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of Transportation

**Federal Railroad
Administration**

Hazardous Materials
Transportation in Tank Cars

Analysis of Risks - Part II

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16. Abstract

The work indicated in this report forms the second phase effort to evaluate the overall risks to the population from the rail transport of certain chemicals. Most of the chemicals studied exhibit one or more hazards such as inhalation toxicity (vapors), flammability (posing fir thermal radiation hazards), and explosivity (causing blast wave damage hazard). A few of the chemicals pose potential hazards from the tendency to self-heat due to the initiation of polymerization reaction caused by loss of inhibitor or by exposure to an external fire. These various hazardous behaviors have been modeled and the risks (in terms of probabilities of occurrence of hazardous events and people exposure hazards) have been evaluated.

It is seen that the overall probability of occurrence of a self-heating induced thermal explosion type accident is rare (10^{-6} per year). The hazardous effects of an explosion of this type has limited range (< 200 m) and consequently the people exposure values are relatively small (1 to 50). However, a great uncertainty exists in the value of the parameter which represents the fraction of the mass of chemical in the tank car which undergoes thermal explosion. In this report, a value of 1.5% is used.

Risk analysis results for toxic, fire and explosion hazards indicates that transportation in DOT 105 tank cars is at best a factor of 10 safer than the transportation in DOT 111A type tank cars.

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Chapter 1

Introduction and Study Scope

1.1 Background

In a previous study, sponsored by the Federal Railroad Administration (FRA) and performed by Technology & Management Systems, Inc. (TMS) *(Raj and Turner, 1993)*, the risk to the U.S. population arising from potential rail accidents involving hazardous materials transported on rail was analyzed. The focus of this study was the development of a risk assessment methodology which considered the differences in structure and strength of different DOT specification tank cars (i.e., their puncture resistance characteristics in accidents), improvements resulting from the provision of increased shell and head thickness, shell head protection, shelf couplers, thermal jacket/insulation, etc. The risk analysis methodology also considered the physical and chemical characteristics and the hazardous nature of a number of commonly transported chemicals. The overall risks were calculated and plotted as annual frequencies of hazardous material exposure from mainline rail accidents against the severity of exposure (in terms of number of people being potentially exposed). The frequencies and severities were expressed in the (semi-quantitative) categories identified in MIL-Std-882B.

The primary purpose of the above study was to review the compatibility of chemicals and tank cars authorized by HM 181 amendment to the Title 49 of the Code of Federal Regulations (49 CFR) and to evaluate (i) whether certain DOT specifications tank cars then authorized to transport certain specific chemicals needed to be strengthened or prohibited from transporting those chemicals because of the "significant" risks such a chemical-tank car combination posed to the population at large, and (ii) the magnitude of reduction in risk if a better protected tank car were used to transport the same chemical(s).

The chemicals of interest in the past study were those that were considered to exhibit "poison by inhalation (PIH)" hazards and others which posed fire/explosion hazards. The list of chemicals considered in the previous study included the following:

1.	Ammonia (anhydrous)	7.	Nitric Acid (fuming)
2.	Chlorine	8.	Sulfuric Acid (fuming)
3.	Ethylene Dibromide	9.	Sulfur Dioxide
4.	Ethylene Oxide	10.	Sulfur Trioxide
5.	Hydrogen Chloride (anhydrous)	11.	Vinyl Chloride
6.	Liquefied Petroleum Gas	12.	Xylene

The thermodynamic properties for several other chemicals were also collected and/or updated in a chemical properties database maintained by TMS.

The tank car puncture probability database, chemical hazard area estimation procedure, and other risk calculation algorithms were codified into a computer program that could be exercised easily to calculate and display graphically the risk "profile" for the transport of a specified chemical (from the list above) in a DOT specification tank car with or without safety enhancing accessories. The risk profiles for different chemical-tank car combinations could be superposed and displayed simultaneously thus facilitating a quick review of the extent of risk reduction due to different options.

Subsequent to the completion of the above discussed work, the FRA desired to expand the list of chemicals to be included in the risk analysis. Some of the chemicals involved in recent rail accidents were to be included. These chemicals, discussed in this report, exhibit certain special behaviors such as self-heating, polymerization (under certain conditions), reaction with moisture after release, etc. This report provides the details of the analyses and calculation methodology developed to analyze the risks from these additional chemicals.

1.2 Project Objective

The principal objective of the present study is to expand the applicability of the risk assessment methodology to additional 25 or more hazardous materials which are carried in bulk in tank cars on the U.S. Railroad System.

1.3 Scope of Work

In order to achieve the above objective, the following scope of work was undertaken.

Task 1:   Development of the List of Additional Chemicals

The Association of American Railroads (AAR) publishes, each year, a list of hazardous materials transported by rail in tank cars. This list condenses the number of tank car origins by commodity in descending order of originations. TMS reviewed a three year history of the materials that originate by rail (i.e., 1990, 1991, and 1992) and, from the three year histories, TMS developed a list of 27 materials for study that were assumed to have a higher-than-average risk to human health or the environment. Special attention was given to selecting the materials for study that exhibit polymerization and/or self-heating reactions. The list did not include materials studied previously, which included predominantly, Division 2.1 materials (flammable gas), Division 2.3 materials (poison gases), and Class 3 materials (flammable liquids) *(Raj and Turner, 1993)*.

METRIC CONVERSION FACTORS

Approximate Conversions to Metric Measures

Symbol	When You Know	Multiply by	To Find	Symbol
LENGTH				
in	inches	*2.5	centimeters	cm
ft	feet	30	centimeters	cm
yd	yards	0.9	meters	m
mi	miles	1.6	kilometers	km
AREA				
in²	square inches	6.5	square centimeters	cm²
ft²	square feet	0.09	square meters	m²
yd²	square yards	0.8	square meters	m²
mi²	square miles	2.6	square kilometers	km²
	acres	0.4	hectares	ha
MASS (weight)				
oz	ounces	28	grams	g
lb	pounds	0.45	kilograms	kg
	short tons (2000 lb)	0.9	tonnes	t
VOLUME				
tsp	teaspoons	5	milliliters	ml
Tbsp	tablespoons	15	milliliters	ml
fl oz	fluid ounces	30	milliliters	ml
c	cups	0.24	liters	l
pt	pints	0.47	liters	l
qt	quarts	0.95	liters	l
gal	gallons	3.8	liters	l
ft³	cubic feet	0.03	cubic meters	m³
yd³	cubic yards	0.76	cubic meters	m³
TEMPERATURE (exact)				
°F	Fahrenheit temperature	5/9 (after subtracting 32)	Celsius temperature	°C

*1 in. = 2.54 cm (exactly). For other exact conversions and more detail tables see NBS Misc. Publ. 286. Units of Weight and Measures. Price $2.25 SD Catalog No. C13 10 286.

Approximate Conversions from Metric Measures

Symbol	When You Know	Multiply by	To Find	Symbol
LENGTH				
mm	millimeters	0.04	inches	in
cm	centimeters	0.4	inches	in
m	meters	3.3	feet	ft
m	meters	1.1	yards	yd
km	kilometers	0.6	miles	mi
AREA				
cm²	square centimeters	0.16	square inches	in²
m²	square meters	1.2	square yards	yd²
km²	square kilometers	0.4	square miles	mi²
ha	hectares (10,000 m²)	2.5	acres	
MASS (weight)				
g	grams	0.035	ounces	oz
kg	kilograms	2.2	pounds	lb
t	tonnes (1000 kg)	1.1	short tons	
VOLUME				
ml	milliliters	0.03	fluid ounces	fl oz
l	liters	2.1	pints	pt
l	liters	1.06	quarts	qt
l	liters	0.26	gallons	gal
m³	cubic meters	36	cubic feet	ft³
m³	cubic meters	1.3	cubic yards	yd³
TEMPERATURE (exact)				
°C	Celsius temperature	9/5 (then add 32)	Fahrenheit temperature	°F

°F -40   0   32   98.6   212
°F -40   0   40   80   120   160   200
°C -40 -20   0   20   37   40   60   80   100

Acknowledgement

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Task 2:   **Compilation of Chemical and Thermodynamic Properties**

In this task, the chemical and thermodynamic properties of the study chemicals were gathered. The properties of interest were those that affect the calculation of consequence of release subsequent to release including exposure to fire. Considerable data were gathered from the open literature and public documents. Where properties were unavailable, solicitations were made with manufacturers of, or dealers in, these chemicals for thermo/physical properties data. This approach yielded limited data.

Task 3:   **Modeling Additional Chemical Behavior Models and Integrating with the Risk Model**

The hazard behavior of some of the study chemicals had not been previously investigated. In this task, attempts were made to mathematically model the release or fire exposure consequence of some chemicals. These included low vapor pressure liquid evaporation and dispersion of vapors, and the self-heating process of reactive/polymerizing chemicals. In some cases, the modeling was successful, and in other cases, while models could be developed, exercise of the models was hampered by lack of important chemical properties data (especially for self heating and polymerizing chemicals).

The models developed were integrated into the risk assessment model. This integration involved modification to the previously developed computer code.

Also, in this task, the revised data obtained from AAR on the conditional release probabilities (given an accident in which a hazardous material tank car is involved) were used and integrated into the release probability model. The AAR data has been expanded to include additional tank car classes and safety enhancing device effects. Also, more accurate conditional release probabilities have been calculated from the tank car accident database maintained by AAR.

Task 4:   **Risk Profile Generation**

Using the data and models developed, the risk profiles for a selected number of study chemicals were developed. The **FRA_RISK** computer program was revised to include all of the study chemicals.

1.4 Overall Study Approach

In general, the approach to conducting the study indicated in this report was the same as that used in the previous study *(Raj and Turner, 1993)*. As such, this report, in effect, should be regarded as an extension of the previous report, except that new chemicals have been included. Because of the significant similarities in the overall approach, types of data used, and risk assessment methodology, many of the details indicated in the previous report *(Raj and Turner, 1993)* have been omitted in this

report in the interest of brevity. However, details of new models developed and revisions to tank car puncture data are indicated.

1.5 Report Organization

The recent modifications to the tank car release (conditional) probability data developed by the Association of American Railroads are discussed in Chapter 2. Also indicated in this chapter is the procedure used to incorporate these results in the overall risk calculations. The effect, if any, of these revised tank car puncture data on the hole size distribution is also discussed.

The list of additional chemicals studied in this project is indicated in Chapter 3. The physical, chemical, and other hazardous properties of each of the study chemicals are discussed. Also, special properties of interest that are difficult to obtain, but are needed in hazard evaluation models are discussed, and reasonable values for these properties are provided. The consequence models developed in this study are elaborated in Chapter 4. These include (i) the evaporation of low vapor pressure toxic liquid spill and dispersion of vapor emanating from such as spill, and (ii) polymerization model. The application of these models to risk analysis is also discussed.

In Chapter 5 the overall risk model is discussed and the results for selected chemicals are presented. The conclusions and recommendations arising from this study are presented in Chapter 6.

1.6 Limitations of the Study

All of the limitations identified in the previous study are equally applicable to this study. These include consideration of only (i) the frequency of accident statistics for mainline rail accidents, (ii) acute hazardous effects posed by the chemicals, and (iii) tank car failures/puncture caused as a direct result of accidents and not due to corrosion, fatigue, or appurtenance failures. In addition, the consequence models developed may not represent the true behavior of the chemical under all circumstances. The secondary consequences of chemical release and combined hazardous effects arising from simultaneous release of two or more chemicals in an accident are not considered. The risk results obtained are expected to be accurate within factors of 3 in frequency estimates and factors of 2 in exposure estimates.

Chapter 2

Lading Release Probabilities and Tank Car Puncture Size Distribution

2.1 Introduction

The magnitude of hazardous consequence arising from the release of a hazardous material (chemical) from a tank car following an accident depends on the rate of release of the chemical among other parameters such as the chemical property, environmental conditions, and the total mass of the chemical in the tank car. The rate of release is directly proportional to the damage (puncture) area. A risk analysis calculation involves the consideration of a spectrum of puncture sizes and assessing their hazardous consequences. The overall accident risk also depends upon the frequency with which a tank car involved in a train accident suffers sufficient damage to result in a lading release. It is, therefore, essential to determine both the probability of release given an accident and the distribution of puncture sizes that can occur consistent with the level of severity of the accident. In this chapter, we discuss the data on these parameters, namely the probability of lading release given an accident and the distribution of puncture sizes.

The research project undertaken by the Association of American Railroads (AAR) and the Railway Progress Institute (RPI) called the Tank Car Safety Research Project has been analyzing the susceptibility of different specification tank cars to punctures in main line and yard accidents under various conditions (speed, improvements to tank car structure, provision of safety devices, etc.). Historical railroad accidents involving tank cars have been analyzed and the results have been synthesized by AAR *(Phillips, 1994)* into a single dependent parameter, namely, the conditional probability of a tank car suffering a lading loss given that the tank car is involved in a railroad accident (main line or yard). Several tank car safety features (or "risk reducing options") and train speed have been used as independent parameters on which the lading loss probability is dependent.

In this chapter we discuss the principal methodology used by AAR and the results. The methodology by which the size distribution of holes on shell and head is determined is also indicated.

2.2 Tank Car lading Release Probability

In the previous report *(Raj and Turner, 1993)* we discussed the details of the Tank Car Accident Database maintained jointly by the AAR and the Railway Progress Institute (RPI). Also presented in the previous report was the statistics on rail accidents involving tank cars and lading losses. The

lading loss probability results, as determined by a previous study by AAR *(Phillips, 1992)* were discussed and sample data were presented.

More recently, AAR has published a more expanded study of the Tank Car Accident Data and the results on lading release probabilities *(Phillips, 1994)*. The following are the features of the latest AAR study.

1. Historical tank car accident data for the period 1965-1987 have been analyzed.

2. Lading loss and damage incidents are enumerated and classified by main line and yard accidents, different DOT Specification tank cars (non-pressure and pressure cars), speed range, tank cars with and without shelf couplers. Also, the count of total number of tank cars derailed and total number damaged with lading loss are provided. Table 2.1 shows a sample table from the AAR Report *(Phillips, 1994)*.

3. Tank car accident data have also been analyzed by considering the number of lading loss incidents with tank cars whose puncture resistance had been improved by the provision of head protection, shell and head thickness increases, insulation and steel jackets, etc. From these data, the effectiveness of each type of protection or risk reduction option, (RRO) in reducing the lading loss probability have been computed. Only mechanical damage caused lading releases have been considered (i.e., no fire induced releases are included) and the probabilities of these releases have been computed.

The lading release probabilities (given that a derailment has occurred) are presented for each DOT Specification tank car and for each and every combination of RROs. Speed independent probability results for five basic types of tank cars are presented, namely

- ◆ Type 1 — 111A Non-Insulated
- ◆ Type 2 — 111A Insulated
- ◆ Type 3 — 112 (114) A
- ◆ Type 4 — 105A
- ◆ Type 5 — 112 (114) S, J, T and 105 S, J

Also, the following types of RROs have been considered:

- ◆ A — Head Protection (increased head thickness, ½ or full height head shields)
- ◆ B — Shell Protection (thickness increase, jacket surrounding the shell)
- ◆ C — Top Fitting Protection (structural protection for fittings)
- ◆ D — Bottom Fitting Protection (structural protection-skids, elimination of bottom outlets)

Table 2.1

NUMBER OF LADING LOSS AND DAMAGE CASES ON MAINLINES BY
CAR TYPE, TRAIN SPEED AND LOSS CAUSE (EXCLUDING RUPTURES DUE TO FIRE),
LOADED CARS ONLY, ALL PRODUCTS, NO SC
(1965-1987)

	Speed									
	0-10 mph					>10 to 20 mph				
	Car Type					Car Type				
Loss Cause ↓	1	2	3	4[1]	5[1]	1	2	3	4[1]	5[1]
H	9	2	5	0	0	11	6	15	1	0
S	6	0	4	1	0	9	0	5	0	0
T	22	26	8	4	0	30	3	7	1	0
B	7	4	1	0	0	6	7	2	0	0
HS	2	0	1	0	0	2	2	3	0	0
HT	0	0	0	0	0	0	0	0	1	0
HB	1	0	0	0	0	0	1	0	0	0
ST	1	0	0	0	0	1	0	2	0	0
SB	0	0	0	0	0	1	0	0	0	0
TB	1	1	0	0	0	5	3	0	0	0
≥3	1	0	0	0	0	4	1	0	0	0
Unknown	0	3	0	0	0	19	2	4	0	0
# damaged w/loss	50	36	19	5	0	88	25	38	3	0
# damaged w/o loss	80	127	82	25	1	60	91	99	19	2
# damaged w & w/o loss	130	163	101	30	1	148	116	137	22	2
# derailed/ damaged	1.80					1.80				
# derailed	234	293	182	54	2	266	209	247	40	4

Symbols

H = head punct.

S = shell punct.

T = loss thru top fitting

B = loss thru bottom fitting

Car Type

1 = 111A carbon steel stub sill non-ins

2 = as above ins

3 = 112(114)A

4 = 105A(120A)

5 = 112(114)S, J, T and 105S, J

1   Values under car types 4 and 5 are not used in the development of loss probabilities and are included here only for completeness.

2   Multiple losses from sources defined under "symbols" i.e., ST = shell puncture and loss thru top fitting.

Source of Table: *Phillips, 1994*

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Table 2.2 shows a sample of the format used in the AAR report to show the results on the lading loss probability. We have used their results, without any change, and coded them into the risk analysis computer program. It should be noted that these probability values are not dependent on the speed and represent speed averaged values.

The principal difference between the release probability results used in our 1993 report and this report is in the expanded scope of tank car types as well as in the changes to the probability values. In the recent AAR report, a more detailed methodology has been used to develop the values for the release probabilities.

2.3 Puncture Size Distribution

A detailed methodology for determining the puncture size distribution for five types of DOT specification tank cars was presented in our earlier report *(Raj and Turner, 1993)*. The accident data and tank car damage data for these calculations had been obtained from AAR *(Phillips, 1992)* and these have not changed. Hence, our previous correlations remain unchanged. For details of these correlations and the distribution of hole area probabilities resulting in accidents, the previous report should be consulted.

For the sake of continuity of discussions, Figure 4.3b of the 1993 report is reproduced and presented in this report as Figure 2.1. Also, the following correlation for hole size distribution was obtained.

$$P = a_2 Z^2 + a_3 Z^3 + a_4 Z^4 \qquad (2.1)$$

where

P = Conditional probability (expressed as a fraction) that given a hole has occurred on a tank car, the hole area is smaller than or equal to A_H

Z = Dimensionless puncture area defined by:

$$Z = \log_{10} \left[\frac{A_H}{1.6 * 10^{-4}} \right] \qquad (2.2)$$

A_H = Hole area in m^2

The following Table 2.3 provides the values of the coefficients a_2, a_3, and a_4 for the various tank car types.

Table 2.2

Sample of Results Developed by AAR-RPI

PERCENT PROBABILITY OF LOSS IN YARDS, GIVEN A LOADED DERAILED
CAR, BY CAR TYPE AND LOSS CAUSE (EXCLUDING RUPTURES DUE TO FIRE)

Base Car Type	Ins	HS	H Base	H +1/8"	H +1/4"	S Base	S +1/8"	S +1/4"	T Base	T Protected	B Base	B Improve prot/elim	M Base	M w/RRO	M Base
1A (111A NI w/o B)	No (base)	0 (base)	3.91	1.62	0.80	1.60	0.54	0.27	7.97	5.51	0.00	0.00	1.12		14.60
		1/2	0.88	0.41	0.23										
		full	0.27	0.17	0.12										
	Yes	0	1.62	0.80	0.45	0.54	0.27	0.17	7.97	5.51	0.00	0.00	0.78		
		1/2	0.50	0.28	0.17										
		full	0.27	0.17	0.12										
1B (111A NI w/ B)	No (base)	0 (base)	3.91	1.62	0.80	1.60	0.54	0.27	7.97	5.51	1.03	0.52/0	1.12		15.63
		1/2	0.88	0.41	0.23										
		full	0.27	0.17	0.12										
	Yes	0	1.62	0.80	0.45	0.54	0.27	0.17	7.97	5.51	1.03	0.52/0	0.96		
		1/2	0.50	0.28	0.17										
		full	0.27	0.17	0.12										
2A (111A I w/o B)	Yes (base)	0 (base)	1.62	0.80	0.45	0.54	0.27	0.17	7.97	5.51	0.00	0.00	0.78		10.91
		1/2	0.50	0.28	0.17										
		full	0.27	0.17	0.12										
2B (111A I w/ B)	Yes (base)	0 (base)	1.62	0.80	0.45	0.54	0.27	0.17	7.97	5.51	1.03	0.52/0	0.96		12.12
		1/2	0.50	0.28	0.17										
		full	0.27	0.17	0.12										

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Figure 2.1

Cumulative Probability vs. Hole Area
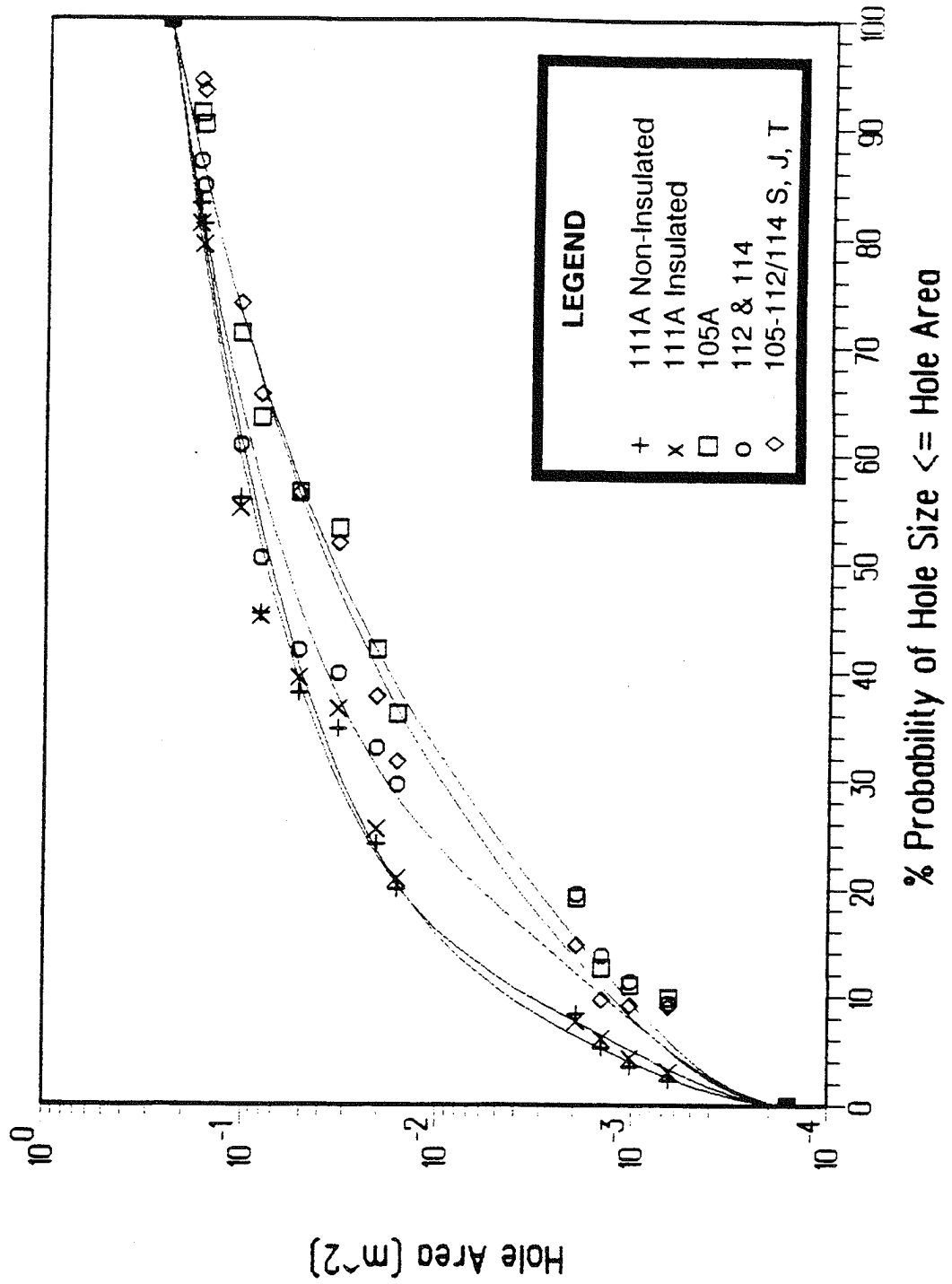
Table 2.3

Hole Probability Correlating Equation Parameters and Mean Hole Areas

Tank Car Specification	a_2	a_3	a_4	Mean Hole Area (m²) $10^{-4} \times$	Hole Std. Deviation (m²) $10^{-4} \times$
DOT 111A Non-Insulated	10.28	-6.72	2.07	897	1193
DOT 111A Insulated	14.03	-9.79	2.66	915	1357
DOT 105A	21.20	-9.52	1.87	654	1330
DOT 112/114	20.35	-12.22	2.80	816	1475
DOT 112/114-105 (S, J, T)	17.56	-7.25	1.52	672	1210

The mean hole area for each of the tank car types is obtained by determining from the respective curves in Figure 2.1 the hole area corresponding to 50% cumulative probability. These mean area values are indicated in the fifth column of Table 2.3. Also indicated in the last column are the standard deviations of the hole area distribution.

The dependency of the hole size distribution was investigated and results were reported in our previous report. It was found that no statistically significant correlation could be obtained for the hole size distribution (or even average hole size) dependency on train speed at the time of accident.

These results and correlations on release probability and puncture size distribution are coded into our risk analysis program. The risk analysis methodology is described in Chapter 5.

Chapter 3

Description of Study Chemical Properties

The physical and thermodynamic properties and hazards associated with the chemicals chosen for study are indicated in this chapter. Twenty seven (27) commonly transported hazardous chemicals were chosen for study in consultations with and approval of the FRA. The details of these chemicals are indicated in Section 3.1. The discussion on property values and their organization in a database, is provided in Section 3.2. Also elaborated in this section is the phenomenon of multiple hazard behavior of some of the chemicals upon release. Additional discussion relevant to chemical properties and hazards is provided in Section 3.3.

3.1 List of Study Chemicals

The twenty seven hazardous chemicals chosen for study in this project are indicated in Table 3.1. The table contains the proper shipping name of the chemical, the three letter code[1], the U.S. DOT designated hazard class, and the United Nations four digit code[2]. Also indicated are the number of tank car shipments of the chemical in 1992 included in the AAR publication of the Top 125 shipment ranking. The list of chemicals included in Table 3.1 consists of flammable gases (Class 2.1), poison gases (Class 2.3), flammable liquids (Class 3), poisonous liquids (Division 6.1, I and II), corrosives (Class 8), and oxidizers (Division 5.1).

Each hazardous material in Table 3.1 was selected for analysis in this project because of its unique chemical properties, historical accidents involving release or damage attributable to its presence in the consist, the potential risk to human health or the environment, and special behavior properties that affect the overall risk or the consequence. The hazard class shown in Table 3.1 for each chemical describes its primary hazard.

Some of the chemicals exhibit different types of hazards when *released* into the environment. The type of behavior upon release from the tank car and the hazards realized will depend on parameters such as the accident scenario, local conditions, environmental, and meteorological conditions.

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[1]The three letter code is used by the U.S. Coast Guard (USCG) to identify the chemicals. These designations are indicated by USCG in the Chemical Hazard Response Information System (CHRIS).

[2]For a definition of hazard classes see the placard substitution table in 49 CFR, §173.2. For an index of correspondence between UN Number and proper shipping name see index listing in 49CFR §172.

