

Memorandum

AIR
PRODUCTS 

To:	D. F. Baker	Dept.:	Executive
From:	A. J. Diglio	Dept./Ext.:	Corporate Environmental/8339
Date:	7 April 1986		
Subject:	Air Products' Air Toxics Control Program and Community Awareness		

Dex:

This is in reply to your request on where do we stand plant-by-plant in communicating with local communities regarding our toxic emissions.

Community Awareness

For accidental releases, plant communities are or will be informed through our Community Awareness and Emergency Response Program (CAER) as appropriate. We also propose to use our CAER program to inform the public concerning our toxic process emissions (continuous releases). Each plant is preparing a status summary, as you requested, on CAER communications.

CMA companies have expressed a concern of potential downside risks associated with improper communications of air toxic information to plant communities. For this reason, CMA plans workshops on effective community communications concerning air toxics. Contingent on the CMA workshops, modification to our program would be proposed.

Air Products' Air Toxics Control Program

According to your request, we have developed a proposed Air Products' Air Toxics Control Program that determines specific toxic emissions, risks and remedies on a stack-by-stack, source-by-source, plant-by-plant basis. The program provides, if need be, for the determination of capital and operating costs for reducing high potential risk process emissions and accidental releases. The program entails:

- Assessing the risks to our employees and the public from our materials if accidentally or continuously released.
- Reducing exposure risks where appropriate.
- Communicating with the appropriate public groups concerning our hazardous emissions.

As appropriate, communications to the public will be a continuous process as the information emerges from our program.

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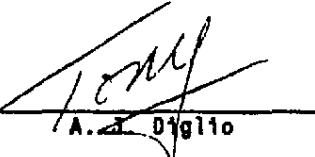
TO: D. F. Baker
FROM: A. J. Diglio

Page 2
7 April 1986

Since your request, we have published a proposed Air Products' Air Toxics Control Program and its implementation. It is in our consensus review and refinement process before its final planned publication in May and presentation to you.

As you know, Air Products has implemented the accidental release portion of the program, and since 1970 has protected the community from process emissions by complying to EPA's increasingly stringent air pollution control regulations.

Please let me know if you wish anything else.



A. J. Diglio

AJD:pbr
0731c

Attachment: Note from D. F. Baker

AP00036705

Dexter F. Baker
President
(215) 481-7531

AIR
PRODUCTS 

6 March 1986

TO: A. J. Diglio

Tony:

Where do we stand, plant by plant, in communicating
with the local communities regarding our toxic
emissions?

DFB

peb
att. - Copy of CMA Air Toxics Control Policy Work
Plan.

AP00036706

Memorandum

AIR 
PRODUCTS

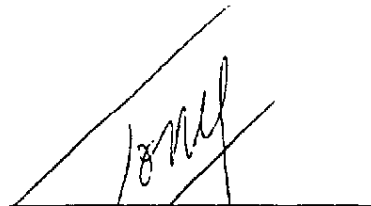
To: Distribution
From: A. J. Diglio
Date: 11 June 1986
Subject:
Dept.:
Dept./Ext.: Corporate Environmental/8339

Distribution:

J. J. Baliker
M. R. Chmura
T. J. Regan
R. C. Sander
J. K. Spata
H. L. Watson

cc: P. L. T. Brian
D. C. Keehn
G. K. Lee
R. E. Linney
J. M. Norwood
R. W. Ormsby

Please find attached, for your information, a fault tree analysis of Calvert City reactor emergency vinyl chloride releases up to 1981. Table I summarizes the frequency and cause of the emergency releases analyzed, and recommendations to abate the frequency of emergency releases are provided on pages 4, 5, and 6 of the report.


A. J. Diglio

AJD:pbr
0941c

Attachment: Memo from A. J. Diglio dated 21 January 1981,
Analysis of Reactor Emergency Vinyl Chloride Releases -
Calvert City

AP00036707

Air Products

Date 21 January 1981

INTEROFFICE
MEMORANDUM

Subject Analysis of Reactor Emergency Vinyl
Chloride Releases - Calvert City

To Distribution

From A. J. Diglio

(Location, Organization, or Department)

Trexlerstown

(Location, Organization, or Department)

Distribution

J. J. Baliker
A. F. Cantor
R. C. Lietzau
R. J. Lomicky

For your information and action is the Task Group Report showing the "Fault Tree" Analysis of various scenarios leading to reactor emergency vinyl chloride releases. Recommendations were developed that show areas where further emphasis may reduce the frequency of reactor emergency releases of those considered by a calculated value of 2.26 yr^{-1} .

These recommendations are in the process of being implemented by Calvert City with the assistance of Corporate Engineering. Corporate Engineering is exploring the use of acoustic emission detection instrumentation for anticipatory replacement of rupture disks.

A. J. Diglio

AJD/gy

Attachments

cc: P. F. Aquila
P. L. T. Brian
T. L. Carey
W. E. Crawford
L. C. Doelp
A. E. Greene
B. D. Helms
R. E. Linney
J. H. McMakin
A. K. McMillan

E. A. Primeau
F. J. Ryan
R. C. Sander
R. H. Schenck
J. R. Schneider
M. J. Scigliano
W. Silowka
L. C. Toney
C. M. Tronolone
H. L. Watson

(770)

AP00036708

SUMMARY

Task Group analyzed the previous emergency vinyl chloride releases from the Calvert City reactors. The purpose of this analysis is to find means to reduce the frequency of the reactor relief system emergency vinyl chloride releases.

A "Fault Tree" methodology was used to generate scenarios that can lead to reactor emergency releases.

Table I summarizes the calculated frequency of emergency releases per year by the causes listed.

TABLE I
CAUSE AND FREQUENCY OF RELEASE

<u>Cause</u>	<u>Frequency yr⁻¹</u>
1. Premature failure of rupture disk (catastrophic)	1.27
2. Critical vapor (inert) heel	0.84
3. Agitator failure	0.44
4. Seal flush overfill	0.42
5. Runaway (high temperature/pressure)	0.098
6. Runaway (high viscosity)	0.077
7. Critical inleakage during reaction	0.077
8. Reactor overfill (overcharge)	0.053
9. Power failure	0.050
10. Computer Error	0.025
11. External uncontrolled fire	0.0001
Total	3.35

The accuracy of the calculated frequency values shown above may vary as much as an order of magnitude.

Recommendations were developed that show areas where further emphasis may reduce the frequency of reactor emergencies of those considered by a calculated value of 2.26 yr⁻¹.

AP00036709

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AP00036710

Introduction

The purpose of this analysis is to evaluate and recommend means to reduce the frequency of emergency vinyl chloride releases from the reactor relief systems at Calvert City. The reactors were chosen as the first system to be analyzed because they were identified as having a higher release frequency than other systems in the plant.

The task group was comprised of the following members:

- A. J. Diglio, Director of Environmental Activities, Chemical Group
- R. E. Linney, Risk Analyst, Corporate Engineering
- E. A. Primeau, PVC Plant Superintendent, Calvert City Operations
- R. H. Schenck, Attorney, Corporate Law
- J. R. Schmieder, Safety Engineer, Corporate Safety
- W. Silowka, Process Manager Polymer Chemicals, Engineering-Chemicals
- C. M. Tronolone, Principal Process Engineer, Engineering-Chemicals
- E. D. Zarytkiewicz, Environmental Coordinator, Manufacturing-Chemicals

Scope and Methodology

The analysis was limited to emergency releases from the polyvinyl chloride reactors relief systems at Calvert City. Other interacting systems were considered only to the degree that they affect reactor releases.

"Fault Tree" methodology was used to systematically generate scenarios of release. Team members were chosen from project, process, plant and safety engineerings in order to have the needed diversity of knowledge and experience. Fault trees were derived in group sessions so they would reflect all points of view.

AP00036711

The quantification techniques used standard relationships for probabilities, reliabilities and availabilities to generate event frequencies. That is, component reliability at time t is,

$$R = e^{-\lambda t}$$

Where λ = component failure rate and steady state availability is,

$$A = 1 - \frac{\lambda}{r}$$

Where r = component repair rate.

All times were expressed in years and all rates or frequencies were in years⁻¹. Demand rates were based on a total capacity of 3800 batches per year for both the homopolymer and copolymer trains (two reactors per train).

Analysis

The undesired event was defined as "Reactor Overpressure" because it will lead directly to a release. This main event was divided into three subevents. The first, "Power Failure", would result in loss of automatic control and agitation, making a release most probable. The second two are "Hydrostatic Overpressure" and "Vapor Phase Overpressure" which are caused by a series of subevents. Identification of these subevents comprised the majority of the analysis. Their interactions are illustrated in the fault trees found in Appendix I. Emergency release statistics are given in Appendix II and a general description of the symbols used in the fault tree analysis is given in Appendix III.

