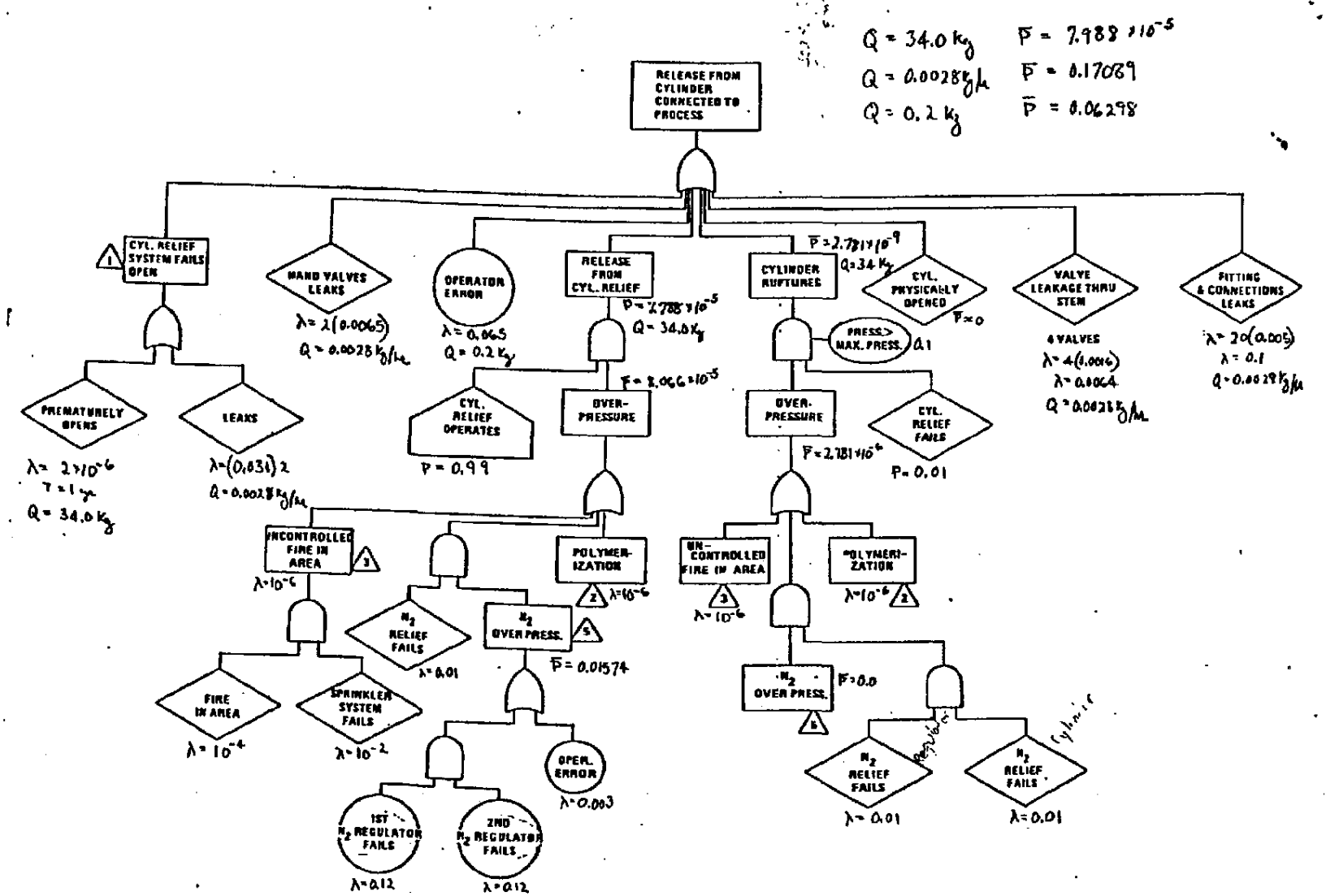
Fault Trees

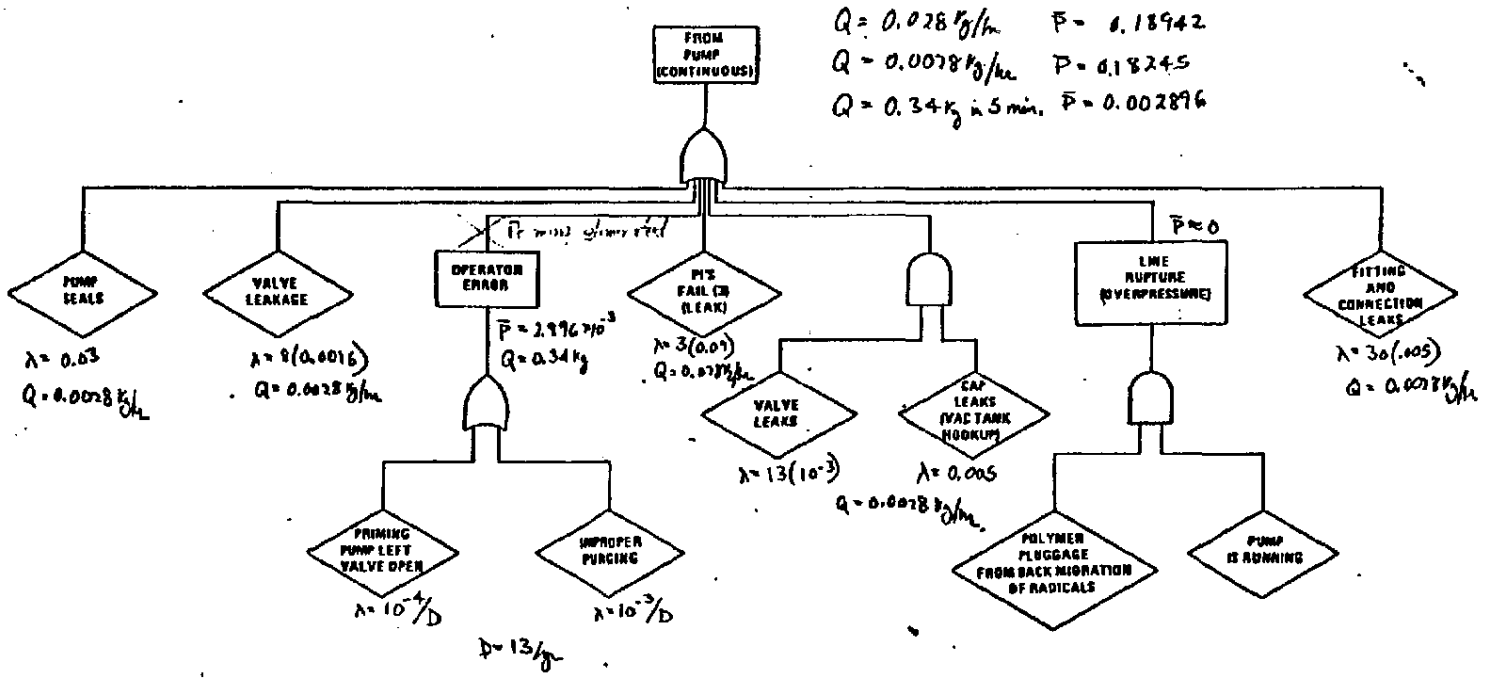


Q = Quantity Released

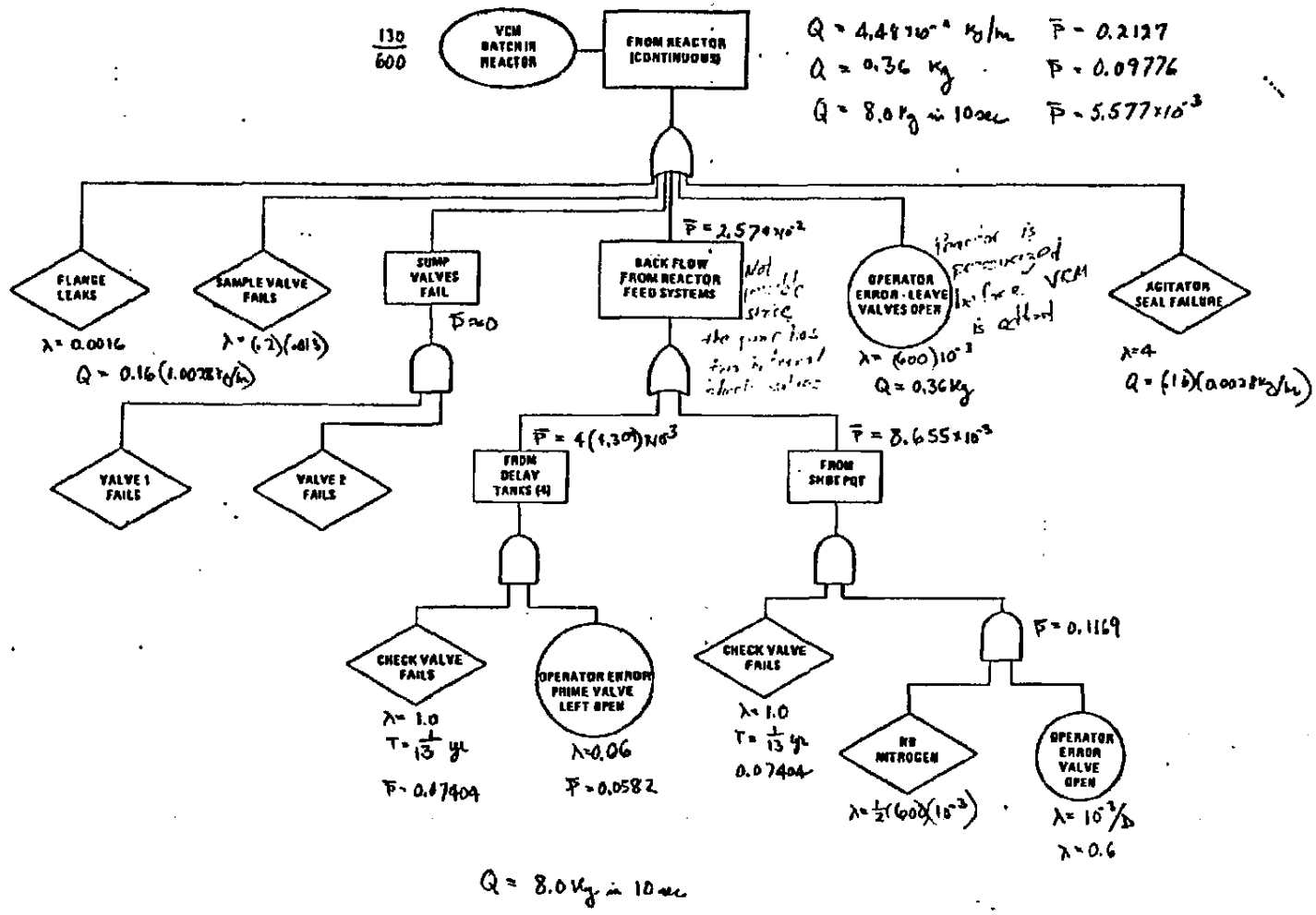
$\bar{p}$ = Probability

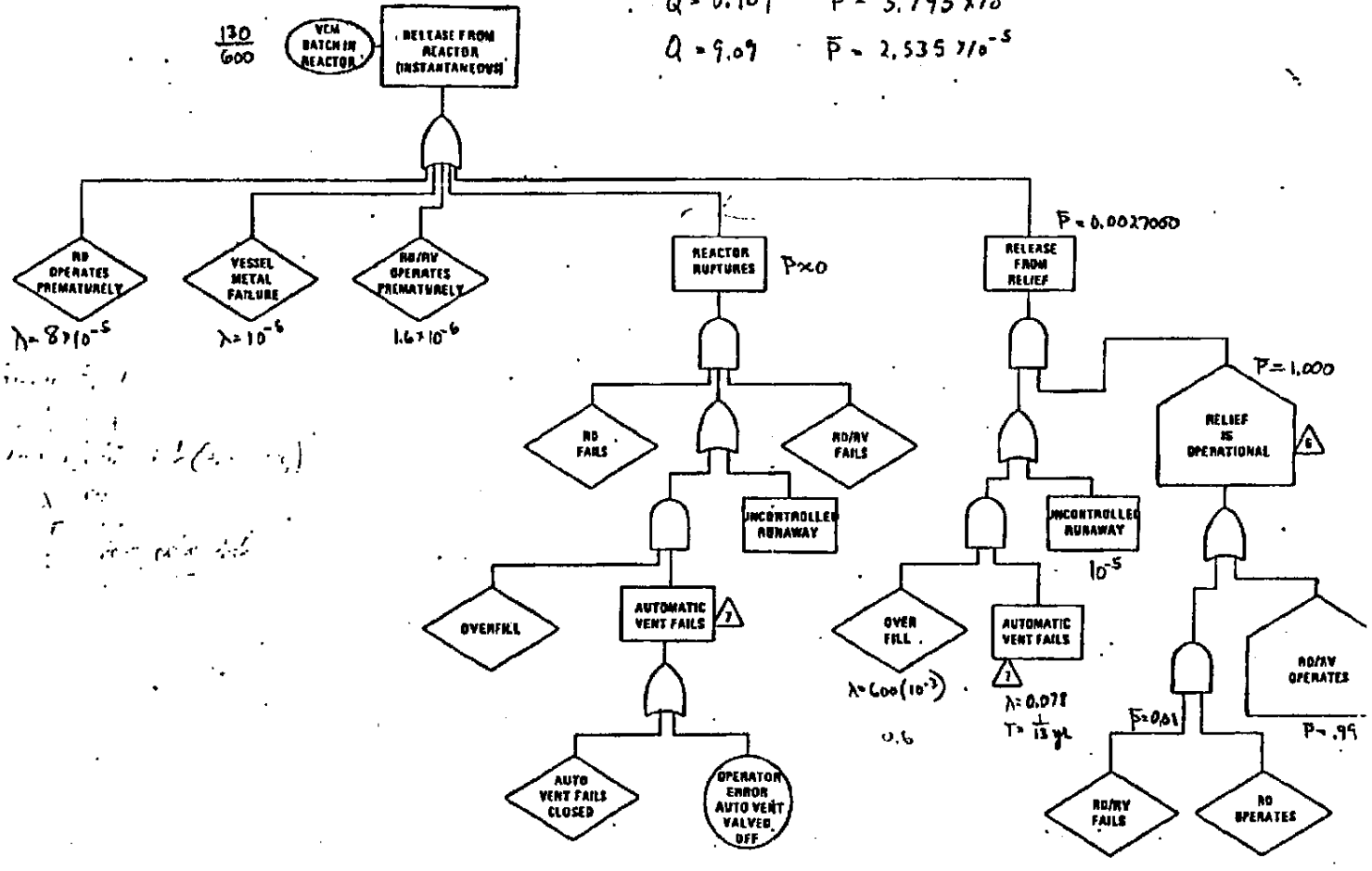
λ = Frequency Rate

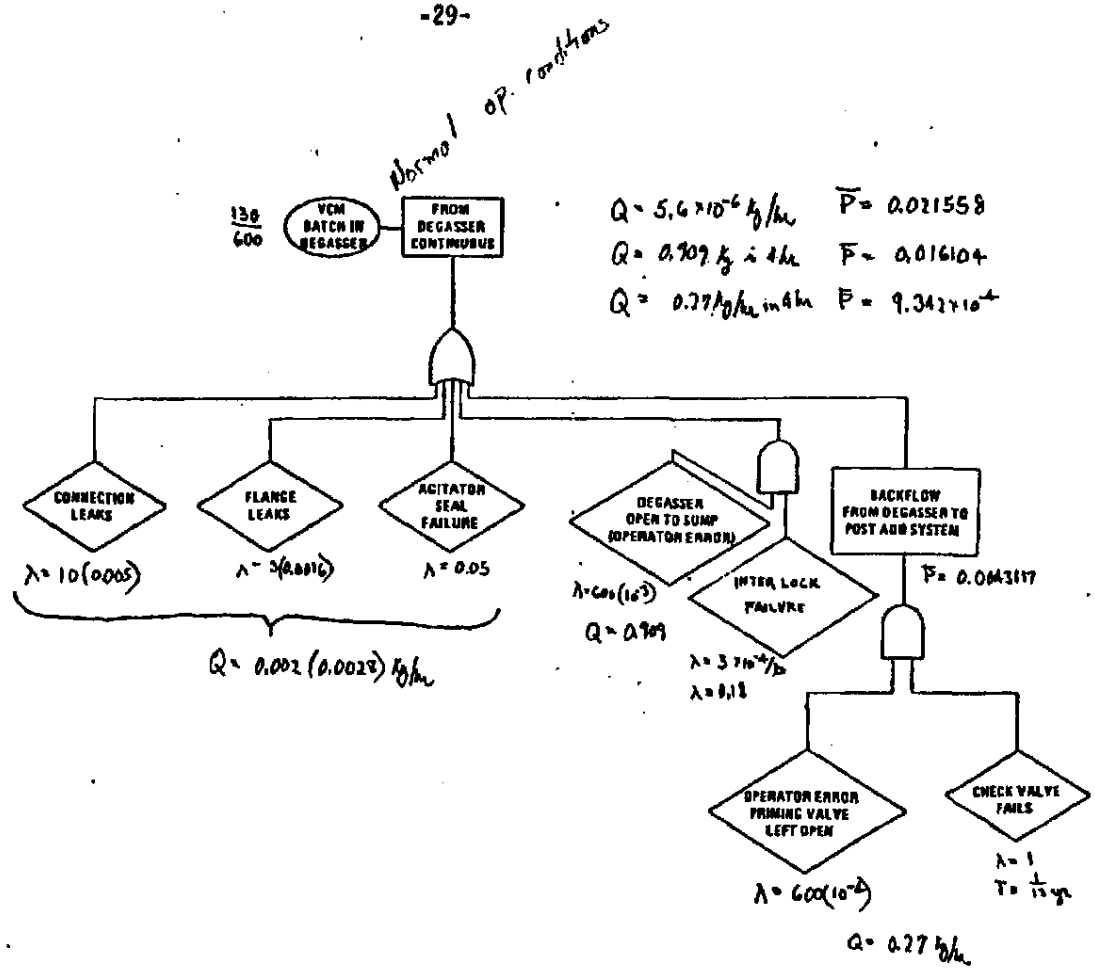

Q = 34.0 kg
Q = 0.0028 kg/hr
Q = 0.2 kg
P̄ = 7.988 x 10⁻⁵
P̄ = 0.17089