Table 3.1

List of Chemical Names

CHEMICAL NAME	CODE	UN ID NUMBER	DOT HAZARD CLASS	# SHIPMENTS IN 1992	AAR TOP 125 RANK
Acetaldehyde	AAD	1089	3	1,899	72
Acetone	ACT	1090	3	2,573	60
Acetone Cyanohydrin	ACY	1541	6.1	*	*
Acrolein, inhibited	ARL	1092	6.1	*	*
Acrylic Acid, inhibited	ACR	2218	8	1,899	71
Bromine	BRX	1744	8	*	*
Carbon Tetrachloride	CBT	1846	6.1	1,216	91
Chloroform	CRF	1888	6.1	*	*
Chloroprene, inhibited	CRP	1991	3	790	116
Chlorosulfonic Acid	CSA	1754	8	*	*
Dimethylhydrazine, unsymmetrical	DMH	1163	6.1	*	*
Ethylene Dichloride	EDC	1184	3	3,931	28
Ethyleneimine, inhibited	EIT	1185	6.1	*	*
Hydrogen Chloride, anh refrigerated	HDC	2186	2.3	*	*
Hydrogen Peroxide, stabilized	HPO	2015	5.1	2,944	55
Isoprene, inhibited	IPR	1218	3	*	*
Methyl Bromide	MTB	1062	2.3	*	*
Nitric Acid, red fuming	NAC	2023	8	*	*
Phenol (Carbolic Acid) solution	PHN	2312	6.1	631	23
Propylene Oxide	POX	1280	3	4,362	39
Sodium Hydroxide (NaOH) solution	SHD	1824	8	78,838	1
Styrene Monomer, inhibited	STY	2055	3	14,324	15
Sulfur, molten	SXX	2448	9	70,812	2
Sulfuric Acid (98%)	SFA	1830	8	58,062	3
Oleum (30%≤SO3≤37%)	OLM	1831	8	2,789	58
Trichloroethylene	TCL	1710	6.1	1,201	93
Vinyl Chloride, inhibited	VCM	1086	2.1	25,130	10

*Not within the top 125 materials shipped in 1992

In general, a particular chemical may pose one or more of the following acute health hazards to human beings:

1.   toxicity due to vapor inhalation (toxic vapor);

2.   burn injury from exposure to thermal radiation heat flux from a pool fire (pool fire);

3.   burn injury due to engulfment in a propagating vapor fire (vapor fire);

4.   blast effects due to a vapor cloud explosion (cloud explosion); or

5.   impact injury by debris ejecta from tank explosion caused by polymerization or decomposition of the material contained within the tank.

The first four hazards listed above require the chemical to be released from the tank car in order for that hazard to be realized. The fifth hazard, however, does not necessarily require a release of the product and may occur if the chemical in the tank is heated above a particular temperature or if contamination of the chemical inside the tank occurs.

Listed in Table 3.2 are the potential multi-hazard behavior of study chemicals *upon release* into the environment. Four principal types of hazards, namely toxic vapor, pool fire, explosion, and vapor fire, are indicated. The potential for a chemical to exhibit a specific one of these four types of hazards is indicated by a conditional probability (fraction). This value indicates the conditional probability that the chemical *released* from the tank exhibits the specified hazard. A value of zero for this conditional probability indicates that the chemical does not pose that type of hazard. In general, the probability of a particular type of behavior is *not* dependent on the chemical (property) only, but is influenced also by external conditions (ignition sources, severity of accident, etc.) and environmental effects.

The probability values depend on the release conditions, environmental conditions, property of the chemical, presence of other chemicals in the accident, and the nature of the accident itself. The values indicated for these conditional behavior probabilities are, at best, approximate and are based on subjective engineering judgement, knowledge of the properties of the chemicals, and our staff experience resulting from review of a number of rail accident reports and an understanding of post accident conditions.

Some of the study chemicals display other hazardous behavior even when *not* released, but when they are subject to certain unique situations. These include polymerization or self-heating of the chemical within the tank car due to inadequate buffering by the inhibitor, loss of inhibitor, heating of chemical from an external fire, etc. Some other chemicals undergo decomposition reactions when exposed to high temperature.

Table 3.2

Conditional Probabilities of Occurrence of Different Types of Hazards Given That the Chemical Has Been Released into the Environment

Chemical Name	Code	Hazard Class	Hazard Type and Chemical Phase	Conditional Probability of Different Behaviors			
				Toxic Vapor	Pool Fire	Explosion	Vapor Fire*
Acetaldehyde	AAD	3	Flammable Liquid	0.30	0.50	0.20	0.00
Acetone	ACT	3	Flammable Liquid	0.00	0.50	0.50	0.00
Acetone Cyanohydrin	ACY	6.1	Poison Liquid	0.60	0.20	0.20	0.00
Acrolein, inhibited	ARL	6.1	Poison, Flammable Liquid	0.60	0.20	0.20	0.00
Acrylic Acid, inhibited	ACR	8	Corrosive Liquid	0.60	0.20	0.20	0.00
Bromine	BRX	8	Corrosive, Poison Liquid	1.00	0.00	0.00	0.00
Carbon Tetrachloride	CBT	6.1	Poison Liquid	1.00	0.00	0.00	0.00
Chloroform	CRF	6.1	Poison Liquid	1.00	0.00	0.00	0.00
Chloroprene, inhibited	CRP	3	Flammable Liquid	0.30	0.50	0.10	0.10
Chlorosulfonic Acid	CSA	8	Corrosive, Poison Liquid	1.00	0.00	0.00	0.00
Dimethylhydrazine, unsymmetrical	DMH	6.1	Poison Liquid	0.50	0.25	0.25	0.00
Ethylene Dichloride	EDC	3	Flammable, Poison Liquid	0.30	0.50	0.20	0.00
Ethyleneimine, inhibited	EIT	6.1	Poison Liquid	0.60	0.20	0.20	0.00
Hydrogen Chloride, anh. refrigerated	HDC	2.3	Corrosive, Poison Gas	1.00	0.00	0.00	0.00
Hydrogen Peroxide, stabilized	HPO	5.1	Oxidizing, Corrosive Liquid	1.00	0.00	0.00	0.00
Isoprene, inhibited	IPR	3	Flammable Liquid	0.20	0.40	0.20	0.20
Methyl Bromide	MTB	2.3	Poison Gas	1.00	0.00	0.00	0.00
Nitric Acid, red fuming	NAC	8	Oxidizer, Poison Corrosive Liquid	1.00	0.00	0.00	0.00

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Chemical Name	Code	Hazard Class	Hazard Type and Chemical Phase	Conditional Probability of Different Behaviors			
				Toxic Vapor	Pool Fire	Explosion	Vapor Fire*
Phenol Solution (Carbolic Acid)	PHN	6.1	Poison Liquid	0.60	0.20	0.20	0.00
Propylene Oxide	POX	3	Flammable Liquid	0.30	0.50	0.20	0.00
Sodium Hydroxide (NaOH) Solution	SHD	8	Corrosive Liquid	1.00	0.00	0.00	0.00
Styrene Monomer, inhibited	STY	3	Flammable Liquid	0.30	0.50	0.20	0.00
Sulfur, molten	SXX	9	Class 9**	0.60	0.20	0.20	0.00
Sulfuric Acid (98%)	SFA	8	Corrosive Liquid	1.00	0.00	0.00	0.00
Oleum (30%≤SO3≤37%)	OLM	8	Corrosive, Poison Liquid	1.00	0.00	0.00	0.00
Trichloroethylene	TCL	6.1	KAFF***	1.00	0.00	0.00	0.00
Vinyl Chloride, inhibited	VCM	2.1	Flammable Gas	0.00	0.70	0.10	0.20

* The probability of vapor fire occurrence is set to 0.0 if the mean vapor concentration at the source is less than the lower flammability limit for combustion of the vapor

** Class 9 consists of miscellaneous hazardous materials

***Keep Away From Food (KAFF)

Table 3.3 lists the materials which exhibit polymerization and/or decomposition hazards and identifies which of the two hazards the chemical is capable of exhibiting. Also listed are some typical causes of these reactions. Note however, that under normal shipping conditions, polymerization and decomposition reactions are usually precluded by the use of a stabilizer or inhibitor in the product. Although these materials effectively retard the onset of these reactions, they must be well mixed within the product and the shipping state of the material must be maintained. In the case of one material, acrylic acid, it is essential that the product remain in the liquid phase. If the product freezes (54°F) and is improperly thawed, the inhibitor may no longer be homogeneously distributed in the material. This may lead to spontaneous and violent polymerization.

3.2 Description of Properties

3.2.1 Conventional Property Parameters

The general thermodynamic property values and the specific hazards posed by the study chemicals are summarized in the format shown in Table 3.4. The properties for each of the selected study chemicals are presented in this format in Appendix A. The information in Table 3.4 were assembled from a number of different literature sources, including: (i) U.S. Coast Guard's Chemical Hazard Response Information System *(CHRIS, manual II, 1984)*; (ii) Emergency Action Guide of the Association of American Railroads (1984); (iii) Pocket Guide to Chemical Hazards published by the National Institute for Occupational Safety and Health *(NIOSH, 1990)*; and (iv) The Fire Protection Handbook published by the National Fire Protection Association *(NFPA, 1981)*. While the data presented in Table 3.4 are useful to understand the types of hazards posed by each of the study chemicals, they are not useful for calculating hazard consequences arising under different release conditions.

Detailed thermodynamic property values were obtained from several published sources, *(Daubert & Danner, 1989; Matheson, 1971; NIOSH, 1990; Reid, Prausnitz, and Poling, 1987)*. For temperature dependent thermodynamic property calculation, the values of coefficients in the publication of Penn State University *(Daubert & Danner, 1989)*, and from the book by Reid *(Reid, et al, 1987)*. These detailed thermodynamic property and coefficient values were added to the chemical properties database maintained by TMS. Table 3.5 shows the list of thermodynamic and other properties, each of which forms a field in TMS' database. (All property values are in the Standard International units.) These property values are used by the TMS' hazard area calculation software, SAFEMODE™.

There are certain chemical behavior modes the analysis of which require special property values which are not in the list of parameters indicated in Table 3.5. These properties include vapor pressure relationship to temperature and solute concentrations, activation energy, and reaction frequency factor (required in analyzing polymerization and self-heating phenomena) and other special properties. These properties are discussed below.

Table 3.3

Chemicals Exhibiting Polymerization and/or Decomposition Hazards

CHEMICAL NAME	ID NUMBER	HAZARD CLASS	CHEMICAL DECOM-POSES	CAUSE OF DECOMPOSITION	CHEMICAL POLYMER-IZES	CAUSE OF POLYMERIZATION
I. Polymerizing Chemicals						
Acetaldehyde	1089	3	Y	Temperatures > 400 °F	Y	Excessive heat, contact with dust, oxidizers, reducing agents
Acetone Cyanohydrin	1541	6.1	Y	Temperatures > 248 °F and contact with alkaline materials	Y	Nitrides, organic acids, certain other materials
Acrolein, inhibited	1092	6.1	N	N/A	Y	Loss of inhibitor, contact with certain materials
Acrylic Acid, inhibited	2218	8	N	N/A	Y	Loss of inhibitor, improper thawing, excessive heat, certain materials
Chloroprene	1991	3	N	Loss of stabilizer or certain conditions	Y	Excessive heat, loss of inhibitor, contact with certain materials
Ethyleneimine	1185	6.1	N	N/A	Y	Excessive heat, contact with acids
Isoprene	1218	3	N	N/A	Y	Excessive heat, loss of inhibitor, contamination from certain materials
Propylene Oxide	1280	3	N	N/A	Y	Excessive heat, contamination from certain materials
Styrene Monomer, inhibited	2055	3	N	N/A	Y	Temperatures > 150 °F, loss of inhibitor, contamination from certain materials
Vinyl Chloride	1086	2.1	N	N/A	Y	Excessive heat, light, or air, loss of inhibitor

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Table 3.3 (continued)

Chemicals Exhibiting Polymerization and/or Decomposition Hazards

CHEMICAL NAME	ID NUMBER	HAZARD CLASS	CHEMICAL DECOMPOSES	CAUSE OF DECOMPOSITION	CHEMICAL POLYMERIZES	CAUSE OF POLYMERIZATION
II. Decomposing Chemicals						
Carbon Tetrachloride	1846	6.1	Y	Elevated temperatures	N	N/A
Chloroform	1888	6.1	Y	Elevated temperatures, air, light	N	N/A
Hydrogen Peroxide, stabilized	2015	5.1	Y	Excessive heat, contact with metals, dirt	N	N/A

Table 3.4

Summary of General Thermodynamic Data and Hazards of Study Chemicals

Acetaldehyde[3]

Chemical Code:	AAD
Formula:	C2H4O
Molecular Weight:	44.05
UN ID Number:	1089
Hazard Class:	3
Hazard Type:	Flammable Liquid
Normal Boiling Point:	68.7 °F
State as Shipped:	Liquid
State as Released:	Liquid
Toxicity:	10,000 ppm IDLH - irritant and moderately toxic
Fire:	Vapors are heavier than air and may travel to an ignition source and flashback. Containers may rupture violently in fire. Will generate large quantity of flammable gas or vapors upon release.
Flashpoint (Closed Cup):	36 °F
Explosion:	Vapors may explode if ignited in confined space.
Stability During Transportation:	Stable
Polymerization:	May occur if exposed to heat, dust, strong oxidizer, or reducing agent.
Decomposition:	Occurs at temperatures > 400F forming methane and carbon monoxide.
Reaction with Water:	No reaction.
NFPA Hazard Classification	
Health Hazard:	2
Flammability:	4
Reactivity:	2
Authorized Tank Cars:	DOT Class 103, 104, 105, 109, 111, 112, 114, and 115. (§ 173.243)

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[3]Data for other study chemicals are indicated in Appendix A

Table 3.5

List of Fields of Thermodynamic Properties for Each Chemical in SAFEMODE™ Chemical Properties Database

PROPERTY NAME	CODE	UNITS
1 Molecular Weight	XMWT	kg/kg mol
2 Critical Point Temperature	TCRI	K
3 Critical Point Pressure	PCRI	N/m^2
4 Normal Boiling Point	XNBP	K
5 Normal Freezing Point	XNFP	K
6 Lower Flammability Limit	XLOFLM	molar %
7 Upper Flammability Limit	UPFLM	molar %
8 Lower Detonation Limit	XLODET	molar %
9 Upper Detonation Limit	UPDET	molar %
10 Liquid Burn Rate	BRAT	m/s
11 Liquid Regression Rate	RGLQ	m/s
12 Molar Ratio Reactants/Products	MRAT	—
13 Air Fuel Ratio	AFRT	—
14 Adiabatic Flame Temperature	ADFT	K
15 Flame Temperature	FLTM	K
16 Effective Fire Temperature	EFLT	K
17 Black Body Emissive Power	BBEP	kW/m^2
18 Grey Body Emissive Power	EMPWR	kW/m^2
19 Emissivity	EMIS	—
20 Limiting Value of Molecular-Function Concentration	XMFRC	—
21 Enthalpy of Fusion	DHF	J/kg
22 Enthalpy of Combustion	DHC	J/kg
23 Enthalpy of Decomposition	DHDC	J/kg
24 Enthalpy of Solution	DHS	J/kg
25 Solubility in H_2O	SOL	kg/100 kg
26 Enthalpy of Reaction with H_2O	DHWR	J/kg
27 Enthalpy of Polymerization	DHPY	J/kg
28 Polymerization Consumption Rate	PRATE	kg/s
29 Aerosol Entrainment Fraction	PHI	—

PROPERTY NAME	CODE	UNITS
Temperature Dependent Properties		
30 Vapor Heat Capacity	CPV	J/kg K
31 Liquid Heat Capacity	CPL	J/kg K
32 Liquid Density	RHOL	kg/m^3
33 Vapor Pressure	PSAT	N/m^2
34 Enthalpy of Saturated Liquid	HLIQS	J/kg
35 Enthalpy of Saturated Vapor	HVAPS	J/kg
36 Enthalpy of Vaporization	XLAMDA	J/kg
37 Liquid Thermal Conductivity	XKL	W/m K
38 Vapor Thermal Conductivity	XKV	W/m K
39 Liquid Viscosity	XMUL	N s/m^2
40 Vapor Viscosity	XMUV	N s/m^2
41 Surface Tension	STEN	N/m
42 Interfacial Surface Tension	XITEN	N/m

3.2.2 Vapor Pressure of Mixtures

Oleum is primarily sulfuric acid in which sulfur trioxide (SO_3) has been dissolved. The "concentration" of oleum depends on the mass fraction of SO_3 that is present in the mixture. The vapor pressure of SO_3 on oleum depends on the temperature of the mixture and the SO_3 concentration in the mixture. Figure 3.1 shows the experimentally obtained vapor pressure — temperature — SO_3 concentration curves. These data for temperature below 100 °C were fit by a general concentration of the type:

$$\log (P/P_o) = C_T (T - 273) \tag{3.1}$$

where:

P = vapor pressure of SO_3 on oleum (N/m^2)

P_o = a pressure constant dependent on the SO_3 concentration in oleum (N/m^2)

C_T = a temperature constant dependent on the SO_3 concentration in oleum (K^{-1})

T = temperature of oleum (K)

The values of the various constants are indicated in Figure 3.1.

Since in an oleum spill the predominant chemical which is released as vapor is sulfur trioxide, all of the "properties" of oleum indicated in the properties database refer to SO_3. The vapor pressure is calculated with assumption that the SO_3 concentration in oleum is 30% by mass.

3.2.3 Polymerization and Decomposition Thermodynamic Properties

A subset of the study chemicals which polymerize or undergo reactive change of composition was identified in Table 3.3. All of these chemicals exhibit exothermic decomposition or polymerization (i.e., heat is liberated). Heat liberated by a part of the chemical undergoing polymerization/ decomposition reaction can lead to a run away reaction depending on the rate of heat liberation, ambient cooling conditions, venting of excess pressure, and several key thermodynamic properties of the chemical. Such an uncontrolled reaction can result in substantial increase in bulk temperature and tank pressure.

Figure 3.1

SO$_3$ Vapor Pressure vs. Temperature
for Different Percentages of Dissolved SO$_3$ in H$_2$SO$_4$

$$\log_{10}(P/P_0) = C_T (T - 273) \qquad T = {}^\circ K$$

P = Vapor Pressure of SO$_3$ (mm Hg)

$P_0 = [2.95 \times 10^{-8} \times (\% \text{ conc})^5 + 0.5]$ (mm Hg)

$C_T = 0.025 \, (1 - e^{-(\% \text{ conc})/5}) \; {}^\circ K^{-1}$ (${}^\circ K^{-1}$)
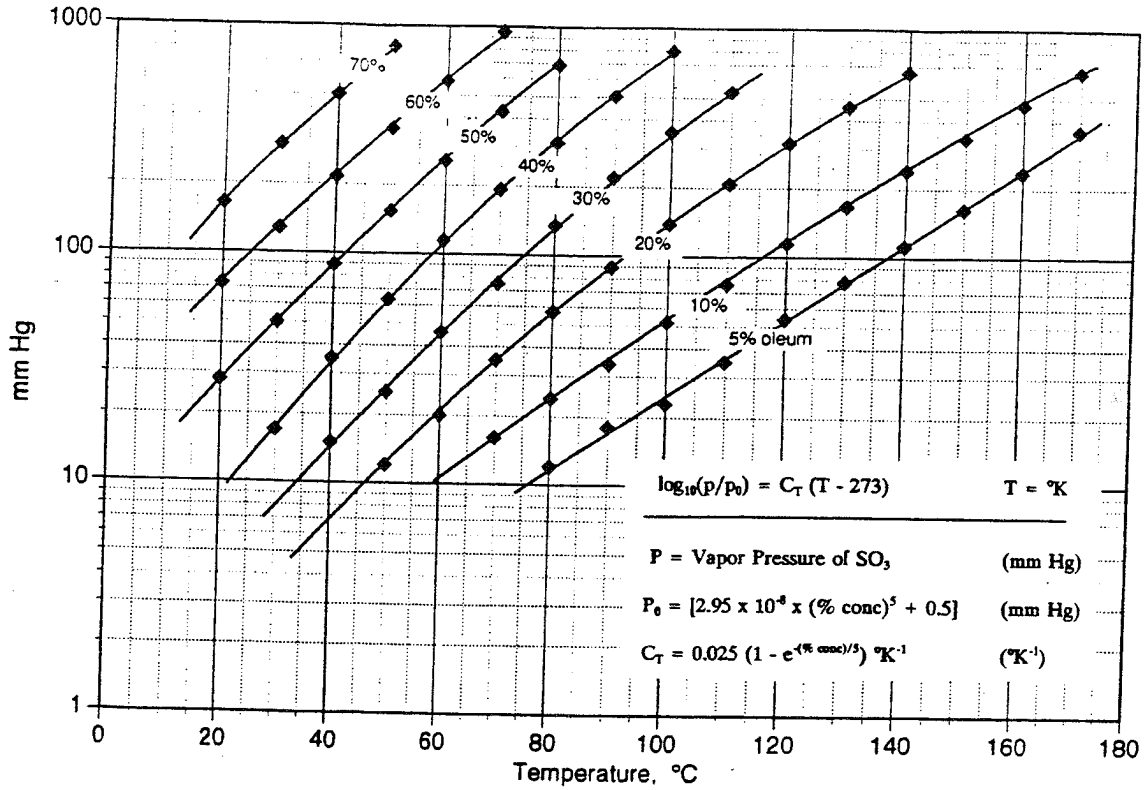
Data Source: Miles et al (1940)
Correlation by TMS

The key thermodynamic properties which characterize the polymerization/decomposition reaction are:

1. Heat of polymerization and/or heat of decomposition, i.e., the quantity of heat liberated when one mole of a compound is formed from its constituent elements.

2. Activation energy which is a measure of the rapidity with which a reaction can be initiated (i.e., it is a measure of the temperature at which the reaction kinetics become important).

3. Reaction rate (pre-exponential) factor. This factor determines the rate at which a certain polymerization or decomposition reactions proceed.

Table 3.6 shows the typical values for the above parameters obtained from the literature. As can be seen, the table is sparsely filled indicating the difficulty of obtaining any data, let alone reliable data, for many of the above properties.

The rate of reaction is generally represented by the Arrhenius equation

$$\dot{r} = A \, e^{-\left(\frac{E}{RT}\right)} \qquad (3.2)$$

where

$\dot{r}$ =   reaction rate (in fraction of mass reactant consumed per unit time)

A =   Arrhenius frequency factor which has a very large numerical value (in general, in units of s^{-1} or in K mole/s m^3)

E =   Activation energy in J/kg

R =   Gas constant for the material (J/kg K)

T =   Temperature (K)

Some of the chemicals exhibit spontaneous polymerization/decomposition reactions at ambient temperature, unless their tendency is inhibited by a buffer/inhibitor. The rate of reaction in these cases is determined by the rate of depletion of the buffer/inhibitor. In the case of acrylic acid, the rate of polymerization reaction is directly a function of the rate at which the dissolved oxygen is depleted *(Levy and Lakin, 1993)*. This is because the effectiveness of the inhibitor (namely, p-methoxyphenol or MEHQ) depends on the concentration of dissolved oxygen in acrylic acid.

The use of the chemical property values discussed in this chapter in the evaluation of hazard areas is elaborated in Chapter 4.

Table 3.6

Property Values Relevant to Self-Heating/Polymerization Phenomena

Chemical	Heat of Polymerization (kJ/kg) (Note 1)	Heat of Decomposition/ Reaction (kJ/kg) (Note 1)	Activation Energy (E) (kJ/kg)	Reaction Rate Pre-Exponential Factor (s^{-1})	Standard Heat of Formation (J/kg) (Note 2)
Polymerizing					
Acetaldehyde	—	—	—	—	-4367 [l]
Acetone cyanohydrin	—	—	—	—	—
Acrolein, inhibited	120.0	—	—	—	-2088 [l]
Acrylic Acid, inhibited	1075.8	—	4094.43 [3]	3.41 x 10^{15} (gmol/h litre)	—
Chloroprene, inhibited	—	—	—	—	—
Ethyleneimine, inhibited	—	—	—	—	—
Isoprene, inhibited	1159.7	—	—	—	—
Propylene Oxide	—	—	—	—	—
Styrene Monomer, inhibited	644.8	—	—	—	1419.6 [l]
Vinyl Chloride	1695.7	2640	—	—	—
Decomposing					
Carbon tetra chloride	—	—	—	—	—
Chloroform	—	—	—	—	—
Hydrogen Peroxide	—	2830.3	—	—	—

Note 1: From Reference Daubert et al (1989)
Note 2: From Reference Kayser (1974)
Note 3: The activation energy refers to dissolved oxygen (depletion reaction). Reference Levy and Lakin (1993).
l = liquid state
g = gaseous state
standard heat of formation is referred to 0 °C and 1 standard atmospheric pressure

Chapter 4

Consequence Models

4.1 Introduction

Hazardous chemicals released from a tank car pose different types of hazards depending on the nature of the chemical and the environmental conditions. In the previous report *(Raj and Turner, 1993)*, the models to assess the consequences of chemicals exhibiting the following types of characteristics were discussed:

♦ vapor inhalation toxicity;

♦ pool fire burning (injury due to thermal radiation);

♦ vapor cloud explosion (blast effects and injury);

♦ vapor cloud burning (burn injury due to fire engulfment); and

♦ corrosivity (skin burn injury due to physical contact).

The models included vapor dispersion (for slow, fast, and catastrophic releases), pool fire thermal radiation model, and explosion hazards. Models describing self-heating or polymerization of chemicals were not included.

In this chapter we describe three additional consequence models. These are:

♦ low vapor pressure chemical release and toxic vapor dispersion;

♦ polymerization of chemicals resulting from exposure to external heat or depletion of inhibitors; and

♦ calculation of the effects of tank car explosion (by over pressure).

In the interest of brevity, the consequence models described in the previous report are not described here; however, these were incorporated during the previous study into the risk assessment computer program.

4.2 Dispersion of Toxic Vapors Generated from a Pool of Low Vapor Pressure Liquid

When a low vapor pressure liquid is released from a tank car it is likely to form first a pool of liquid which then evaporates, relatively slowly, generating vapors that will be dispersed by wind. In these cases, the area of vapor toxicity hazard is relatively small because of low vapor evolution rates. Table 4.1 lists study chemicals, organized by their primary hazard class. The table also indicates the vapor concentration levels in air which are assumed to pose an Immediate Danger to Life and Health (IDLH) as defined by NIOSH (1990) for a 30 minute exposure. Several of these chemicals have very low vapor pressures (at 20 °C) compared to the atmospheric pressure.

We have developed two models to determine the toxic hazard area for the low vapor pressure chemical release. The first model applicable to the ultra low vapor pressures (i.e., vapor pressure so low that the total evaporation rate from a liquid pool formed by the spill of the entire content of a tank car is less than 1 kg/s. The second model is applicable to moderately low vapor pressure chemicals. These are discussed below.

4.2.1 Hazard Concentration Dependence on Exposure Time

The IDLH values presented in Table 4.1 are NIOSH values which are based on the 30 minute exposure criterion. In the case of a slowly evaporating pool, it is likely that the toxic vapor exposure time will exceed 30 minutes. The potential variability in exposure time and its effect on hazard concentration are considered by modifying the hazard concentration level as follows.

$$
C_{Haz} = \begin{cases} 2 * IDLH & \text{for } t_e \leq 15 \\ (30/t_e) * IDLH & \text{for } 15 \leq t_e \leq 60 \\ 0.5 * IDLH & \text{for } t_e \geq 60 \end{cases}
$$

where

C_{Haz} = Ground level concentration used for hazard area calculation

t_e = Exposure time in minutes (exposure time is assumed to be the same as the liquid pool evaporation time)

 = $\left(\rho_l \dfrac{V_{ch}}{\dot{M}_e} \right)$

$\dot{M}_e$ = Mass rate of evaporation from the chemical pool (kg/min)

Table 4.1

IDLH Concentrations and Maximum Volume Shipped in Tank Cars
(Ranked by Primary Hazard)

Chemical Name	IDLH (ppm)	Max. Volume** (gallons)	Max. Volume** (m³)
POISONOUS MATERIALS			
Acetone Cyanohydrin	17	21,700	82.0
Acrolein, inhibited	5	23,700	89.8
Carbon Tetrachloride	300	15,000	55.6
Chloroform	1,000	15,500	58.6
Dimethylhydrazine, unsymmetrical	50	25,800	97.8
Phenol (Carbolic Acid) Solution	250	22,300	84.8
Ethyleneimine	100	24,000	90.8
Trichloroethylene	1,000	16,800	63.8
Hydrogen Chloride, refrigerated	100	15,900	60.2
Methyl Bromide	2,000	10,500	39.6
FLAMMABLE MATERIALS			
Acetaldehyde	10,000	29,700	112.5
Acetone	20,000	29,300	110.8
Chloroprene, inhibited	400	22,400	84.6
Ethylene Dichloride	1,000	18,100	68.5
Isoprene, inhibited	75	34,100	128.9
Propylene Oxide	2,000	28,100	106.8
Styrene Monomer inhibited	5,000	27,400	104.1
Vinyl Chloride, inhibited	N/A	32,900	124.9
CORROSIVE MATERIALS			
Acrylic Acid, inhibited	20*	22,000	83.2
Bromine	10	9,200	16.0
Chlorosulfonic Acid	100	11,600	43.7
Nitric Acid, red fuming	100	13,700	52.1
Sodium Hydroxide (NAOH) Solution	145	15,300	58.1
Sulfuric Acid (98%)	20	13,500	51.0
Oleum (30%≤SO_3≤37%)		10,600	40.3
OXIDIZERS			
Hydrogen Peroxide, stabilized	75	18,000	68.2
MISCELLANEOUS MATERIALS			
Sulfur, molten	300	12,600	47.7

*IDLH unavailable, STEL value listed

**The shipment volumes indicated are nominal values used for risk calculations. The actual shipment volumes may vary depending on the loading conditions, tank car, and outage requirements. Please refer to 49 CFR §173.24b for outage requirements.

