U.S. Department of Transportation

Federal Railroad Administration

TANK CAR RELIEF VALVE REQUIREMENTS FOR LIQUID POISON INHALATION HAZARD (PIH) LADING

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16. Abstract

Analyses were performed by Transportation Technology Center, Inc., a subsidiary of the Association of American Railroads, to determine if the changes made to Chapter 49 of the Code of Federal Regulations under docket HM-181 for the selection pressure relief valves used on tank cars transporting liquid materials designated as poison inhalation hazard (PIH) would affect safety. Also considered were the implications for other materials that are thermally reactive, polymerizable, or dangerous when wet. Key findings are:

- The start-to-discharge pressure of a pressure relief valve on a tank car used to transport PIH materials is not a significant factor in the survival of the car when subjected to a 100-minute pool fire provided a large enough flow capacity is chosen for the valve.

- If the overturned car case is to be included in the conditions to be considered by the regulations, it is recommended that the criterion for the pressure in the tank not exceeding the flow capacity of the valve not apply.

- Although pressure relief design methods for polymerizable and thermally reactive materials are not considered in current regulations, survival of a 100-minute fire is likely for most cases.

- The relatively high start to discharge pressures used in present tank car safety relief devices are an impediment to achieving practical sized pressure relief for most runaway reaction scenarios.

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METRIC CONVERSION FACTORS

Approximate Conversions to Metric Measures

Symbol	When You Know	Multiply by	To Find	Symbol

LENGTH

Symbol	When You Know	Multiply by	To Find	Symbol
in	inches	*2.50	centimeters	cm
ft	feet	30.00	centimeters	cm
yd	yards	0.90	meters	m
mi	miles	1.60	kilometers	km

AREA

Symbol	When You Know	Multiply by	To Find	Symbol
in²	square inches	6.50	square centimeters	cm²
ft²	square feet	0.09	square meters	m²
yd²	square yards	0.80	square meters	m²
mi²	square miles	2.60	square kilometers	km²
	acres	0.40	hectares	ha

MASS (weight)

Symbol	When You Know	Multiply by	To Find	Symbol
oz	ounces	28.00	grams	g
lb	pounds	0.45	kilograms	kg
	short tons (2000 lb)	0.90	tonnes	t

VOLUME

Symbol	When You Know	Multiply by	To Find	Symbol
tsp	teaspoons	5.00	milliliters	ml
Tbsp	tablespoons	15.00	milliliters	ml
fl oz	fluid ounces	30.00	milliliters	ml
c	cups	0.24	liters	l
pt	pints	0.47	liters	l
qt	quarts	0.95	liters	l
gal	gallons	3.80	liters	l
ft³	cubic feet	0.03	cubic meters	m³
yd³	cubic yards	0.76	cubic meters	m³

TEMPERATURE (exact)

Symbol	When You Know	Multiply by	To Find	Symbol
°F	Fahrenheit temperature	5/9 (after subtracting 32)	Celsius temperature	°C

* 1 in. = 2.54 cm (exactly)

Approximate Conversions from Metric Measures

LENGTH

Symbol	When You Know	Multiply by	To Find	Symbol
mm	millimeters	0.04	inches	in
cm	centimeters	0.40	inches	in
m	meters	3.30	feet	ft
m	meters	1.10	yards	yd
km	kilometers	0.60	miles	mi

AREA

Symbol	When You Know	Multiply by	To Find	Symbol
cm²	square centim.	0.16	square inches	in²
m²	square meters	1.20	square yards	yd²
km²	square kilom.	0.40	square miles	mi²
ha	hectares (10,000 m²)	2.50	acres	

MASS (weight)

Symbol	When You Know	Multiply by	To Find	Symbol
g	grams	0.035	ounces	oz
kg	kilograms	2.2	pounds	lb
t	tonnes (1000 kg)	1.1	short tons	

VOLUME

Symbol	When You Know	Multiply by	To Find	Symbol
ml	milliliters	0.03	fluid ounces	fl oz
l	liters	2.10	pints	pt
l	liters	1.06	quarts	qt
l	liters	0.26	gallons	gal
m³	cubic meters	36.00	cubic feet	ft³
m³	cubic meters	1.30	cubic yards	yd³

TEMPERATURE (exact)

Symbol	When You Know	Multiply by	To Find	Symbol
°C	Celsius temperature	9/5 (then add 32)	Fahrenheit temperature	°F

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

inches / cm scale: 9 8 7 6 5 4 3 2 1 inches ; 23 22 21 20 19 18 17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 cm
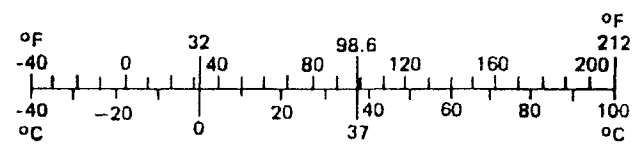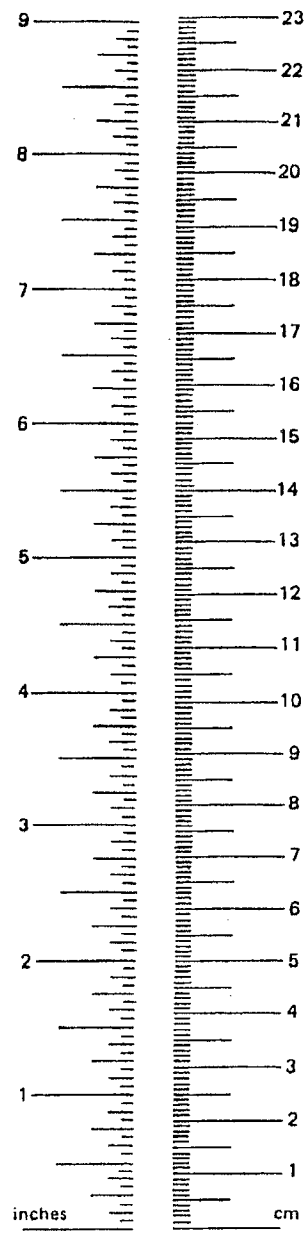
EXECUTIVE SUMMARY

Analyses were performed by Transportation Technology Center, Inc., a subsidiary of the Association of American Railroads (AAR), to determine if the changes made to the DOT packaging requirements in Chapter 49 of the Code of Federal Regulations (CFR) under HM-181 for the selection of pressure relief valves used on cars transporting liquid materials designated as poison inhalation hazard (PIH) materials would affect safety. Implications for other liquid materials that are thermally reactive (TR), polymerizable (P), or dangerous when wet (W) were also considered.

Five observations were made:

- None of the tank cars containing the PIH products was predicted to fail. A wide margin between the pressure in the tank and burst strength of the tank was maintained continuously.

- The analyses showed a wide range in pressure relief valve flow capacities required for the cars. Smaller capacities were generally associated with the higher density products having low vapor pressures.

- For all but three of the products — acetone cyanohydrin, acrolein and hydrogen cyanide — the regulations would permit the selection of a pressure relief valve with a start-to-discharge pressure as low as 75 psi. The analyses showed no particular advantage for using the lower pressure valve. While the use of a lower pressure valve usually resulted in a larger margin between the pressure in the tank and the burst strength of the tank for the upright car case, it sometimes resulted in a lower margin for the overturned car case. Also, especially in the overturned car case, it resulted in more product being released from the car.

- In many of the overturned car cases, a larger flow capacity valve was required to meet the requirement to limit the pressure to the flow rating pressure. In several cases, it was impossible to get a valve with a large enough flow capacity to meet this requirement.

- The use of high temperature thermal insulation does not appear necessary for the survival of cars containing PIH materials for the 100-minute pool fire environment. The jacket on the tank, together with the air space between the jacket and the tank after the fiberglass insulation has deteriorated, appears to provide sufficient protection.

Four major conclusions and recommendations were made from the work:

- The start-to-discharge pressure of a pressure relief valve on a tank car used to transport liquid PIH materials is not a significant factor in the survival of the car when subjected to a 100-minute pool fire provided a large enough flow capacity is chosen for the valve. When conducting the analyses to determine the required flow capacity of the valve, it is recommended that the FRA full fire engulfment condition be used instead of the AAR fire criterion because it gives a more conservative result.