Results

The table below gives the calculated frequency of emergency releases by cause.

The above frequencies include operator error when a task is required by operating procedures. Also included in the fault tree analysis, but not specifically quantified as a major cause is a category of "General Operator Error". This subevent is intended to account for other incidents created by errors made in performing normal tasks. An example would be when an operator inadvertently closes a wrong valve which initiates a cascading series of errors leading to a release. This shortfall illustrates one of the reasons why this type of quantification is not an exact science. Reporting frequencies to three significant figures perhaps gives undue credence to its accuracy. A frequency such as 3.35 yr^{-1} is at best a calculated average with a large variance. The actual frequency may vary as much as an order of magnitude. Therefore, Calvert City PVC Plant history (post startup) of 5 reactor releases per year is consistent with this analysis.

These recommendations are now being implemented in Manufacturing with the exception of recommendation (1.C). Recommendation (1C) requires instituting a Research Program to explore the use of acoustic emission detection for anticipatory replacement of rupture disks.

of magnitude. Therefore, Calvert City PVC Plant history (post startup) of 5 reactor releases per year is consistent with this analysis.

The utility of quantification in this study is not to predict an absolute frequency but rather to calculate relative frequencies by cause. The results of the study are best used to determine where emphasis for improvement or further study should be placed.

Recommendations

The following are recommendations to abate emergency releases. Note that the same serialization as for the tabulated results is used.

1. Premature Failure of Rupture Disk

- a) Replace rupture disk on a preventive schedule of no greater than 600 batches.
- b) Commission a special team of safety relief device repairmen. These people would receive more extensive training in proper installation and maintenance of both rupture disks and relief valves. They would be the only people permitted to work on such devices.
- c) Consider instituting a research program to explore the use of acoustic emission detection for anticipatory replacement of rupture disks on an as needed basis. This technique has not been proven in this service, but may have the potential for achieving lower emissions frequencies more economically than a).

2. Critical Vapor (Inert) Heel

The major cause of a critical vapor heel is the pressure indicating control (PIC) failing high on the copolymer reactors. This PIC tells the computer that the evacuation pressure is low enough and that charging may begin. If the actual pressure is higher than the PIC indicates, then the reactor will overpressure when heated due to residual inerts not evacuated.

- a) It is recommended another pressure indicating device be installed. Reprogram the computer to compare signals from the two separate pressure indicating devices on the reactors. If the signals vary by more than a predetermined amount, the computer would cease the reactor sequence and inform the operators of the discrepancy. This technique gives immediate indication of instrument failure and would virtually eliminate this as a cause of release. The burden would then be on the operators to determine the cause of failure and to repair the fault before charging.
- b) Reprogram the computer so a minimum reactor evacuation time is embedded in the procedures. The length of time should be determined using the operating capacity of the evacuation equipment plus an additional margin for safety.

3. Agitator Failure

Expansion of the existing maintenance program is warranted by the criticality of the agitator. While the task group recognizes the criticality, we do not possess the needed expertise to prescribe a detailed program. It is recommended that a task group of maintenance and machinery experts be formed to develop the most effective means of improving agitator reliability. Technicians

that should be considered include scheduled replacement of wear parts (bearings, gears, etc.) and monitoring indicators of impending failure (oil analysis, vibration/displacement probes, non-destructive material tests, etc.). Emphasis should be placed on parts that would cause catastrophic failures. It is further suggested that quantification be incorporated in the analysis and that a final report be issued to management.

4. Seal Flush Overfill

The postulated release scenario is that both reactors are full and a failure of downstream equipment occurs. If the equipment repair time exceed the critical three day limit for seal flush influx, the reactor would hydrostatically overfill.

To avert this type of release, the following procedures should be adopted.

- a) Discontinue charge sequence if any necessary equipment downstream of the reactors is out of service.
- b) If the reaction is in progress and downstream equipment fails, pinch seal flush to minimum flow.
- c) If failed equipment cannot be repaired before the critical three day limit, strip reactants of monomer in reactor and dump to an appropriate location.
- d) If hydrostat is imminent, shut off seal flush flow and risk plugging seal cavity.

Impact of Recommendations

1. Premature Rupture Disk Failure

Assuming that premature failures are normally distributed with a mean of 1000 cycles and a variance of 200 (manufacturing and installation), the probability of failure before replacement is

$$P = 0.02$$

for a replacement schedule of 600 cycles. This probability multiplied by the required 6.3 replacements per year yields an event frequency of,

$$F = 0.02 (6.3) = 0.127 \text{ yr}^{-1}$$

which is an order of magnitude improvement. If the disks were replaced during the opportune plant turnaround (~ 475 batches), the probability of failure before replacement would be,

$$P = 0.005$$

This would require 8 replacements per year, yielding an event frequency of

$$F = 0.005 (8) = 0.040 \text{ yr}^{-1}$$

2. Critical Vapor (Inert) Heel

Because probability of both the PIC and the PT simultaneously drifting into the same direction is much smaller than other factors (e.g. computer failure), the changes should virtually eliminate this as a cause of release.

3. Agitator Failure

The effectiveness of improving on a preventive maintenance program is difficult to assess. In consulting with machinery and maintenance experts, it was suggested that a 50% decrease in catastrophic failures would not be overly optimistic. If this were the case, the release frequency would be reduced to 0.22 yr^{-1} .

4. Seal Flush Overfill

If the postulated scenario occurs and the procedures are followed, there should be no release of monomer. The problem is that all situations are unique. Human interpretations and judgements would continue to play an important role. Inherent to these human factors are the probabilities of the error. The level of these errors would be approximately 10%, leaving a residual frequency of,

$$F = 0.1 (0.42) = 0.042 \text{ yr}^{-1}$$

Conclusions

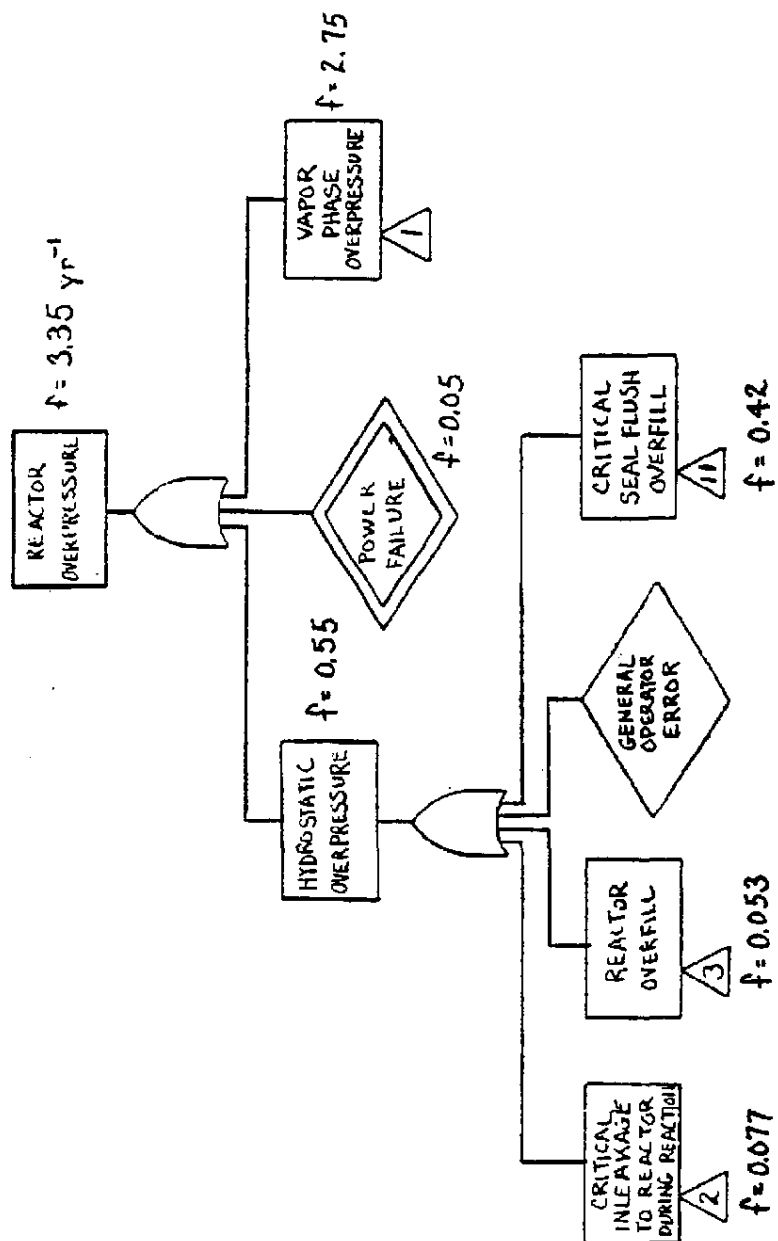
1. The analysis indicates that Calvert City should have experienced between 3 and 4 emergency reactor releases per year as calculated by the fault tree methodology. During fiscal 1980, the plant had 5 such releases which is consistent with the accuracy of this technique.
2. If all reported recommendations are implemented, the analysis predicts that approximately 2.6 releases per year could be prevented.