V_{ch} = Volume of the chemical contained in the tank car (all of which is assumed to be spilled to form the pool) (m³)

ρ_l = Liquid density (kg/m³)

The mass rate of evaporation ($\dot{M}_e$) is calculated by assuming the liquid pool depth to be 1 cm (0.01 m) and using the pool evaporation model developed in an earlier project *(Raj and Morris, 1987)*. This model is built into the TMS' SAFEMODE™ program code. Maximum tank car capacities were obtained from Union Tank Car Co. (Woodall, 1992) and the GATX Tank Car Manual. The shipment volume in each tank car for each chemical is then calculated noting the outage requirements specified in 49 CFR, Section 173.24b(a). These shipment volumes are indicated in Table 4.1.

4.2.2 Toxicity Hazard Area for Extremely Low Vapor Pressure Liquid Chemicals

Some of the study chemicals have very low vapor pressure compared to atmospheric pressure. Hence, their evaporation rate at 20 °C is relatively low.[1] Table 4.2 shows the vapor pressure and pool evaporation rates for a number of chemicals. We consider those chemicals whose evaporation rate to be less than 1 kg/s at 20 °C from a liquid pool to pose limited hazard area. These chemicals include:

- Acetone cyanohydrin
- Acrylic Acid
- Chlorosulfonic Acid
- Hydrogen Peroxide

- Nitric Acid
- Phenol
- Sodium Hydroxide
- Sulfuric Acid

Therefore, in general, there will be no toxic hazard at any significant distance down wind from the liquid pool boundary. However, to account for wind (or turbulent) gusts and to err on the conservative side we have assumed that the hazard area extends to a distance of 2.5 pool diameters[2] from the downwind edge of the pool and that the hazard area width remains constant and equal to the diameter of the pool. Figure 4.1 illustrates schematically the *assumed* hazard area.

The toxic vapor hazard area thus calculated for the above listed chemicals are indicated in Table 4.2. (Note that because of the above assumption, the hazard area is independent of the atmospheric stability.) It is noted that the total hazard areas for very low vapor pressure chemicals are relatively small, of the order of magnitude 3×10^{-2} sq. km.

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[1]The model does not consider the evaporation rate of the material at an elevated temperature.

[2]This distance is somewhat arbitrary.

Table 4.2

Toxic Vapor Hazard Area Results for Selected Chemicals

Chemical Name	Shipment Vol. in a Tank Car (m³)*	Vapor Pressure at 20°C (N/m²)	Liquid Pool Evaporation Under Neutral Weather Conditions (Atmosphere D)					Liquid Pool Evaporation Under Stable (F) Atmospheric Conditions				
			Evaporation Rate (kg/s)	Duration of Evaporation (min)	Vapor Concentration at Pool Edge (ppm)	Hazard Concentration (ppm)	Toxic Hazard Area (sq. km)	Evaporation Rate (kg/s)	Duration of Evaporation (min)	Vapor Concentration at Pool Edge (ppm)	Hazard Concentration (ppm)	Toxic Hazard Area (sq. km)
Acetaldehyde	112.5	99177.	74.9	19.5	5322	15322	N/A	43.7	33.5	15693	8955	.0046
Acetone	110.8	24420.	51.6	29.12	8371	20604	N/A	28.5	52.72	23455	11381	.048
Acetone Cyanohydrin	82.0	39.6	.066	8456	10045	34	.013	.027	20671	25394	34	.013
Acrolein, inhibited	89.8	29501.	47.6	39.68	8246	4	.034	26.2	72.09	22974	2	.034
Acrylic Acid	83.2	374.4	1.46	1032.53	13984	5	.029	.63	2409.23	30526	5	.029
Bromine	16.0	22549.	22.4	37.17	3974	8	.677	12.6	66.07	11312	5	1.82
Carbon Tetrachloride	55.6	12050.	56.2	28.44	5113	316	.323	29.3	54.36	13592	166	4.91
Chloroform	58.6	20942.	57.9	25.7	5032	1166	0.0658	31.9	46.7	14091	642	0.789
Chloroprene	84.6	32482.	56.2	21.25	6274	565	0.273	30.1	39.68	17077	303	1.7
Chlorosulfonic Acid	43.7	40.0	.236	6747	7953	200	.030	.100	24689	17307	200	.030
Dimethylhydrazine, unsy	97.8	16334.	27.8	51.2	6765	29	3.4	14.1	25.4	17578	25	32.5
Ethylene Dichloride	68.5	8210.9	33.6	55.01	7278	545	.423	16.6	111.34	18393	500	2.7

*The shipment volumes indicated are nominal values used for risk calculations. The actual shipment volumes may vary depending on the loading conditions, tank car, and outage requirements. Please refer to 49 CFR §173.24b for outage requirements.

Chemical Name	Shipment Vol. in a Tank Car (m³)	Vapor Pressure at 20°C (N/m²)	Liquid Pool Evaporation Under Neutral Weather Conditions (Atmosphere D)					Liquid Pool Evaporation Under Stable (F) Atmospheric Conditions				
			Evaporation Rate (kg/s)	Duration of Evaporation (min)	Vapor Concentration at Pool Edge (ppm)	Haz. and Concentration (ppm)	Toxic Haz. and Area (sq. km.)	Evaporation Rate (kg/s)	Duration of Evaporation (min)	Vapor Concentration at Pool Edge (ppm)	Haz. and Concentration (ppm)	Toxic Haz. and Area (sq. km.)
Ethyleneimine	90.8	22017.	29.5	50.97	10314	59	2.3	16.0	93.97	28366	50	34.
Hydrogen Chloride *	60.2	4127500.	n/a	n/a	n/a	n/a	21.7	n/a	n/a	n/a	n/a	80.6
Hydrogen Peroxide	68.2	180.7	.20	9053.75	19946	38	.027	.086	21055.23	42161	38	.027
Isoprene	128.9	60465.	130.	11.09	5624	150	.409	76.6	18.83	16762	119	.9540
Methyl Bromide	39.6	183060.	n/a	n/a	n/a	1000	0.01	n/a	n/a	n/a	1000	0.02
Nitric Acid, red fuming *	52.1	6348.2	8.67	183.40	8506	50	.022	4.04	393.59	20286	50	.022
Phenol, (Carbolic Acid)	84.8	214.6	.92	1676.84	8597	125	.031	.377	4092.02	18222	125	.031
Propylene Oxide	106.8	34879.	54.3	49.74	7345	1206	.1705	30.4	88.85	20791	1000	1.13
Sodium Hydroxide (NAOH)	58.1	0.0296	1.8	1083.73	9817	73	.022	7.4	263.61	20288	73	.022
Styrene Monomer inhibited	104.1	592.6	5.7	307.25	11787	2500	.153	2.48	706.18	26304	2500	2.54
Sulfur, molten	47.7	0.0003	n/a	n/a	n/a	300	.083	n/a	n/a	n/a	300	.156
Sulfuric Acid (98%) *	51.0	0.0042	1.4	1.12e08	10144	13	.018	5.7	274.27	21979	13	.018
Oleum (35 SO3)	40.3	25466.	1.59	968	321.	17.5	.2812	.655	2351	683	17.5	1.213
Trichloroethylene	63.8	7698.4	33.5	46.97	6094	639	.1846	15.6	100.87	15393	500	1.37
Vinyl Chloride *	124.9	340110.	n/a	n/a	n/a	n/a	N/A	n/a	n/a	n/a	n/a	N/A

*The shipment volumes indicated are nominal values used for risk calculations. The actual shipment volumes may vary depending on the loading conditions, tank car, and outage requirements. Please refer to 49 CFR §173.24b for outage requirements.

Figure 4.1

Determination of Liquid Pool and Toxic Vapor Hazard Areas for Materials with Extremely Low Evaporation Rates

Pool formed is assumed .01 m deep and contains entire contents of tank car

Hazard area contained within this line

D

A_1 D A_2

2D

Total Down Wind Distance

POOL h = .01 m

➡ U_{WIND}
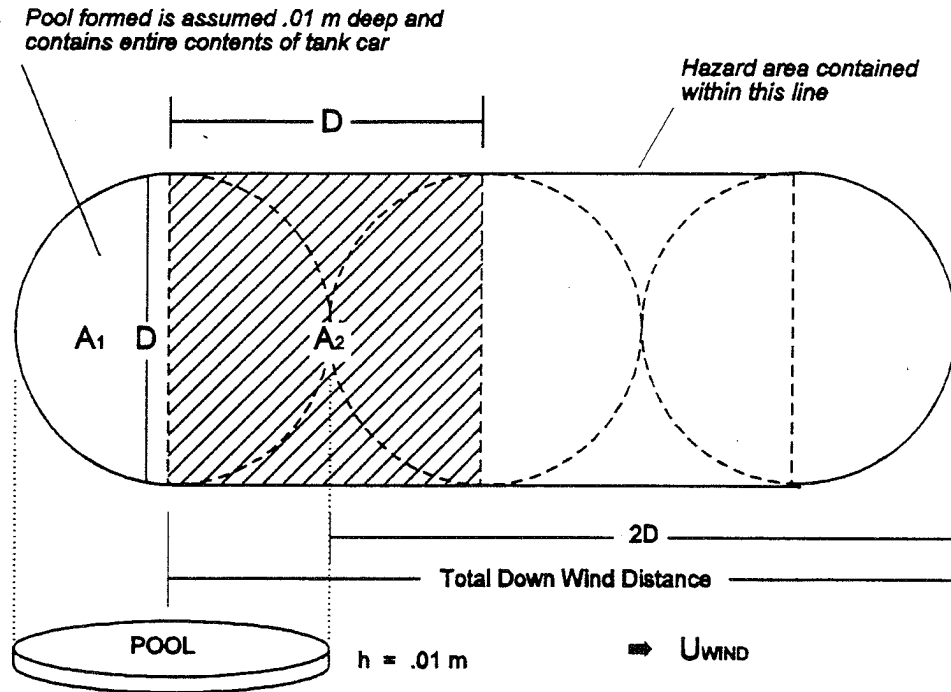
V = Volume of chemical in tank car = pool volume = $\Pi/4\ D^2 h$

$$D = \sqrt{\frac{4V}{\Pi h}} \qquad h:\ 0.01\,m$$

Total area for toxic liquid material spills = $2A_1 + 2A_2 = 2(A_1 + A_2)$

$$A_1 = \tfrac{1}{2}\ \tfrac{\Pi}{4}\ D^2\ ,\quad A_2 = D^2 \quad \therefore\ Hazard\ Area\ = D^2\ (\tfrac{\Pi}{4} + 2)\ =\ \frac{4V}{\Pi h}\ (\tfrac{\Pi}{4} + 2)\ =\ \frac{V}{h}\ (1 + \tfrac{8}{\Pi})$$

$$= 100\ *\ V\ (1 + \tfrac{8}{\Pi})\ ,\ h\ =\ .01\,m$$

$$= 354.6\ *\ V\ m^2$$

$$= 3.54\ *\ 10^{-4}\ *\ V\ km^2$$

It is also seen from Table 4.2 that for a few other chemicals, the hazard area is essentially restricted to the liquid pool area because the vapor concentration at the downwind edge of the pool is lower than the limit concentration for hazard (after adjusting the IDLH for the exposure time). This is so even though the absolute vapor pressure is relatively large (see for example, Acetaldehyde in Table 4.2). In these cases, the hazard area is indicated as "N/A" in Table 4.2.

4.2.3 Toxic Vapor Hazard Areas from Liquid Chemicals with Moderate to High Evaporation Rates

When the vapor evolution rate from a liquid chemical pool is relatively high (» 1 kg/s) and the level of hazard concentration of vapor is low it is necessary to calculate the toxic vapor hazard area using a vapor dispersion model which takes into account the pool size, evaporation rate, density, and other characteristics of the chemical vapor, atmospheric and wind conditions, etc. A dispersion model, which considers the vapor density (relative to that of the ambient air) was developed and is given in detail in Appendix B. The essential features of this model are described below.

The vapors generated over the different parts of the pool area are entrained by the prevailing wind[3]. The developed model assumes that the chemical vapor together with the ambient air issues out at the down wind edge of the pool through a "source window" of width equal to pool diameter. The pool evaporation rate, the air entrainment rate, thermodynamic conditions of vapor (such as temperature, vapor concentration, etc.) at the down wind pool edge source window are calculated by the pool evaporation model described in a report by Raj and Morris, 1987. The model described in Appendix B simulates the dispersion of the vapor air mixture issuing out of the "source window." If the vapor air mixture exiting from the source window is heavier than air, it will disperse close to the ground. The expansion of the vapor plume in the cross wind direction is effected, initially, by the higher than air density (gravity flow) and subsequently by the atmospheric turbulence. In the case of a near neutral density vapor air mixture exiting from the "source window" atmospheric turbulence disperses the plume and dilutes the vapor concentration. These physical phenomenon are expressed mathematically in the model described in Appendix B. The output of the model include the dimensions on the ground (footprint) of the area contained within the hazard concentration contour.

The results obtained by exercising the model detailed in Appendix B are indicated in Table 4.2 for two specific conditions of weather, namely, neutral atmosphere (D) and stable atmosphere (F). It is seen that toxic areas are, in general, larger in the case of stable atmosphere than in neutral atmosphere. Also the toxic areas can range from 10^{-2} km^2 to about 3 sq. km.

The model described above has been incorporated into the risk analysis program developed in this project.

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[3]Figure B.1 in Appendix B shows schematically, the physical situation describing the evaporation of vapors from a liquid pool and their subsequent dispersion.

4.3   Models for Polymerization or Self-Reaction of Chemicals

The principal hazard posed by run away reactions (self reactions or polymerization of monomers) of chemicals inside a tank car is the explosion caused by over pressure inside the tank car. Depending on the characteristics of the chemical and the quantity of chemical contained in the tank car, the severity can range from a release of chemical (vapor or liquid) from the safety relief device to an explosion in which pieces of the tank car metal are hurled several hundreds of meters.

There are three important parameters that a hazard model needs to calculate if the potential severity of the thermal explosion hazard is to be evaluated. These parameters include:

1.   A dimensionless critical parameter which will indicate whether the conditions to which the tank car containing the chemical under consideration is subject will interact in such a way as to precipitate a self-heating explosion.

2.   The induction time. That is, the duration of time over which the temperature of the chemical increases from the ambient temperature to a critical temperature. The greater the induction time, the larger the margin of safety for the emergency responders to undertake corrective action to suppress the self-heating reaction.

3.   The total energy released by the run away reaction (which depends on the quantity of chemical inside the tank car and the value of heat of reaction/polymerization) determines the magnitude of the explosion.

In the following sections, we discuss first the physical situation that may lead to a polymerization/self-heating reaction of a chemical in a tank car. Subsequently, important mathematical analyses are presented and methods for solving the equations are discussed.

4.3.1   Description of Physical Situations Which Lead to Polymerization Hazards

In general, a chemical with a potential for polymerization or self-heating is transported in tank cars with a suitable inhibitor or buffer mixed in with the chemical. The self-heating reactions may be initiated due to several reasons including (i) loss of inhibitor[4]; (ii) steam cleaning of tank cars

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[4]Zolotorofe (1994) discusses the conditions under which this can happen in the case of acrylic acid.

containing some left over chemical[5]; or (iii) heating of the tank car by an external fire. In the case of loss of inhibitor, the reaction is self-initiated and could become a runaway reaction if cooling is inadequate or the required venting capacity exceeds the venting capacity of the valve. A model for acrylic acid polymerization reaction is discussed in Section 4.3.3. When the tank car is exposed to an external fire, the heat input to the chemical raises the chemical temperature. The increased temperature will result in a higher self-heating/polymerization reaction rate which may lead to a runaway reaction if cooling of the contents is not adequate. Figure 4.2 represents schematically the scenario of exposure of a part of the tank car surface to an external fire. A model describing the heating up of the chemical and its temperature change with time due to heat transfer and self-heating effects is discussed below.

4.3.2 Equations and Parameters Describing the Self-Heating/Reaction Process

Extensive literature exists on the phenomenon of material self-heating and its modeling for different types of environmental conditions *(Churney and Garvin, 1980)*.[6] It is, therefore, intended in this report to only summarize certain important equations, parameter definitions, and results.

The simplest situation modeled is that of a material (say, the self-heating bulk liquid chemical in a tank car) suddenly exposed to an external temperature higher than its current stable temperature. Assuming a homogeneous temperature within the mass of the material and that the material thermally interacts with the environment (i.e., it exchanges heat with the outside environment) the following energy balance equation is written.

$$M C_P \frac{dT}{dt} = Q\dot{r} - hA_s (T - T_o)$$

(4.1)

where

M = Total mass material

C_P = Specific heat of material

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[5]A tank car with isoprene residue which was being steam cleaned exploded at the cleaning rack in the Rescar Tank Car facility, Longview, TX, on December 30, 1987. The manway bonnet fell through the roof of a building 175 feet away from the tank car.

[6]A review of the different models is indicated in the cited report. Also, this report's focus is on the self-heating problems in chemicals transported and exposed to different conditions.

Figure 4.2

Exposure of a Part of Tank Car Surface to a Pool Fire and Consequent Heating of the Chemical in Tank Car
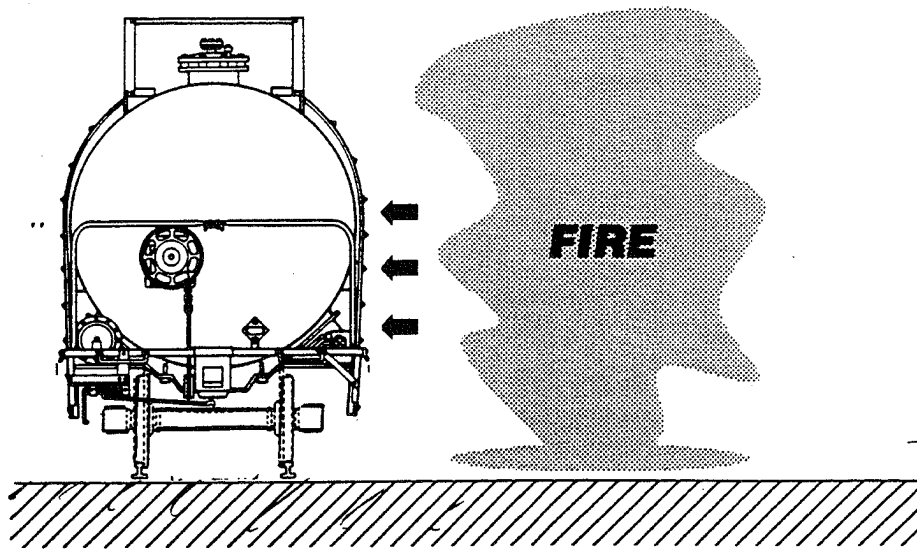
T = Instantaneous (bulk) temperature of material

Q = Heat of polymerization or reaction per unit mass of material reacting

$\dot{r}$ = Reaction rate. That is, the mass rate of consumption of chemical reactant per unit time.

A_s = Surface area for heat transfer

T_o = Ambient temperature

Assuming an Arrhenius type of (zeroth order) reaction the reaction rate can be written as

$$\dot{r} = -M \frac{dn}{dt} = M\, f(\eta)\, A_F\, e^{-\frac{E}{RT}} \tag{4.2}$$

where

η = Fraction of reactant remaining at any time

$f(\eta)$ = A function of η

A_F = Pre-exponential Arrhenius frequency factor

E = Activation energy

R = Chemical specific gas constant

Certain non-dimensional parameters are defined as follows to facilitate solving equation (4.1) using the reaction rate formula in equation (4.2).

$$\delta = \frac{M\, Q\, f(\eta)\, A_F\, e^{-\frac{E}{RT_o}}}{h\, A_s \left(\dfrac{RT_o^2}{E} \right)} = \frac{\text{Heat release rate at } T_o}{\text{Cooling rate for a characteristic temperature difference}} \tag{4.3a}$$

$$\theta = \frac{T - T_o}{(R T_o^2 / E)} = \text{Dimensionless temperature} \qquad (4.3b)$$

$$t_{ch} = \frac{M \, C_P \, T_o}{h \, A_s \, T_o} = \frac{\text{Enthalpy of material at } T_o}{\text{Cooling rate for a temperature difference of } T_o} \qquad (4.3c)$$

$$\tau = \frac{t}{t_{ch}} = \text{Dimensionless time} \qquad (4.3d)$$

Assuming that

1. The function $f(\eta)$ is a constant; and

2. the temperature of the material is **NOT** substantially higher than T_o

equation (4.1) is written in dimensionless form (using equations (4.2) and (4.3)) as

$$\frac{d\theta}{d\tau} = \delta \, e^\theta - \theta \qquad (4.4a)$$

with

$$\theta = \theta_i \quad at \ \tau = o \qquad (4.4b)$$

It can be shown (see Churney and Garvin, 1980) that for

$$\delta > \delta_{cr} = e^{-1} \qquad (4.5)$$

the temperature θ rapidly increases resulting in a thermal explosion. When the value of δ is close to the critical value (δ_{cr}) as given by equation (4.5), a rough measure of the temperature at which the thermal explosion is initiated is given by

$$T_{EX} \text{ (at explosion)} \approx T_o + \frac{2 R T_o^2}{E} \qquad (4.6)$$

The duration of time it takes the material to heat up from initial temperature T_i to T_o (when exposed to the external temperature, $T_o > T_i$) is termed the "warm-up" time. This warm up time is given by

$$t_{warmup} \approx 2 t_{ch} \equiv \frac{2 M C_P}{h A_s} \qquad (4.7)$$

"Induction time" is defined as the duration it takes for the material to reach a temperature T_{EX} from the time the material temperature has attained T_o. The induction time is a function of the value of δ, with induction time being very close to zero when δ approaches the value δ_{cr}. The induction time is approximated by

$$t_{induction} = \left[\frac{1}{\delta} - \frac{1}{\delta_{cr}} \right] \frac{M C_P}{h A_s} \qquad (4.8)$$

If t_{ex} is the total time for initiation of a thermal explosion from the time the material is "exposed" to an external high temperature then from the above two equations we can see that

$$t_{ex} = \left[2 + \frac{1}{\delta} - \frac{1}{\delta_{cr}} \right] \frac{M C_P}{h A_s} \qquad (4.9)$$

Where δ is the thermal explosion parameter defined in equation (4.3a) and δ_{cr} is the critical value for δ indicated in equation (4.5).

The above analysis is conditioned on the assumption that the critical (explosion) temperature T^* is higher than the ambient temperature T_o which the material is exposed. T^* is calculated by solving the implicit equation (4.3a) in which the left hand side of the equation is replaced by a value e^{-1} (i.e., δ_{cr}) and on the right hand side all T_o s are replaced by T^*.

Given a material whose properties (i.e., C_p, Q, A_F, E, and R) are known, the environmental conditions are specified (h, T_o, T_i) and the quantity and dimensions (M, A_s) are provided, then using the above set of equations, one can calculate, (i) whether a critical condition for self-heating will occur or not, and (ii) if it does occur, the approximate time for criticality to occur.

In applying the above model to the case of a polymerizable material in a tank car which is exposed to an external fire the following issues and phenomena are to be noted.

1. Not all thermodynamic properties required to perform the above discussed criticality condition assessment are available for all chemicals exhibiting self-heating or polymerization phenomenon.

2. The bulk (uniform temperature) analysis indicated above may be applicable only approximately to the case of a liquid in a tank car. This is because of: (i) finite thermal conductivity of the liquid; (ii) internal circulation created by heating of liquid over the hot tank car wall and the effects of buoyancy; (iii) mass loss due to venting from the tank car; and (iv) non uniform heating due to exposure of only a part of the tank car walls to an external fire (unless the tank car is fully engulfed in the fire).

3. Thermal explosion may be initiated in a small pocket of liquid which may be overheated and which attains a significantly higher temperature compared to the liquid bulk temperature. In view of this the values calculated for the criticality condition and the explosion time duration, respectively from equations (4.3a), (4.5), and (4.9), may not be conservative. That is, the mass of tank car material that may be subject to overheating and suffering the thermal explosion phenomenon may be substantially smaller than the total mass of the chemical in the tank car. Hence, explosions may occur sooner or at a lower "ambient" fire temperature. Detailed analysis of the real situation is extremely complex and is beyond the scope of this study.

4.3.3 Model for Thermal Explosion Resulting from Loss of Inhibitor

Some materials are unstable even at room temperature. The rail transportation of these chemicals is possible only because the self-reaction can be quenched effectively by the addition of small quantities of inhibitors to the chemical. For example, acrylic acid is typically inhibited with 200 ppm of methyl ether hydroquinone (MEHQ).

The effectiveness of inhibitors may be reduced if the distribution of inhibitor within the chemical is not uniform or the overall inhibitor concentration is decreased. The effectiveness of inhibitors can also be reduced when the temperature of the chemical is increased, say, due to exposure to a fire. Also, in some cases such as MEHQ, the presence of dissolved oxygen is necessary for the inhibitor to be effective. Properly aerated acrylic acid with MEHQ is known to be stable at 25 °C for several years. At a temperature of 54 °C (approximately the temperature of tank car wall reached when it is sitting in bright sun in southwestern U.S.) a properly inhibited acrylic acid is expected to be stable for 75 days (Zolotorofe, 1994). It is theorized that an insulated rail tank car containing acrylic acid with the correct amount of inhibitor exposed to an external fire (with a nominal heat input rate equivalent to the rate of temperature rise of the bulk liquid at 0.5 °C/min) will begin to polymerize at about 120 °C and lead to an explosion. The time to onset of explosion is about 3 hours (Zolotorofe, 1994).

A model for the initiation of polymerization reaction in materials such as acrylic acid due to the decrease in dissolved oxygen and its effect on the effectiveness of the inhibitor is discussed by Levy and Lakin (1993). The decrease in dissolved oxygen concentration is assumed to result from the increase in the bulk liquid temperature as a result of exposure to an external fire. The objective of the model is to determine the time duration of exposure to the fire within which the oxygen concentration decreases to such a value as to initiate a runaway polymerization reaction. The model is based on the following assumptions:

♦ oxygen consumption rate as a function of temperature can be represented by an Arrhenius type equation (see equation (4.10) below)

♦ the temperature increase of the bulk liquid (say, in a tank car exposed to an external fire) is proportional to the duration of exposure (see equation (4.11) below)

♦ the oxygen concentration everywhere within the bulk of the fluid is the same (i.e., homogenous mixture). Also the state of the bulk liquid can be represented by a single temperature at every instant of time.

Based on the above assumptions, the following equations are developed.

$$\frac{dc}{dt} = - A_F \ e^{-\frac{E}{R_u T}} \tag{4.10}$$

$$T = a + bt \tag{4.11}$$

where,

c   =   Dissolved oxygen concentration (mol/m^3)

A_F =   Arrhenius frequency factor
(= 9.47 x 10^{11} kmol/m^3 s for dissolved oxygen depletion rate in acrylic acid)

E   =   Activation energy (J/mol)
(= 131,022 J/mol for oxygen)

T   =   Temperature (K)

R_u =   Universal gas constant
(= 8.314 J/mol K)

The following additional parameters are defined to assist in obtaining the solution to equation (4.10) with equation (4.11).

$$t_{ch} \quad = \quad \text{characteristic oxygen depletion time} \quad = \quad \frac{E}{b \, R_u} \qquad (4.12a)$$

$$\tau \quad = \quad \text{dimensionless time} \quad = \quad \frac{t}{t_{ch}} \qquad (4.12b)$$

$$\alpha \quad = \quad \text{dimensionless constant} \quad = \quad \frac{R_u}{E} a \qquad (4.12c)$$

$$\theta \quad = \quad \text{dimensionless temperature} \quad = \quad T \frac{R_u}{E} \qquad (4.12d)$$

$$A^* \quad = \quad \text{dimensionless Arrhenius factor} \quad = \quad A_F \, t_{ch} \qquad (4.12e)$$

Using the above definitions, equation (4.10) is reduced to

$$\frac{dc}{d\tau} = -A^* \, e^{-\left[\frac{1}{(\alpha + \tau)}\right]} \qquad (4.13a)$$

with

$$c = c_i \quad \text{at} \quad \tau = 0 \qquad (4.13b)$$

It can be shown that the solution to the above equation is given by

$$(c_i - c) = A^* \left[\left((\alpha + \tau) \, e^{-\left(\frac{1}{\alpha + \tau}\right)} - \alpha \, e^{-\frac{1}{\alpha}} \right) + \left(E_1 \left(\frac{1}{\alpha + \tau} \right) - E_1 \left(\frac{1}{\alpha} \right) \right) \right]$$

$$(4.14)$$

4-17

Where E_1 is the exponential integral function (for a definition of this function and its associated properties, see Abramowitz & Stegun (1965), pp. 228, §5.1.1). Using the above equation, the dissolved oxygen concentration (C) at any time t can be calculated.