- If the overturned car case is to be included in the conditions to be considered in fulfillment of 49 CFR 179.18(b), it is recommended that the criterion for the pressure in

the tank not exceeding the flow rating pressure of the valve not apply. This is because it is likely to result in an unreasonably large flow capacity requirement for the valve.

- Pressure relief design methods for polymerizable and thermally reactive compounds are not considered in current standards for railroad tank cars. However, survival of a 100-minute duration pool fire is likely for most compounds. The unresolved issues clearly reside in the time domain beyond 100 minutes for which further research is recommended. Runaway reaction prevention through proper use and understanding of inhibitors and related thermal stability issues and control and/or prevention of contamination are the most effective pro-active safety measures.

- The relatively high start-to-discharge pressures used in present tank car safety relief devices are an impediment to achieving practical sized pressure relief for most runaway reaction scenarios. Insulation could conceivably be an effective component in runaway reaction prevention however is not without adverse effects that also require consideration. Any attempt to include runaway exothermic reactions in the standards for tank car pressure relief vent sizing would be a difficult undertaking with prospects for only limited success on a case-by-case basis.

In conducting the analyses, a list of liquid commodities classified as PIH, TR, P, or W that can be shipped in railroad tank cars was compiled. It was then determined how many tank car loads per year of each of these products were shipped over the four-year period, 1996-1999 using AAR TRAIN II annual shipment data. Only those liquid PIH commodities where an average of 100 or more tank-car loads were shipped in the four-year period were considered. This reduced the list to 11 PIH materials. The thermal properties of these commodities were determined so that analyses could be run to predict the behavior of tank cars loaded with these products when subjected to a pool fire. The source for the property data was the American Institute of Chemical Engineers (AIChE), Design Institute for Physical Properties.

Analyses were then conducted on tank cars containing the selected PIH products. The analyses were conducted to determine the pressure relief valve characteristics required to prevent failure when a tank car is exposed to the effects of a 100 minute duration pool fire as defined in Appendix B to 49 CFR 179. The analyses also showed how much of the product would be released through the valve because of liquid expansion in the tank as the product is heated and vapor flow through the valve, if any. Both the upright and overturned car positions were considered.

Special attention was given to the TR and P products. This included consideration to the conditions under which these commodities thermally react, or polymerize, and whether or not these conditions might be reached during fire exposure. Also, since most of these products are inhibited, the conditions under which the inhibitor might become inactive as a result of fire exposure were considered.

Table of Contents

List of Tables

1.0 INTRODUCTION

Transportation Technology Center, Inc. (TTCI), a subsidiary of the Association of American Railroads (AAR), performed analyses to determine if the changes made to the Department of Transportation's (DOT) packaging regulations under HM-181 for the selection pressure relief valves used on cars transporting liquid poison inhalation hazard (PIH) materials would affect safety. Also considered were the implications for other liquid materials that are classified as thermally reactive (TR), polymerizable (P), or dangerous when wet (W). The work described in this report was conducted under authorization of Federal Railroad Administration (FRA) Contract No. DTFR53-93-C-00001, Task Order Number 124.

1.1 OBJECTIVE

The objective of this research was to determine if those changes made under docket HM-181 would affect safety. Several low vapor pressure liquid materials were added to the PIH category under the docket. Changes to packaging requirements were also made that required liquid PIH's to be transported in higher test pressure tank cars with pressure relief valves that had higher start-to-discharge pressures. The concern was that under some fire exposure conditions, a tank car might fail before the pressure relief valve functioned. If that were to occur, a large quantity of poisonous material would be released into the environment. If determined necessary through this research, selection parameters for pressure relief valves were to be recommended. The implications for other low vapor pressure liquid materials that have an acute hazard such as thermal reactivity (TR), polymerization (P), or dangerous when wet (W) were also to be considered.

1.2 SCOPE

The scope of work included:

- Evaluation of the present standards for the selection of pressure relief devices.
- Consideration of the failure of a tank car due to the improper selection of a pressure relief valve.
- The development and recommendation of standards for the proper selection of pressure relief devices.
- Provide, if needed, recommendations for a test program to verify valve selection parameters.

1.3 BACKGROUND

Previous studies, in addition to changes to the regulations, led to the initiation of this project. Extensive studies have been conducted to determine the effects of fire on tank cars containing liquefied gases such as propane or anhydrous ammonia. Those studies have shown the need to have large capacity pressure relief valves and insulation systems that are resistant to high temperature for the cars to survive the effects of 100-minute exposure to a pool fire. Similar studies to determine fire effects on tank cars containing liquid PIH, TR, or P materials have been much more limited. These

1

products can be shipped in tank cars that do not have high temperature insulation systems thus leading to some concern about their behavior when exposed to fire.

In 1996 the pressure relief valve requirements were removed from 49 CFR 179.100-1 for each of the specific pressure car classes and from 49 CFR 179.200-1 for each of the non-pressure car cases. For example, a pressure car with a 300 pounds per square inch (psi) test pressure would have been equipped with a pressure relief valve having a 225 psi start-to-discharge pressure. Pressure relief valve requirements were made much more general and placed in § 179.15. This section permits pressure relief valve start-to-discharge pressure as low as 75 psi for low vapor pressure products. Thus, there is the potential for lowering the start-to-discharge pressure of the pressure relief valve on a tank car if a fire analyses showed that the car, with a PIH product, was predicted to fail if equipped with a higher start-to-discharge pressure valve.

2.0 PROCEDURE

The first step in conducting the work was to compile a list of liquid commodities classified as PIH, TR, P, or W that could be shipped in railroad tank cars. It was then determined how many tank-car loads per year of each of these products were shipped over the 4-year period from 1996 to 1999 using the AAR TRAIN II data. The results of this analysis are displayed in Table 2.1.

To make the work more manageable, the list of PIH, TR, P, and W commodities were then reduced to consider only those where an average of 100 or more tank can loads were shipped annually in the 4-year period. This reduced the list to 32 products: 11 PIH and 21 TR, P, and W, shown in Table 2.2.

The Analysis of Fire Effects on Tank Cars (AFFTAC) computer model[1] was used to determine the behavior of tank cars loaded with these commodities when subjected to an external fire. The source of the physical property data is the American Institute of Chemical Engineers (AIChE), Design Institute for Physical Properties (DIPPR).[2] The source data is represented in a highly compact form of property correlation coefficients with absolute temperature as the independent variable. In order to provide a user friendly and useful database for AFFTAC analysis, the DIPPR property correlation equations and primary correlation coefficients were assembled into Microsoft® Excel work sheets, with appropriate tabulations of thermodynamic and transport physical properties. In all, 40 compounds are included in a project reference database.[3] The compounds included in the database are listed in Table 2.3.

AFFTAC analyses were carried out on a selected subset of the compounds included in the database. These analysis show bulk heat-up rates, inventory loss due to liquid thermal expansion and due to bulk boiling, as well as the safety relief valve size required to prevent failure in a 100-minute duration external fire. All of the selected products were considered in a separate analysis that indicated the physical property factors, which determine the relative response rankings. This property sensitivity analysis demonstrated that those products selected for detailed AFFTAC

2

analysis adequately represent the likely response of any product of interest included in the project database. The details of the property sensitivity analysis are included in the Appendix.

Finally, special attention was given to the TR and P products. This included consideration to the conditions under which these commodities thermally react or polymerize, and whether or not these conditions might be reached during fire exposure. Also, since most of these products are inhibited, the conditions under which the inhibitor might become inactive as a result of fire exposure were considered.