P̄ = 0.06298
RELEASE FROM CYLINDER CONNECTED TO PROCESS
CYL. RELIEF SYSTEM FAILS OPEN
PREMATURELY OPENS
λ = 2 x 10⁻⁶
T = 1 yr
Q = 34.0 kg
LEAKS
λ = (0.631) 2
Q = 0.0028 kg/hr
HAND VALVES LEAKS
λ = 2(0.0065)
Q = 0.0028 kg/hr
OPERATOR ERROR
λ = 0.065
Q = 0.2 kg
RELEASE FROM CYL. RELIEF
P̄ = 2.788 x 10⁻⁵
Q = 34.0 kg
CYL. RELIEF OPERATES
P = 0.99
OVER-PRESSURE
P̄ = 2.066 x 10⁻⁵
CYLINDER RUPTURES
P̄ = 2.781 x 10⁻⁹
Q = 34 kg
CYL. PHYSICALLY OPENED
P̄ = 0
PRESS > MAX. PRESS.
Δ1
OVER-PRESSURE
P̄ = 2.781 x 10⁻⁶
CYL. RELIEF FAILS
P = 0.01
VALVE LEAKAGE THRU STEM
4 VALVES
λ = 4(1.0016)
λ = 0.0064
Q = 0.0028 kg/hr
FITTING & CONNECTIONS LEAKS
λ = 20(0.005)
λ = 0.1
Q = 0.0028 kg/hr
UNCONTROLLED FIRE IN AREA
λ = 10⁻⁶
FIRE IN AREA
λ = 10⁻⁴
SPRINKLER SYSTEM FAILS
λ = 10⁻²
N2 RELIEF FAILS
λ = 0.01
N2 OVER PRESS.
P̄ = 0.01574
POLYMERIZATION
λ = 10⁻⁶
1ST N2 REGULATOR FAILS
λ = 0.12
2ND N2 REGULATOR FAILS
λ = 0.12
OPER. ERROR
λ = 0.003
UNCONTROLLED FIRE IN AREA
λ = 10⁻⁶
POLYMERIZATION
λ = 10⁻⁶
N2 OVER PRESS.
P̄ = 0.0
N2 RELIEF FAILS
λ = 0.01
N2 RELIEF FAILS
λ = 0.01