Levy and Lakin present results for a number of different heating rate assumptions for acrylic acid and dissolved oxygen depletion at different times. It is seen from their results that as heating rate increases the difference in the time duration between when the oxygen concentration is zero and when oxygen concentration is 50% decreases. At heating rates greater than 10 °C/hr there is practically no difference between the time to reach 50% of initial dissolved oxygen concentration and time to reach 0%. That is, the time at which 50% of initial oxygen concentration is reached can be considered to be the time at which thermal explosion occurs.

Figure 4.3 shows the dependence of the "thermal explosion" time on the initial temperature of the bulk liquid and the heating rate (expressed in °C/hr). It is seen that for acrylic acid at an initial temperature of 40 °C (103.4 °F) in an insulated tank car exposed to a fire (approximate heating rate = 20 °C/hr) the thermal explosion time is of the order of 2.5 hours.

In the next section, we discuss a model to determine the consequence of thermal explosion from the perspective of damage assessment and risk analysis.

4.4 Model to Evaluate the Consequences of Thermal Explosion in a Tank Car

When the chemical in a tank car self-heats or polymerizes leading to a thermal explosion, it can be assumed that all of the lading has undergone the reaction. The explosion itself occurs due to the significant heat release which leads to tank car over pressurization and its subsequent bursting. The small mass of the lading vented before a thermal explosion can be neglected in comparison with the mass of the chemical in the tank car. Calculations can then be made of the total explosive yield from a thermal explosion and the consequences can be evaluated. The model presented below addresses these calculations.

4.4.1 Explosive Yield

The total heat released in a thermal explosion which is converted to mechanical energy in propelling metal fragments is[7]

$$Q = Y M_T Q'$$

(4.15)

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[7]neglecting the small amount of energy carried away by venting and the fraction of energy that causes the increase in lading temperature

Figure 4.3

Variation of Thermal Explosion Time with Initial Temperature and Heating Rate for Acrylic Acid
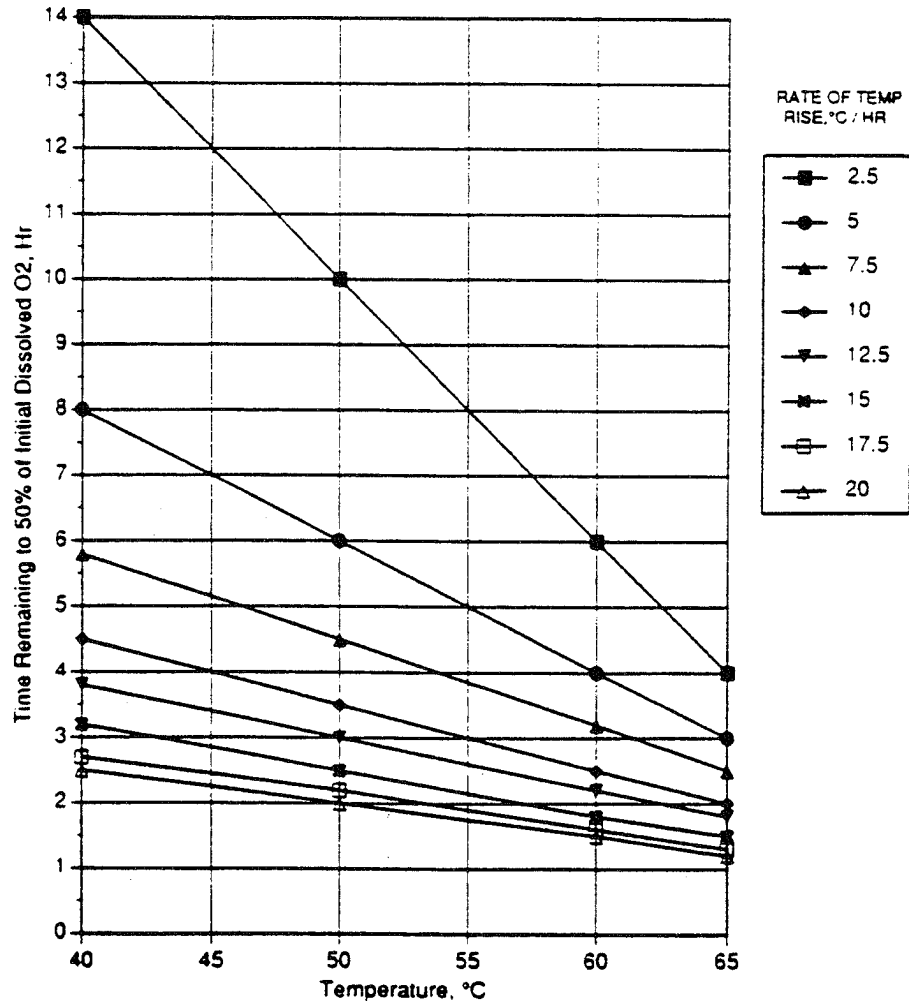
Source: *Levy and Lakin (1993)*

where

Q = Total heat energy converted to explosion[8] (J)

Q' = Heat of polymerization or self-reaction (J/kg)

M_T = Total mass of chemical in the tank car (kg)

Y = Yield: that is, the fraction of the mass in the tank car which participates in the self-heating or polymerization reaction

No data are available from railroad industry experience on which to base the value of Y. However, from hypergolic propellant tests reported by Baker, et al (1977), it is known that 5 to 15 percent of propellant mass reacts. For polymerization in tank cars it is our premise that a yield fraction of 1% to 2% is appropriate.

The energy released will initially pressurize the tank car. When the tank car burst pressure is exceeded, it is likely that the shell of the car will rupture and result in pieces of metal flying in all directions. A part of the energy released is expended in bursting the shell and propelling the metal pieces. The remaining fraction of the energy will manifest itself as a rapidly spreading blast wave. The blast effect may be similar to that from an explosive charge detonation. We consider below the modeling of each of the two phenomena.

4.4.2   Blast Effect Calculation

The "air blast" effects resulting from a thermal explosion in a tank car are determined by calculating the energy released using equation (4.15). Subsequently, the blast caused direct-on-overpressure is calculated at any specified distance as follows:

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[8]For a typical case of acrylic acid transported in a 111A100W1 tank car, we have the following values:

Q'	=	1.0758×10^6 J/kg	=	Heat of polymerization
V	=	23,500 gallons	=	$89\ m^3$
M_T	=	Total mass in the car	=	82×10^3 kg
Y	=	Yield (assumed)	=	0.015
Q	=	Heat of polymerization released	=	1.32×10^9 J
TNT equivalent mass of energy released into the blast			=	316 kg

1. For any specified distance X from the tank car, the non-dimensional distance $\bar{X}$ is determined from the equation

$$\bar{X} = X \left[\frac{P_a}{Q} \right]^{\frac{1}{3}}$$ (4.16)

where P_a = ambient pressure

2. The dimensionless overpressure $\bar{P}$ is obtained from the correlation presented in Figure 4.4.

3. The dimensional overpressure P at distance X is the obtained from the relation

$$\bar{P} = \left[\frac{P}{P_a} - 1 \right]$$ (4.17)

The reflected overpressure due to ground reflection is generally assumed to be twice the direct-on-overpressure. Different magnitudes of overpressure cause different levels and types of damage from structural collapse, human injury, and glass breakage. These overpressure damage criteria were presented in our earlier report (Raj and Turner, 1993). The model for calculating the air blast damage area has been incorporated into the computer program developed for tank car transportation risk assessment.

4.4.3   Fragmentation Damage Assessment Model

The tank shell will rupture when the pressure inside exceeds the burst pressure consistent with the shell plate thickness and the ultimate yield strength of the steel used. Results from tests on pressurizing propellant tanks to destruction have shown that the mass of different size fragments are distributed log normally[9] (Baker, et al, 1977). Also, it is found that the mass (size) distribution of the tank fragments depends on the tank volume, pressure at burst, and to some extent, on the shape of the tank.

S   =   Standard deviation of the log normal distribution of fragment masses t
(=1.695 from experimental data)

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[9]i.e., the probability density distribution of the masses of fragments is a Gaussian when the logarithm of the mass of fragments is the independent variable.

Figure 4.4

Variation Direct-on-Overpressure with Distance for a Blast Wave

$\bar{P} = 4.59 \ (\bar{X})^{-1.17}$

$\bar{X} < 0.7$

$\bar{P} = 0.942 \ (\bar{X})^{-1.90}$

$0.1 \leq \bar{X} \leq 4$

$\bar{P} = 0.321 \ (\bar{X})^{-1.17}$

$\bar{X} > 4$

LEGEND

$\bar{P} = \left[\dfrac{P}{P_a} - 1 \right]$

$\bar{X} = X \left[\dfrac{P_a}{Q} \right]^{\frac{1}{3}}$

P = Overpressure

Q = Energy Released in Blast

P_a = Ambient Air Pressure

X = Dimensional Distance

$\bar{P}$ Dimensionless Direct on Overpressure

$\bar{X}$
Dimensionless Distance

Source: Baker, et al (1977)

4-22
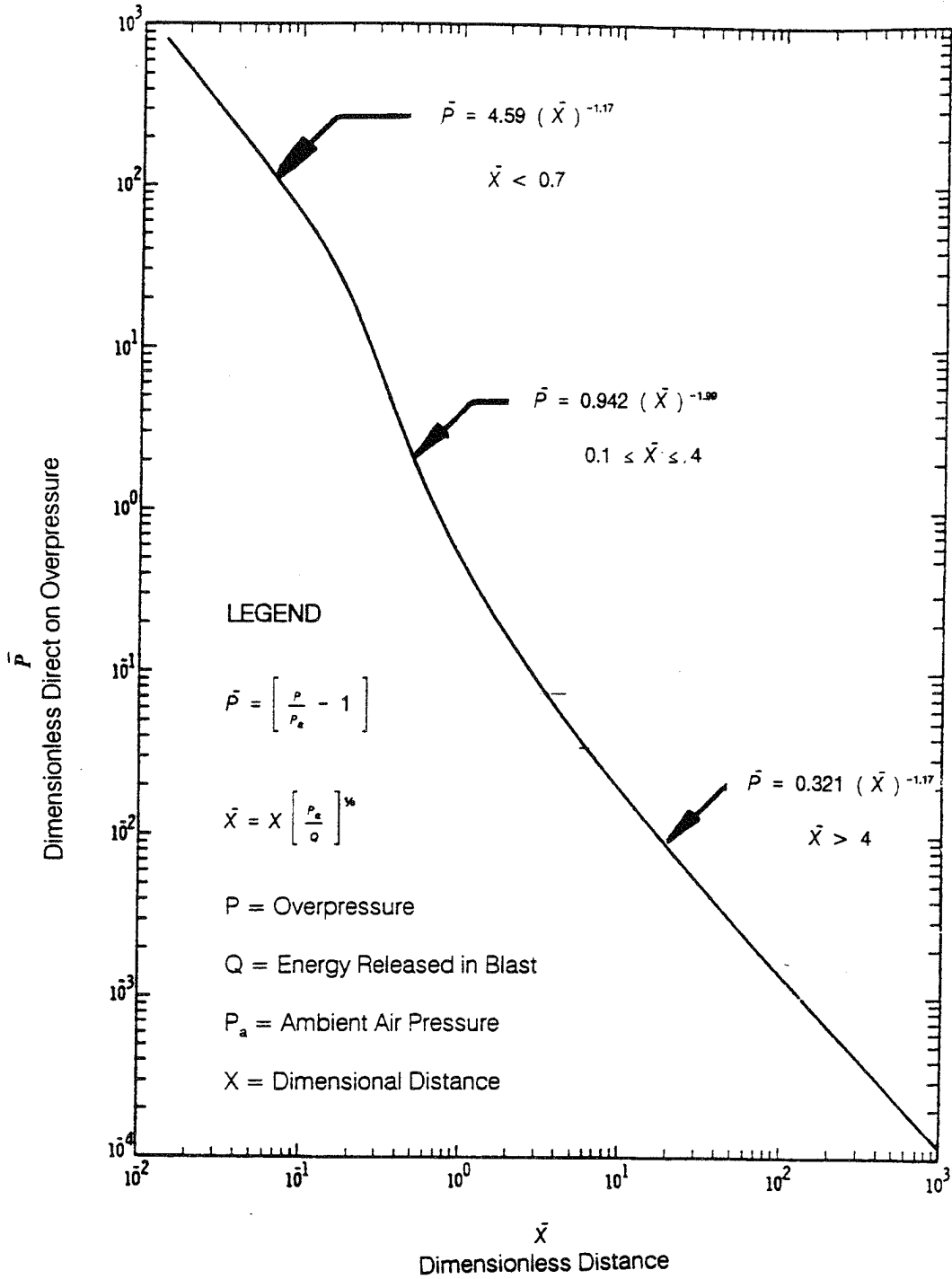
Indicated below are equations to determine the tank car explosion debris characteristics and the distance to which the pieces may be propelled.

Debris Size Distribution. Based on the results presented by Baker, et al (1977) for propellant tank bursts[10], we have developed the following correlation for the mean size (mass) of steel chunks resulting from a tank car rupture.

$$\bar{W} = 0.32 \ Y^{0.871} \tag{4.18}$$

where

$\bar{W}$ = Average mass of the tank car shell debris (kg)

Y = Normalized yield (TNT equivalent mass) (kg)

$$Y = \frac{P_B \ V}{E_o} \tag{4.19}$$

P_B = Burst pressure of tank car (see 49 CFR §179.201-1) (N/m²)

V = Volume within the tank car (m³)

E_o = Energy released in the detonation of a unit mass of TNT (J/kg)
(=4.19 MJ/kg)

The debris size (mass) distribution has been found to follow a log normal distribution. For any specified percentile of confidence (p) the cardinal mass[11] (W_p) of the debris can be found by the formula:

$$W_p = \bar{W} \ e^{(Z_p S)} \tag{4.20}$$

_____

[10]It is noted that the results presented by Baker, et al are applicable to normalized yield values less than 2000.

[11]This is, the probability of finding a debris mass lower than Wp is p.

4-23

where

$\bar{W}$ = mean debris mass (equation 4.18)

Z_p = value of normal parameter for the Gaussian probability = p
[Z_{50} = 0, Z_{90} = 1.28, Z_{95} = 1.645, Z_{99} = 2.33]

p = percentile value

In the next section we discuss the velocity of the projectile and their range.

Fragment Initial Velocity Calculation. The analysis of bursting of a cylinder, initially pressurized by a gas, is extremely complex. It involves the consideration of cylinder strength, cylinder size, gas pressure, and mass of gas in the cylinder. The analysis requires the calculations of strain energy stored in the walls of the cylinder, partitioning of the gas energy into metal strain energy, initial kinetic energy, of fragments, and energy lost by gas escaping through the cracks between the fragments. Baker et al (1977) report a computer program developed to perform the complex calculations. There are no simple formulas by which one can calculate the initial velocities of the fragments. Even the complex code assumes that all fragments formed are identical in shape, size, and mass!

Figure 4.5 illustrates the variation of fragment velocity with mass of the cylinder and internal gas pressure (note that the results are dependent on the initial cylinder diameter; hence, different figures of the type indicated in Figure 4.5 will have to be drawn for other cylinder diameters). The axes of the graph in Figure 4.5 are defined as follows:

a	=	Speed of sound in the gas within the cylinder at standard temperature and pressure	(m/s)	(4.21a)
U	=	Velocity with which the fragments are released due to the tank explosion	(m/s)	(4.21b)
P	=	Internal gas pressure in the cylinder before explosion	(N/m²)	(4.21c)
P_o	=	Ambient pressure	(N/m²)	(4.21d)
M_{os}	=	Mass of gas inside the cylinder at standard temperature and pressure	(kg)	(4.21e)
M_t	=	Mass of the tank metal confining the gas (i.e., only that part of the tank that is likely to fragment)	(kg)	(4.21f)
$\bar{U}$	=	U/a = Dimensionless fragment initial velocity		(4.21g)
$\bar{P}$	=	P/P_o = Dimensionless gas pressure		(4.21h)

Figure 4.5

Initial Velocity of Fragments from a Cylinder Tank Gas Explosion

$M_{os}/M_t = 1.40 \times 10^{-1}$

1.40×10^{-2}

4.67×10^{-2}

4.67×10^{-3}

1.40×10^{-3}

4.67×10^{-4}

Cylinder Diameter = 1.52 m

$\bar{U}$

$\bar{P}$
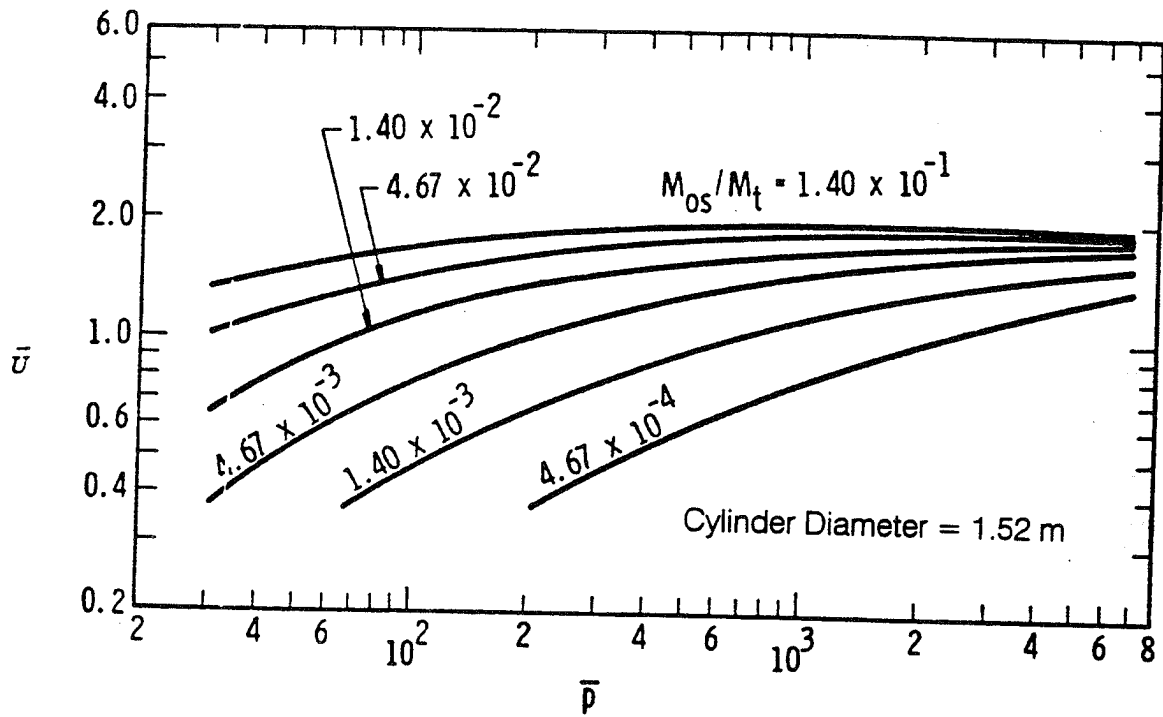
Source: Baker, et al (1977)

The procedure by which the fragment velocity can be calculated is illustrated in the numerical example in Section 4.4.4.

Fragment Range. The distance to which a piece metal fragment from the tank car is hurled depends on a number of factors including the size, shape, initial velocity, and the angle of release of the piece with respect to the horizon. The range will be particularly affected by the shape. The motion of the fragment and its trajectory in air depends on whether the object is: disk-like, in which case it may sail like a Frisbee; flat but tumbling, in which case the drag on the body is significant, limiting its range; or is some what spherical, in which case a "drag surface" is presented to the air in the direction of its motion, limiting the range significantly.

Figure 4.6 shows a typical "range diagram" in which the distance to which fragments of different areal density are hurled is indicated for different angles of release, all fragments being released at the same velocity. The results indicated in Figure 4.6 specifically refer to disk-like fragments (with a diameter to thickness ratio of 10) being released at 200 m/s. Other results such as those indicated in this figure can be developed for other object shapes, initial velocities, and aspect ratios. A number of these types of figures are presented by Baker et al (1977). Unfortunately, calculation of the results indicated in Figure 4.6 involves the use of a complex computer code (which was not accessible in this study).

In the next section, we illustrate the use of the above equations and graphical results for the specific case of a tank car explosion.

4.4.4   Numerical Example

As an example, we consider the application of the above equations to the hypothetical case of a DOT111A tank car suffering a thermal explosion. The size of fragments, their initial velocity, and range are calculated below. The values for the various parameters assumed are as follows:

DOT111A Car Details.

D	=	Internal shell diameter	=	110 inch	=	2.79 m
t	=	Shell thickness	=	7/16"	=	1.11×10^{-2} m
V	=	Internal (water volume)	=	23,500 gallon	=	89 m^3
σ	=	Ultimate tensile strength of shell steel plate	=	70,000 psi	=	4.83×10^8 N/m^2
ρ_s	=	Density of Steel Plate			=	7800 kg/m3
P_B	=	Calculated burst pressure			=	3.84×10^6 N/m^2

Figure 4.6

Range of Tank Explosion Fragment with Size and Release Angle
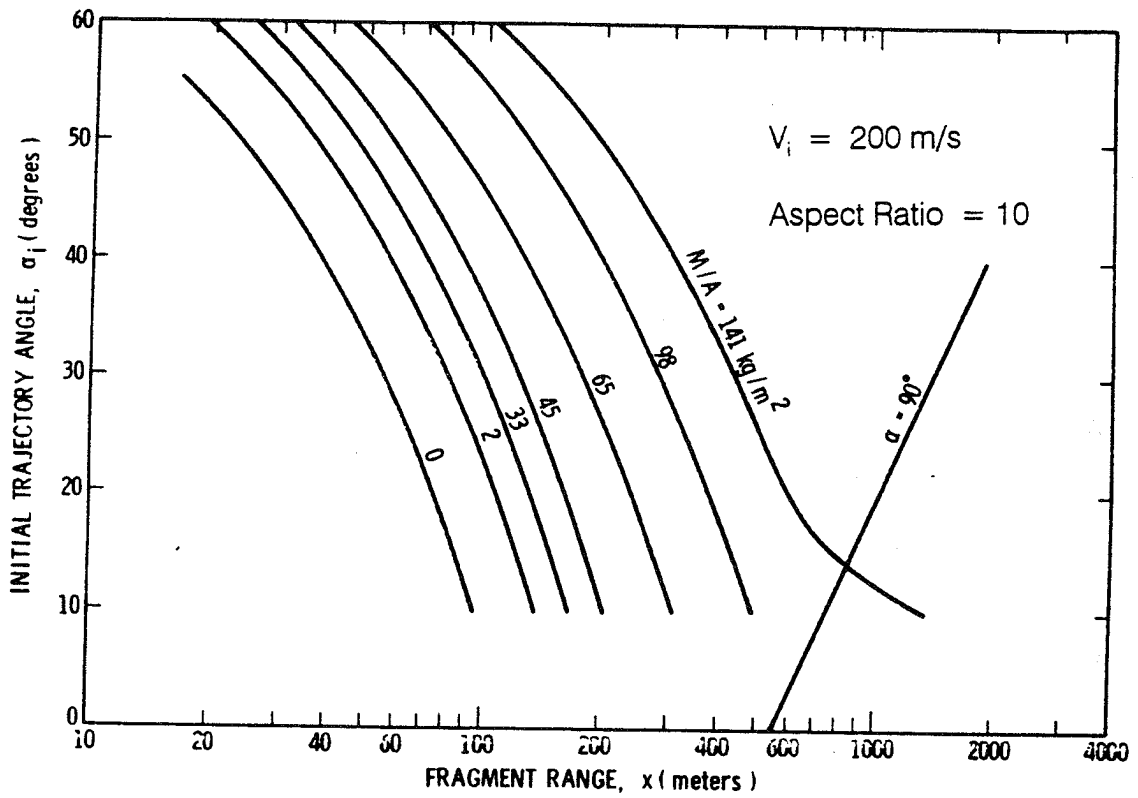
Source: Baker et al (1977)

P_B	=	Specification burst pressure (49 CFR §179.201-1)	=	500 psi	=	3.38×10^6 N/m^2
L	=	Length of tank car	=	37 ft	=	11.3 m

Debris Size.

Y	=	TNT mass equivalent t yield due to tank bursting (equation 4.19)	=	$\dfrac{3.38 \times 10^6 \times 89}{4.19 \times 10^6}$	=	71.8 kg
$\bar{W}$	=	Mean mass of fragment (equation 4.18)	=	$0.32 \times 71.8^{0.871}$	=	13.2 kg
W_{90}	=	90th percentile fragment mass (from equation 4.20)	=	$13.2 e^{(1.28 \ast 1.695)}$	=	115.6 kg

Initial Projectile Velocity. Assuming that the entire tank car is filled with vapors[12] at burst pressure we have:

ρ_a	=	Density of gas (air) in the tank car at 500 psig and 125 °C	=	31 kg/m^3
$\rho_{a,s}$	=	Density of air at standard temperature and pressure		=	1.2 kg/m^3
M_{os}	=	$V \rho_a$	=	89×1.2	=	106.8 kg
M_t	=	Mass of Steel	=	$\pi (2.79 \times 11.3 + 2.79^2/4) \times 1.11 \times 10^{-2} \times 7800$	=	9105 kg

Hence,

$$M_{os}/M_t = 1.2 \times 10^{-2}$$

Also,

$$\bar{P} \text{ (equation 4.21h)} = 34$$

---

[12] It is very obvious that in a real tank car at burst condition, over 95% of volume is filled with liquid. No analysis is available to describe the burst of a liquid filled tank and the subsequent motion of the fragments. Hence, we use the gas filled tank burst analysis result.

and,

a   =   Sonic velocity in air   =   340 m/s

From Figure 4.5, we get

$\bar{U}$ =   0.59

Hence,

U   = $a\bar{U}$ =   200 m/s

We consider now the hurling range for a piece of metal whose size and mass are consistent with the mean debris size ($\bar{W}$), i.e., 13.2 kg.

d   =   Diameter of the "average"   = $\left[\dfrac{4 * 13.2}{\pi * 1.11 \times 10^{-2} * 7800} \right]^{\frac{1}{2}}$ =   0.44 m
          fragment (of thickness t)

          Aspect ratio of the disk   =   d/t   =   40

          Mass per unit area of disk (M/A)   = $13.2/(4 * 0.44^2)$ =   86.8 kg/m^2

Assuming a 30° angle of initial trajectory, from Figure 4.6[13] we get,

          Distance to which a 13.2 kg object is hurled   =   270 m

Similar calculation for the 90th percentile mass fragment (i.e., W = 115.6 kg) leads to the same distance if the same initial velocity is assumed. However, since the fragment is more massive, we can assume a release velocity inversely proportional to the square root of the mass relative to the mean size fragment. Based on this, it can be shown that:

$$X_{90} = X_{50} * \left[\frac{U_{90}}{U_{50}} \right]^2$$ (4.22)

---

[13]Since a diagram for an aspect ratio 40 is not available, we have used the largest aspect ratio value curves from Baker, et al (1977)

where

X_{90} = distance to which the 90th percentile mass is hurled

X_{50} = distance to which the average size fragment is hurled

U_{90} = initial velocity of 90th percentile mass

U_{50} = initial velocity of the average mass fragment

Using the above equation, it can be shown that the 90th percentile mass (115 kg) will be hurled to a distance of about 35 m.