Table 2-1. Annual Tank Car Shipments of Materials with PIH, TR, P, and W Classifications, 1996-1999

	Hazard	4 Yr. Avg.	Total	1999	1998	1997	1996
Hazard Key:							
1: Poison by Inhalation (PIH)							
2: Thermally Reactive							
3. Dangerous When Wet							
4. Polymerization Hazard							
Shaded Area Indicates Average Annual Shipments of 100 or More Cars							
Trimethoxysilane	1	0	1	0	1	0	0
Sulfuryl Chloride	1	0	1	0	1	0	0
Ethyl Nitrate Solution	1	1	3	3	0	0	0
Toxic Liquid Flammable Chloropicrin	1	2	6	0	0	6	0
Flammable Liquid NOS (Chloropicrin)	1	3	10	2	3	4	1
Ethylene Dibromide	1	4	14	0	0	4	10
Toxic Liquid Organic NOS	1	6	25	15	3	5	2
Hexachlorocyclopentadiene	1	25	98	27	25	23	23
Chloropicrin	1	46	184	63	48	35	38
Toxic Liquid Flammable Organic NOS	1	61	243	51	81	56	55
Allyl Alcohol	1	102	408	122	105	86	95
Phosphorus Trichloride	1	187	749	42	208	257	242
Chlorosulfonic Acid	1	260	1038	243	251	265	279
Titanium Tetrachloride	1	302	1206	321	260	313	312
Acetone Cyanohydrin	1	664	2657	691	610	662	694
Sulfuric Acid, Fuming	1	1931	7724	1786	2030	1958	1950
Hydrogen Fluoride, Anhydrous	1	3070	12281	3266	3308	2997	2710
Nitroethane	2	0	1	0	0	1	0
Motor Fuel Antiknock Mixtures	2	34	134	19	19	39	57
Vinyl Toluenes	2	87	349	51	88	101	109
Vinylidene Chloride	2	806	3222	809	800	773	840
Dinitrotoluenes	2	1091	4362	2	1178	1479	1703
Hydrogen Peroxide, Aqueous Solutions	2	1152	4608	1189	1217	1162	1040
Acetaldehyde	2	1914	7654	1874	1771	2060	1949
Acrylic Acid	2	4245	16980	5190	4054	4099	3637
Vinyl Acetate	2	6766	27064	6996	6358	6774	6936
1,2-Dichloroethylene	3	0	1	0	0	0	1
Octadiene	3	1	2	0	0	0	2
Isobuty Methacrylate	3	4	14	0	1	8	5

Table 2-1. Annual Tank Car Shipments of Materials with PIH, TR, P, and W Classifications, 1996-1999 (continued)

n-Butyl Methacrylate	3	122	487	128	107	121	131
Methyltrichlorosilane	3	268	1071	283	314	265	209
Furfural	3	295	1180	13	363	439	365
Acrylamide	3	825	3301	1147	584	614	956
Epichlorohydrin	3	1036	4142	1048	1025	1029	1040
Ethyl Acrylate	3	1486	5942	1506	1493	1414	1529
Methylallyl Chloride	4	3	10	0	0	4	6
Flourobenzene	4	8	33	9	14	0	10
Isobutyl Acetate	4	334	1336	387	337	304	308
Toxic Liquid Flammable NOS Methylchlorosilane	1, 3	0	1	0	0	1	0
Tocix Liquid Organic NOS Antimony Pentachloride	1, 3	1	5	1	2	1	1
Toxic Liquid Organic NOS Sulfur Dichloride	1, 3	41	164	20	47	43	54
Toxic Liquid Corrosive Inorganic NOS Sulfur Chloride	1, 3	144	576	151	142	146	137
Isopropyl Isocyanate	1,2	1	2	0	0	0	2
Ethyl Phosphonothiotic Dichloride, Anhydrous	1,2	1	2	0	0	1	1
Allyl Chloroformate	1,2	1	2	0	0	2	0
n Butyl Chloroformate	1,2	1	3	0	0	3	0
Bromine	1,2	105	420	95	131	147	47
Hydrogen Cyanide, Anhydrous	1,2	391	1563	389	391	412	371
Sulfur Trioxide	1,2	717	2869	1027	641	661	540
Nitric Acid, Red Fuming	1,2,3	1	2	0	0	1	1
Methyl Chloroformate	1,2,3	1	4	0	0	4	0
Crotonaldehyde	1,2,3	15	59	59	0	0	0
Ethyl Chloroformate	1,2,3	15	60	11	14	19	16
Acrolein	1,2,3	32	129	28	32	29	40
Toxic Liquid Inorganic NOS	1,3	20	79	56	5	6	12
Toxic Liquid Corrosive Organic NOS	1,3	34	137	0	0	0	137
Dimethyl sulfate	1,3	70	280	74	58	73	75
Pentaborane	1,3,4	1	4	0	0	4	0
Ethyl Methacrylate	2,3	0	1	0	0	1	0
Methyl Isopropenyl Ketone	2,3	1	2	0	1	1	0
Isobutyl Acrylate	2,3	6	24	1	5	7	11
Methyl Acrylate	2,3	380	1519	456	458	302	303
Chloroprene	2,3	886	3543	762	900	915	966
Isoprene	2,3	1187	4749	1253	1216	1157	1123
Butyl Acrylates	2,3	3877	15509	4232	3850	3655	3772
Acrylonitrile	2,3	3998	15992	3522	3596	4072	4802
Methyl Methacrylate Monomer	2,3	5378	21510	5242	5148	5656	5464
Propylene Oxide	2,3	6892	27567	7234	6959	6798	6576
Styrene Monomer	2,3	19984	79937	20258	19122	20448	20109

**Table 2-2. PIH, TR, P, and W Commodities Shipped in Quantities
Greater than 100 Carloads Per Year 1996-99**

PIH Commodities

Acetone Cyanohydrin, stabilized
Allyl Alcohol
Bromine or Bromine Solutions (also TR)
Chlorosulfonic Acid
Hydrogen Cyanide, anhydrous (also TR)

Hydrogen Fluoride, anhydrous
Phosphorus Trichloride
Sulfur Chloride (also W)
Sulfur Trioxide, or Sulfur Trioxide, stabilized (also TR)
Sulfuric Acid, fuming (30 percent or more sulfur
trioxide)
Titanium Tetrachloride

TR, P, and W Commodities

Acetaldehyde	TR
Acrylamide	W
Acrylic Acid, inhibited	TR
Acrylonitrile	TR,W
Butyl Acrylates	TR,W
Chloroprene, inhibited	TR,W
Dinitrotoluenes	TR
Epichlorohydrin	W
Ethyl Acrylate	TR,W
Furfural	W
Hydrogen Peroxide Solution	TR
Isobutyl Acetate	P
Isoprene, inhibited	TR,W
Methyl Acrylate, inhibited	TR,W
Methyl Methacrylate Monomer	TR,W
Methyltrichlorosilane	W
n-Butyl Metharcylate, inhibited	W
Propylene Oxide	TR,W
Styrene Monomer, inhibited	TR,W
Vinyl Acetate, inhibited	TR
Vinylidene Chloride, inhibited	TR