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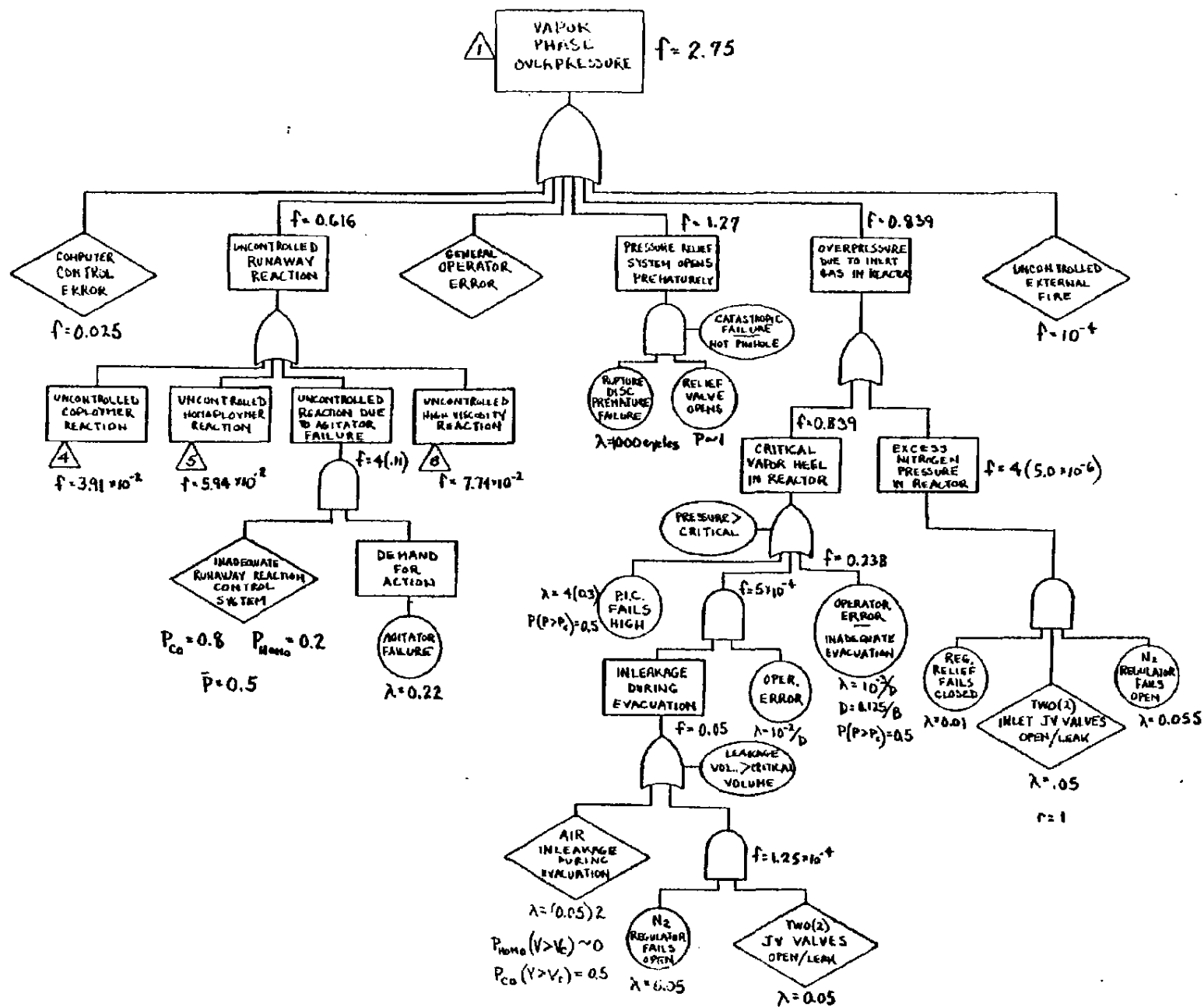
Appendix I