Chapter 5

Risk Analysis Results

5.1 Introduction

In the previous report *(Raj and Turner, 1993)* were discussed the details of the MIL-STD-882B classes of frequency of occurrence of hazardous events and categories of hazard consequences. Also discussed in the report were the equivalence between the numerical values calculated from classical risk analysis for annual probabilities of occurrence of accidental events and hazard consequence and MIL-STD-882B categories. Details of probability calculations for tank car accidents with different levels of severity were provided. The methods by which the variations in tank car puncture size distribution, the population density distribution, and the occurrence of other (stochastic) environmental conditions were considered in the risk assessment and have been described. Hence, these descriptions are not repeated in this report. However, for the convenience of the reader, the "Undesired Event Probability" categories in MIL-STD-882B and their definitions are indicated in Table 5.1. In Table 5.2 the "Undesired Event Severity" categories are shown. The "Risk Assessment Matrix" which illustrates the various risk acceptability conditions is shown in Figure 5.1.

In this chapter, we discuss the application of the Risk Analysis approach developed previously to study the chemicals identified in Chapter 3. Risk profiles for a selected set of the study chemicals which exhibit either toxic vapor hazards, fire thermal radiation, or combustion explosion hazards are presented. An approach has been indicated for performing risk analysis for the case of hazardous materials which exhibit polymerization and/or self-heating caused thermal explosion hazards. Complete risk results for polymerizing chemicals in the form of risk profiles are not presented because of lack of pertinent data on chemical properties, as well as due to the difficulty in evaluating the consequences (for use in a risk analysis) of tank car pieces being hurled in a thermal explosion.

Table 5.1

Undesired Event Probability Categories

CATEGORY	LEVEL	SPECIFIC EVENT
A	Frequent	Not an unusual event, could occur several times in annual operations.
B	Probable	Event could occur several times in the lifetime of the system.
C	Occasional	Expected to occur at least once in the lifetime of the system.
D	Remote	Event is unlikely to occur during the lifetime of the system.
E	Improbable	Event is so unlikely that it is not expected to occur in the lifetime of the system.

Table 5.2

Undesired Event Severity Categories

CATEGORY	SEVERITY	CHARACTERISTICS
I	Catastrophic	Death to person or employee, loss of system.
II	Critical	Severe injury to public or employee, or major system damage.
III	Marginal	Minor injury not requiring hospitalization or the hazard present does not by itself threaten the safety of the public. Also minor system damage.
IV	Negligible	Less than minor injury. Does not impair any of the critical systems.

Figure 5.1

Risk Assessment Matrix

Frequency of Occurrence	Undesired Event Categories			
	I Catastrophic	II Critical	III Marginal	IV Negligible
(A) Frequent	IA	IIA	IIIA	IVA
(B) Probable	IB	IIB	IIIB	IVB
(C) Occasional	IC	IIC	IIIC	IVC
(D) Remote	ID	IID	IIID	IVD
(E) Improbable	IE	IIE	IIIE	IVE
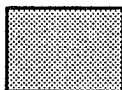
Risk Index

IA, IB, IC, IIA, IIB, IIIA	▨	Unacceptable
ID, IIC, IID, IIIB, IIIC	▨	Unacceptable (Management Decision Required)
IE, IIE, IIID, IIIE, IVA, IVB	▨	Acceptable With Review by Management
IVC, IVD, IVE	▨	Acceptable Without Review

The risk assessment procedure developed in our previous study is quantitative in its approach. The risk results are calculated in numerical terms of annual probabilities of occurrence of accident events, and consequence impacts (in terms of number of people being exposed). To interpret these numerical results in terms of the qualitative, the measures of risk of MIL-STD-882B, TMS developed a correspondence table. These correspondences between numerical probability values and MIL-STD-882B frequency categories are shown in Table 5.3. Similar correspondence between the consequence categories and numerical population exposure values are shown in Table 5.4. *It is to be noted that these correspondences are valid only for the rail transport or hazardous chemicals.* Using these correspondence table values, the numerical probability and consequence results obtained from the risk model are expressed in MIL-STD-882B categories. Details of these results are discussed below.

5.2 Risk Results for Chemicals Posing Toxic Vapor and/or Fire Hazards

5.2.1 Risk Results

In Chapter 3 we discussed the chemical properties and indicated a list of the subset of study chemicals that pose toxic, fire, and combustion explosion hazards (see Table 3.2). The risk posed by the transportation of these chemicals was calculated using the methodology detailed in our earlier report *(Raj and Turner, 1993)*. This methodology was applied to a selected number of the study chemicals. The chemicals for which the toxic vapor, fire, and combustion explosion (if relevant) hazard caused risks were calculated are indicated in Table 5.5. The results of the risk analysis are presented in the form of risk profiles with the Y-axis representing the annual probabilities and the X-axis the consequences.

A risk profile indicates the annual probability of *exceeding* a consequence level (in this case, the exposure of a number of people) given by the abscissa (X coordinate) on the risk profile curve corresponding to the ordinate (i.e., the Y-axis value) representing the probability. In other words, risk profile provides a measure of the cumulative probability value for a consequence to be equal or higher than a specified number value. Any point on the risk curve should read as "the annual probability of occurrence of events which exceed the X level of consequence is Y," where (X and Y are the coordinate points of the chosen point on the risk curve). The region below or to the left of the risk curve represents "inherently" a safer region of operations. Correspondingly the region to the right or top of the risk curve represents less safe operating conditions than the present. It is emphasized that, in general, there are significant errors in the estimation of both the probability of occurrence of events and their consequence impact. Therefore, even though the risk is represented by a line on the diagram, it should be represented by a band. The "width" of this band is probably a factor of 3 to 5 in probability direction and a factor of about 2 in the consequence coordinate.

Table 5.3

Relationship Between Numerical Risk Values and MIL Standard 882B Categories
Probability Categories

MIL Standard Probability Categories	Number of Events Assumed to Occur Per Year*	Mean Frequency of Events #/Year**	Events Occur Approximately Once In	Ratio of Event Frequency to that of "Frequent"	
				Range	Mean**
Frequent	>500	500	a day	1	1
Probable	10 - 500	70	a week	2×10^{-2} to 1	1.4×10^{-1}
Occasional	1 - 10	3	a season	2×10^{-3} to 2×10^{-2}	6.3×10^{-3}
Remote	0.1 - 1	0.3	3 years	2×10^{-4} to 2×10^{-3}	6.3×10^{-4}
Improbable	0.01 - 0.1	0.03	30 years	2×10^{-5} to 2×10^{-4}	6.3×10^{-5}

Table 5.4

Relationship Between Numerical Risk Values and MIL Standard 882B Categories
Severity Categories

MIL Standard Categories	Number of Persons Exposed		Ratio of Exposures to Catastrophic	
	Range*	Mean**	Range	Mean**
Catastrophic	> 1000	1000	1	1
Critical	30 - 1000	170	0.33 to 1	170×10^{-3}
Marginal	1 - 30	6	10^{-3} to 3.3×10^{-1}	5.5×10^{-3}
Negligible	≤ 1	< 1	$< 10^{-3}$	$< 10^{-3}$

*TMS' definitions
**Represents the logarithmic mean of the extremum values of the range.

In this project, several different combinations of tank cars and chemicals (from the study list indicated in Table 3.1) were considered and the risk profile for each combination was generated. Not all combinations are realistic nor are some of the combinations allowed under the 49CFR Regulations. However, the purpose of the exercise was to determine the *extent of reduction* in risk that may be realized if a (study) chemical is transported in a least protected car and in an extremely well protected car. A selected sample of these results is presented in a series of figures presented below.

The risk profiles for several chemicals indicated in Table 5.5 and exhibiting hazards due to toxic vapors, fire, or explosion, are shown in Figures 5.2a through 5.2j. In each figure, two profiles are presented; one for the transport of the identified chemical in an as built DOT 111A specification tank car with no protections, and the other risk profile for the transport of the same chemical in a DOT 105J500W tank car. The latter car has a thicker shell and head materials, is surrounded by jacketed thermal protection, has a shelf coupler, and is equipped with a half height tank head shield. In other words, 105J500W cars are extremely well protected.[1] The principal features of these two tank cars used in our analysis are indicated in Table 5.6. It is seen that, as can be expected, transportation of the studied chemicals in 105J cars provides increased safety (in some cases, by one order of magnitude reduction in probability of release).

An attempt has been made to generate and compare for the case of the risk results in transporting chemicals (with nearly similar behavior properties) in two cars which are more or less identical except for increased shell and head thickness. Figures 5.3a and 5.3b illustrate the results. Figure 5.3a shows the risk profiles for transporting in a single tank car acetone in DOT 111A60W1 tank car and in DOT 105A300W.[2] The features of these two cars are also indicated in Table 5.6. Similar comparative risk profiles for chloroform are shown in Figure 5.3b. The risk profiles for carbon tetrachloride transport are shown in Figure 5.2c. It is again seen that the increase in shell and head thicknesses has significant effect in reducing the risk. Depending on the chemical, however, the frequency category at the lowest consequence category may or may not be different for the case of the two tank cars studied. More detailed discussion on the results are indicated below.

5.2.2 Discussion on the Risk Results

By examining the results presented in Figures 5.2a through 5.2j, the following observations can be made. It is emphasized again that the purpose of executing the model for DOT 111A and DOT 105J500W tank cars was to discern the maximum risk reduction that could be achieved. The discussion below has to be viewed in the context of this premise.

---

[1]It is again noted that the fact that 111A or 105J cars were used in the analysis **does not mean** that either car is required to be used under the 49 CFR.

[2]Realistically, DOT105A100W should have been used in the analysis. However, puncture probability data are not available for this specification tank car. Hence, 105A300W is used for which the puncture probability data are available.

Table 5.5

Subset of Study Chemicals for Which Toxic Vapor, Fire, and Explosion Risks Were Calculated

Chemical Name	Risk Profiles Indicated in:
Acetone Cyanohydrin	Figure 5.2a
Acrolein, inhibited	Figure 5.2b
Carbon Tetrachloride	Figure 5.2c
Chloroprene, inhibited	Figure 5.2d
Hydrogen Peroxide, stabilized	Figure 5.2e
Methyl Bromide	Figure 5.2f
Oleum (30% SO_2)	Figure 5.2g
Propylene Oxide	Figure 5.2h
Styrene Monomer, inhibited	Figure 5.2i
Trichloroethylene	Figure 5.2j

Figure 5.2a

Risk Profile for Acetone Cyanohydrin

Single Tank Car Transport
Annual Probability of Exceeding
Specified Consequence Level

Probable
Occasional
Remote
Improbable

DOT 111A Tank Car
DOT 105J500W Tank Car

Negligible   Marginal   Critical   Catastrophic

Population Exposure Severity
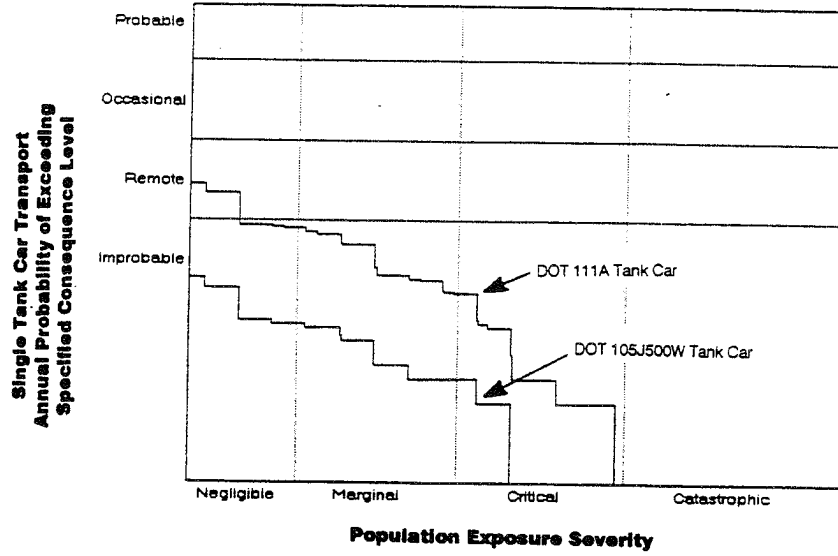
Figure 5.2b

Risk Profile for Acrolein

Single Tank Car Transport
Annual Probability of Exceeding
Specified Consequence Level

Probable
Occasional
Remote
Improbable

DOT 111A Tank Car
DOT 105J500W Tank Car

Negligible   Marginal   Critical   Catastrophic

Population Exposure Severity

5-8

Table 5.3

Relationship Between Numerical Risk Values and MIL Standard 882B Categories
Probability Categories

MIL Standard Probability Categories	Number of Events Assumed to Occur Per Year*	Mean Frequency of Events #/Year**	Events Occur Approximately Once In	Ratio of Event Frequency to that of "Frequent"	
				Range	Mean**
Frequent	>500	500	a day	1	1
Probable	10 - 500	70	a week	2×10^{-2} to 1	1.4×10^{-1}
Occasional	1 - 10	3	a season	2×10^{-3} to 2×10^{-2}	6.3×10^{-3}
Remote	0.1 - 1	0.3	3 years	2×10^{-4} to 2×10^{-3}	6.3×10^{-4}
Improbable	0.01 - 0.1	0.03	30 years	2×10^{-5} to 2×10^{-4}	6.3×10^{-5}

Table 5.4

Relationship Between Numerical Risk Values and MIL Standard 882B Categories
Severity Categories

MIL Standard Categories	Number of Persons Exposed		Ratio of Exposures to Catastrophic	
	Range*	Mean**	Range	Mean**
Catastrophic	> 1000	1000	1	1
Critical	30 - 1000	170	0.33 to 1	170×10^{-3}
Marginal	1 - 30	6	10^{-3} to 3.3×10^{-1}	5.5×10^{-3}
Negligible	≤ 1	< 1	$< 10^{-3}$	$< 10^{-3}$

*TMS' definitions
**Represents the logarithmic mean of the extremum values of the range.

Figure 5.1

Risk Assessment Matrix

Frequency of Occurrence	Undesired Event Categories			
	I Catastrophic	II Critical	III Marginal	IV Negligible
(A) Frequent	IA	IIA	IIIA	
(B) Probable	IB	IIB	IIIB	
(C) Occasional	IC	IIC	IIIC	IVC
(D) Remote	ID	IID		IVD
(E) Improbable				IVE

Risk Index
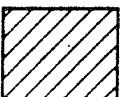
IA, IB, IC, IIA, IIB, IIIA	▒	Unacceptable
ID, IIC, IID, IIIB, IIIC	▨	Unacceptable (Management Decision Required)
IE, IIE, IIID, IIIE, IVA, IVB	■	Acceptable With Review by Management
IVC, IVD, IVE	▨	Acceptable Without Review

Figure 5.2e

Risk Profile for Hydrogen Peroxide

Single Tank Car Transport
Annual Probability of Exceeding
Specified Consequence Level

Probable

Occasional

Remote

Improbable

DOT 111A Tank Car

DOT 105J500W Tank Car

Negligible   Marginal   Critical   Catastrophic

Population Exposure Severity
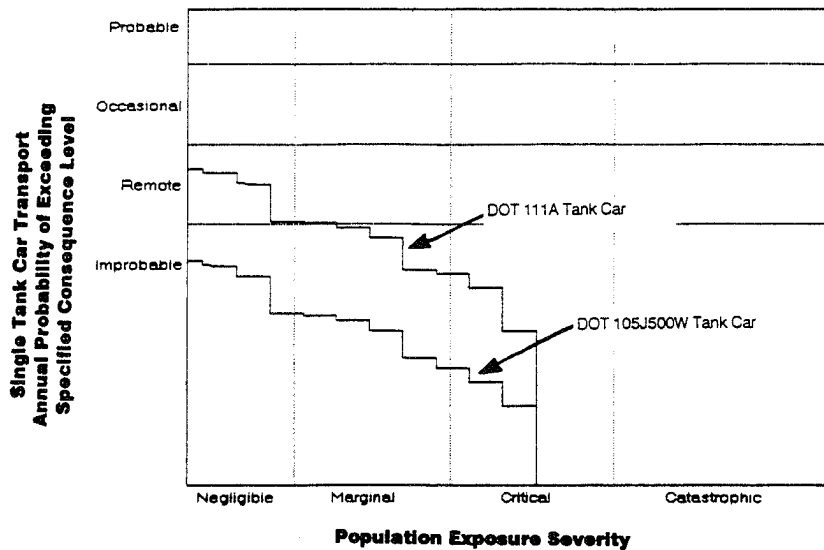
Figure 5.2f

Risk Profile for Methyl Bromide

Single Tank Car Transport
Annual Probability of Exceeding
Specified Consequence Level

Probable

Occasional

Remote

Improbable

DOT 111A Tank Car

DOT 105J500W Tank Car

Negligible   Marginal   Critical   Catastrophic

Population Exposure Severity

5-10
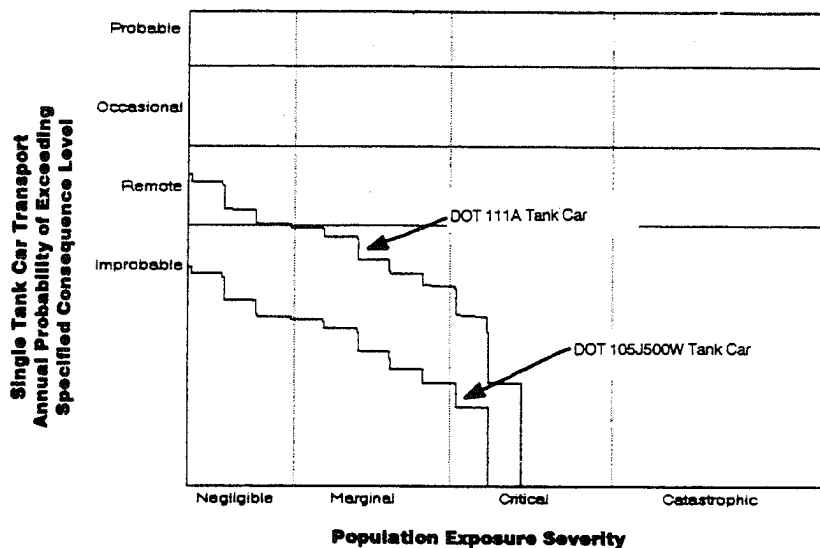
Figure 5.2c

Risk Profile for Carbon Tetrachloride
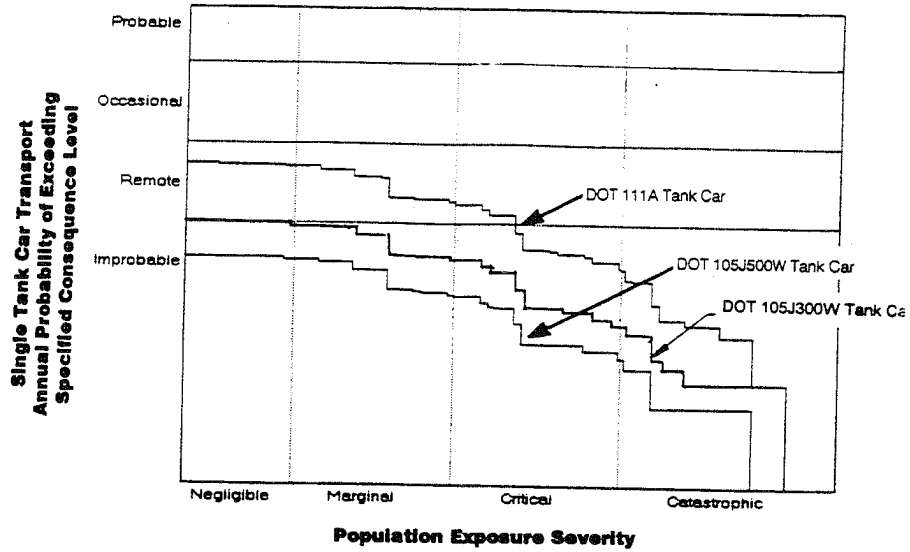
Figure 5.2d

Risk Profile for Chloroprene
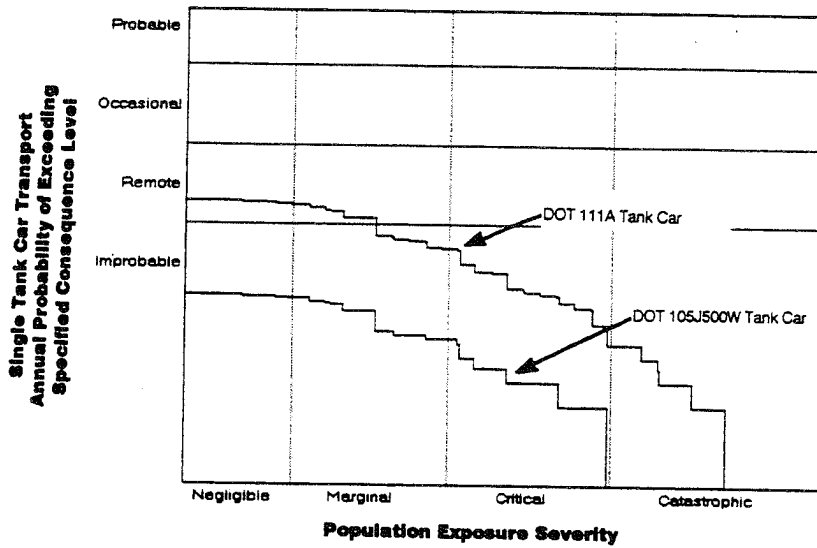
Table 5.6

Features of Tank Cars Used in Generating the Risk Profiles

Risk Reduction Feature	DOT Specification Tank Car			
	111A60W1	105A300W	111A	105J500W
Insulation	Y	Y	N	Y
Head Shields	N	N	N	Y
Thermal Protection	N	N	N	Y
Jacket Thickens	N/A	N/A	N/A	0.25"
Bottom Outlets	N	N[A]	Y	N
Improved Bottom Fitting Protection	N	N/A	N	N/A
Improved Top Fitting Protection	N	N	N	N
Shell Thickness	7/16"[B]	9/16"[B]	7/16"[B]	13/16"[C]
Head Thickness	7/16"[B]	9/16"[B]	7/16"[B]	13/16"[C]
Tank Volume	[D]	[D]	[D]	[D]

N = No   Y = Yes   N/A = Not Applicable

Notes:

[A]   105A300W car is not equipped with bottom outlets and therefore, by default, "N" is indicated for bottom outlet RRF.

[B]   Minimum table thicknesses as specified in 49CFR §179.100-6 (Pressure cars) and §179.200-6 (Non-pressure cars)

[C]   Minimum required thickness of 9/16" plus additional 1/4" thickness increase.

[D]   Tank car volumes are commodity dependent.

Figure 5.3a
Risk Profiles for Transporting Acetone in Very Similar Tank Cars
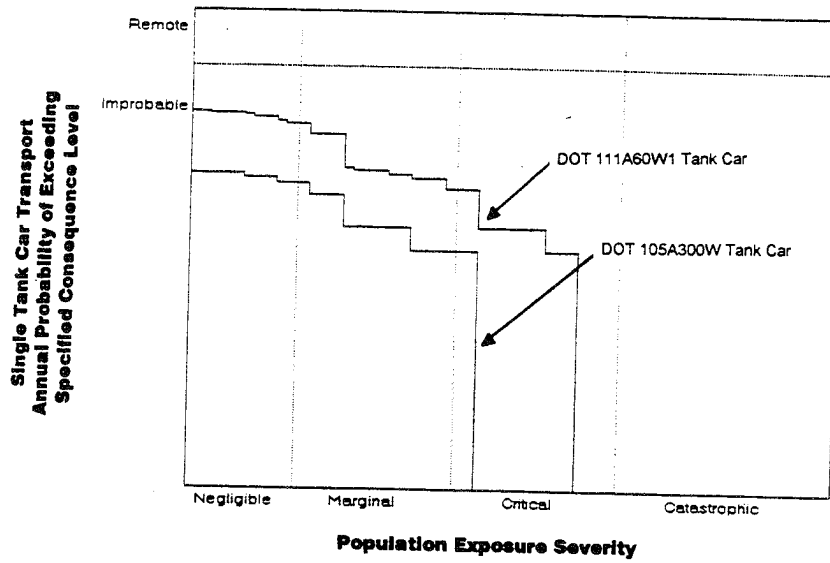
Figure 5.3b
Risk Profiles for Transporting Chloroform in Very Similar Tank Cars
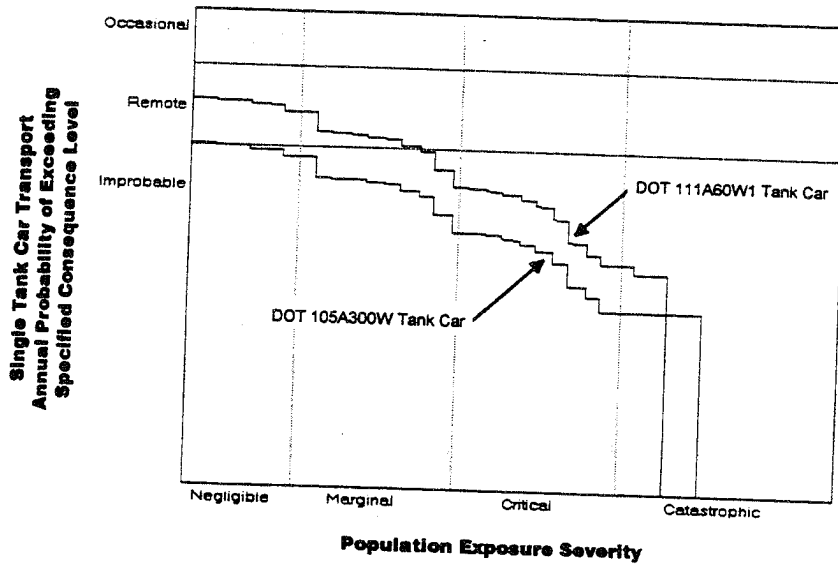
Figure 5.2i

Risk Profile for Styrene Monomer

Single Tank Car Transport / Annual Probability of Exceeding Specified Consequence Level

Probable — Occasional — Remote — Improbable

DOT 111A Tank Car

DOT 105J500W Tank Car

Negligible — Marginal — Critical — Catastrophic

Population Exposure Severity
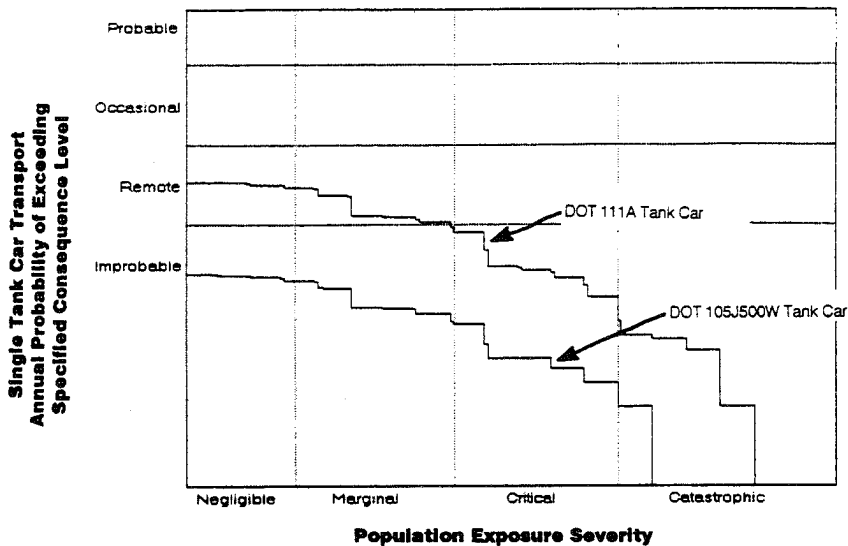
Figure 5.2j

Risk Profile for Trichloroethylene

Single Tank Car Transport / Annual Probability of Exceeding Specified Consequence Level

Probable — Occasional — Remote — Improbable

DOT 111A Tank Car

DOT 105J500W Tank Car

Negligible — Marginal — Critical — Catastrophic

Population Exposure Severity

5-12
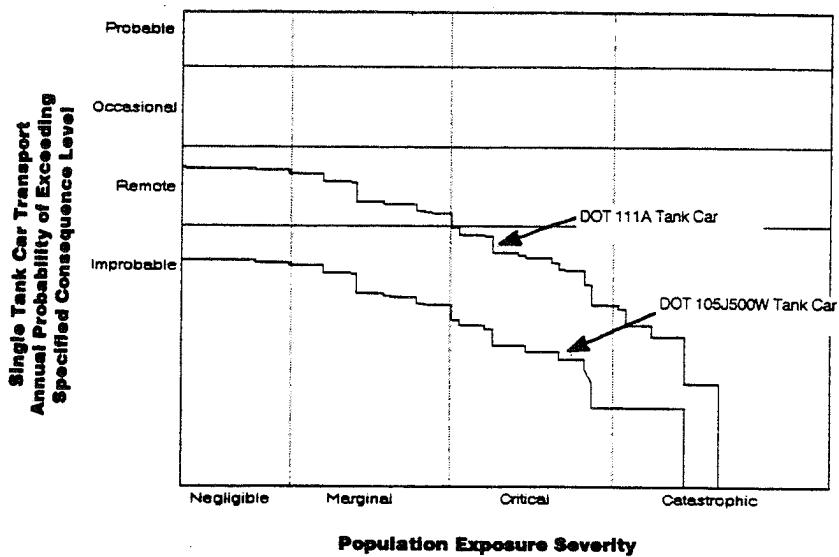
Figure 5.2g

Risk Profile for Oleum (30% SO$_2$)
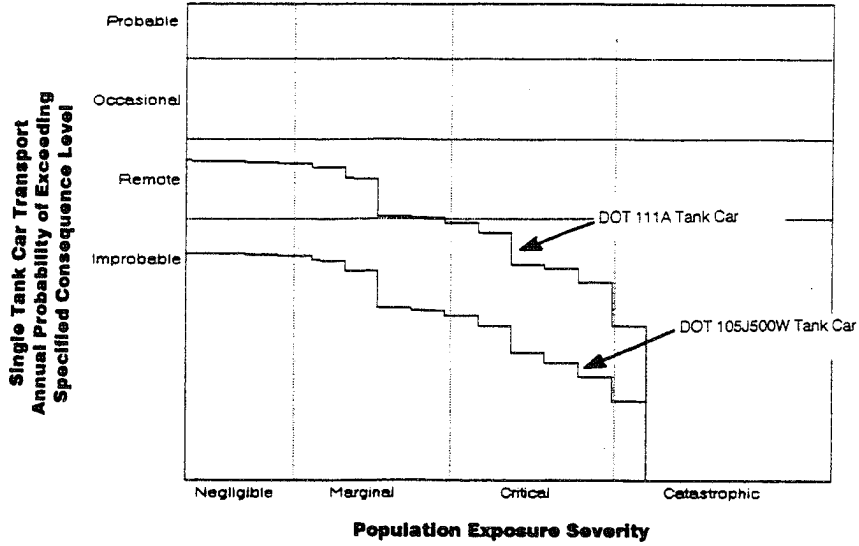
Figure 5.2h

Risk Profile for Propylene Oxide
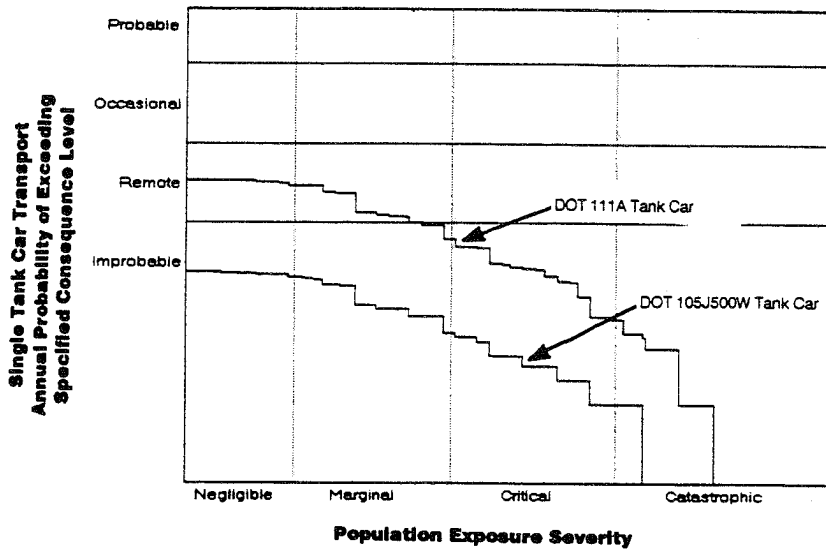
1. The frequency with which lower exposure levels ("negligible" category) occur is always higher than (in some cases by several orders of magnitude) the frequency for the occurrence of very high exposure levels ("catastrophic"). This is because lower levels of exposure can be caused by small leaks of the chemical. These types of leaks and accidents causing such leaks are significantly more frequent in their occurrence.