5

Table 2-3. Compounds Included in Physical Property Database

Compound	Formula	Molecular Weight	Melting Temperature [°C]	Normal Boiling Temperature [°C]	Liquid Density at 25 °C	Type	Index No.
Bromine	Br2	159.808	-7.25	58.75	3104.33	PIH	1
Vinylidene chloride	C2H2Cl2	96.943	-122.50	31.56	1116.66	TR	2
Acetaldehyde	C2H4O	44.053	-123.00	20.85	779.91	TR	3
Dimethyldichlorosilane	C2H6Cl2Si	129.061	-76.10	70.20	1064.81	W	4
Dimethylchlorosilane	C2H7ClSi	94.616	-111.00	35.50	860.80	W	5
Acrylonitrile	C3H3N	53.064	-83.52	77.35	801.12	P,TR	6
Acrolein	C3H4O	56.064	-87.70	52.69	834.41	PIH	7
Acrylic Acid	C3H4O2	72.064	13.50	141.00	1045.51	P,TR	8
Epichlorohydrin	C3H5ClO	92.525	-57.20	118.50	1173.89	PIH	9
Acrylamide	C3H5NO	71.079	84.50	240.85	933.25	PIH	10
Propylene oxide	C3H6O	58.080	-111.93	33.90	823.27	P.TR	11
Allyl Alcohol	C3H6O	58.080	-129.23	97.08	847.49	PIH	12
Trimethylchlorosilane	C3H9ClSi	108.643	-57.70	57.60	853.47	W	13
Chloroprene	C4H5Cl	88.536	-130.00	59.40	950.97	P,TR	14
Vinyl acetate	C4H6O2	86.090	-92.80	72.50	926.21	TR	15
Methyl acrylate	C4H6O2	86.090	-76.83	80.20	949.05	TR	16
Methacrylic acid	C4H6O2	86.090	15.00	161.00	1009.45	P,TR	17
Acetone cyanohydrin	C4H7NO	85.106	-20.00	170.85	926.39	PIH	18
Furfural	C5H4O2	96.086	-36.50	161.70	1154.53	W	19
Isoprene	C5H8	68.118	-145.88	34.06	675.94	P,TR	20
Ethyl acrylate	C5H8O2	100.117	-71.20	99.50	918.26	P,TR	21
Methyl methacrylate	C5H8O2	100.170	-48.20	100.30	937.17	P,TR	22
Butyl acrylate	C7H12O2	128.171	-64.60	147.85	894.09	P,TR	23
n-Butyl methacrylate	C8H14O2	142.198	-75.37	163.00	890.92	PIH	24
Styrene monomer	C8H8	104.152	-30.61	145.16	900.08	P,TR	25
2-Vinyl toluene	C9H10	118.178	-68.57	169.81	907.69	P,TR	26
3-Vinyl toluene	C9H10	118.178	-86.34	171.60	907.57	P,TR	27
4-Vinyl toluene	C9H10	118.178	-34.13	172.78	915.63	P,TR	28
Methyl-trichlorosilane	CH3Cl3Si	149.478	65.40	66.40	1266.30	PIH	29
Hydrogen cyanide	CHN	27.026	-13.32	25.70	679.56	PIH	30
Sulfur chloride	Cl2S	102.970	-122.00	59.60	1611.36	PIH	31
Titanium tetrachloride	Cl4Ti	189.691	-24.10	135.85	1714.03	PIH	32
Chlorosulfonic acid	ClHO3S	116.525	-80.00	153.85	1740.71	PIH	33
Hydrogen fluoride	FH	20.006	-83.36	19.52	955.17	PIH	34
Water	H2O	18.000	0.00	100.00	1000.00	nr	35
Hydrogen peroxide	H2O2	34.015	-0.04	150.20	1442.72	TR	36
Sulfuric Acid (fuming)	H2SO4	98.079	10.31	274.80	1832.90	PIH	37
Sodium	Na	22.990	97.83	882.85	921.78	W	38
Sulfur trioxide	O3S	80.064	16.80	44.75	1897.48	PIH	39
Phosphorus Trichloride	PCl3	137.330	-92.00	76.10	1566.18	PIH	40

	indicates PIH compound considered in AFFTAC case evaluation.

3.0   ANALYSES OF TANK CARS CONTAINING PIH PRODUCTS

Tank cars containing the 11 PIH materials listed in Table 2-2 and acrolein were analyzed to determine their behavior when exposed to the effects of a pool fire for 100 minutes. Survival of the tank car in a 100-minute pool fire is the performance standard given in 49 CFR 179.18(a). Analysis of the pool fire effects to verify that the standard has been met is permitted by 49 CFR 179.18(b).

3.1   TANK CAR CHARACTERISTICS

Tank cars carrying PIH products are subject to certain restrictions published in the DOT regulations. For example, 49 CFR 173.31(b)(2) requires the tank have a self-closing pressure relief device (excluding shipments of chloroprene, inhibited shipped in Class 115 tank cars). Also, 49 CFR §173.31(e)(2) requires that a tank car used for a PIH material must have a tank test pressure of 300 psi or greater, if required, head protection, and a metal jacket. The Hazardous Material Table (HMT), at 49 CFR 172.101, also specifies restrictions for individual products in a series of notes following the table. Finally, 49 CFR 173.24b(a)(1) requires PIH liquids and liquefied gases be loaded so that the outage is at least 5 percent at the following reference temperatures:

- 115°F for an uninsulated tank
- 110°F for a tank car having a thermal protection system that incorporates a metal jacket and provides an overall thermal conductance at 60°F of no more than 0.5 BTU/hr-ft^2-°F
- 105°F for an insulated tank

This meant that the initial outages for the PIH products analyzed were different for each product because of the different rates of product expansion with temperature, even though the same initial temperature was used for each of the products.

The tank cars analyzed in the first and second sets of AFFTAC calculations were assumed to be insulated with 4 inches of fiberglass covered by a steel jacket. (An exception to this was cars containing acrolein where a high temperature insulation system is required.) A fiberglass insulation system does not qualify as a high temperature thermal insulation system (one that meets the performance standards given in Appendix B to 49 CFR 179). Tests have shown that the fiberglass tends to deteriorate over about a 15-minute period after the fire impinges on the jacket.[4] However, the jacket itself would continue to provide a significant barrier to heat flow into the tank after the fiberglass became ineffective.

An additional assumption was that the tank cars were constructed of AAR TC-128 Grade B steel, which has a minimum tensile strength of 81,000 psi.

3.2   HEAT INPUT FOR POOL FIRE ANALYSES

There are two options for selecting the heat flux to use when analyzing tank cars subjected to the effects of a pool fire. In this report these are designated as the AAR heat flux and the FRA heat flux.

3.2.1 AAR Heat Flux

The AAR heat flux is used to address the requirements of 49 CFR 179.15(a), which states that each tank must have a pressure relief system with flow capacity sufficient to prevent pressure buildup in the tank to no more than the flow rating pressure of the pressure relief device in fire conditions, as defined in Appendix A of the AAR Specifications for Tank Cars.[5] Section A9.02 of these specifications states that the formulas presented for pressure relief valve flow capacities under vapor flowing conditions for a bare, un-insulated tank are based on a heat flux of 34,500 BTU/hr-ft^2. If the tank car is insulated the heat flux is reduced by the factor:

$$8U(1,200 - t)/34,500 \qquad\qquad (1)$$

where, U is the thermal conductance of the insulation system at 100°F, and t is the temperature of the gas entering the valve in degrees Fahrenheit.

The above factor shows that the heat flux of 34,500 BTU/hr-ft^2 is canceled out. The heat flux is now based on the assumption that the outside surface of the insulation system is at 1,200°F. The factor 8 is used to account for unknowns. The conductance of the insulation system is multiplied by 2 to account for its higher conductivity in a fire, then again by 2 to account for it being 50 percent ineffective in a fire, and then by 2 again to account for heat transferred through discontinuities. A typical conductance for 4 inches of fiberglass is 0.075 BTU/hr-ft^2-°F at ambient conditions. It would imply a conductance of 0.60 BTU/hr-ft^2-°F under fire conditions.

Tests have shown that a typical fiberglass insulation will allow much higher heat transfer than that accounted for by the factor of 8 because the fiberglass would deteriorate and become ineffective after about 15 minutes of fire impingement. The effective conductance of the jacket and the charred fiberglass would be in the range of 6-10 BTU/hr/ft^2/°F.

Calculations made with the AFFTAC program using the AAR heat flux would incorporate a heat flux of 34,500 BTU/hr-ft^2 to a cold plate surface. A flame temperature of 1,654°F can represent this. The AAR Heat Flux would also be applied to a fraction of the surface area defined as (area)$^{0.82}$ of the tank. In the case of a typical tank car considered in this study, this would mean the heat flux would be applied to 27 percent of the surface area of the tank.

3.2.2 FRA Heat Flux

The FRA heat flux considers full engulfment of the car in the fire with a flame temperature of 815.5°C (1,500°F). This results in a heat flux of 25,500 BTU/hr-ft^2 to a cold plate surface. These conditions are close to those observed in the two full-scale fire tests on tank cars.[6] These conditions have been accepted by the FRA for the analysis of a tank car in a fire in fulfillment of 49 CFR 179.18(b).

The total heat flux to a tank car is about 2.7 times greater for the FRA heat flux than for the AAR heat flux because of the larger area coverage, even though the AAR flame temperature is higher.

8

For this reason, and because of the uncertainties associated with the application of the AAR assumptions, the analyses in this study were conducted using the FRA heat flux.

3.3   INITIAL CONDITIONS AND PROCEDURE

An initial temperature of 60°F was used in each of the analyses. Both the upright and overturned (120°) car cases were analyzed.

First, a set of AFFTAC analyses were conducted for each product using a pressure relief valve with a start-to-discharge pressure of 225 psi, except for acetone cyanohydrin and acrolein which require a start-to-discharge pressure of 150 psi. A series of analyses were performed with this valve to determine the minimum flow capacity that would keep the pressure in the tank below the flow rating pressure of the valve and allow the car to survive the pool fire effects for 100 minutes as specified in 49 CFR 179.15(a) and 179.18(a)(1). The valve flow capacity changes were made in 1,000 standard cubic feet per minute (SCFM) increments.