Fault Trees

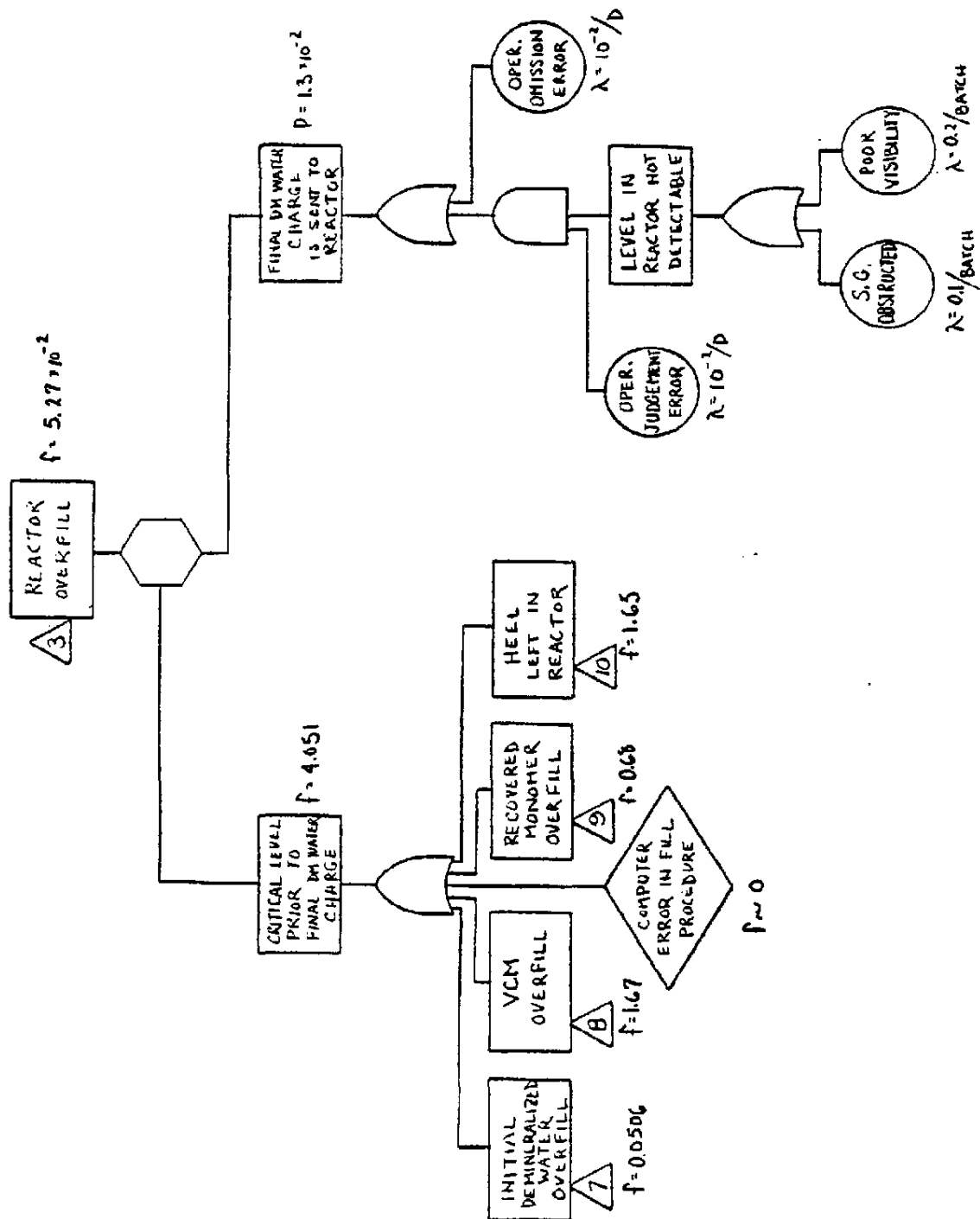
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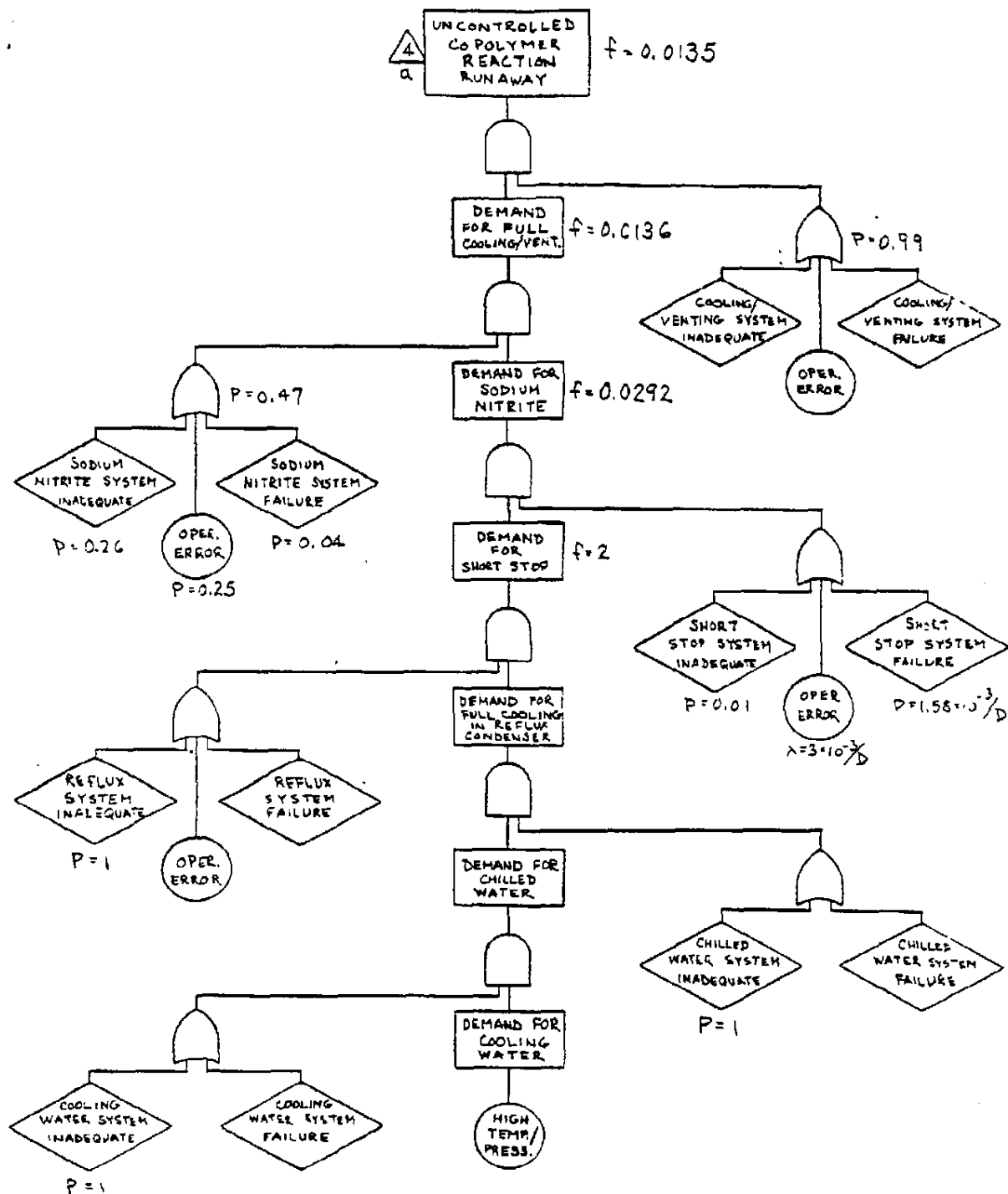
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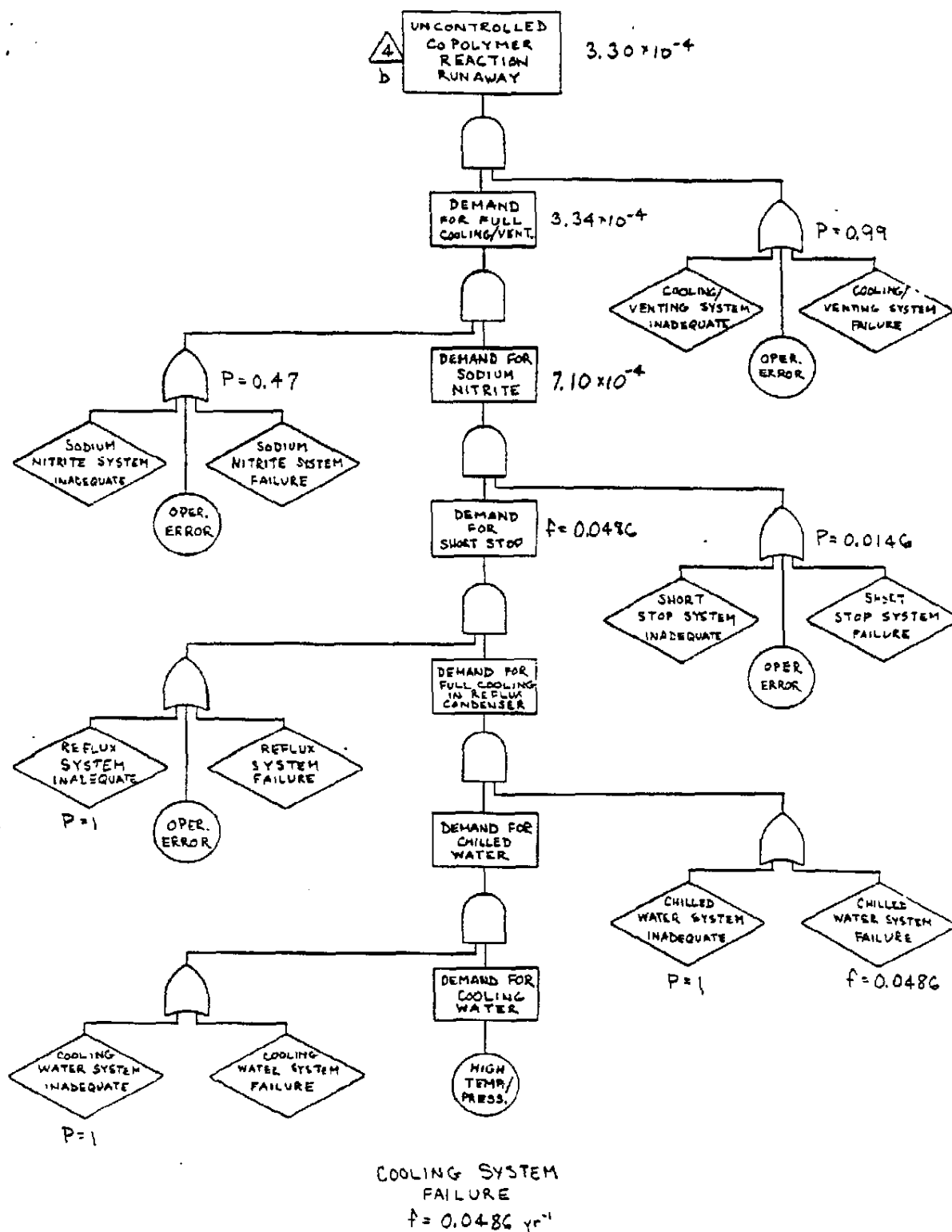