2. The risk of transporting any chemical in DOT 105J500W tank car is lower than that of transporting the same chemical in DOT 111A car. "Risk" in this comparison can be either the annual probability evaluated at the same exposure level or exposures evaluated at a specified annual probability value. In many cases the reduction in probability is about an order of magnitude at lower exposure levels. Much higher reduction in risk can be seen at higher exposure levels for transport in DOT 105J cars.

    The above result is primarily due to the better structural integrity of DOT 105J500W cars. That is, if a rail accident occurs, the probability of release is much lower in the case of 105J cars compared to 111A cars. Also, for a given severity of an accident, the mean puncture size in the case of 105J cars is lower than in the case of 111A cars. The hole size, of course, does not matter if the material released is a liquid with relatively low vapor pressure. In such a case, the toxic hazard area and pool fire hazard area are dependent on the size of the liquid pool formed on the ground (which depends on the total quantity released and not on the rate of release).

3. The "catastrophic" category exposure in the risk profile results, invariably, from postulated toxic vapor chemical releases in very densely populated areas and the liquid pool spreading to its maximum extent on a flat land. Also it is assumed in the risk models that no remedial action is taken following the accident releases. These assumptions are, of course, idealistic and are not realized in real accidents. Therefore, the actual exposure will be far less than the calculated exposure.

    Finally, the toxic vapor cloud depths resulting from the pool evaporation of many low vapor pressure liquids is relatively shallow (less than 1 m, in many cases). In densely populated areas, generally population is located in multi-tier dwellings whose heights are far greater than 1 m. To this extent, the actual population density exposed to a shallow vapor will be at least an order of magnitude smaller than the "theoretical" exposure. Therefore, the "catastrophic" exposure result indicated for such chemicals as Acetone Cyanohydrin, Acrolein, Carbon Tetrachloride, Chloroprene, Propylene Oxide, Trichloroethylene, should be viewed very skeptically. It is, however, comforting to note that in each of these cases the probability of calculated catastrophic exposure is "improbable".

4.   The risk profile results in some cases present seeming inconsistencies. For example, in the case of Methyl Bromide (Figure 5.2f) there is no "catastrophic" exposure category (even in the "improbable" probability category) while for propylene oxide (Figure 5.2h) the catastrophic exposure exists. However, methyl bromide is transported as a compressed gas, whereas, propylene oxide is a low vapor pressure liquid. Intuitively one would expect a larger hazard area for methyl bromide, because of a larger vapor rate of release than in the case of propylene oxide.

An examination of the basic data used in the risk calculation indicates that methyl bromide has a higher IDLH value (2000 ppm compared to propylene oxide's 1000 ppm). Also, it should be noted that the volumes of these two chemicals transported in the tank cars are different; 36 m^3 for methyl bromide vs. 96.7 m^3 for propylene oxide.

In this risk assessment effort, our focus has been to compare the relative risk reduction in the transport of a specified chemical in the least protected car and the best protected car. These comparisons are illustrated in the various figures identified earlier. In performing these assessments, the volume of the chemical in the tank cars was kept constant for each chemical. However, different chemicals are transported with different volumes (depending on the chemical density and consistent with the maximum load allowed on the rails—263,000 lbs.) even though the same specification tank car (such as DOT 111A or DOT 105J500W, etc.) may be used for different chemicals. That is, in the results presented no attempt has been made to develop risk profiles for *all chemicals* with the same volume of transport in each tank car. This can be, of course, performed using the model developed; but it would not be consistent with the shipping practice. Therefore, *the results presented should NOT be used for comparing risks between chemicals*, but only for the purpose of comparing risks between different tank cars carrying the same chemical and the same volume in each tank car.

5.3   Analysis of Risks Posed by Polymerizing and/or Self-Heating Chemicals

For a polymerizing or self-heating chemical in transportation, it is extremely difficult to perform a generalized risk assessment in the same vein as discussed in Section 5.2. This is because the frequency of the primary causes which initiate these reactions, namely, loss of inhibitor and/or exposure to fires cannot be determined easily. For example, loss of inhibitor may be attributable to human failures in not mixing enough quantity of inhibitor before the chemical is shipped. Also, the frequency of occurrence of polymerization reactions due to wrong procedures (human failures) being used in tank car cleaning stations cannot be currently quantified. Even the fire exposure phenomenon is extremely difficult to quantify stochastically.

An attempt is made in this section to evaluate an average probability of exposure of polymerizing/self-heating chemicals to rail accident caused fires. This result may provide a broad measure of the seriousness of, if any, of this phenomenon. An approach is also discussed to evaluate the potential exposure (i.e., the consequence).

5.3.1 Probability of Exposure of a Tank Car Containing a Polymerizing Chemical to a Fire Caused by a Rail Accident

In this analysis we are interested in rail accidents in which there exists in the train consist a tank car containing the polymerizing chemical *and* at least one tank car containing a flammable material. More specifically, we consider the presence of only combustible/flammable liquid chemicals. This is because, in general, to initiate a polymerization reaction the *thermally protected* tank car containing the chemical has to be exposed to a fire for hours before a runaway reaction occurs. Such long duration fires occur only in the case of combustible/flammable liquid releases (and not in the case of compressed flammable gas releases). We note, however, that most flammable liquids which are also monomers are **NOT** transported in thermally protected tank cars. In these cases, run away reactions may occur significantly sooner than in the case of thermally protected tank cars.

We now define the following probabilities

P = Annual frequency of exposing a tank car containing a polymerizing/self-heating chemical[3] to a long duration fire caused by a railroad accident (5.1a)

N_c = Number of tank car shipments of chemical C per year (5.1b)

N_{FT} = Total number of freight trains moving/year in the U.S. (5.1c)

N_{FT}^A = Number of freight train accidents/year (per the FRA's Accident & Incident Bulletin) (5.1d)

$P(A_{FT})$ = Probability that a given freight train suffers an accident (5.1e)

$P(F/FT)$ = Conditional probability that a freight train accident leads to a long duration fire caused by the release of flammable/combustible liquid chemical (5.1f)

Assuming a one chemical "C" tank car per train it can be shown that:

$$P = N_c \, P(A_{FT}) \, P(F/FT)$$ (5.2)

---

[3]For brevity, hence forth such a chemical will be called "C" chemical.

where

$$P(A_{FT}) = \left[\dfrac{N_{FT}^{A}}{N_{FT}} \right]$$
(5.3)

Table 5.7 shows the statistics of train accidents over the period 1987-1991. The assumptions made in calculating the number of freight trains per year are indicated as foot notes in the table. It is seen that an average value for the probability of an accident to a freight train is:

$$P(A_f) = 3.6 \times 10^{-3}$$
(5.4)

Now the conditional probability P(F/FT) can be calculated by the equation:

$$P(F/FT) = P(HT/FT) \times P(R/HT) \; P(FL/R) \; P(F/FL) \; P(t/F) \; P(E/A)$$
(5.5)

where

P(HT/FT)   =   Conditional probability that the accident involves a hazardous material carrying train assuming that a train accident has occurred.

P(R/HT)   =   Conditional probability that a hazardous material is released given that an accident has occurred to a freight train with hazmat consist.

P(FL/R)   =   Conditional probability that the released hazmat is either a flammable or a combustible liquid.

P(F/FL)   =   Conditional probability that there occurs an ignition and fire given that a combustible or flammable liquid has been released.

P(t/F)   =   Conditional probability that the duration of fire is long (> 2 hours) given that a pool fire ensues after the rail accident.

P(E/A)   =   Probability that the chemical C tank car ends up "close" to fire given that an accident has occurred and it has resulted in a fire.

Table 5.7

Train Accident Statistics

Year	Total Train Miles (Note 1) $= 10^3 x$	Total # of Freight Trains (Note 2) $= 10^3 x$ (N_{FT})	Total # of Freight Train Accidents N_{FT}^A	Total # of Hazmat Train Accidents	Number of Accidents with Hazmat Releases
1988	469,132	938	3,051	475	44
1989	483,727	967	3,081	517	55
1990	477,459	955	3,045	466	35
1991	460,204	920	2,814	525	47
1992	481,800	964	2,531	482	27
Avg.	474,464	949	2,904	493	42

Source: *Accident/Incident Bulletin No. 161, Calendar Year 1992, Federal Railroad Administration, Washington, DC 20590.*

Note 1: Only locomotive train miles are considered

Note 2: It is assumed that on the average a freight train travels 500 miles

$$P(A_F) = \frac{N_{FT}^A}{N_{FT}} = \frac{2904}{949 \times 10^3} = 3.6 \times 10^{-3}$$ = Probability of a freight train suffering an accident

$$P(HT/FT) = \frac{493}{2904} = 0.17$$ = Conditional probability that the accident involves a hazmat carrying train given that a train accident has occurred

$$P(R/HT) = \frac{42}{493} = 0.085$$ = Conditional probability that a hazmat is released given that a train accident involving hazardous materials has occurred.

The values of P(HT/FT) and P(R/HT) are indicated in Table 5.7. It is known from a previous work *(Raj, 1990)* that on the average for mainline accidents,

$$P\,(FL/R) = 0.4$$

Table 5.8 shows the results obtained from a review of recent RSPA data on hazardous material accidents. It shows that,

$$P\,(F/FL) = 0.021$$

No data are available to determine the length of duration of fires (or their size) resulting from the release of flammable liquids in rail accidents. It may be assumed that the 90th percentile duration is 2 hours. That is, only 10% of fires will have a burning duration of longer than 2 hours, i.e.,

$$P\,(t/F) = 0.1$$

For illustration purposes, we use the shipment data for acrylic acid. Table 5.9 shows the annual shipment data (from AAR) on the number of tank cars shipped. Hence, on an average, the annual shipment volume is

$$N_c = 1992$$

Using the probability values indicated above and using the shipment volumes of acrylic acid we calculate the annual probability of exposing at least one acrylic acid tank car to a rail accident fire of duration longer than 2 hours. This is, using equation (5.2),

$$P = 1992 \ x \ 3.6 \ x \ 10^{-3} \ x \ 0.17 \ x \ 0.085 \ x \ 0.4 \ x \ 0.021 \ x \ 0.1 \ x \ \frac{1}{50} \tag{5.4}$$

$$= 1.74 \ x \ 10^{-6} \ per \ year$$

Where the number 1/50 represents the probability that the acrylic acid car lies next to a fire after the accident. The number 50 represents the average number of freight cars in an average size freight train.

Table 5.8

Rail Accidents Resulting in Fires

Hazardous Material Class Released	Total Number of Accidents with Release in Which			P(F/R)
	There Was No Fire	There Was Fire	Total	
Combustible Liquid	223	0	223	0
Flammable Liquid	653	14	667	0.021
Flammable Compressed Gas	139	2	141	0.014
Flammable Solid	22	7	29	0.241

Source: RSPA Hazardous Materials Rail Accident Data for the period 1990-1993

P(F/R) =   Probability of fire given that the material is released

Table 5.9

Annual Number of Tank Car Shipments of Acrylic Acid

Calendar Year	Number of Tank Car Shipments
1988	1797
1989	2207
1990	2053
1991	N/A
1992	1911
Average	1922

Source: AAR Top 125 Shipment List, 1992

The result indicated in equation (5.4) represents the annual probability of realizing a fire induced thermal explosion incident in an acrylic acid tank car. This probability will be even smaller if the potential emergency response action is considered within the 2 hour limit. As the fire duration factor $P_{(t/F)}$ approaches a limiting value of 1; the probability of occurrence, per year, is higher by a factor of 10. (1.74 x 10⁻⁵ per year).

5.3.2 Thermal Explosion Consequence in Terms of People Exposure

The consequence of a thermal explosion is the generation of a blast wave (that can inflict structural damage and human injury at hundreds of meters from the location of explosion), and the hurling of pieces of tank car metal to several tens of meters. It is very hard to predict the injury to people from pieces of metal flying. Spectacular as the missile (debris) hurling may be, the total direct human injury will be limited to, at best, a few people (probably less than 10). This is because the total surface area of the missiles hurled is, at best, equal to the tank car surface area. This area will also form the ground impact area (not including secondary damage caused by roof collapse or structural damage). The total number of persons in an area equal to the surface area of a tank car even in the most densely populated area is very small.

Blast Effects. Using the model presented in Section 4.42 and assuming a yield of 1.5% (i.e., 1.5% of the mass in the tank car participates in the polymerization initiated reaction), we calculated a blast yield equivalent to 1.32 x 10⁹ J of energy or 316 kg of TNT for an acrylic acid tank car explosion (see page 4.20).

The following human injury hazard criteria are indicated in the literature *(Zabetakis, 1967)* for blast over pressure effects:

♦   Overpressure for Lung Damage   =   6 psi   = $4.14 \times 10^4 \, N/m^2$

♦   Overpressure for Ear Drum Damage   =   2.5 psi   = $1.72 \times 10^4 \, N/m^2$

We calculate the distance to the hazards (using Figure 4.4 and equations 4.16 and 4.17) as,

$$X_{Lung\ Damage} \quad = \quad 30 \ m$$

$$X_{Ear\ Drum\ Rupture} \quad = \quad 50 \ m$$

Assuming a population density of 5,000 persons per sq. km. (representative of urban population density) it is estimated that the exposure index from acrylic acid polymerization blast effects is

$$N_{Lung\ Damage} \approx 14$$

$$N_{Ear\ Drum\ Rupture} \approx 40$$

It should be noted that the above estimates are dependent on two key assumptions, namely for the values for the fraction of the mass of the chemical in the tank car that participates in the polymerization reaction and the population density in the immediate vicinity of the tank car accident.

Fragmentation Effects. The chunks of steel from a tank car rupture can injure (or even fatally injure) a person if the missile directly impacts the person. Because of the relative small size of the pieces of metal that would be released the probability that a missile hits a person is very small. At best the number of people that may be *directly impacted*[4] is given by

$$N_{Missile\ Impact} = \rho_{Pop}\ A_{Missiles} \tag{5.5}$$

where

ρ_{Pop} = Population density in the vicinity of the tank car accident ($\#/m^2$)

$A_{missiles}$ = Sum total projected area presented by all pieces of the missiles (debris) (m^2)

The total surface area $A_{Missiles}$ can at best be equal to the total surface area of the tank car shell, if it is assumed that the entire shell is blown up into smaller fragments.

For a DOT 111A100W tank car, we estimate

$$A_{Missiles} = 190\ m^2 = 190 \times 10^{-6}\ sq.\ km.$$

Hence,

$$N_{Missile\ Impact} = 5,000 \times (190 \times 10^{-6}) \approx 1$$

---

[4]Secondary effects such as roof or building collapse as a direct consequence of the missile impacting the structures are not considered.

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5.4 Discussion on the Thermal Explosion Risk Results

The calculations of the probability of a thermal explosion induced by the exposure of a tank car containing a polymerizing/self-heating chemical to a rail accident caused fire indicate that this probability is extremely small (10^{-6} per year). Even though it is very difficult to calculate a similar probability value for thermal explosion initiation due to loss of inhibitor, it can be argued that this probability will be either of the same order of magnitude as the accidental fire exposure or less. It should be noted that while the occurrence of a thermal explosion in a tank car does not require the product to be released (i.e., the tank car be punctured), the exposure to a fire requires the occurrence of puncture in other tank cars carrying flammable or combustible liquids. That is, *a rail accident occurrence is essential* for this scenario of thermal explosion to play out. However, thermal explosions caused by loss of (or lack of sufficient amount of) inhibitor *does not* require the occurrence of rail accidents. Hence the parameters that govern the occurrence probability are completely different from those for a fire induced thermal explosion.

The analysis of the consequences of a thermal explosion (using acrylic acid as an example) indicates that substantially more injury to people may result from the blast over pressure rather than by impacting missiles. The absolute numbers for people exposed depends very importantly on the mass of the lading in the tank car that "explodes" and on the local population density. We have not considered some of the mitigating factors which may reduce the effects of over pressures such as the protection from buildings. On the other hand, we have not considered the potential detrimental effects of building appurtenances (glass windows) in causing secondary injuries to people. The blast effect injury calculation is complex and needs to consider a whole set of other parameters. Such a study, in our opinion, is beyond the scope of this study.

Chapter 6

Conclusions and Recommendations

This report evaluates the potential risk that the twenty-seven (27) selected chemicals pose during transportation in tank cars on the U.S. railroad system. Most of the chemicals studied exhibit one or more hazards, e.g., inhalation toxicity (vapors), flammability (posing fire thermal radiation hazards), and explosivity (causing blast wave damage hazard). A few of the chemicals pose potential hazards from their tendency to self-heat due to the initiation of polymerization reaction caused by loss of inhibitor or by exposure to an external fire. These various hazardous behaviors have been modeled and the risks (in terms of probabilities of occurrence of hazardous events and people exposure hazards) have been evaluated.

6.1 Conclusions

Based on the analysis performed and the results obtained from the models we conclude the following:

1. Substantial number of chemical property values of relevance to risk/hazard analysis are unavailable in the literature. This is particularly true for chemicals that pose polymerization or self-heating hazards.

    Because of this some of the analyses may not be completely accurate or the results may be incorrect-to-incomplete.

2. The risk profiles generated for liquid chemicals exhibiting conventional hazards (vapor toxicity, fire or explosive behavior) and having low vapor pressures may overstate the magnitude of the consequences. It is very likely that calculated people exposure values may be overstated by a factor with values between 5 and 10.

    This is because of the very low vapor plume depths developed during the dispersion of vapors generated by the evaporation of low to very low vapor pressure liquids. While the ground level area calculated may be correct, the inclusion of all of the population within this area in calculating the potential exposure numbers may be grossly incorrect because of the extremely low depth of vapor plumes.

3. The risk profile results are useful more for comparative assessment of risks posed when a chemical is transported in different specification tank cars, rather than for obtaining absolute values of the risks.

4. The probability of a tank car explosion induced by a runaway self-heating reaction of the chemical when the tank car is exposed to a rail accident caused fire is extremely low (of the order of 10^{-6}/year for acrylic acid).

5. Calculation of the probability of thermal explosion caused by either the depletion of the inhibitor (or due to insufficient inhibitor concentration at the time of shipment) is extremely difficult. This is because it requires the consideration and quantification of human error occurrence frequency and in some cases the occurrence of special conditions of weather.

6. The consequences of a thermal explosion are the development of a blast wave and the fragmentation of the tank car shell. The effect of the blast wave seems to be more serious than the impact injury effects from the debris falling. In the example considered, the total number of people "exposed" to blast wave effects is of the order of 40 while the "exposure" number from the missiles is at best 1.

7. The hazard consequence of the self-heating reaction is very much dependent on the mass fraction of the tank car contents that undergo thermal explosion. No experimental or accidental investigation data exist to evaluate this very important number. An estimate of 1.5% for the "efficiency of thermal reaction" is made in this report based entirely on propellant tank destruction test data from the literature.

8. In general, all other conditions being equal, a thermally protected DOT 105 specification tank car provides about an order of magnitude less risk than an unprotected DOT 111A specification tank car for the transport of any of the chemicals studied.

6.2 Recommendations

We recommend that the FRA:

1. Initiate a more thorough chemical property gathering project to collect much needed and important chemical and thermodynamic property values for many of the commonly transported hazardous materials. This project should involve cooperative efforts among the Government agencies, hazardous material (rail) shippers, academic institutions, etc.

2. Support a research activity to develop a detailed model to analyze the self-heating/ polymerization process in a tank car when it is exposed to a fire. This model should consider the thermal and fluid dynamic complexities involved as well as categories of different size and location of fires.

Listing of References

Abramowitz, M., and I.A. Stegun, 1965; "Handbook of Mathematical Functions," Dover Publications, New York.

Baker, W.E., J.J. Kulesz, R.E. Ricker, R.L. Bessey, P.S. Westine, V.B. Parr, and G.A. Oldhams, 1977; "Workbook for Predicting Pressure Wave and Fragment Effects of Exploding Propellant Tanks and Gas Storage Vessels," NASA Contractor Report No. 134906, NTIS No. N76-19296-19302, Southwest Research Institute, San Antonio, TX, 78284.

CHRIS, 1984; "Hazardous Chemical Data," Manual II, Chemical Hazard Response Information System. U.S. Government Printing Office, Washington, DC 20402.

Churney, K.L. and D. Garvin, 1980; "A Third Appraisal of Methods for Estimating Self-Reaction Hazards," Report No. NBSIR-80-2018 (DOT), National Bureau of Standards, Washington, DC, 20590.

Conlon, P.C., 1984; "Emergency Action Guides" Association of American Railroads, Washington, DC 20036.

Daubert, T.E., and R.P. Danner, 1989; "Physical and Thermodynamic Properties of Pure Chemicals — Data Compilation," Design Institute for Physical Property Data, American Institute for Chemical Engineers, Department of Chemical Engineering, The Pennsylvania State University, University Park, PA. Published by Hemisphere Publishing Corporation, New York.

Domalski, E.S., 1977; "A Second Appraisal of Methods for Estimating Self-Reaction Hazards," DOT Report No. DOT/MTB/OHMO-7616, prepared by the National Bureau of Standards, Washington, DC, 20234.

Kayser, E.G., 1974; "The Thermal Decomposition of Thirty Commercially Available Materials at 300 °C," Report No. TES-20-74-1. U.S. DOT/Office of Hazardous Materials, Naval Ordnance Laboratory, Silver Spring, MD 20910.

Levy, L.B., and M.B. Lakin, 1993; "Emergency Response Shortstop Inhibition During the Approach to an Acrylic Acid Runaway Polymerization," Process Safety Progress, V. 12, N. 2, pp. 111-114.

Matheson, 1971; "Matheson Gas Data Handbook," 5th Edition. Matheson Gas Products, Inc., Rutherford, NJ.

Miles, F.D., et al. Trans. of Faraday Soc., V. 36, 1940, pp. 352. Communicated by T.L. Muller, Sulfuric Acid Technology Center, E.I. DuPont de Nemours & Co., Deepwater, NJ. April 1994.

NFPA, 1981; "Fire Protection Handbook," 15th Edition. National Fire Protection Agency, Quincy, MA.

NIOSH, 1990; "Pocket Guide to Chemical Hazards." U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, Superintendent of Documents, Washington, DC.

Phillips, E.A., 1994; "Probability of Lading Loss from Tank Cars Damaged in Accidents," Report No. RA-02-7-61, Tank Car Research Project. Association of American Railroads, Chicago, IL.

Phillips, E.A, 1992; "Tank Car Damage Statistics 1965-1988," Personal Communication. Chicago: Association of American Railroads, 31 March 1992.

Raj, P.K., and J.A. Morris, 1988; "Source Characterization and Heavy Gas Dispersion Models for Reactive Chemicals," Final Report, Volume I, submitted to USAF, Contract No. F19628-86-C-0036, by Technology & Management Systems, Inc., Burlington, MA 01803.

Raj, P.K., Morris, J., and Reid, R.C., 1987; "A Hybrid Box-Gaussian Dispersion Model Including Considerations of Chemical Reactions & Liquid Aerosol Effects," Paper presented at the International Conference on Vapor Cloud Modeling, Cambridge, MA.

Raj, P.K., and C.K. Turner, May 1993; "Hazardous Materials Transportation in Tank Cars — Analysis of Risks," Report No. DOT/FRA/ORD-92/34, by Technology & Management Systems, Inc., Burlington, MA. Federal Railroad Administration, Washington, DC 20590.

Raj, P.K., 1990; "Conditional Probability of Hazmat Releases from Rail Tank Cars in Accidents," TMS Report No. 90-62, Submitted to Arthur D. Little, Inc.

Reid, R.C., J.M. Prausnitz, and B.E. Poling, 1987; "The Properties of Gases & Liquids," 4th Edition. McGraw Hill Book Company, New York, NY.

Slade, D.H. (editor), 1968; "Meteorology and Atomic Energy," NTIS Report No. TID-24190, Office of Information Services, U.S. Atomic Energy Commission, Oak Ridge, TN.

Tsang, W., and E.S. Domalski, 1974; "An Appraisal of Methods for Estimating Self-Reaction Hazards," DOT Report no. TES-20-74-8, prepared by the National Bureau of Standards, Washington, DC, 20234.

Woodall, W.J., 1993; "Tank Car Capacities," Personal Communication, Union Tank Car Company, East Chicago, IN.

Zabetakis, M.G., 1967; "Safety with Cryogenic Fluids" Plenum Press, New York.

Zolotorofe, D.L., 1994; Rohm & Haas Company, Spring House, PA, 19477, July 1994; Private Communication.