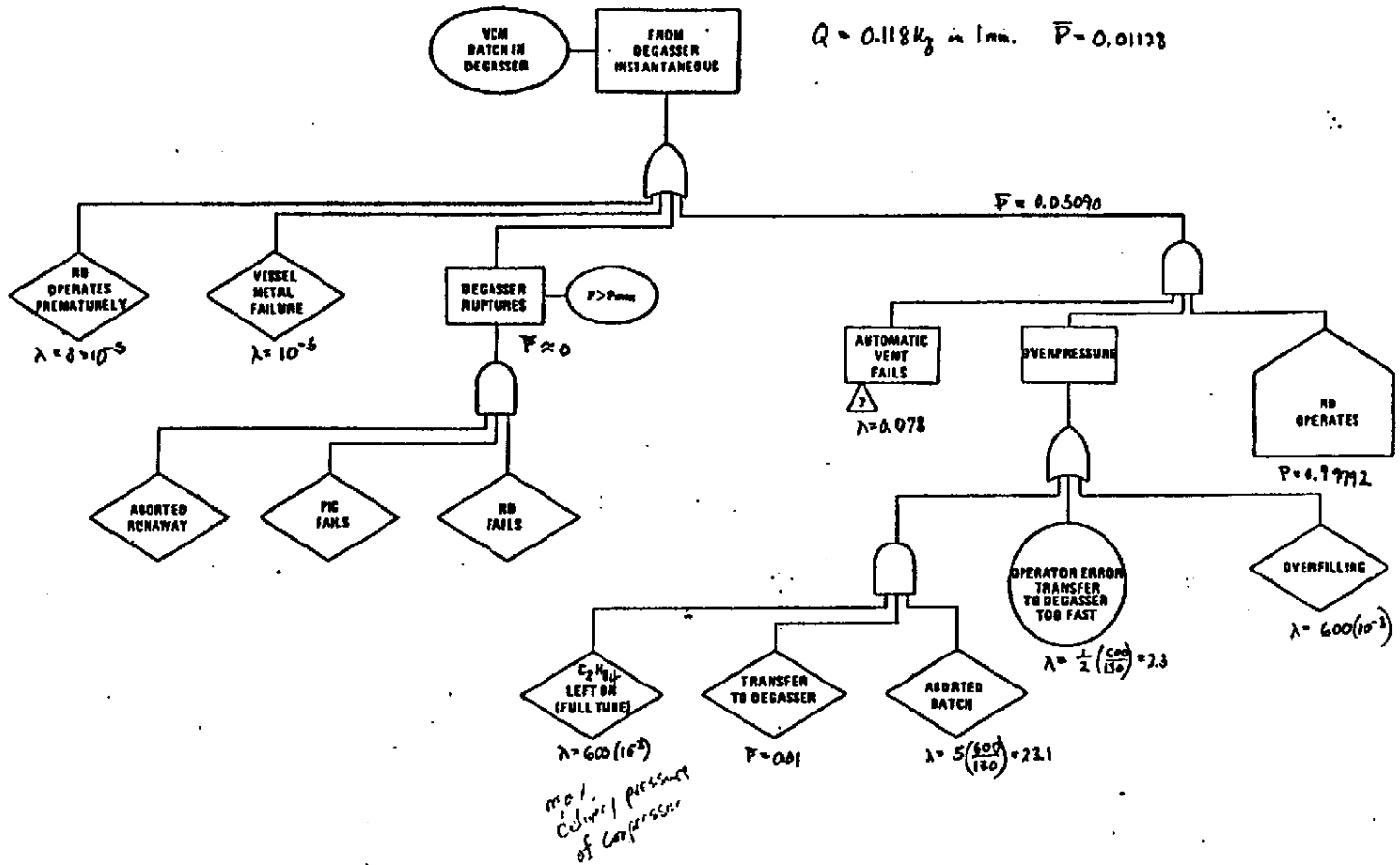


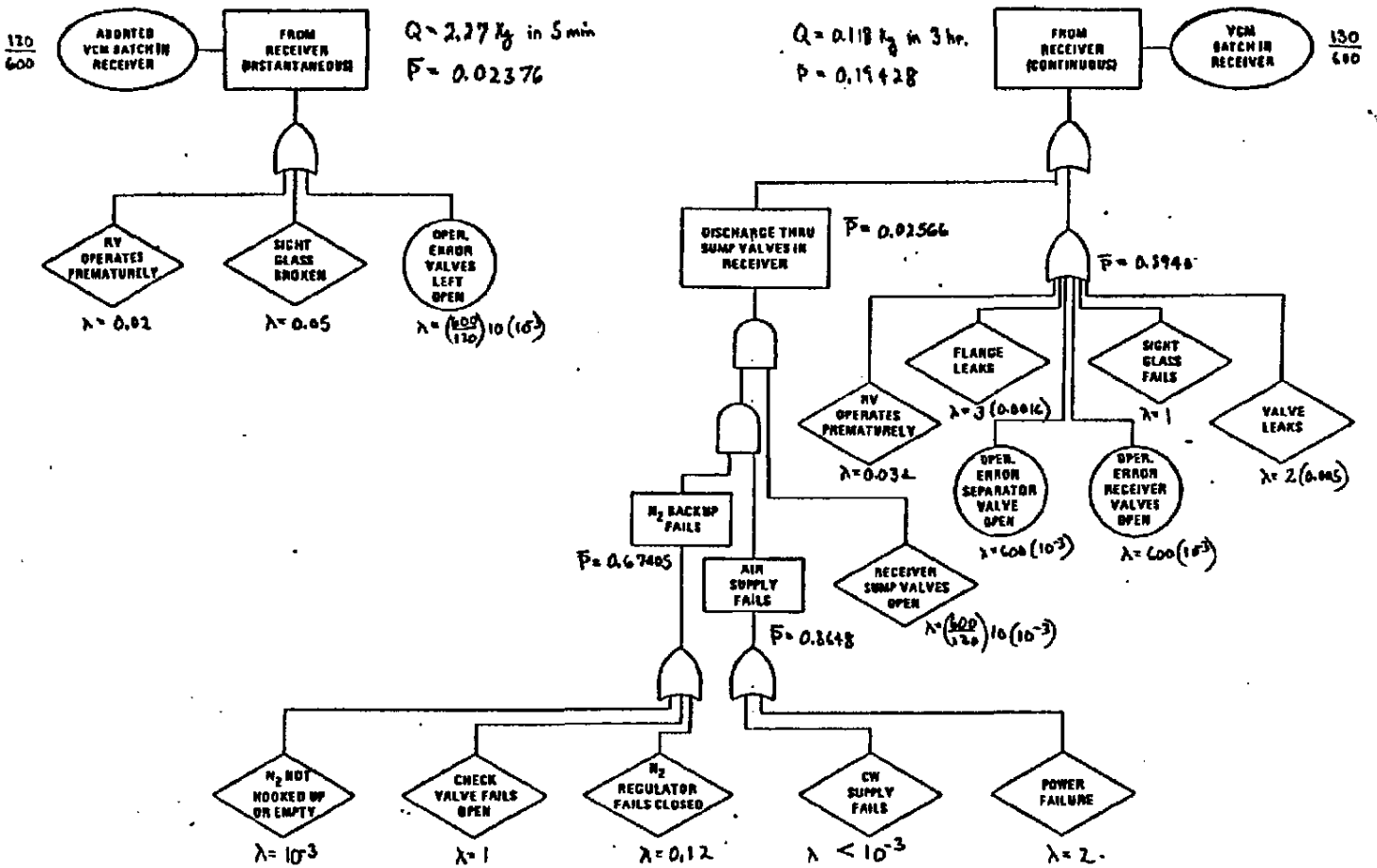
Priming 1 cylinder × 3 cylinders / batch , batches ...