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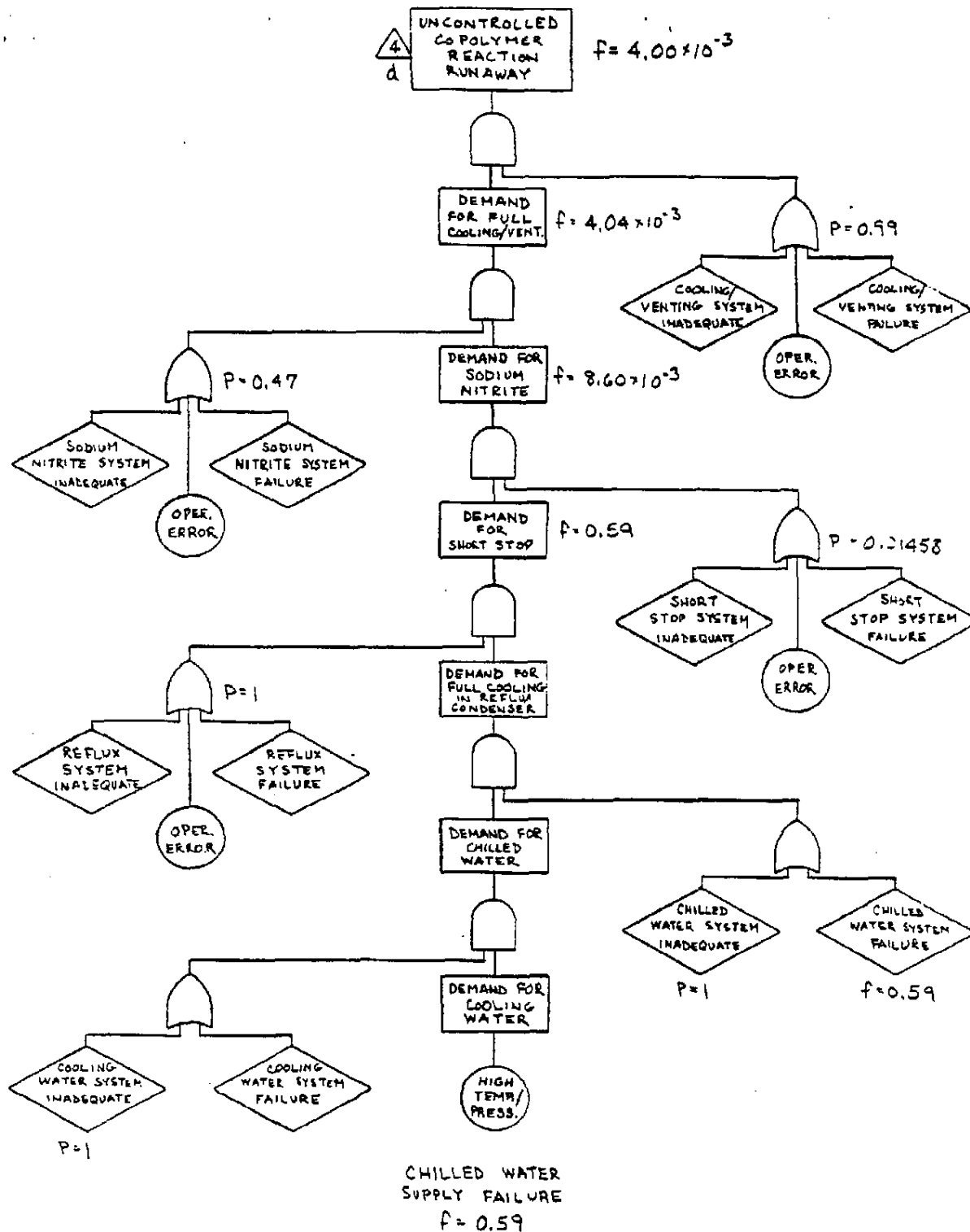
JACKET CIRCULATION
PUMP FAILURE
 $\lambda = 1 \text{ yr}^{-1}$
 $f = 2(1) = 2 \text{ DEMANDS/yr}$

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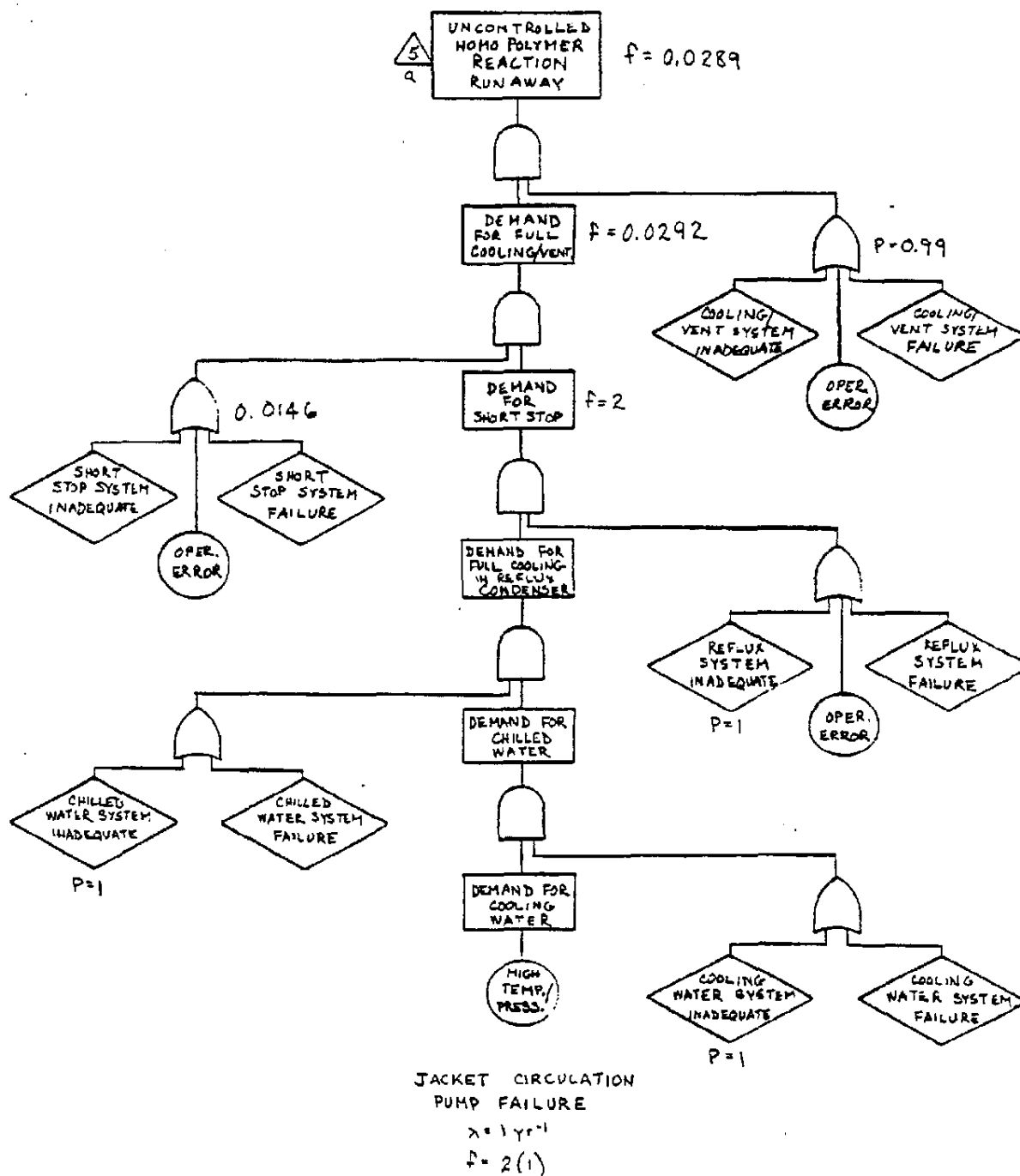