49 CFR 179.15(b)(2) permits a pressure relief valve to have a start-to-discharge as low as 75 psi. Therefore, if not prohibited by other regulations, second sets of analyses were conducted using a pressure relief valve with this start-to-discharge pressure. All of the products for which AFFTAC analyses were run met this criterion except for acetone cyanohydrin, acrolein, and hydrogen cyanide, which require a specific start-to-discharge pressure. Again the analyses were repeated until a valve size was found that would prevent the pressure in the tank from rising above the flow rating pressure of the valve.

Finally, a third set of analyses was conducted for each product (where a high temperature insulation system was not required) assuming the tank was equipped with a high temperature insulation system. These analyses were conducted to determine the consequences of shipping the commodities in tank cars equipped with high temperature insulation systems. The cars would be designated as "J" cars. The pressure relief valve start-to-discharge pressures used in the first set of analyses were also used in these analyses. Again the analyses were repeated until a valve size was found that would prevent the pressure in the tank from rising above the flow rating pressure of the valve.

3.4   SUMMARY OF RESULTS

Table 3-1 provides a summary of results for the first and second sets of analyses. It gives the pressure relief valve start-to-discharge pressure and flow capacity, the maximum pressure experienced over the 100-minute analysis period, and the fraction of the original product remaining in the tank after the 100-minute analysis period.

Table 3-1. Summary of Results from First and Second Sets of Analyses

Product	Tank Capacity (gallons)	Orientation of Tank	Start-to-Discharge Pressure (psi)	Valve Flow Capacity (SCFM)	Maximum Pressure (psi)	Remaining Fraction at 100 Minutes
Acetone Cyanohydrin, stabilized, 7.8 lbs/gal	22,000	Upr.	150	1,000	152	.973
		Ovr.	150	1,000	153	.965
Acrolein, 7.1 lbs/gal	20,000	Upr.	150	3,000	152	.977
		Ovr.	150	3,000	152	.968
Allyl Alcohol, 7.2 lbs/gal	22,000	Upr.	225	1,000	232	.963
		Ovr.	225	1,000	227	.958
	22,000	Upr.	75	1,000	76	.963
		Ovr.	75	1,000	76	.944
Bromine, 26.3 lbs/gal	4,000	Upr.	225	5,000	232	.684
		Ovr.	225	5,000	436	.124
		Ovr.	225	15,000	243	.101
	4,000	Upr.	75	4,000	78	.730
		Ovr.	75	4,000	244	.089
		Ovr.	75	25,000	82	.066
Chlorosulfonic Acid, 14.7 lbs/gal	12,000	Upr.	225	1,000	232	.974
		Ovr.	225	1,000	227	.969
	12,000	Upr.	75	1,000	76	.974
		Ovr.	75	1,000	76	.957
Hydrogen Cyanide, 5.9 lbs/gal	20,000	Upr.	225	12,000	237	.663
		Ovr.	225	12,000	407	.318
		Ovr.	225	30,000	284	.146
Hydrogen Fluoride, Anhydrous, 8.2 lbs/gal	20,000	Upr.	225	2,000	232	.816
		Ovr.	225	2,000	232	.817
	20,000	Upr.	75	16,000	80	.743
		Ovr.	75	16,000	217	.253
		Ovr.	75	30,000	166	.096
Phosphorus Trichloride, 13.3 lbs/gal	12,000	Upr.	225	5,000	246	.773
		Ovr.	225	5,000	247	.732
	12,000	Upr.	75	10,000	79	.646
		Ovr.	75	10,000	208	.109
		Ovr.	75	30,000	109	.070
Sulfur Dichloride, 13.6 lbs/gal	12,000	Upr.	225	8,000	245	.777
		Ovr.	225	8,000	296	.671
		Ovr.	225	30,000	269	.390
	12,000	Upr.	75	8,000	80	.717
		Ovr.	75	8,000	254	.120
		Ovr.	75	30,000	111	.085
Sulfur Trioxide, 16.4 lbs/gal	11,000	Upr.	225	1,000	230	1.000
		Ovr.	225	1,000	228	.999
	11,000	Upr.	75	1,000	76	1.000
		Ovr.	75	1,000	75	.981
Sulfuric Acid, fuming 30 percent SO_3 16.3 lbs/gal	12,000	Upr.	225	1,000	228	1.000
		Ovr.	225	1,000	227	.994
	12,000	Upr.	75	1,000	76	1.000
		Ovr.	75	1,000	75	.982
Titanium Tetrachloride, 14.5 lbs/gal	12,000	Upr.	225	1,000	232	.851
		Ovr.	225	1,000	229	.849
	12,000	Upr.	75	1,000	76	.850
		Ovr.	75	1,000	83	.806

Examination of the results permits a number of observations to be made. First, none of the tank cars containing the PIH products were predicted to fail. A wide margin between the pressure in the tank and the burst strength of the tank was maintained at all times.

Second, the analyses showed there was a wide range in pressure relief valve flow capacities required for the cars. Smaller capacities are generally associated with the higher density products having low vapor pressures.

Third, for all but three of the products (acetone cyanohydrin, acrolein and hydrogen cyanide) the regulations would permit the selection of a pressure relief valve with a start-to-discharge pressure as low as 75 psi. The analyses showed no particular advantage for using the lower pressure valve. While its use usually resulted in a larger margin between the pressure in the tank and the burst strength of the tank for the upright car case, it sometimes resulted in a lower margin for the overturned car case. Also, especially in the overturned car case, it resulted in more product being released from the car.

Fourth, in many of the cases for the overturned car, a larger flow capacity valve was required to meet the flow rating pressure requirement. In several cases it was impossible to get a valve with a large enough flow capacity to meet the flow rating pressure requirement.

Finally, the results show that the use of high temperature thermal insulation does not appear necessary for the survival of cars containing PIH materials for the 100-minute pool fire environment. The jacket on the tank, together with the air space between the jacket and the tank after the fiberglass insulation has deteriorated, appears to provide sufficient protection.

Table 3.2 summarizes the results for the third set of analyses where the tanks were assumed to be equipped with a high temperature insulation system. The results show a significantly reduced outflow of the products as a result of the pool fire exposure when compared with the preceding table. Also note, except for the bromine car, pressure relief valves of 1,000 SCFM capacity would suffice.

Table 3-2. - Summary of Results from Third Set of Analyses

Product	Tank Capacity (gallons)	Orientation of Tank	Start-to-Discharge Pressure (psi)	Valve Flow Capacity (SCFM)	Remaining Fraction at 100 Minutes
Acetone Cyanohydrin, Stabilized	22,000	Upr.	150	1,000	1.000
		Ovr.	150	1,000	1.000
Allyl Alcohol	22,000	Upr.	225	1,000	1.000
		Ovr.	225	1,000	1.000
Acrolein	20,000	Upr.	150	1,000	.977
		Ovr.	150	1,000	.968
Bromine	4,000	Upr.	225	3,000	.846
		Ovr.	225	7,000	.523
Chlorosulfonic Acid	12,000	Upr.	225	1,000	1.000
		Ovr.	225	1,000	1.000
Hydrogen Cyanide	20,000	Upr.	225	1,000	.902
		Ovr.	225	1,000	.899
Hydrogen Fluoride, Anhydrous	20,000	Upr.	225	1,000	.962
		Ovr.	225	1,000	.961
Phosphorus Trichloride	12,000	Upr.	225	1,000	.948
		Ovr.	225	1,000	.943
Sulfur Dichloride	12,000	Upr.	225	1,000	.953
		Ovr.	225	1,000	.945
Sulfur Trioxide	11,000	Upr.	225	1,000	1.000
		Ovr.	225	1,000	1.000
Sulfuric Acid, fuming, 30 percent SO_3	12,000	Upr.	225	1,000	1.000
		Ovr.	225	1,000	1.000
Titanium Tetrachloride	12,000	Upr.	225	1,000	.970
		Ovr.	225	1,000	.965

3.5   DETAILED RESULTS OF ANALYSES

3.5.1 Acetone Cyanohydrin, Stabilized

49 CFR 173.244 allows acetone cyanohydrin, stabilized, to be shipped in Class 105, 109, 112, 114, or 120 tank cars. However, Note B76 to the HMT allows only Class 105S, 112J, 114J, or 120S cars with a test pressure of 300 psi or greater to be used, and the pressure relief valve must have a start-to-discharge pressure of 150 psi.