Appendix A

Acetaldehyde

Chemical Code:	AAD
Formula:	C_2H_4O
Molecular Weight:	44.05
UN ID Number:	1089
Hazard Class:	3
Hazard Type:	Flammable Liquid
Normal Boiling Point:	68.7 °F
State as Shipped:	Liquid
State as Released:	Liquid
Toxicity:	10,000 ppm IDLH - irritant and moderately toxic
Fire:	Vapors are heavier than air and may travel to an ignition source and flashback. Containers may rupture violently in fire. Will generate large quantity of flammable gas or vapors upon release.
Flashpoint (Closed Cup):	36 °F
Explosion:	Vapors may explode if ignited in confined space.
Stability During Transportation:	Stable
Polymerization:	May occur if exposed to heat, dust, strong oxidizer, or reducing agent.
Decomposition:	Occurs at temperatures > 400F forming methane and carbon monoxide.
Reaction with Water:	No reaction.

NFPA Hazard Classification

Health Hazard:	2
Flammability:	4
Reactivity:	2
Authorized Tank Cars:	DOT Class 103, 104, 105, 109, 111, 112, 114, and 115. (§ 173.243)

Acetone

Chemical Code:	ACT
Formula:	C3H6O
Molecular Weight:	58.08
UN ID Number:	1090
Hazard Class:	3
Hazard Type:	Flammable Liquid
Normal Boiling Point:	133.2 °F
State as Shipped:	Liquid
State as Released:	Liquid
Toxicity:	20,000 ppm IDLH - low to moderate toxicity by potential pathways of exposure.
Fire:	Vapors are heavier than air and may travel to an ignition source and flash back. Containers may rupture violently in fire. May generate large quantity of flammable gas or vapors upon release.
Flashpoint (Closed Cup):	0 °F
Explosion:	Explosion may result if vapors are ignited in confined space.
Stability During Transportation:	Stable
Polymerization:	Not pertinent.
Decomposition:	Not pertinent.
Reaction with Water:	No reaction.
NFPA Hazard Classification	
Health Hazard:	1
Flammability:	3
Reactivity:	0
Authorized Tank Cars:	DOT Class 103, 104, 105, 109, 111, 112, 114, and 115, and AAR Class 206W. (§ 173.242)

Acetone Cyanohydrin

Chemical Code:	ACY
Formula:	C4H7NO
Molecular Weight:	85.11
UN ID Number:	1541
Hazard Class:	6.1
Hazard Type:	Poison Liquid
Normal Boiling Point:	330 °F
State as Shipped:	Liquid
State as Released:	Liquid
Toxicity:	50 mg/m3 IDLH (17 ppm) - highly toxic by ingestion or inhalation, moderately toxic by skin absorption.
Fire:	Combustible liquid. Containers may rupture violently in fire. Heat will cause decomposition to acetone and highly toxic hydrogen cyanide.
Flashpoint (Closed Cup):	165 °F
Explosion:	Reactive at high temperature or pressure. Explosion may occur if vapors are heated in a confined space. Contact with certain materials may cause violent polymerization or formation of explosive materials.
Stability During Transportation:	Stable
Polymerization:	May occur under contact with nitrides, alkali or alkaline earth metals, organic acids, isocyanates, epoxies, or certain other substances.
Decomposition:	Decomposes at 248F and at lower temperatures under alkaline conditions with evolution of toxic hydrogen cyanide. Some decomposition may occur even at ambient conditions.
Reaction with Water:	Will not react.

NFPA Hazard Classification

Health Hazard:	4
Flammability:	1
Reactivity:	2
Authorized Tank Cars:	DOT 105S300ALW, 105S300W, 112J340W, 114J340W and these type tank car having higher tank test pressure or/and tank protective devices. Tank cars must be stenciled DOT 105_200_, 112J200W, and 114J200W, respectively. (§ 173.244, B76)

Acrolein, inhibited

Chemical Code:	ARL
Formula:	C3H4O
Molecular Weight:	56.1
UN ID Number:	1092
Hazard Class:	6.1
Hazard Type:	Poison Liquid, Flammable Liquid
Normal Boiling Point:	655 °F
State as Shipped:	Liquid
State as Released:	Liquid
Toxicity:	5 ppm IDLH - highly toxic by all pathways or exposure.
Fire:	Vapors are heavier than air and may travel to an ignition source and flash back. Containers may rupture violently in fire. Exposure to excessive heat may cause violent polymerization. May generate large quantities of flammable gas or vapor upon release.
Flashpoint (Closed Cup):	13 °F
Explosion:	Containers may rupture violently in fire. Explosion may result if confined vapors are ignited. Loss of inhibitor or contact with certain materials may cause spontaneous violent polymerization.
Stability During Transportation:	Stable if inhibited.
Polymerization:	Violent polymerization may result from loss of inhibitor, excessive heat or light, or contact with alkaline materials, amines, metal salts, oxidants, sulfur dioxide, and acids.
Decomposition:	Not pertinent.
Reaction with Water:	No reaction.
NFPA Hazard Classification	
Health Hazard:	3
Flammability:	3
Reactivity:	2
Authorized Tank Cars:	DOT 105J500W and 105J600W. (§ 173.244, B72)

Acrylic Acid, inhibited

Chemical Code:	ACR
Formula:	C3H4O2
Molecular Weight:	72.06
UN ID Number:	2218
Hazard Class:	8
Hazard Type:	Corrosive
Normal Boiling Point:	286.3 °F
State as Shipped:	Liquid
State as Released:	Liquid (will solidify at 56F)
Toxicity:	IDLH n/a - corrosive and highly toxic to bodily tissues by all pathways of exposure.
Fire:	Combustible material. Containers may rupture violently in fire.
Flashpoint (Closed Cup):	118 °F
Explosion:	Explosion may result if vapors of warm liquid are ignited in confined area. Loss of inhibitor, improper thawing, excessive heat, or certain contaminants may cause explosion due to spontaneous violent polymerization.
Stability During Transportation:	Shipped with 200 ppm hydroquinone inhibitor but considered unstable in normal transportation due to possibility of polymerization.
Polymerization:	Violent polymerization may result from loss of inhibitor, improper thawing, excessive heat, or upon contact with acids, amines, ammonia, iron salts, and other chemicals.
Decomposition:	Not pertinent.
Reaction with Water:	No reaction.
NFPA Hazard Classification	
Health Hazard:	3
Flammability:	2
Reactivity:	2
Authorized Tank Cars:	DOT Class 103, 104, 105, 109, 111, 112, 114, and 115, and AAR Class 206W. (§ 173.242)

Bromine

Chemical Code:	BRX
Formula:	Br2
Molecular Weight:	159.81
UN ID Number:	1744
Hazard Class:	8
Hazard Type:	Corrosive, Poison
Normal Boiling Point:	138 °F
State as Shipped:	Liquid (above 19F)
State as Released:	Liquid (above 19F)
Toxicity:	10 ppm IDLH - highly toxic by all pathways of exposure.
Fire:	Non-flammable liquid. Container may rupture violently in fire due to over pressurization. Will generate large quantities of toxic fumes upon release.
Flashpoint (Closed Cup):	Not Flammable
Explosion:	Non-flammable but container may rupture violently in fire due to over pressurization. Contact with certain substances may result in formation of explosive mixtures.
Stability During Transportation:	Stable.
Polymerization:	Not pertinent.
Decomposition:	Not pertinent.
Reaction with Water:	No reaction.

NFPA Hazard Classification

Health Hazard:	4
Flammability:	0
Reactivity:	0
Authorized Tank Cars:	DOT 105S300W (105A300W built before 1991) and this type tank car having higher tank test pressure or/and tank protective devices. (§ 173.249, B64)

Carbon Tetrachloride

Chemical Code:	CBT
Formula:	CCl4
Molecular Weight:	153.83
UN ID Number:	1846
Hazard Class:	6.1
Hazard Type:	Poison
Normal Boiling Point:	170 °F
State as Shipped:	Liquid
State as Released:	Liquid
Toxicity:	300 ppm IDLH - highly toxic by ingestion or inhalation, less toxic by skin absorption. May be a carcinogen.
Fire:	Containers may rupture in fire due to over pressurization. May decompose at elevated temperatures.
Flashpoint (Closed Cup):	Not Flammable
Explosion:	Non-flammable but container may rupture violently in fire due to over pressurization. Contact with certain substances may result in formation of explosive mixtures.
Stability During Transportation:	Stable.
Polymerization:	Not pertinent.
Decomposition:	Decomposes at elevated temperatures to form toxic substances such as hydrogen chloride, chlorine, phosgene, and carbon monoxide.
Reaction with Water:	No reaction.
NFPA Hazard Classification	
Health Hazard:	3
Flammability:	0
Reactivity:	0
Authorized Tank Cars:	DOT Class 103, 104, 105, 109, 111, 112, 114, and 115. (§ 173.243)

Chloroform

Chemical Code:	CRF
Formula:	CHCl3
Molecular Weight:	119.39
UN ID Number:	1888
Hazard Class:	6.1
Hazard Type:	Poison
Normal Boiling Point:	142 °F
State as Shipped:	Liquid
State as Released:	Liquid
Toxicity:	1000 ppm IDLH - low to moderate toxicity. Suspected carcinogen.
Fire:	Containers may rupture in fire due to over pressurization. May evolve toxic gases or vapors upon release.
Flashpoint (Closed Cup):	Not Flammable
Explosion:	Containers may rupture in fire due to over pressurization. Contact with a mixture of water and alkalis may result in explosion.
Stability During Transportation:	Stable.
Polymerization:	Not pertinent.
Decomposition:	May decompose at high temperatures to form toxic phosgene, chlorine, carbon monoxide, and hydrogen chloride gas. May also decompose very slowly to form phosgene and hydrogen chloride if exposed to air or light.
Reaction with Water:	No reaction.

NFPA Hazard Classification

Health Hazard:	2
Flammability:	0
Reactivity:	0
Authorized Tank Cars:	DOT Class 103, 104, 105, 109, 111, 112, 114, and 115 and AAR Class 203W, 206W, and 211W. (§ 173.241)

Chloroprene, inhibited

Chemical Code:	CRP
Formula:	C4H5Cl
Molecular Weight:	88.54
UN ID Number:	1991
Hazard Class:	3
Hazard Type:	Flammable Liquid, Poison
Normal Boiling Point:	138.9 °F
State as Shipped:	Liquid
State as Released:	Liquid
Toxicity:	400 ppm IDLH - moderate to high toxicity by potential pathways of exposure. Suspected carcinogen in chronic exposures.
Fire:	May generate large quantities of flammable vapor upon release. Vapors are heavier than air, may persist in low areas, and may travel to an ignition source and flash back. Containers exposed to fire may result in violent polymerization and container rupture.
Flashpoint (Closed Cup):	4 °F
Explosion:	Explosion may result if vapors are ignited in a confined space. Loss of inhibitor or excessive heat may cause spontaneous polymerization resulting in violent container rupture.
Stability During Transportation:	Shipped with inhibitor but may still be unstable under certain conditions.
Polymerization:	Loss of inhibitor, excessive heat, or contact with acids, peroxides, or oxidizing materials may cause violent self-polymerization. Product temperature should be maintained below 75F.
Decomposition:	Not pertinent.
Reaction with Water:	No reaction.
NFPA Hazard Classification	
Health Hazard:	2
Flammability:	3
Reactivity:	0
Authorized Tank Cars:	DOT Class 103, 104, 105, 109, 111, 112, 114, and 115. (§ 173.243)

Chlorosulfonic Acid

Chemical Code:	CSA
Formula:	ClSO3H
Molecular Weight:	116.53
UN ID Number:	1754
Hazard Class:	8
Hazard Type:	Corrosive, Poison
Normal Boiling Point:	311 °F
State as Shipped:	Liquid
State as Released:	Liquid
Toxicity:	IDLH n/a - highly corrosive to bodily tissues by all pathways of exposure.
Fire:	Non-flammable substance. May generate large quantities of corrosive fumes and vapors upon release.
Flashpoint (Closed Cup):	Not Flammable
Explosion:	Contact with yellow or red phosphorous or certain other materials may result in formation of explosive mixtures. Hydrogen gas formed from contact with some metals may explode if ignited in a confined space.
Stability During Transportation:	Stable.
Polymerization:	Not pertinent.
Decomposition:	Not pertinent.
Reaction with Water:	Reacts violently with formation of sulfuric acid, hydrochloric acid, and evolution of heat and large quantities of dense white acid fumes.
NFPA Hazard Classification	
Health Hazard:	3
Flammability:	0
Reactivity:	2
Authorized Tank Cars:	DOT 105S300ALW or 105S300W (105A built before 1991), 112J340W, 114J340W, and these types tank car having higher tank test pressure or/and tank protective devices. (§ 173.244, B74)

Dimethylhydrazine, unsymmetrical

Chemical Code:	DMH
Formula:	C2H8N2
Molecular Weight:	60.11
UN ID Number:	1163
Hazard Class:	6.1
Hazard Type:	Poison, Flammable Liquid, Corrosive
Normal Boiling Point:	146 °F
State as Shipped:	Liquid
State as Released:	Liquid
Toxicity:	50 ppm IDLH - highly toxic by all pathways of exposure.
Fire:	Poison gases are produced when heated. Vapors may travel to an ignition source and flashback. Heat of fire may cause container to rupture.
Flashpoint (Closed Cup):	N/A °F
Explosion:	Vapors may explode if ignited in a confined space.
Stability During Transportation:	Stable.
Polymerization:	Not pertinent.
Decomposition:	Not pertinent.
Reaction with Water:	No reaction.

NFPA Hazard Classification

Health Hazard:	3
Flammability:	3
Reactivity:	1

Authorized Tank Cars:	DOT 105S300ALW or 105S300W (105A built before 1991), 112J340W, 114J340W, and these types tank car having higher tank test pressure or/and tank protective devices. (§ 173.244, B74)

Ethylene Dichloride

Chemical Code:	EDC
Formula:	C2H4Cl2
Molecular Weight:	98.96
UN ID Number:	1184
Hazard Class:	3
Hazard Type:	Flammable Liquid, Poison
Normal Boiling Point:	182.3 °F
State as Shipped:	Liquid
State as Released:	Liquid
Toxicity:	1000 ppm IDLH - toxic by inhalation in high concentrations.
Fire:	Toxic phosgene and hydrogen chloride are produced in fire. Vapors may travel to an ignition source and flash back. Heat of fire may cause container to rupture.
Flashpoint (Closed Cup):	55 °F
Explosion:	Vapors may explode if ignited in a confined space.
Stability During Transportation:	Stable.
Polymerization:	Not pertinent.
Decomposition:	Not pertinent.
Reaction with Water:	No reaction.

NFPA Hazard Classification

Health Hazard:	3
Flammability:	3
Reactivity:	1
Authorized Tank Cars:	DOT Class 103, 104, 105, 109, 111, 112, 114, and 115. (§ 173.243)

Ethyleneimine, inhibited

Chemical Code:	EIT
Formula:	C2H5N
Molecular Weight:	43.07
UN ID Number:	1185
Hazard Class:	6.1
Hazard Type:	Poison, Flammable Liquid
Normal Boiling Point:	133 °F
State as Shipped:	Liquid
State as Released:	Liquid
Toxicity:	100 ppm IDLH - highly toxic by all pathways of exposure.
Fire:	Irritating vapors are generated upon heating. Vapors are heavier than air and may travel to an ignition source and flash back. May polymerize in fires resulting in evolution of heat and violent container rupture.
Flashpoint (Closed Cup):	12 °F
Explosion:	Vapors may explode if ignited in a confined space. Heat of fire or contact with acids may cause violent polymerization and explosion.
Stability During Transportation:	Stable unless heated under pressure.
Polymerization:	Excessive heat or contact with acids results in explosive polymerization.
Decomposition:	Not pertinent.
Reaction with Water:	Mild non-hazardous reaction may result.
NFPA Hazard Classification	
Health Hazard:	3
Flammability:	3
Reactivity:	3
Authorized Tank Cars:	DOT 105J500W and 105J600W. (§ 173.244, B72)

Hydrogen Chloride, refrigerated

Chemical Code:	HDC
Formula:	HCl
Molecular Weight:	36.46
UN ID Number:	2186
Hazard Class:	2.3
Hazard Type:	Poison Gas, Corrosive
Normal Boiling Point:	-121 °F
State as Shipped:	Compressed Liquefied Gas
State as Released:	Gas or Boiling Liquid
Toxicity:	100 ppm IDLH - highly toxic by inhalation. Corrosive to bodily tissue by all pathways of exposure.
Fire:	Containers may rupture violently in fire due to over pressurization. Will generate large quantities of corrosive gas or fumes upon release.
Flashpoint (Closed Cup):	Not Flammable
Explosion:	Containers may rupture violently in fire due to over pressurization. Contact with most metals produces hydrogen gas that may explode if ignited in confined space.
Stability During Transportation:	Stable.
Polymerization:	Not pertinent.
Decomposition:	Not pertinent.
Reaction with Water:	Moderate reaction with evolution of heat.
NFPA Hazard Classification	
Health Hazard:	3
Flammability:	0
Reactivity:	0
Authorized Tank Cars:	DOT 105S600W (105A600W built before 1991) and this type tank car having tank protective devices. (§ 173.314)

Hydrogen Peroxide, stabilized

Chemical Code:	HPO
Formula:	H2O2
Molecular Weight:	34.01
UN ID Number:	2015
Hazard Class:	5.1
Hazard Type:	Oxidizer, Corrosive
Normal Boiling Point:	302 °F
State as Shipped:	Liquid
State as Released:	Liquid
Toxicity:	75 ppm IDLH - irritating and injurious to body tissue by all pathways of exposure at high concentrations.
Fire:	Not flammable. Containers may rupture violently in fire due to over pressurization.
Flashpoint (Closed Cup):	Not Flammable
Explosion:	Contact with combustible materials or some metals may result in explosive mixtures in cases where the product is concentrated. Container may rupture violently if contaminated by metals or dirt.
Stability During Transportation:	Stable unless contaminated by metals or dirt.
Polymerization:	Not pertinent.
Decomposition:	Will undergo rapid decomposition if heated or placed in contact with metals or dirt.
Reaction with Water:	No reaction.
NFPA Hazard Classification	
Health Hazard:	2
Flammability:	0
Reactivity:	3
Authorized Tank Cars:	DOT Class 103, 104, 105, 109, 111, 112, 114, and 115. (§ 173.243)

Isoprene, inhibited

Chemical Code:	IPR
Formula:	C5H8
Molecular Weight:	68.12
UN ID Number:	1218
Hazard Class:	3
Hazard Type:	Flammable Liquid
Normal Boiling Point:	93.4 °F
State as Shipped:	Liquid
State as Released:	Liquid (boils at 93.4F)
Toxicity:	75 ppm IDLH - low to moderate toxicity by all pathways of exposure.
Fire:	May generate large quantities of flammable gas or vapor upon release. Vapors are heavier than air and may travel to an ignition source and flash back. Heat of fire may cause violent self-polymerization. Containers may rupture violently in fire.
Flashpoint (Closed Cup):	65 °F
Explosion:	Explosion may result if confined vapors ignited. Loss of inhibitor, excessive heat, or chemical contamination may cause spontaneous violent polymerization resulting in container rupture. Explosions possible in presence of certain metals and alloys.
Stability During Transportation:	Stable.
Polymerization:	Excessive heat or chemical contamination may cause spontaneous violent self-polymerization.
Decomposition:	Not pertinent.
Reaction with Water:	No reaction.
NFPA Hazard Classification	
Health Hazard:	2
Flammability:	4
Reactivity:	2
Authorized Tank Cars:	DOT Class 103, 104, 105, 109, 111, 112, 114, and 115. (§ 173.243)

Methyl Bromide, anhydrous

Chemical Code:	MTB
Formula:	CH2Br2
Molecular Weight:	94.95
UN ID Number:	2032
Hazard Class:	2.3
Hazard Type:	Poison Gas
Normal Boiling Point:	38.4 °F
State as Shipped:	Liquefied Gas
State as Released:	Gas, Boiling Liquid, Evaporating Liquid
Toxicity:	2000 ppm IDLH - highly toxic by all pathways of exposure.
Fire:	Practically non-flammable. Containers may rupture violently in fire due to over pressurization.
Flashpoint (Closed Cup):	Practically Not Flammable
Explosion:	Contact with certain substances may result in explosive mixture.
Stability During Transportation:	Stable.
Polymerization:	Not pertinent.
Decomposition:	Not pertinent.
Reaction with Water:	No reaction.

NFPA Hazard Classification

Health Hazard:	3
Flammability:	0
Reactivity:	0
Authorized Tank Cars:	DOT 111A100W4, 105A100W, 112T340W, 114T340W, and these types tank car having higher tank test pressure or/and tank protective devices. (§ 173.314)

Nitric Acid, fuming

Chemical Code:	NAC
Formula:	HNO3
Molecular Weight:	63.01
UN ID Number:	2032
Hazard Class:	8
Hazard Type:	Corrosive, Oxidizer, Poison
Normal Boiling Point:	192 °F
State as Shipped:	Liquid
State as Released:	Liquid
Toxicity:	100 ppm IDLH - highly toxic and corrosive to body tissue by all pathways of exposure.
Fire:	Limited potential that containers may rupture violently in fire due to over pressurization. May generate large quantities of toxic and corrosive vapors and fumes upon release.
Flashpoint (Closed Cup):	Not Flammable
Explosion:	Contact with numerous chemicals and materials may result in violent or explosive reactions. Contact with most metals produces hydrogen gas which may explode if ignited in a confined space.
Stability During Transportation:	May give off toxic red oxides if heated.
Polymerization:	Not pertinent.
Decomposition:	Not pertinent.
Reaction with Water:	Produces heat and toxic fumes.
NFPA Hazard Classification	
Health Hazard:	3
Flammability:	0
Reactivity:	0
Authorized Tank Cars:	DOT 105S300ALW, 105S300W, 112J340W, 114J340W, and these types tank car having higher tank test pressure or/and tank protective devices. (§ 173.244, B74)

Phenol (Carbolic Acid)

Chemical Code:	PHN
Formula:	C6H6O
Molecular Weight:	94.11
UN ID Number:	1671-Solid 2313-Molten 2821-Liquid
Hazard Class:	6.1
Hazard Type:	Poison
Normal Boiling Point:	359.2 °F
State as Shipped:	Solid, Molten, or Liquid Solution
State as Released:	Solid, Molten, or Liquid Solution
Toxicity:	250 ppm IDLH - highly toxic, especially if ingested or absorbed through skin. Fumes are irritating to bodily tissue by all pathways of exposure.
Fire:	Combustible. Difficult to ignite, but will burn if heated.
Flashpoint (Closed Cup):	175 °F
Explosion:	May explode if vapors are ignited in a confined area.
Stability During Transportation:	Stable.
Polymerization:	Not pertinent.
Decomposition:	Not pertinent.
Reaction with Water:	No reaction.

NFPA Hazard Classification

Health Hazard:	3
Flammability:	2
Reactivity:	0

Authorized Tank Cars: Molten Phenol & Liquid Phenol Solutions: DOT Class 103, 104, 105, 109, 111, 112, 114, and 115. (§173.243)

Solid Phenol: DOT Class 103, 104, 105, 109, 111, 112, 114, and 115, and AAR Class 203W, 206W, and 211W. (§ 173.240)

Phosphorous Red

Chemical Code:	PPR
Formula:	P4
Molecular Weight:	123.89
UN ID Number:	1338
Hazard Class:	4.1
Hazard Type:	Flammable Solid
Normal Boiling Point:	N/A °F
State as Shipped:	Solid
State as Released:	Solid
Toxicity:	n/a - harmful if swallowed. Solid red phosphorous is reported to be of negligible toxicity.
Fire:	Flammable. Poisonous, irritating, and flammable gases are produced in fire. Can react violently with oxidizing agent in presence of air and moisture liberating phosphorous acids and toxic, spontaneously flammable phosphine gas. Heat of fire may cause reversion to toxic white phosphorous.
Flashpoint (Closed Cup):	Flammable Solid °F
Explosion:	N/A
Stability During Transportation:	Stable.
Polymerization:	Not pertinent.
Decomposition:	Not pertinent.
Reaction with Water:	No reaction.

NFPA Hazard Classification

Health Hazard:	0
Flammability:	1
Reactivity:	1
Authorized Tank Cars:	N/A (§ N/A)

> **NOTE**
> This chemical is **NOT** authorized for shipment on rail in the U.S. However, it's properties are indicated for informational purposes only.

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Propylene Oxide

Chemical Code:	POX
Formula:	C3H6O
Molecular Weight:	58.08
UN ID Number:	1280
Hazard Class:	3
Hazard Type:	Flammable Liquid
Normal Boiling Point:	93.7 °F
State as Shipped:	Liquid
State as Released:	Liquid (boils at 93.7F)
Toxicity:	2000 ppm IDLH - moderately toxic. Vapor irritating to eyes, nose, and throat.
Fire:	May generate large quantities of flammable vapors upon release. Vapors are heavier than air and may travel to an ignition source and flash back. Exposure of containers to fire may cause violent self-polymerization and container rupture.
Flashpoint (Closed Cup):	-35 °F
Explosion:	Explosion may result if vapors are ignited in a confined area. Containers may rupture violently in fire due to violent self-polymerization. Contamination by certain chemicals may also cause violent spontaneous polymerization resulting in container rupture.
Stability During Transportation:	Stable.
Polymerization:	May occur due to high temperatures or contamination by alkalines, aqueous acids, amines, and acidic alcohols.
Decomposition:	Not pertinent.
Reaction with Water:	No reaction.
NFPA Hazard Classification	
Health Hazard:	2
Flammability:	4
Reactivity:	2
Authorized Tank Cars:	DOT Class 103, 104, 105, 109, 111, 112, 114, and 115. (§ 173.243)

Sodium Hydroxide

Chemical Code:	SHD
Formula:	NaOH
Molecular Weight:	40
UN ID Number:	1824-Liquid Solution 1823-Solid Anhydrous NaOH
Hazard Class:	8
Hazard Type:	Corrosive
Normal Boiling Point:	388-73% NaOH Solution; 2470-Solid NaOH °F
State as Shipped:	Solid NaOH (anhydrous) or Liquid Solution
State as Released:	Solid NaOH (anhydrous) or Liquid Solution
Toxicity:	200 mg/m3 IDLH (145 ppm) - Corrosive to bodily tissues by all pathways of exposure.
Fire:	No special hazards apparent. Remote chance of container rupture in fire.
Flashpoint (Closed Cup):	Not Flammable
Explosion:	Contact with nitro compounds and certain other chemicals may result in the formation of explosive mixtures. Contact with some metals may result in the formation of hydrogen gas that may explode if ignited in confined spaces. Container rupture possible.
Stability During Transportation:	Stable.
Polymerization:	Not pertinent.
Decomposition:	Not pertinent.
Reaction with Water:	Dissolves with liberation of much heat. May steam and spatter while dissolving.