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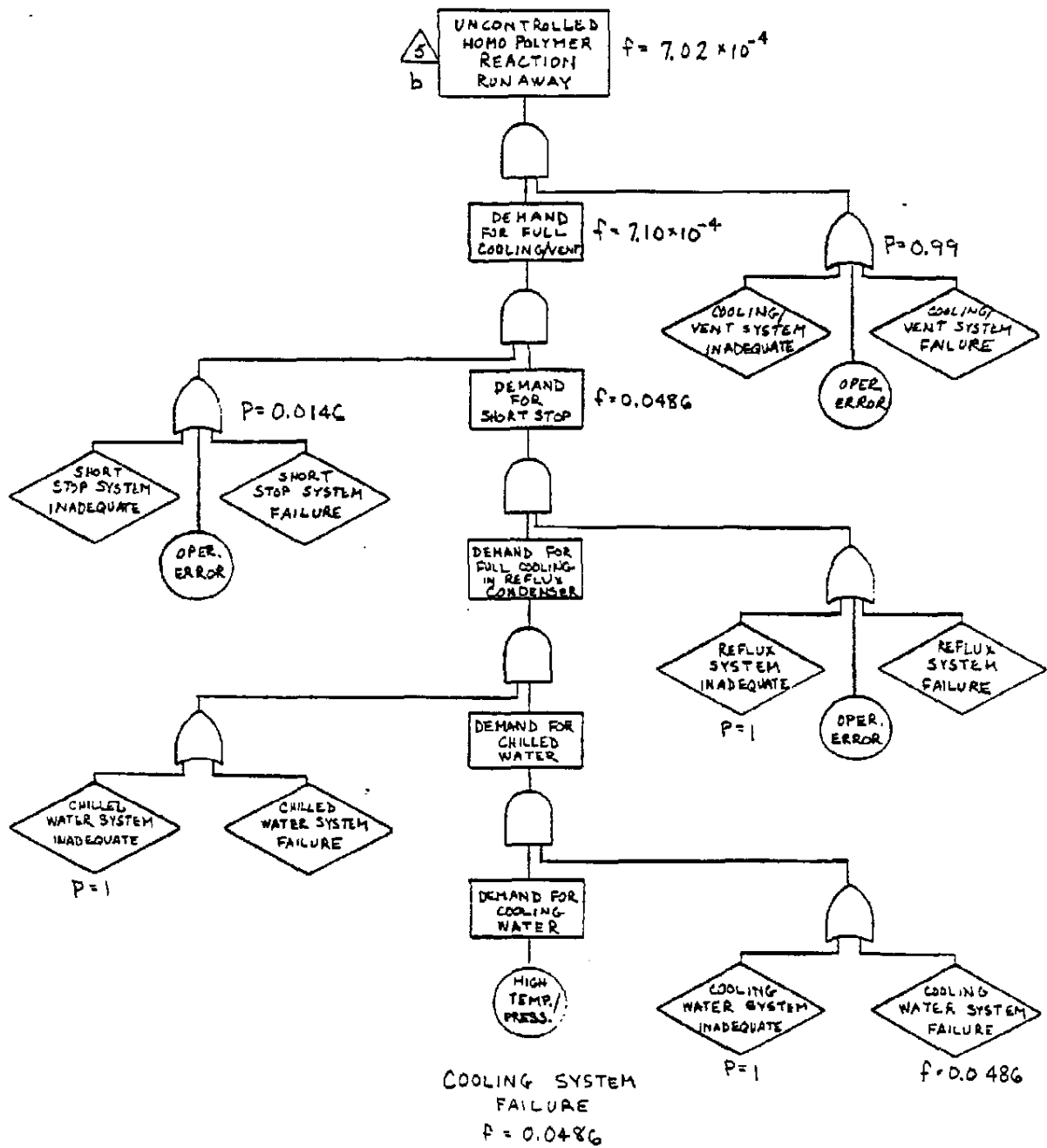




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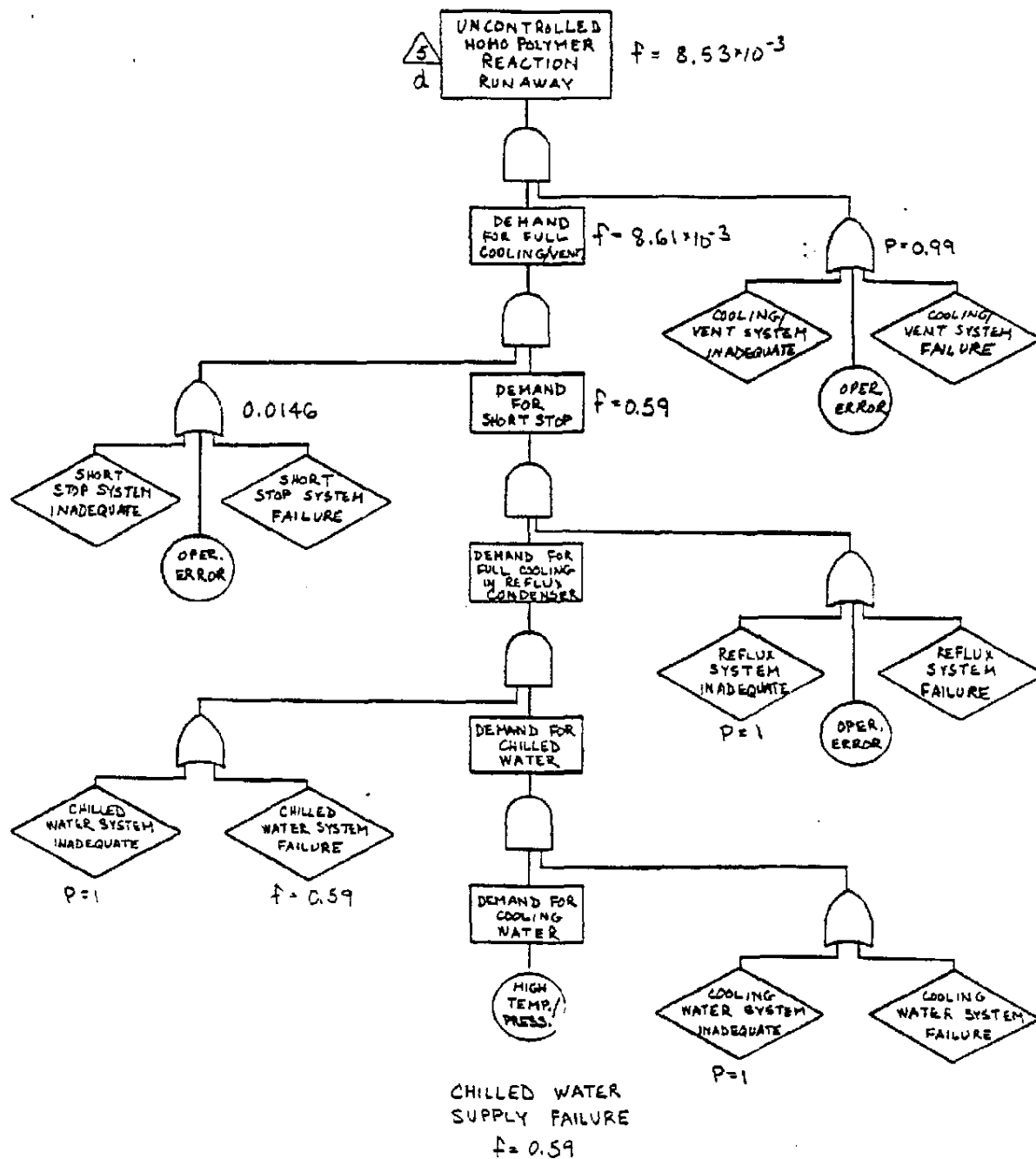


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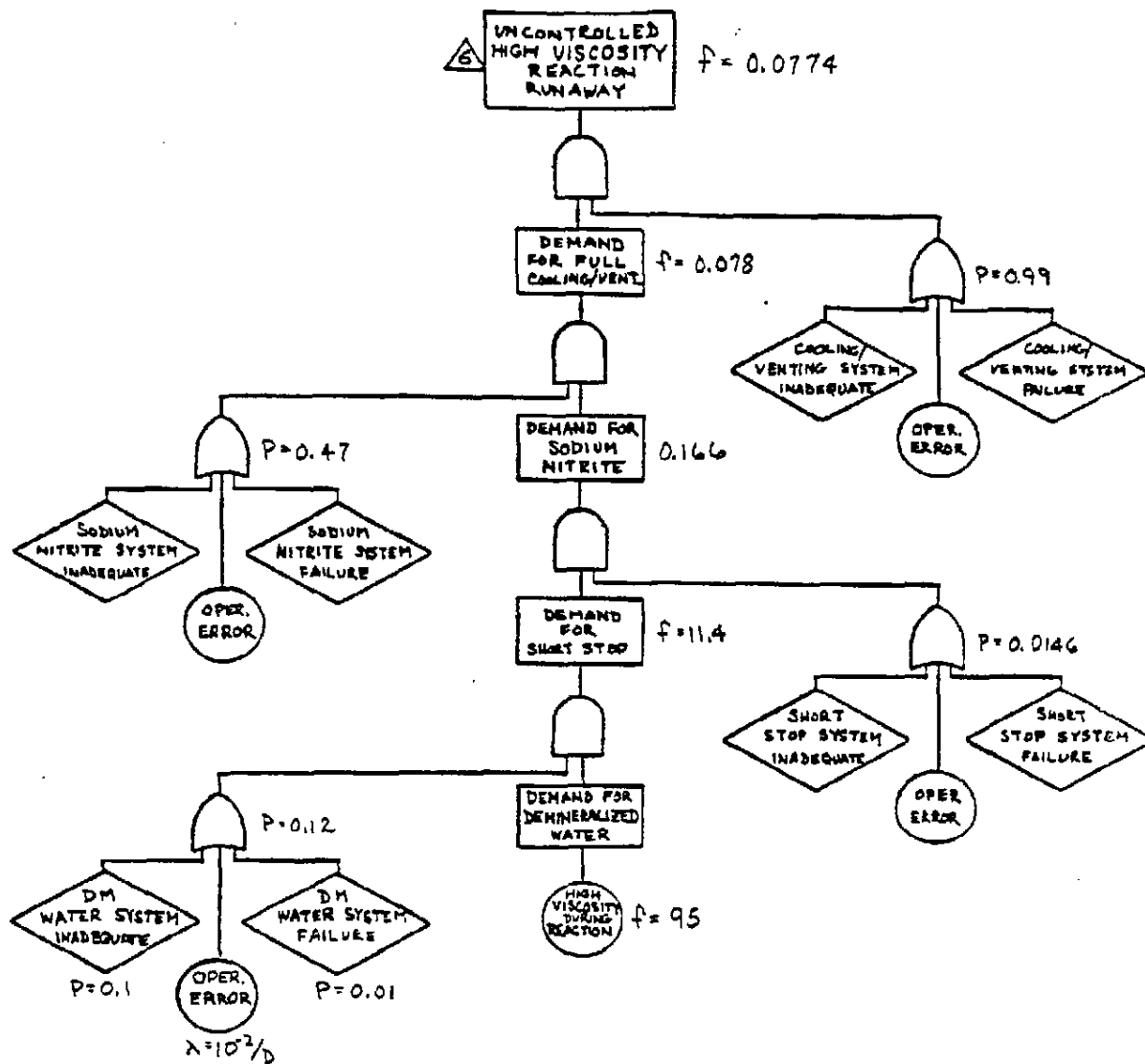