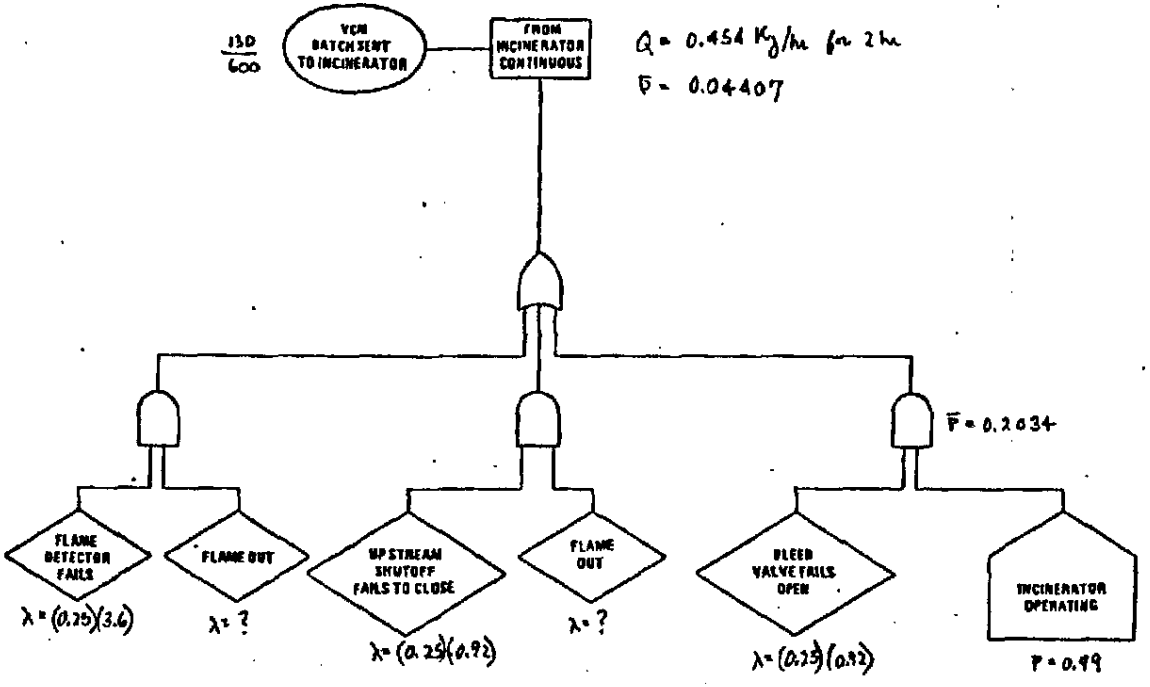

130/600
VCM BATCH IN REACTOR
FROM REACTOR (CONTINUOUS)
Q = 4.48 x 10⁻⁴ kg/hr
Q = 0.36 kg
Q = 8.0 kg in 10 sec
P̄ = 0.2127
P̄ = 0.09776
P̄ = 5.577 x 10⁻³
FLANGE LEAKS
λ = 0.0016
Q = 0.16 (1.0028 x 0/hr)
SAMPLE VALVE FAILS
λ = (.2)(.013)
SUMP VALVES FAIL
P̄ = 0
P̄ = 2.57 x 10⁻²
BACK FLOW FROM REACTOR FEED SYSTEMS
Not possible since the pump has two in series and check valves
OPERATOR ERROR - LEAVE VALVES OPEN
λ = (600)10⁻³
Q = 0.36 kg
Pressure is increased VCM in reactor is allowed
AGITATOR SEAL FAILURE
λ = 4
Q = (1.6)(0.0028 kg/hr)
VALVE 1 FAILS
VALVE 2 FAILS
P̄ = 4(1.30³)10⁻³
P̄ = 8.655 x 10⁻³
FROM DELAY TANKS (4)
FROM SHOT POT
CHECK VALVE FAILS
λ = 1.0
T = 1/13 yr
P̄ = 0.07404
OPERATOR ERROR PRIME VALVE LEFT OPEN
λ = 0.06
P̄ = 0.0582
CHECK VALVE FAILS
λ = 1.0
T = 1/13 yr
0.07404
P̄ = 0.1169
NO NITROGEN
λ = ½(600)(10⁻³)
OPERATOR ERROR VALVE OPEN
λ = 10⁻³/D
λ = 0.6
Q = 8.0 kg in 10 sec


130/600
VCM BATCH IN REACTOR
RELEASE FROM REACTOR (INSTANTANEOUS)
RD OPERATES PREMATURELY
λ = 8 x 10⁻⁵
VESSEL METAL FAILURE
λ = 10⁻⁶
RD/RV OPERATES PREMATURELY
1.6 x 10⁻⁶
REACTOR RUPTURES
P = 0
RD FAILS
RD/RV FAILS
UNCONTROLLED RUNAWAY
OVERFILL
AUTOMATIC VENT FAILS
7
AUTO VENT FAILS CLOSED
OPERATOR ERROR AUTO VENT VALVED OFF
Q = 0.909
P̄ = 5.795 x 10⁻⁴
Q = 9.09
P̄ = 2.535 x 10⁻⁵
P̄ = 0.0027050
RELEASE FROM RELIEF
P = 1.000
RELIEF IS OPERATIONAL
6
UNCONTROLLED RUNAWAY
10⁻⁵
OVER FILL
λ = 600 (10⁻³)
0.6
AUTOMATIC VENT FAILS
7
λ = 0.078
T = 1/13 yr
P = 0.81
RD/RV OPERATES
P = .99
RD/RV FAILS
RD OPERATES


Normal OP. conditions
138/600
VCM BATCH IN DEGASSER
FROM DEGASSER CONTINUOUS
Q = 5.6 x 10⁻⁶ kg/hr
P̄ = 0.021558
Q = 0.909 kg in 4 hr
P̄ = 0.016104
Q = 0.27 kg/hr in 4 hr
P̄ = 9.342 x 10⁻⁴
CONNECTION LEAKS
λ = 10(0.005)
FLANGE LEAKS
λ = 3(0.0016)
AGITATOR SEAL FAILURE
λ = 0.05
Q = 0.002 (0.0028) kg/hr
DEGASSER OPEN TO SUMP (OPERATOR ERROR)
λ = 6.0 (10⁻³)
Q = 0.909
INTER LOCK FAILURE
λ = 3 x 10⁻⁴/D
λ = 0.11
BACKFLOW FROM DEGASSER TO POST AGIT SYSTEM
P̄ = 0.0043117
OPERATOR ERROR PRIMING VALVE LEFT OPEN
λ = 6.0(10⁻⁴)
CHECK VALVE FAILS
λ = 1
T = 1/12 yr
Q = 0.27 kg/hr