A typical Class 105S300W tank car with the following characteristics was selected for the analyses:

- Inside diameter: 120 inches
- Wall thickness: 0.5625 inch
- Capacity: 22,000 gallons
- Tank test pressure: 300 psi

- Minimum tank burst pressure: 750 psi
- Actual burst pressure: 759.4 psi
- TC128B steel construction

The initial filled fraction of the car was 0.9255.

Analyses with a 225 psi start-to-discharge valve found that a valve flow capacity as low as 1,000 SCFM would satisfy the requirements for both the upright and overturned car conditions. The reason such a low capacity relief valve could be used was due to the low vapor pressure of acetone cyanohydrin, its vapor pressure not reaching one atmosphere until its temperature rises to 340°F. The maximum pressures are listed as follows:

	Valve Flow Capacity (SCFM)	Maximum Pressure (psi)	Time at Maximum Pressure (min)	Tank Burst Strength at Maximum Pressure (psi)
Upright car	1,000	152.1	69.1	496
Overturned car	1,000	153.0	69.2	497

The results show a margin of about 340 psi between the burst strength of the tank and the pressure within the tank for both conditions.

In the upright car condition there was no vapor released through the valve because of boiling of the liquid. The tank became shell full after 75 minutes after which a limited amount of liquid was released through the valve as the fluid expanded. Over 97 percent of the product remained in the tank after 100 minutes of fire exposure. In the overturned car condition a relatively small amount of liquid product began to be released after 70 minutes. After 100 minutes of fire exposure 96.5 percent of the product remained in the tank.

3.5.2 Acrolein

49 CFR 173.244 allows acrolein to be shipped in Class 105, 109, 112, 114, or 120 tank cars. However, Note B42 to the HMT allows only Class 105J500 cars to be used, and the pressure relief valve must have a start-to-discharge pressure of 150 psi.

A Class 105J500W tank car with the following characteristics was selected for the analyses:
- Inside diameter: 102 inches
- Wall thickness: 0.7871 inch
- Capacity: 20,000 gallons
- Tank test pressure: 500 psi
- Minimum tank burst pressure: 1,250 psi
- Actual burst pressure: 1,250.1 psi
- TC128B steel construction

The initial filled fraction of the car was 0.9196.

Analyses with a 150 psi start-to-discharge valve found that a valve flow capacity as low as 1,000 SCFM would satisfy the requirements for both the upright and overturned car conditions. The

reason such a low capacity relief valve could be used was due to the requirement that a "J" car be used, which meant a high temperature thermal insulation system was used on the car. The maximum pressures are listed as follows:

	Valve Flow Capacity (SCFM)	Maximum Pressure (psi)	Time at Maximum Pressure (min)	Tank Burst Strength at Maximum Pressure (psi)
Upright car	1,000	152.1	76.4	1,073
Overturned car	1,000	151.6	76.3	1,073

The results show a wide margin between the burst strength of the tank and the pressure within the tank for both conditions.

In the upright car condition there was no vapor released through the valve. The tank became shell full after 85 minutes. A limited amount of liquid was released through the valve as the fluid expanded. After 100 minutes of fire exposure, 97.7 percent of the product remained in the tank. In the overturned car condition, a small amount of liquid product began to be released through the valve after 77 minutes. After 100 minutes of fire exposure, 96.8 percent of the product remained in the tank.

3.5.3 Allyl Alcohol

49 CFR 173.244 allows allyl alcohol to be shipped in Class 105, 109, 112, 114, or 120 tank cars. However, Note B74 to the HMT allows only Class 105S, 112J, 114J, or 120S cars with a test pressure of 300 psi or greater to be used.

A Class 105S300W tank car with the following characteristics was selected for the analyses:
- Inside diameter: 120 inches
- Wall thickness: 0.5625 inch
- Capacity: 22,000 gallons
- Tank test pressure: 300 psi
- Minimum tank burst pressure: 750 psi
- Actual burst pressure: 759.4 psi
- TC128B steel construction

The initial filled fraction of the car was 0.9232.

Analyses with a 225 psi start-to-discharge valve found that a valve flow capacity of 1,000 SCFM would satisfy the requirements for both the upright and overturned car conditions. The maximum pressures are listed as follows:

	Valve Flow Capacity (SCFM)	Maximum Pressure (psi)	Time at Maximum Pressure (min)	Tank Burst Strength at Maximum Pressure (psi)
Upright car	1,000	231.8	69.2	507
Overturned car	1,000	227.1	69.0	506

14

The results show a wide margin between the burst strength of the tank and the pressure within the tank for both conditions.

The tank became shell full after 73.4 minutes in the upright car case and liquid began to be released through the valve. At the end of 100 minutes the tank was still shell full and 96.3 percent of the allyl alcohol remained in the tank. Liquid product began to be released after 69.0 minutes in the overturned car case. At the end of 100 minutes 95.8 percent of the allyl alcohol remained in the tank.

Analyses made for a car equipped with a valve having a 75 psi start-to-discharge pressure and an 82.5 psi flow rating pressure showed that in both the upright and overturned car cases a valve flow capacity of 1,000 SCFM was acceptable. The maximum pressures are listed as follows:

	Valve Flow Capacity (SCFM)	Maximum Pressure (psi)	Time at Maximum Pressure (min)	Tank Burst Strength at Maximum Pressure (psi)
Upright car	1,000	76.2	60.0	486
Overturned car	1,000	75.5	72.2	486

The results show an ample margin between the burst strength of the tank and the pressure within the tank for all conditions.

The tank became shell full after 72.8 minutes in the upright car case and liquid began to be released through the valve. At the end of 100 minutes, 64.6 percent of the allyl alcohol remained in the tank. Liquid product began to be released after 32.5 minutes in the overturned car case. At the end of 100 minutes 94.4 percent of the allyl alcohol remained in the tank.

3.5.4 Bromine

Bromine is a high-density product (26.3 lbs/gal) that is subject to a larger number of requirements than most PIH materials.

49 CFR 173.249(d) requires a 3/16-inch lead lining if the tank is made from steel plate. § 173.249 together with § 172.102 requires bromine to be shipped in Class 105S300W or 105S500W tank cars. § 173.249(e) specifies maximum and minimum filling densities of 300 and 287 percent, respectively, of the water capacity of the tank. It also states that for Class 105A300W tank cars the maximum water capacity is 20,400 pounds with a maximum quantity of lading of 60,000 pounds. For Class 105A500W tank cars the maximum water capacity is 37,400 pounds with a maximum quantity of lading of 110,000 pounds. The range of filling densities given in § 173.249(e) includes an outage of 5 percent which is specified in § 173.24b(a)(1) for PIH materials, at 105°F for an insulated tank. Note, however, that no temperature is given for the filling density range requirement. This causes some uncertainty in the way that the requirement is to be applied.

Because of the above requirements, a Class 105S500W tank car was chosen for the analyses. This allowed for a 55-ton product load, but the high density of the product results in a tank car with a capacity of only 4,000 gallons.

The other car characteristics are given as follows:

- Inside diameter: 60 inches
- Wall thickness: 0.5625 inch
- Lead Lining: 3/16 inch
- Tank test pressure: 500 psi
- Minimum tank burst pressure: 1,250 psi
- Actual burst pressure: 1,518.8 psi
- TC128B steel construction

Analyses made for a car equipped with a valve having a 225 psi start-to-discharge pressure and a 247.5 psi flow rating pressure showed that in the upright car case a valve flow capacity of 5,000 SCFM was required. If the 5,000 SCFM valve is used for the overturned car condition, the pressure exceeds the flow rating pressure by a wide margin although the maximum pressure still remains below the burst pressure of the tank. The maximum pressure is reduced if a larger capacity valve is used. It was found that a 15,000 SCFM valve would keep the pressure below the flow rating pressure. The results and maximum pressures are summarized as follows:

	Valve Flow Capacity (SCFM)	Maximum Pressure (psi)	Time at Maximum Pressure (min)	Tank Burst Strength at Maximum Pressure (psi)
Upright car	5,000	232.0	27.2	1,161
Overturned car	5,000	436.2	69.7	795
Overturned car	15,000	242.8	59.0	872

The results show a wide margin between the burst strength of the tank and the pressure within the tank for all conditions.