NFPA Hazard Classification

Health Hazard:	3
Flammability:	0
Reactivity:	1

Authorized Tank Cars:	Liquid Solution: DOT Class 103, 104, 105, 109, 111, 112, 114, and 115, and AAR Class 206W. (§ 173.242)
	Solid NaOH: DOT Class 103, 104, 105, 109, 111, 112, 114, and 115, and AAR Class 203W, 206W, and 211W. (§ 173.240)

Styrene Monomer, inhibited

Chemical Code:	STY
Formula:	C8H8
Molecular Weight:	104.15
UN ID Number:	2055
Hazard Class:	3
Hazard Type:	Flammable Liquid
Normal Boiling Point:	293.4 °F
State as Shipped:	Liquid
State as Released:	Liquid
Toxicity:	5000 ppm IDLH - low to moderate toxicity by various pathways of exposure (inhalation, ingestion, skin contact).
Fire:	May generate flammable vapors upon release. Vapors are heavier than air and may travel to an ignition source and flash back. Exposure of containers to fire may result in polymerization and violent container rupture.
Flashpoint (Closed Cup):	88 °F
Explosion:	Explosion may result if vapors are ignited in confined area. Loss of inhibitor, excessive heat, or chemical contamination may cause spontaneous polymerization and violent container rupture.
Stability During Transportation:	Stable, but may polymerize under certain conditions.
Polymerization:	Self-polymerization may occur if heated above 150F. Contamination by metal salts, peroxides, and strong acids may also cause polymerization. 10-15 ppm Teritarybutylcatechol normally used as an inhibitor.
Decomposition:	Not pertinent.
Reaction with Water:	No reaction.
NFPA Hazard Classification	
Health Hazard:	2
Flammability:	3
Reactivity:	2
Authorized Tank Cars:	DOT Class 103, 104, 105, 109, 111, 112, 114, and 115, and AAR Class 206W. (§ 173.242)

Sulfur, molten

Chemical Code:	SXX
Formula:	S8
Molecular Weight:	256.51
UN ID Number:	2448
Hazard Class:	4.1
Hazard Type:	Flammable Solid (International)
Normal Boiling Point:	832.3 °F
State as Shipped:	Molten
State as Released:	Molten
Toxicity:	IDLH n/a - liquid will burn skin and eyes. Harmful if swallowed. Possible hydrocarbon constituents may react with molten material to form combustible and highly toxic hydrogen sulfide.
Fire:	Combustible. Poisonous sulfur dioxide gas is produced in fire.
Flashpoint (Closed Cup):	405 °F
Explosion:	Vapor fumes and finely divided vapor dust may form explosive mixtures with air. Also forms highly explosive and easily detonable mixtures with chlorates and perchlorates and forms gun powder when mixed with potassium nitrate and charcoal.
Stability During Transportation:	Stable.
Polymerization:	Not pertinent.
Decomposition:	Not pertinent.
Reaction with Water:	No reaction.
NFPA Hazard Classification	
Health Hazard:	1
Flammability:	1
Reactivity:	0
Authorized Tank Cars:	DOT Class 103, 104, 105, 109, 111, 112, 114, and 115, and AAR Class 203W, 206W, and 211W. (§ 173.247)

Sulfuric Acid (98%) (<30% SO₃)

Chemical Code:	SFA
Formula:	H2SO4
Molecular Weight:	98.08
UN ID Number:	1830
Hazard Class:	8
Hazard Type:	Corrosive
Normal Boiling Point:	644 °F
State as Shipped:	Liquid
State as Released:	Liquid
Toxicity:	80 mg/m3 (20 ppm) IDLH - highly corrosive to bodily tissue by all pathways of exposure. Harmful if swallowed.
Fire:	May generate large quantities of corrosive fumes or vapor upon release.
Flashpoint (Closed Cup):	Not Flammable
Explosion:	Contact with most metals produces hydrogen gas that may explode if ignited in confined spaces. Contact with certain other materials may result in explosive mixtures.
Stability During Transportation:	Stable.
Polymerization:	Not pertinent.
Decomposition:	Not pertinent.
Reaction with Water:	Reacts violently with evolution of heat.
NFPA Hazard Classification	
Health Hazard:	3
Flammability:	0
Reactivity:	2
Authorized Tank Cars:	DOT Class 103, 104, 105, 109, 111, 112, 114, and 115, and AAR Class 206W. (§ 173.242)

Oleum (fuming sulfuric acid, $SO_3 \geq 30\%$)

Chemical Code: OLM

Formula: H2S2O7

Molecular Weight: 98.08

UN ID Number: 1831

Hazard Class: 8

Hazard Type: Corrosive, Poison

Normal Boiling Point: 186.4 - 287.6, depending on % SO3 content) °F

State as Shipped: Liquid

State as Released: Liquid

Toxicity: IDLH n/a - highly corrosive to bodily tissues by all pathways of exposure.

Fire: Some potential of container rupture due to over pressurization. May generate large quantities of corrosive vapors and fumes upon release. Toxic and irritating gases may evolve in fire.

Flashpoint (Closed Cup): Not Flammable

Explosion: Contact with certain chemicals and substances may result in violent or explosive reactions. Contact with many metals produces hydrogen gas which may explode if ignited in confined spaces.

Stability During Transportation: Stable.

Polymerization: Not pertinent.

Decomposition: Not pertinent.

Reaction with Water: Reacts vigorously or violently producing much heat and spattering.

NFPA Hazard Classification

   Health Hazard: 3

   Flammability: 0

   Reactivity: 2

Authorized Tank Cars: DOT 105S300ALW, 105S300W, 112J340W, 114J340W, and these types tank car having higher tank test pressure or/and tank protective devices. (§ 173.244, B74)

Trichloroethylene

Chemical Code:	TCL
Formula:	C2HCL3
Molecular Weight:	131.4
UN ID Number:	1710
Hazard Class:	6.1
Hazard Type:	Keep Away From Food
Normal Boiling Point:	189 °F
State as Shipped:	Liquid
State as Released:	Liquid
Toxicity:	1000 ppm IDLH - moderately toxic.
Fire:	Will burn but is very difficult to ignite. Containers may rupture due to over pressurization. May generate significant quantities of gas or vapor upon release. May produce toxic or irritating gases in fire.
Flashpoint (Closed Cup):	90 °F
Explosion:	Stable, generally not explosive. Contact with certain materials may generate explosive mixtures. Chance of explosion if warm vapors are ignited in confined area.
Stability During Transportation:	Stable.
Polymerization:	Not pertinent.
Decomposition:	Not pertinent.
Reaction with Water:	No reaction.

NFPA Hazard Classification

Health Hazard:	2
Flammability:	1
Reactivity:	0
Authorized Tank Cars:	DOT Class 103, 104, 105, 109, 111, 112, 114, and 115, and AAR Class 203W, 206W, and 211W. (§ 173.241)

Vinyl Chloride, inhibited

Chemical Code: VCM

Formula: C2H3Cl

Molecular Weight: 62.5

UN ID Number: 1086

Hazard Class: 2.1

Hazard Type: Flammable Gas

Normal Boiling Point: 7.2 °F

State as Shipped: Liquefied Gas

State as Released: Gas or Liquid (Boils at 7.2F)

Toxicity: IDLH n/a. Toxic effects and tissue damage expected upon ingestion of liquid vinyl chloride. Inhalation of gaseous vinyl chloride may cause nervous system disorders. Possible carcinogen.

Fire: Large quantities of flammable gas or vapor generated upon release. Vapors are heavier than air and may travel to an ignition source and flash back. Exposure of containers to fire may cause violent polymerization.

Flashpoint (Closed Cup): 0 °F

Explosion: Excessive heat, light, or air may cause spontaneous violent polymerization and container rupture. Contact with monel, copper, and copper alloys may form explosive mixtures. Unconfined vapor clouds may explode if ignited.

Stability During Transportation: Stable, but may polymerize under certain conditions.

Polymerization: May polymerize violently in presence of excessive heat, light, or air unless stabilized with inhibitor (40-100 ppm phenol).

Decomposition: Not pertinent.

Reaction with Water: No reaction.

NFPA Hazard Classification

    Health Hazard: 2

    Flammability: 4

    Reactivity: 1

Authorized Tank Cars: DOT 111A100W4, 105A100W, 112T340W, 114T340W, and these types tank car having higher tank test pressure or/and tank protective devices. (§ 173.314)

Appendix B

Appendix B

A Model to Describe the Dispersion of Vapors Emanating From an Evaporating Pool of Liquid Chemical

B.1 Introduction

In this appendix, we discuss a model describing the dispersion of vapors generated by the evaporation of a liquid chemical from a pool on the ground. The evaporation rate is assumed to be low because of the low vapor pressure of the liquid at ambient temperature. The objective of the model is to describe the ground level concentration of vapor down wind of the pool.

Figure B.1 shows schematically vapor generating liquid pool and the dispersing vapor plume down wind of the pool. The liquid evaporates due to heat transfer from the wind blowing over the pool and the ground. The evaporated vapors mix with the wind stream and are carried down wind. Beyond the down wind edge of the pool the vapor plume entrains air and gets diluted. The plume spreads both laterally and vertically. The lateral spread is enhanced if the average vapor density in the plume is higher than that of the ambient air. Depending on the magnitude of the negative buoyancy,[1] the initial phases of dispersion near the down wind edge of the pool may be dominated by the gravity driven flow. Correspondingly, the air entrainment rate in this phase will be dependent on the vapor density. Once the negative buoyancy effects become small, the dispersion of vapors is dominated by the atmospheric turbulence. The dispersion is essentially as a neutral density vapor. These physical phenomena are modeled by the following equations.

B.2 Dispersion Model Assumptions

In formulating the model described below, the following assumptions are made:

1. Evaporation rate from the pool is constant and steady.

2. Temperature of the vapor generated by the evaporating pool is essentially the same as the air temperature.

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[1]Gravity driven flow in the lateral direction and entrainment are functions of the local Richardson number (i.e., ratio of gravity induced vapor velocity to the atmospheric turbulence friction velocity).

Figure B.1

Schematic Representation of Dispersion of Vapors Generated by the Evaporation of a Low Vapor Pressure Liquid Pool
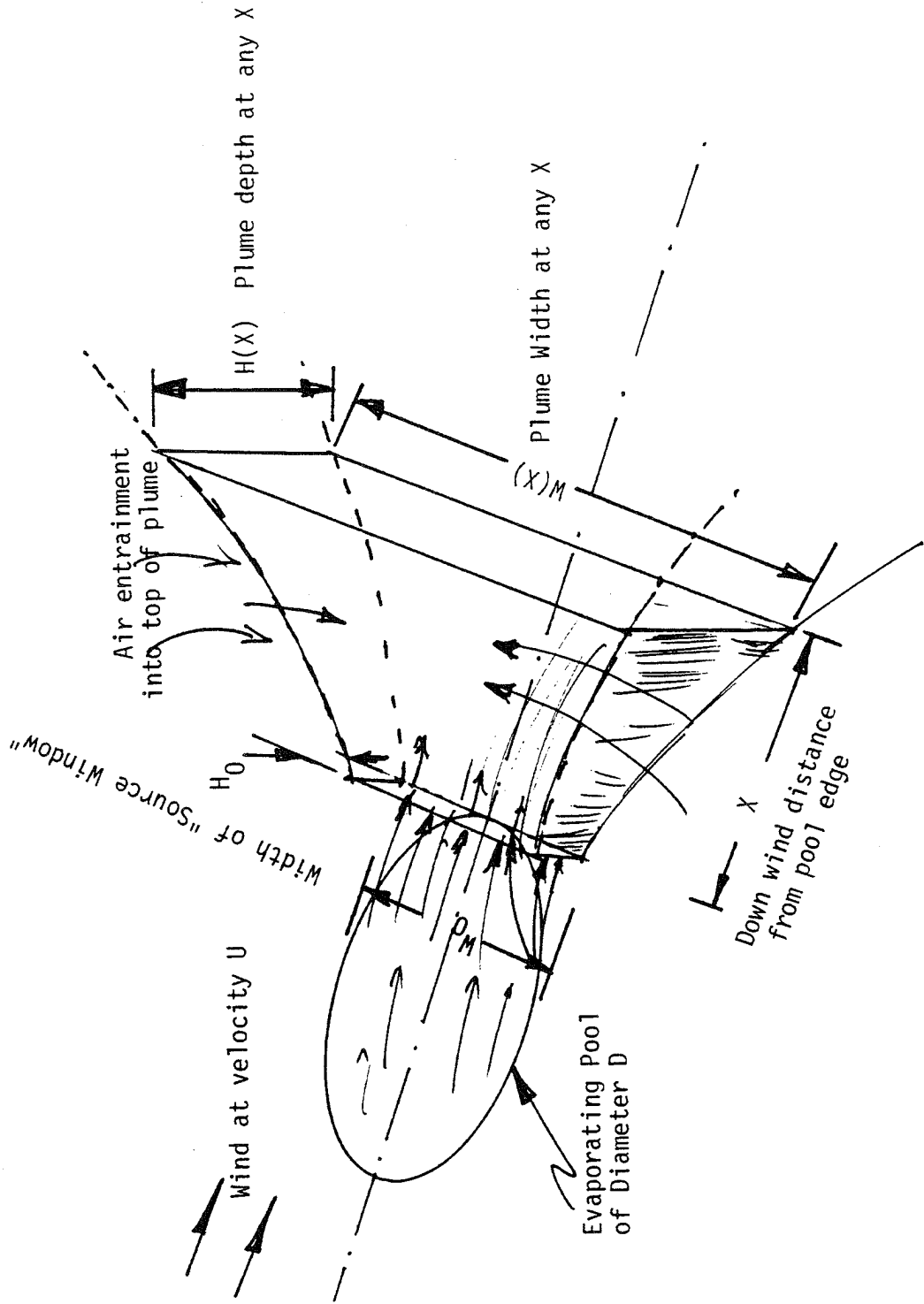
3. The vapors and air can be considered to be perfect gases with the same value for the molar specific heat.

4. Vertical extent of the plume (i.e., the depth) is small compared to its width. Therefore, air entrainment into the plume can be assumed to occur only at its top surface.

5. The vapor plume traverses downward at a constant speed equal to wind speed. The ambient air velocity at a distance above the ground (representing the maximum expected plume depth) is used.

6. All intensive plume properties such as vapor concentration, plume density (of air-vapor mixture), temperature, velocity are uniform within the plume at any specified down wind distance from the pool edge.

Other assumptions made in the derivation of the model are indicated at the appropriate places.

B.3 Vapor Plume Characteristics at Down Wind Pool Edge

Let,

$\dot{M}_e$ = Total mass rate of vapor evaporation over the pool[2][3]

$\dot{M}_{a,o}$ = Mass rate of entrainment of ambient air over the pool

$\dot{M}_o$ = Mass flow rate of vapor air mixture at the down wind edge of the pool

Hence,

$$\dot{M}_o = \dot{M}_e + \dot{M}_{a,o} \tag{B.1}$$

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[2] The model by which $\dot{M}_e$ and $\dot{M}_{a,o}$ can be calculated given the vapor pressure of the liquid, wind speed, and pool diameter is described in a report by Raj and Morris (1988).

[3] All symbols are defined in the nomenclature list provided in Section B.6 at the end of this appendix.

Also if,

$\dot{V}_e$ = Volume rate of the flow vapor generated over the pool at temperature Ta

$\dot{V}_{a,o}$ = Volume rate of flow air entrained over the pool

$\dot{V}_o$ = Total volume flow rate of gases at the down wind pool edge

Then it can be shown, as a consequence of assumption 3, that

$$\dot{V}_o = \dot{V}_e + \dot{V}_{a,o} \qquad (B.2)$$

Noting that,

$$\dot{M}_e = \dot{V}_e \, \rho_v \qquad (B.3a)$$

$$\dot{M}_{a,o} = \dot{V}_{a,o} \, \rho_a \qquad (B.3b)$$

and with

$$\dot{M}_o = \dot{V}_o \, \rho_o \qquad (B.3c)$$

ρ_o the mean density of vapor air mixture in the plume at the down wind edge of the pool can be shown to be

$$\frac{1}{\rho_o} = \frac{1}{(1 + r_o)} \left[\frac{1}{\rho_v} + \frac{r_o}{\rho_a} \right]$$

and

$$C_o = \frac{\dot{V}_e}{\dot{V}_o} \qquad \qquad = \text{Vapor concentration at} \qquad (B.5)$$
$$\text{down wind edge of pool}$$

where,

$$r_o \quad = \quad \frac{\dot{M}_{a,o}}{\dot{M}_e} \qquad\qquad\qquad = \quad \text{dilution ratio over the pool}$$

$$\rho_v \quad = \quad \text{vapor density at generation} \quad = \quad \frac{P_v^{sat}(T_a)\,\mu_v}{R_u\,T_a} \qquad\qquad (B.6)$$

Also, the physical dimensions of the "source window" at the down wind edge of the pool are calculated as follows:

$$W_o \quad = \quad \text{Width at down wind edge} \qquad = \quad D \qquad\qquad (B.7a)$$

$$H_o \quad = \quad \text{Plume depth at down wind edge} \quad = \quad \frac{\dot{V}_o}{U\,W_o} \qquad\qquad (B.7b)$$
$$\text{of pool}$$

B.4 Heavy Gas Dispersion Phase Near the Down Wind Edge of Pool

In this derivation we assume that the overall plume density ρ is greater than ρ_a, the air density.

Let

X	$=$	Down wind distance from the down wind edge of the pool
α	$=$	Air entrainment rate coefficient
H	$=$	Plume depth at any distance X
$W(x)$	$=$	Width of plume at any distance X
$\dot{V}$	$=$	Total volume rate of flow of air and vapor in the plume at X
$\dot{M}$	$=$	Mass flow rate in the plume at X
$\dot{V}_a$	$=$	Volume rate of entrainment of air into the plume between $X=0$ and any down wind distance X

At any X distance we have

$$\dot{M} = \dot{M}_o + \dot{M}_a$$
$$(\textit{Mass Continuity})$$

(B.8)

$$\dot{V} = \dot{V}_o + \dot{V}_a$$
$$(\textit{Volumetric Continuity}$$
$$\textit{in View of Assumption 3})$$

(B.9)

$$\dot{V} = U \, H \, W$$

(B.10)

Equation (B.8) is rewritten as

$$\rho \, \dot{V} = \rho_o \, \dot{V}_o + \rho_a \, \dot{V}_a$$

(B.11)

Using (B.9) and (B.11) it can be shown that

$$\dot{V} \left(\rho - \rho_a \right) = \dot{V}_o \left(\rho_o - \rho_a \right) = \dot{B}_o = \text{Buoyancy} = \text{Constant}$$
$$\text{Flux}$$

(B.12)

The air entrainment equation is written as

$$\frac{d \dot{V}}{d X} = \alpha \, U \, W$$

(B.13)

The lateral spread of the plume due to gravity is given by

$$\frac{d W}{d X} = 2 k \sqrt{g \, \frac{\left(\rho - \rho_a \right)}{\rho_a} \, H}$$

(B.14)

B-6

Substituting for $\dot{H}$ in terms of $\dot{V}$ from equation (B.10) and using equation (B.12) we can show that

$$U \frac{d W}{d X} = 2 k \sqrt{\frac{g \dot{B}_o}{U W \rho_a}}$$

(B.15)

Integration of the above equation gives

$$\left[\left(\frac{W}{W_o} \right)^{\frac{3}{2}} - 1 \right] = 3 k \sqrt{\frac{g \dot{B}_o}{U^3 W_o^3 \rho_a}} \ X$$

(B.16)

We now define the following parameters to simplify other equations

$$X_{ch} = \frac{1}{3 k} \sqrt{\frac{U^3 W_o^3 \rho_a}{g \dot{B}_o}}$$
= A characteristic dispersion length scale

(B.17a)

$$\xi = X/X_{ch}$$
= Non-dimensional distance

(B.17b)

$$\eta = W/W_o$$
= Non-dimensional plume width

(B.17c)

In view of the definitions in (B.17a), (B.17b), and (B.17c), equation (B.16) can be rewritten as

$$\left(\eta^{\frac{3}{2}} - 1 \right) = \xi$$

(B.18)

The *volume of air entrained* into the plume up to X is determined from

$$\dot{V}_a (X) = \int_o^x \dot{V}_a' (X) \ dx = \int_o^x \alpha \ U \ W \ dx$$

(B.19)

B-7

Substituting for $\dot{W}$ from (B.18) and integrating, we can show that

$$\dot{V}_a(X) = \frac{3}{5} \alpha \, U \, W_o \, X_{ch} \left[(1 + \xi)^{\frac{5}{3}} - 1 \right] \qquad (B.20)$$

Now the total volume flow at any point X is

$$\dot{V}(X) = U \, W \, H = \dot{V}_o + \dot{V}_a \qquad (B.21)$$

$$\dot{V}_o = U \, W_o \, H_o \qquad (B.22)$$

Substituting for $\dot{V}_a$ from equation (B.20) and using the results from equation (B.18) and (B.22) it can be shown that,

$$\frac{H}{H_o} (1 + \xi)^{\frac{3}{4}} = 1 + \frac{3}{5} \alpha \left(\frac{X_{ch}}{H_o} \right) \left[(1 + \xi)^{\frac{5}{3}} - 1 \right] \qquad (B.23)$$

The above result describes the variation of plume depth H with down wind distance X (or ξ).

The molar concentration of vapor in the plume at any X is determined by

$$C(X) = \frac{\dot{V}_e}{\dot{V}(X)} \qquad (B.24)$$

i.e.,

$$C = \frac{\dot{V}_e}{\dot{V}_o} \frac{\dot{V}_o}{\dot{V}(X)} = C_o \frac{W_o \, H_o}{W \, H} \qquad (B.25)$$

B-8

Substituting for W/W_o from (B.18) and for H/H_o from equation (B.23) we get

$$C = C_o \cfrac{1}{1 + \cfrac{3}{5} \alpha \left(\cfrac{X_{ch}}{H_o} \right) \left[(1 + \xi)^{\frac{5}{3}} - 1 \right]} \tag{B.26}$$

B.5　Dispersion in Neutral Density Regime

B.5.1　Transition Parameter Values

When the fractional density deviation[4] of the vapor plume is very small then the vapor can be considered to be neutrally buoyant. The dispersion models applicable to a neutral density (with respect to that of air) vapors can be used. These models are basically Gaussian models, suitably modified to take into account the different geometrical shapes of the vapor source.

The most often used criterion for determining the cessation of the heavy gas type dispersion and the beginning of Gaussian dispersion phase is the Richardson number criterion. Gaussian (or neutral density) dispersion is said to begin when

$$R_i \leq 1 \tag{B.27}$$

where

$$R_i = \cfrac{g \left(\cfrac{\rho}{\rho_a} - 1 \right) H}{U^2} = \cfrac{Gravitational\ Force}{Inertial\ Force} \tag{B.28}$$

R_i　=　Densimetric Richardson number

H　=　Cloud depth

U　=　Wind speed

---

[4]Fraction density deviation = $(\rho/\rho_a - 1)$

B-9

$$\rho \quad = \quad \text{Density of vapor cloud}$$

From the equation of conservation of buoyancy (equation (B.12)) we get,

$$U \, W \, H \, (\rho - \rho_a) = U \, W_o \, H_o \, (\rho_o - \rho_a) \tag{B.29}$$

i.e.,

$$(\rho - \rho_a) \, H = H_o \, \frac{(\rho_o - \rho_a)}{(W/W_o)} \tag{B.30}$$

Substituting equation (B.30) in (B.28) and using the result in equation (B.18) we can show that

$$R_i = (R_i)_o \, \frac{1}{(1 + \xi)^{\frac{2}{3}}} \tag{B.31}$$

where

$$(R_i)_o = \frac{g \, (\rho_o - \rho_a) \, H_o}{\rho_a \, U^2} = \begin{array}{l} Richardson \; number \; at \; the \\ down \; wind \; edge \; of \; pool \end{array} \tag{B.32}$$

The above equation shows that the Richardson number continuously decreases with distance down wind of the pool edge. When the local Richardson number is unity, we can assume that the heavy gas dispersion regime is complete and neutral density dispersion begins.

We define the following *transition* parameter values:

X_{tr} = down wind distance at which R_i=1 (i.e., transition distance)

C_{tr} = mean plume concentration at $X=X_{tr}$ (mole fraction)

C_{tr}^m = mean mass concentration of vapor at $X=X_{tr}$ (kg/m^3)

W_{tr} = plume width at transition location

H_{tr} = plume depth at transition location

The neutral density dispersion model is discussed in the next section.

B.5.2   Modified Gaussian Dispersion Model

We define a new down wind distance coordinate as follows:

$$X' = X - X_{tr} \tag{B.33}$$

where

X' =   Distance from the transition point

X =   Distance from the down wind edge of pool

Also the cross wind dispersion parameter (σ_y) and the vertical dispersion parameter (σ_z) are dependent on the distance X' and the stability of the atmosphere. These values are obtained from the correlations presented by Slade (1968).

At the transition location, the plume cross section is rectangular with uniform concentration distribution, both horizontally and vertically. The source for calculating the concentration variation in the Gaussian phase is assumed to be rectangular (of dimensions equal to the plume cross sectional dimensions at transition location). In the Gaussian phase of dispersion, the vapor concentration varies both horizontally from the plume center and vertically above ground. The peak concentration is at the ground level and at plume center.

The vapor concentration (in mass units) at any point X', Y, Z, can be shown to be given by

$$C^m(X', Y, Z) = C_{tr}^m \; \tfrac{1}{2} \left[erf \left[\frac{0.5 \; W_{tr} - Y}{\sqrt{2} \; \sigma_Y} \right] + erf \left[\frac{0.5 \; W_{tr} + Y}{\sqrt{2} \; \sigma_Y} \right] \right]$$

$$x \; \tfrac{1}{2} \left[erf \left[\frac{H_{tr} + Z}{\sqrt{2} \; \sigma_Z} \right] + erf \left[\frac{H_{tr} - Z}{\sqrt{2} \; \sigma_Z} \right] \right]$$

$$\tag{B.34}$$

Where "erf" represents the error function.

If,

c_{Haz}^{m} =   Vapor hazard concentration in mass units (kg/m^3)

Y_{Haz} =   Cross wind distance at ground level to the   (m)
hazard concentration contour

then the value of Y_{Haz} at every X' distance can be calculated from the equation below (obtained from equation B.34).

$$c_{Haz}^{m} = C_{tr}^{m} \ erf \left(\frac{H_{tr}}{\sqrt{2} \ \sigma_z} \right) \left[erf \left[\frac{0.5 \ W_{tr} - Y_{Haz}}{\sqrt{2} \ \sigma_Y} \right] + erf \left[\frac{0.5 \ W_{tr} + Y_{Haz}}{\sqrt{2} \ \sigma_Y} \right] \right]$$

(B.35)

The above implicit equation has to be solved for Y_{haz} for every value of X', given the hazard concentration c_{Haz}^{m}.

If the gas does not display any heavy gas behavior, that is, the value of Richardson number (Ri_o) at the down wind edge of the pool is less than unity then all of the dispersion phase can be considered to be in the neutral density regime. In this case the only equation of relevance is equation (B.34) in which all "transition" parameter values are replaced by their respective values at the pool edge. The distance X' will be the same as the distance X.

B.6 Nomenclature

Symbol	Definition	Units
$\dot{B}$	buoyancy flow rate at any point $= (\rho - \rho_a) \ V$	(kg/s)
C	mole concentration of vapor at any down wind distance	
C_o	mole concentration of vapor at pool dow wind edge	
C^m	mass concentration of vapor at any point	(kg/m^3)
D	diameter of evaporating liquid pool	(m)
H	plume vertical depth	(m)

k	a constant in the gravity spread equation	
$\dot{m}''$	evaporation rate from the pool	(kg/m² s)
$\dot{M}$	mass flow rate of gases at any X	(kg/s)
$\dot{M}_a$	total mass rate of air entrained between down wind edge of pool and X	(kg/s)
$\dot{M}_o$	mass flow rate of gases at the down wind edge of pool	(kg/s)
P_a	partial pressure of chemical vapor over pool surface $(= P_{atm} - P_v)$	(N/m²)
P_{atm}	atmospheric pressure	(N/m²)
P_v	partial pressure of chemical vapor over pool $= P_v^{Sat}(T_a)$ i.e., its saturation pressure at ambient air temperature	(N/m²)
r	dilution ratio; i.e., mass of air entrained per unit mass of chemical	
Ri	Richardson number (see equation B.28)	
R_u	universal gas constant	(J/mole K)
T	temperature	(K)
T_a	ambient air temperature	(K)
U	wind speed (considered constant)	(m/s)
$\dot{V}$	total volume flow rate at any section	(m³/s)
$\dot{V}_a(X)$	total volume rate of air entrained into the plume between X=0 and x=X	(m³/s)
$\dot{V}_{a,o}$	total volume flow rate of air over the evaporating liquid pool which mixes with the chemical vapor	(m³/s)
$\dot{V}_c$	volume rate of generation of vapors at ambient pressure (by the evaporation of liquid pool)	(m³/s)
$\dot{V}_o$	total volumetric flow of gases at the down wind edge of pool	(m³/s)
W	width of plume at any point	(m)

X_{ch}	a characteristic distance	(m)
X	down wind distance from the edge of pool	(m)
y	cross wind distance	(m)
z	vertical distance above ground	(m)

Greek Letters:

α	entrainment coefficient	
η	dimensionless width of plume (W/W_o)	
μ	molecular weight	(kg/mole)
ξ	dimensionless down wind distance (X/X_{ch})	
ρ	density of gases at any X	(kg/m^3)
ρ_a	ambient air density	(kg/m^3)
ρ_o	density of gases (air and vapor mixture) at the down wind edge of pool	(kg/m^3)

Superscripts:

'	represents "per unit down wind distance"
.	represents temporal rate of change

Subscripts:

a	pertains to ambient air conditions
c	pertains to pure chemical vapor
ch	a characteristic condition
e	entrainment condition
o	refers to the conditions at the down wind edge of pool
p	pool conditions
tr	transition condition
v	pertains to vapor