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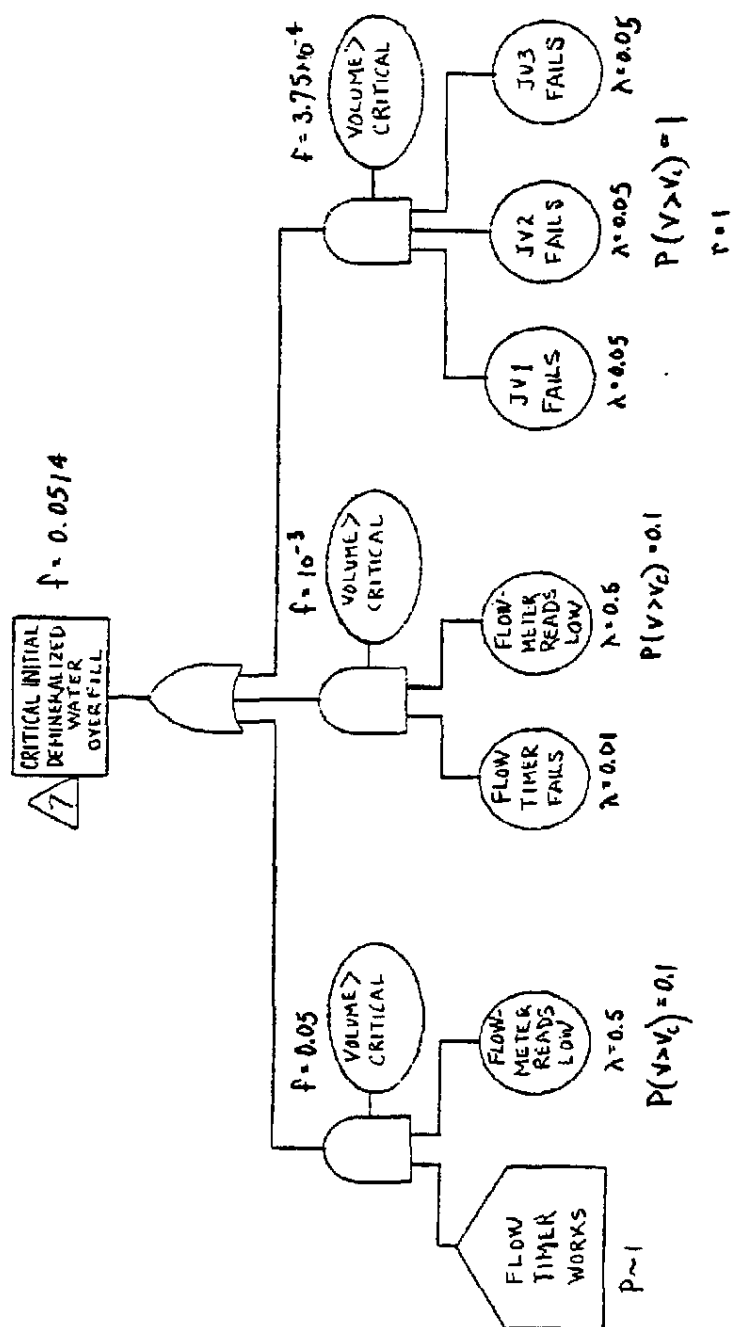