The tank became shell full after 30 minutes in the upright car case and liquid began to be released through the valve. After 50 minutes the vapor pressure of the bromine was high enough for vapor to be released through the valve. At the end of 100 minutes 68.4 percent of the bromine remained in the tank.

Liquid product began to be released after 27.5 minutes in the overturned car case with the 5,000 SCFM valve. This was followed by vapor flow, when the level of the liquid reached the valve at 75 minutes. At the end of 100 minutes, only 12.4 percent of the bromine remained in the tank. Liquid product again began to be released after 27.5 minutes in the overturned car case with the 15,000 SCFM valve followed by vapor flow at 65 minutes. At the end of 100 minutes, 10.1 percent of the bromine remained in the tank.

Analyses made for a car equipped with a valve having a 75 psi start-to-discharge pressure and an 82.5 psi flow rating pressure showed that in the upright car case a valve flow capacity of 4,000 SCFM was required. If the 4,000 SCFM valve is used for the overturned car condition, the pressure exceeds the flow rating pressure by a wide margin, although the maximum pressure remains below the burst pressure of the tank. If a larger capacity valve is used the maximum pressure is reduced. It was found that a 25,000 SCFM valve must be used to keep the pressure below the flow rating pressure. The results and maximum pressures are summarized as follows:

	Valve Flow Capacity (SCFM)	Maximum Pressure (psi)	Time at Maximum Pressure (min)	Tank Burst Strength at Maximum Pressure (psi)
Upright car	4,000	78.1	40.4	1,079
Overturned car	4,000	244.0	56.4	792
Overturned car	25,000	81.8	43.8	907

The results show a wide margin between the burst strength of the tank and the pressure within the tank for all conditions.

The tank became shell full after 30 minutes in the upright car case and liquid began to be released through the valve. After 40 minutes the vapor pressure of the bromine was high enough for vapor to be released through the valve. At the end of 100 minutes, 73.0 percent of the bromine remained in the tank.

Liquid product began to be released after 25.0 minutes in the overturned car case with the 4,000 SCFM valve. This was followed by vapor flow, when the level of the liquid reached the valve, at 60 minutes. At the end of 100 minutes, only 8.9 percent of the bromine remained in the tank. Liquid product again began to be released after 27.5 minutes in the overturned car case with the 25,000 SCFM valve followed by vapor flow at 47.5 minutes. At the end of 100 minutes, 6.6 percent of the bromine remained in the tank.

3.5.5 Chlorosulfonic Acid

49 CFR 173.244 allows chlorosulfonic acid to be shipped in Class 105, 109, 112, 114, or 120 tank cars. However, Note B74 to the HMT allows only Class 105S, 112J, 114J, or 120S cars with a test pressure of 300 psi or greater to be used. Chlorosulfonic acid is a relatively high-density product (about 14.7 lbs/gal), thus a smaller capacity tank car would be used for transport. A Class 105S300W tank car was selected for the analyses.

Its characteristics were:
- Inside diameter: 110 inches
- Wall thickness: 0.5625 inch
- Capacity: 12,000 gallons
- Tank test pressure: 300 psi
- Minimum tank burst pressure: 750 psi

- Actual burst pressure: 828.4 psi
- TC128B steel construction

The initial filled fraction of the car was 0.9320.

Analyses with a 225 psi start-to-discharge valve found that a valve flow capacity as low as 1,000 SCFM would satisfy the requirements for both the upright and overturned car conditions. The reason such a low capacity valve could be used was due to the low vapor pressure of chlorosulfonic acid; its vapor pressure does not reach one atmosphere until its temperature rises to 309°F. There was no vapor flow of the product through the valve, only liquid flow after the tank became shell full. The maximum pressures are listed as follows:

	Valve Flow Capacity (SCFM)	Maximum Pressure (psi)	Time at Maximum Pressure (min)	Tank Burst Strength at Maximum Pressure (psi)
Upright car	1,000	231.8	77.2	564
Overturned car	1,000	227.4	72.1	551

The results show a wide margin between the burst strength of the tank and the pressure within the tank for both conditions.

The tank became shell full after 80 minutes in the upright car case and liquid began to be released through the valve. At the end of 100 minutes, 97.4 percent of the chlorosulfonic acid remained in the tank. Liquid product began to be released after 72.5 minutes in the overturned car case. At the end of 100 minutes, 96.9 percent of the chlorosulfonic acid remained in the tank.

Analyses made for a car equipped with a valve having a 75 psi start-to-discharge pressure and an 82.5 psi flow rating pressure showed that in both the upright and overturned car cases a valve flow capacity of 1,000 SCFM would be sufficient. There was no vapor flow of the product through the relief valve; only liquid flow after the tank became shell full.

The results for this case are shown as follows:

	Valve Flow Capacity (SCFM)	Maximum Pressure (psi)	Time at Maximum Pressure (min)	Tank Burst Strength at Maximum Pressure (psi)
Upright car	1,000	75.7	63.0	528
Overturned car	1,000	75.5	62.9	528

The results show a wide margin between the burst strength of the tank and the pressure within the tank for both conditions.

The tank became shell full after 77.5 minutes in the upright car case and liquid began to be released through the valve. At the end of 100 minutes, 97.4 percent of the chlorosulfonic acid remained in the tank. Liquid product began to be released after 65.0 minutes in the overturned car case. At the end of 100 minutes, 95.7 percent of the chlorosulfonic acid remained in the tank.

3.5.6 Hydrogen Cyanide

CFR 173.244 allows hydrogen cyanide to be shipped in Class 105, 109, 112, 114, or 120 tank cars. However, Note B65 to the HMT allows only Class 105A, cars with a test pressure of 500 psi or greater to be used. The pressure relief valve must have a start-to-discharge pressure of 225 psi.

A Class 105S500W tank car with the following characteristics was selected for the analyses:
- Inside diameter: 102 inches
- Wall thickness: 0.7871 inch
- Capacity: 20,000 gallons
- Tank test pressure: 500 psi
- Minimum tank burst pressure: 1,250 psi
- Actual burst pressure: 1,250.1 psi
- TC128B steel construction

The initial filled fraction of the car was 0.8954.

Analyses with a 225 psi start-to-discharge valve found that a valve flow capacity of 12,000 SCFM was required in the upright car case. The pressure exceeds the flow rating pressure by a wide margin if the 12,000 SCFM valve is used for the overturned car condition, although the maximum pressure remains below the burst pressure of the tank. If a larger capacity valve is used the maximum pressure is reduced. Even if a 30,000 SCFM valve is used the pressure still exceeds the flow rating pressure. The results and maximum pressures are summarized as follows:

	Valve Flow Capacity (SCFM)	Maximum Pressure (psi)	Time at Maximum Pressure (min)	Tank Burst Strength at Maximum Pressure (psi)
Upright car	12,000	236.7	78.2	876
Overturned car	12,000	407.0	100.0	701
Overturned car	30,000	283.5	92.1	704

The results show a wide margin between the burst strength of the tank and the pressure within the tank for all conditions.

The tank became shell full after 40 minutes in the upright car case and liquid began to be released through the valve. After 80 minutes, the vapor pressure of the hydrogen cyanide was high enough for vapor to be released through the valve. At the end of 100 minutes, 66.3 percent of the hydrogen cyanide remained in the tank.

Liquid product began to be released after 40.0 minutes in the overturned car case with the 12,000 SCFM valve. There was no vapor flow from the tank. At the end of 100 minutes, 31.8 percent of the hydrogen cyanide remained in the tank. Liquid product again began to be released after 40.0 minutes in the overturned car case with the 30,000 SCFM valve. This was followed by

vapor flow at 95.0 minutes. At the end of 100 minutes, 14.6 percent of the hydrogen cyanide remained in the tank.

3.5.7 Hydrogen Fluoride, Anhydrous

49 CFR 173.243 allows hydrogen fluoride, anhydrous, to be shipped in Class 103, 104, 105, 109, 111, 112, 114, 115, or 120 tank cars. However, Note B71 to the HMT allows only Class 105, 112, 114, or 120 cars with a test pressure of 300 psi or greater to be used.