VCM BATCH IN DEGASSER
FROM DEGASSER INSTANTANEOUS
Q = 0.118 kg in 1mn. P = 0.0112B
P = 0.05090
RD OPERATES PREMATURELY
λ = 8×10⁻⁵
VESSEL METAL FAILURE
λ = 10⁻⁶
DEGASSER RUPTURES
P>Pmax
P ≈ 0
AUTOMATIC VENT FAILS
?
λ = 0.078
OVERPRESSURE
RD OPERATES
P = 4.9 ppm
ABORTED RUNAWAY
PIC FAILS
RD FAILS
OPERATOR ERROR TRANSFER TO DEGASSER TOO FAST
λ = 1/2 (600/150) = 2.3
OVERFILLING
λ = 600(10⁻³)
C2H4 LEFT ON (FULL TUBE)
λ = 600(10⁻³)
TRANSFER TO DEGASSER
P = 081
ABORTED BATCH
λ = 5(600/150) = 22.1
mol. Column pressure of compressor


120/600
ABORTED VCM BATCH IN RECEIVER
FROM RECEIVER (INSTANTANEOUS)
Q = 2.27 kg in 5 min
P = 0.02376
RV OPERATES PREMATURELY
λ = 0.02
SIGHT GLASS BROKEN
λ = 0.05
OPER. ERROR VALVES LEFT OPEN
λ = (600/120) 10 (10⁻³)
Q = 0.118 kg in 3 hr.
P = 0.19428
FROM RECEIVER (CONTINUOUS)
VCM BATCH IN RECEIVER
130/600
DISCHARGE THRU SUMP VALVES IN RECEIVER
P = 0.02566
P = 0.3948
FLANGE LEAKS
λ = 3 (0.0016)
SIGHT GLASS FAILS
λ = 1
RV OPERATES PREMATURELY
λ = 0.034
VALVE LEAKS
λ = 2 (0.005)
OPER. ERROR SEPARATOR VALVE OPEN
λ = 600 (10⁻³)
OPER. ERROR RECEIVER VALVES OPEN
λ = 600 (10⁻³)
N₂ BACKUP FAILS
P = 0.67405
AIR SUPPLY FAILS
P = 0.3648
RECEIVER SUMP VALVES OPEN
λ = (600/120) 10 (10⁻³)
N₂ NOT HOOKED UP OR EMPTY
λ = 10⁻³
CHECK VALVE FAILS OPEN
λ = 1
N₂ REGULATOR FAILS CLOSED
λ = 0.12
CW SUPPLY FAILS
λ < 10⁻³
POWER FAILURE
λ = 2.


1.5D / 600
VCM BATCH SENT TO INCINERATOR
FROM INCINERATOR CONTINUOUS
Q = 0.454 Kg/h for 2 h
P = 0.04407
P = 0.2034
FLAME DETECTOR FAILS
λ = (0.25)(3.6)
FLAME OUT
λ = ?
UP STREAM SHUTOFF FAILS TO CLOSE
λ = (0.25)(0.92)
FLAME OUT
λ = ?
BLEED VALVE FAILS OPEN
λ = (0.25)(0.92)
INCINERATOR OPERATING
P = 0.99

Memorandum

AIR PRODUCTS

To:	M. R. CHMURA	Dept.:	CHEMICALS MANUFACTURING
From:	H. J. SMITH	Dept./Ext.:	CHEMICALS MANUFACTURING/8374
Date:	31 MARCH 1986		
Subject:			

SCOTT
VCM Pol

cc: H. L. Watson

The Safety and Health Work Practice Standard for Vinyl Chloride at Escambia has been fully approved. I will retain a copy in my files.

for H. J. SMITH

HJS:mcs
3864L

Attachment

RECEIVED
APR - 3 1986
H. L. WATSON

FORM 1520-17(84)

AP00022522

SAFETY AND HEALTH

WORK PRACTICE STANDARD

- Vinyl Chloride -

ESCAMBIA PLANT

REVISED 29 JANUARY 1986

SAFETY AND HEALTH WORK PRACTICE STANDARD

VINYL CHLORIDE

ESCAMBIA PLANT

REVISED 29 JANUARY 1986

Approvals:

Chemicals Group Manager of Safety	6 March 86 Date
Manager of Manufacturing Services	6 March 86 Date
Plant Manager - Escambia	2/14/86 Date
Production Manager - Escambia	2/13/86 Date
Safety, Health and Environmental Manager	2/12/86 Date

J. J. BALIKER
MANUFACTURING MANAGER

3/20/86
DATE

F. FISHER
GENERAL MANAGER - PLASTICS

3/14/86
DATE

R. E. GADOMSKI
VICE PRESIDENT AND GENERAL MANAGER
INDUSTRIAL CHEMICALS

3/19/86
DATE

R. C. SANDER
VICE PRESIDENT AND GENERAL MANAGER
MANUFACTURING

25 MAR 1986
DATE

NOTE: The purpose of this Standard is to promote safe conditions through the avoidance of exposure and prevent accidents affecting the safety and health of employees, visitors, and contractors through proper instruction and implementation of safe operating procedures, so as to protect the well being of individuals and minimize product or property losses. It addresses the safety and industrial hygiene concerns involved with the handling of vinyl chloride monomer. As the need for new procedures is recognized, it is intended that they will be developed and added to this standard.