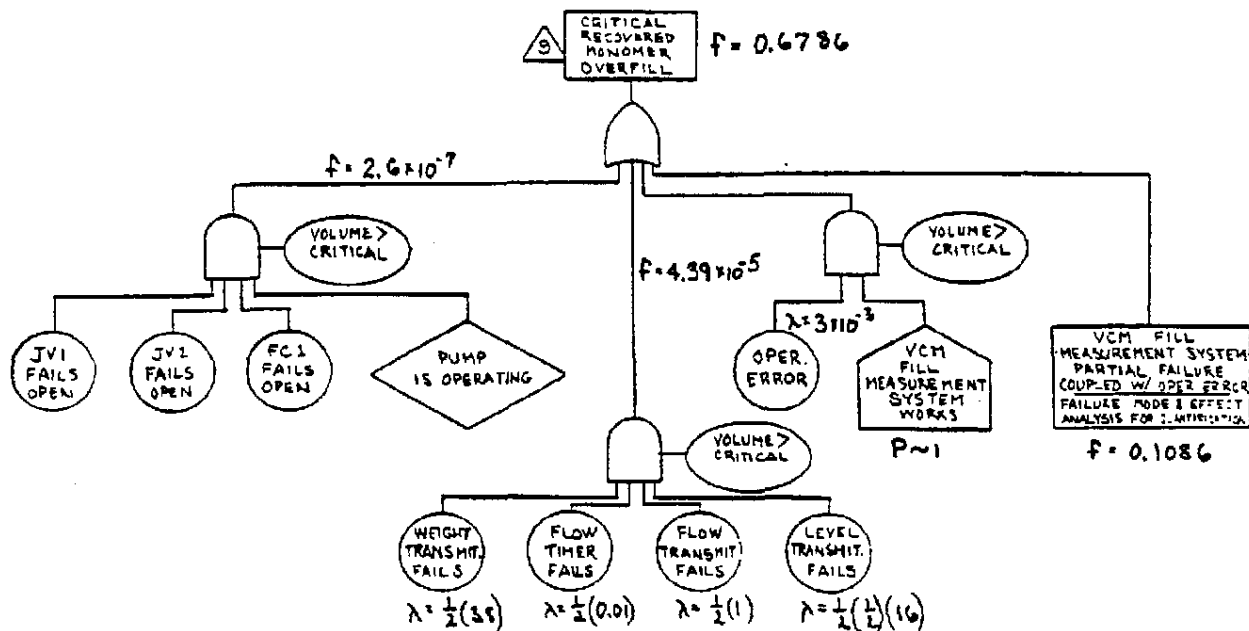
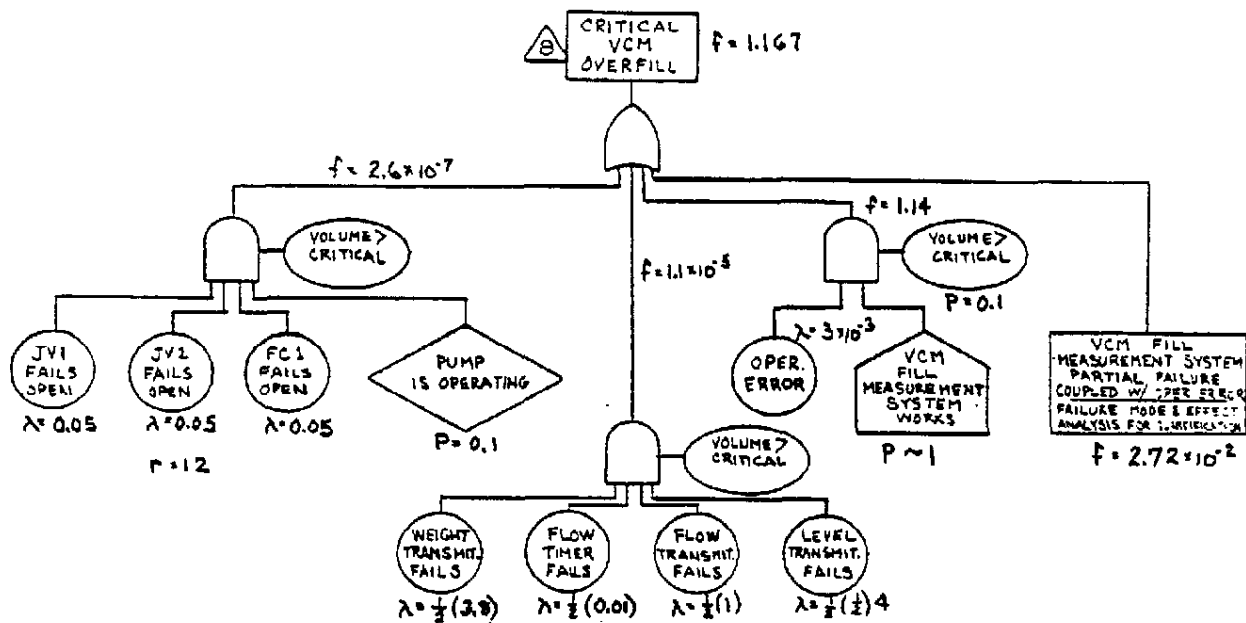
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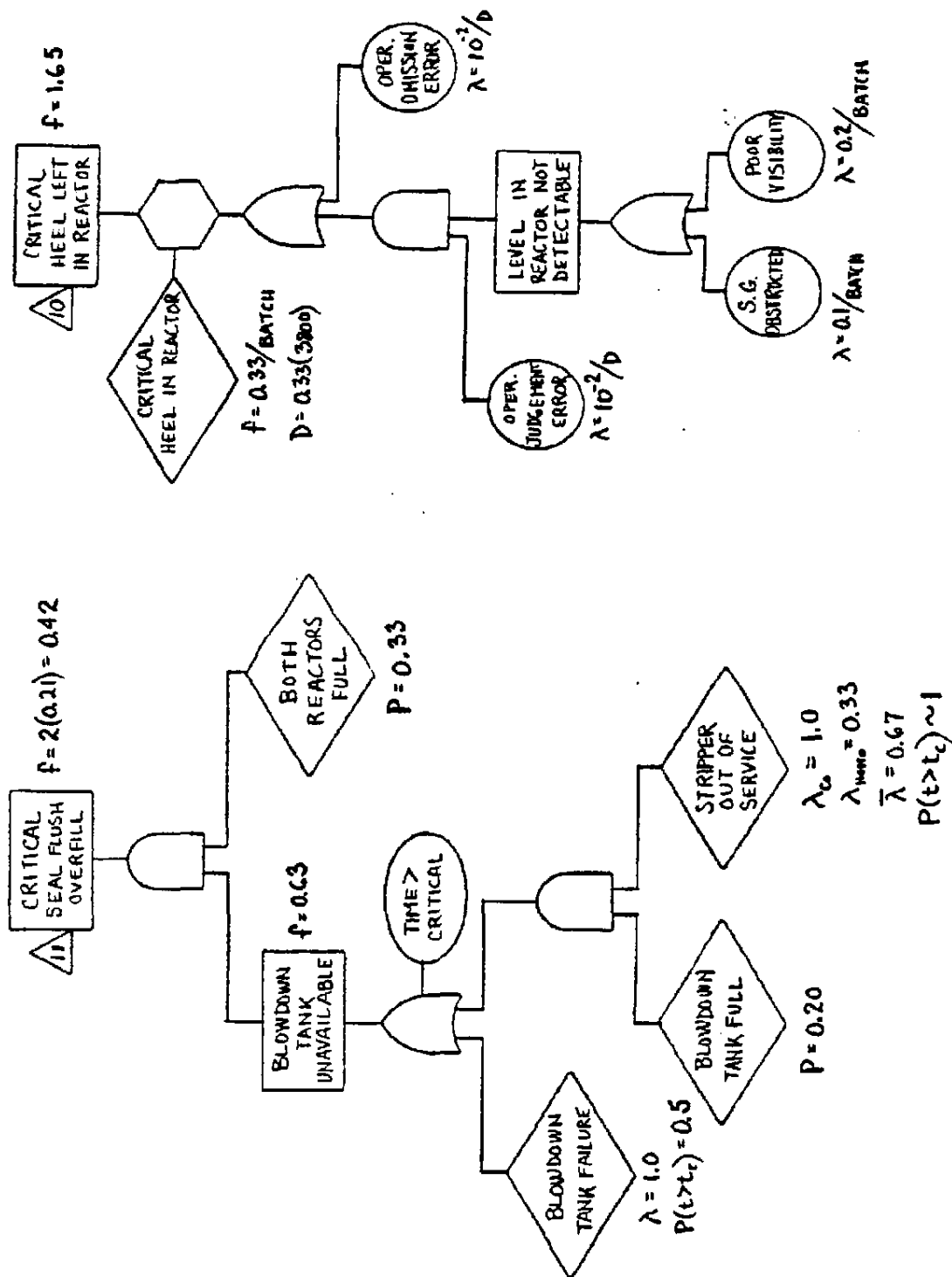
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AP00036735

Appendix II
Emergency Release Statistics

	PVC Industry* 1979	APCI Calvert City ⁺ 1 Oct. '79 - 30 Sept. '80
Total Emergency Releases	238	11
Emergency Releases from Reactors	164	5
 Total lbs. Released	 543,317	 9610
Lbs. Released from Reactors	374,387 (est.)	305
 Average lbs/Release	 2284.6	 873.6
Average lbs/MM lbs Production	111.38	103.64
Average No. of Releases/MM lbs Prod.	0.0488	0.1186

* Vast majority homopolymer production

+ Approximately half homopolymer and half copolymer production

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Appendix III

Fault Tree Analysis Method

(Extracted from APCI "Process Hazards Analysis Seminar")

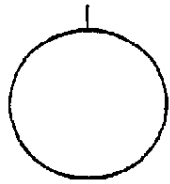
"Fault Tree" analysis, probably the most complex method used in process hazards reviews, is nonetheless the most systematic and concise. It defines basic causes and their relationships in leading to a single, undesired event. The method was originated by Bell Telephone in 1961, and further developed by the Boeing Company during the '60's. Fault trees were initially limited to the aerospace field, and only recently have begun to emerge within the chemicals industry.

Hazards reviews of plants or extensive modifications to existing ones are best suited to the fault tree method, especially where a team has been assigned to do the review. However, individuals may find the fault tree a useful tool in reviewing smaller-scale processes for safety adequacy. Although references are made throughout this text to the team concept, an individual's approach would be quite similar.

The procedure for applying this method is discussed in the following.

I. Define the Undesired Event

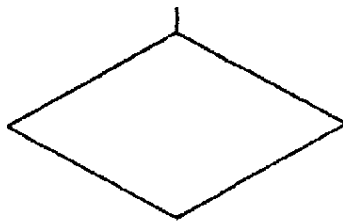
The fault tree is a logical sequence of events which could result in the undesired event, such as an explosion or chemical spill. Generally, the meeting prior to the hazards review provides an excellent opportunity to generate the undesired events and where they may occur. Often, the coordinator may determine those events for analysis based on results of previous hazards reviews or from recent incidents at the facility. Which-ever approach is taken, a list of the undesired events should be developed so that team members can refer to it as an agenda of topics for the review.



Primary Cause

Represents either a system component primary failure, or an independent basic fault that requires no further explanation.

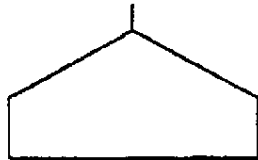
e.g., primary failure: relief valve fails closed; basic fault: operator smoking in area



Secondary Cause

Accounts for a basic fault which cannot or is not desired to be developed further because of a lack of information or its low probability of occurrence.

e.g., steam pressure regulator fails



Normal Operation

Represents an event or element which occurs because of design or normal conditions.

e.g., air (oxygen for combustion)



Transfer

Transfers one part of a tree to another location on the same tree or to a separate page for more elaborate development.

II. Construct Fault Tree

The undesired event is placed at the top of the fault tree schematic. Team members then generate possible causes of this event, called sub-events, in descending order of occurrence, building on the "stump" of the tree. Each subevent forms a branch of the fault tree and is developed independently of the other branches. The cause should be direct and immediate, and reflect its failed state only on the subevent to which it is connected.

Subevents can be related to one another through the use of "AND" or "OR" gates. A single subevent will cause the next higher event to occur if the two events are connected by an "OR" gate. The "AND" gate is used when the next higher event is the result of all subevents happening simultaneously. Construction of the tree continues until the review team has considered all possible causes for each subevent and developed the basic cause for each branch of the tree.