A Class 105S300W tank car with the following characteristics was selected for the analyses:
- Inside diameter: 120 inches
- Wall thickness: 0.5625 inch
- Capacity: 20,000 gallons
- Tank test pressure: 300 psi
- Minimum tank burst pressure: 750 psi
- Actual burst pressure: 759.4 psi
- TC128B steel construction

The initial filled fraction of the car was 0.8875

Analyses with a 225 psi start-to-discharge valve found that a valve flow capacity as low as 2,000 SCFM would satisfy the requirements for both the upright and overturned car cases. There was no vapor flow through the valve in the upright case, only liquid flow after the tank became shell full. The maximum pressures are listed as follows:

	Valve Flow Capacity (SCFM)	Maximum Pressure (psi)	Time at Maximum Pressure (min)	Tank Burst Strength at Maximum Pressure (psi)
Upright car	2,000	231.9	47.7	508
Overturned car	2,000	231.8	47.9	509

The results show a wide margin between the burst strength of the tank and the pressure within the tank for both conditions.

The tank became shell full after 50 minutes in the upright car case and liquid began to be released through the valve. At the end of 100 minutes, 81.6 percent of the hydrogen fluoride remained in the tank. Liquid product began to be released after 50 minutes in the overturned car case. At the end of 100 minutes, 81.7 percent of the hydrogen fluoride remained in the tank.

Analyses made for a car equipped with a valve having a 75 psi start-to-discharge pressure and an 82.5 psi flow rating pressure showed that a valve flow capacity of 16,000 SCFM was required in the upright car case. If the 16,000 SCFM valve is used for the overturned car condition, the pressure exceeds the flow rating pressure by a wide margin, although the maximum pressure remains below the burst pressure of the tank. If a larger capacity valve is used the maximum pressure is reduced. However, it was found that even if a 30,000 SCFM valve were used the

20

pressure would still exceed the flow rating pressure. The results and maximum pressures are summarized as follows:

	Valve Flow Capacity (SCFM)	Maximum Pressure (psi)	Time at Maximum Pressure (min)	Tank Burst Strength at Maximum Pressure (psi)
Upright car	16,000	79.9	80.0	512
Overturned car	16,000	216.9	100.0	381
Overturned car	30,000	165.8	89.9	381

The results show an ample margin between the burst strength of the tank and the pressure within the tank for all conditions.

The tank became shell full after 47.5 minutes in the upright car case and liquid began to be released through the valve. After 72.5 minutes, the vapor pressure of the hydrogen fluoride was high enough for vapor to be released through the valve. At the end of 100 minutes, 74.3 percent of the hydrogen fluoride remained in the tank.

Liquid product began to be released after 47.5 minutes in the overturned car case with the 16,000 SCFM valve. At the end of 100 minutes, 25.3 percent of the hydrogen fluoride remained in the tank. Liquid product again began to be released after 47.5 minutes in the overturned car case with the 30,000 SCFM valve. This was followed by vapor flow at 97.5 minutes. At the end of 100 minutes, only 9.6 percent of the hydrogen fluoride remained in the tank.

3.5.8 Phosphorus Trichloride

49 CFR 173.244 allows phosphorus trichloride to be shipped in Class 105, 109, 112, 114, or 120 tank cars. However, Note B74 to the HMT allows only Class 105S, 112J, 114J, or 120S cars with a test pressure of 300 psi or greater to be used.

Phosphorus trichloride is a relatively high-density product (about 13.3 lbs/gal), thus a smaller capacity tank car would be used for transport. A Class 105S300W tank car was selected for the analyses. Its characteristics were:

- Inside diameter: 110 inches
- Wall thickness: 0.5625 inch
- Capacity: 12,000 gallons
- Tank test pressure: 300 psi
- Minimum tank burst pressure: 750 psi
- Actual burst pressure: 828.4 psi
- TC128B steel construction

The initial filled fraction of the car was 0.9213.

Analyses with a 225 psi start-to-discharge valve found that a valve flow capacity of 5,000 SCFM would satisfy the requirements for both the upright and overturned car conditions.

The maximum pressures are listed as follows:

	Valve Flow Capacity (SCFM)	Maximum Pressure (psi)	Time at Maximum Pressure (min)	Tank Burst Strength at Maximum Pressure (psi)
Upright car	5,000	246.3	100.0	548
Overturned car	5,000	247.1	100.0	496

The results show a wide margin between the burst strength of the tank and the pressure within the tank for both conditions.

The tank became shell full after 38.7 minutes in the upright car case and liquid began to be released through the valve. After 97.5 minutes, the vapor pressure of the phosphorus trichloride was high enough for vapor to be released through the valve. At the end of 100 minutes, 77.3 percent of the phosphorus trichloride remained in the tank. Liquid product began to be released after 36.8 minutes in the overturned car case with the 5,000 SCFM valve. At the end of 100 minutes, 73.2 percent of the phosphorus trichloride remained in the tank.

Analyses made for a car equipped with a valve having a 75 psi start-to-discharge pressure and an 82.5 psi flow rating pressure showed that in the upright car a valve flow capacity of 10,000 SCFM was required. The pressure exceeds the flow rating pressure by a wide margin if the 10,000 SCFM valve is used for the overturned car condition, although the maximum pressure remains below the burst pressure of the tank. If a larger capacity valve is used the maximum pressure is reduced. However, it was found that even if a 30,000 SCFM valve were used the pressure would still exceed the flow rating pressure. The results and maximum pressures are summarized as follows:

	Valve Flow Capacity (SCFM)	Maximum Pressure (psi)	Time at Maximum Pressure (min)	Tank Burst Strength at Maximum Pressure (psi)
Upright car	10,000	78.7	82.0	554
Overturned car	10,000	207.7	92.3	343
Overturned car	30,000	109.0	80.1	433

The results show an ample margin between the burst strength of the tank and the pressure within the tank for all conditions.

The tank became shell full after 38.6 minutes in the upright car case and liquid began to be released through the valve. After 72.0 minutes the vapor pressure of the phosphorus trichloride was high enough for vapor to be released through the valve. At the end of 100 minutes, 64.6 percent of the phosphorus trichloride remained in the tank.

Liquid product began to be released after 32.5 minutes in the overturned car case with the 10,000 SCFM valve followed by vapor flow at 92.3 minutes. At the end of 100 minutes, 10.9 percent of the phosphorus trichloride remained in the tank. Liquid product again began to be released after 32.5 minutes in the overturned car case with the 30,000 SCFM valve followed by vapor flow at

80.2 minutes. At the end of 100 minutes, only 7.0 percent of the phosphorus trichloride remained in the tank.

3.5.9 Sulfur Chloride/Sulfur Dichloride

Sulfur chloride and sulfur dichloride are closely related chemically and are both PIH materials. The DIPPR chemical property database used in this study only contained information on sulfur dichloride so this product was analyzed as being representative of the sulfur chlorides.

49 CFR 173.243 allows sulfur dichloride to be shipped in Class 103, 104, 105, 109, 111, 112, 114, 115, or 120 tank cars. However, 49 CFR 173.31(e)(2) requires that a tank car used for a material poison by inhalation must have a tank test pressure of 300 psi or greater. This eliminates from consideration the non-pressure tank car Classes 103, 104 and 111.

A Class 105S300W tank car with the following characteristics was selected for the analyses:
- Inside diameter: 110 inches
- Wall thickness: 0.5625 inch
- Capacity: 12,000 gallons
- Tank test pressure: 300 psi
- Minimum tank burst pressure: 750 psi
- Actual burst pressure: 828.4 psi
- TC128B steel construction

The initial filled fraction of the car was 0.9230.

Analyses with a 225 psi start-to-discharge valve found that a valve flow capacity of 8,000 SCFM was required in the upright car case. If the 8,000 SCFM valve is used for the overturned car condition, the pressure exceeds the flow rating pressure by a wide margin, although the maximum pressure remains below the burst pressure of the tank. If a larger capacity valve is used the maximum pressure is reduced. However, it was found that even if a 30,000 SCFM valve were used the pressure would still exceed the flow rating pressure.

The results and maximum pressures are summarized as follows:

	Valve Flow Capacity (SCFM)	Maximum Pressure (psi)	Time at Maximum Pressure (min)	Tank Burst Strength at Maximum Pressure (psi)
Upright car	8,000	245.4	100.0	546
Overturned car	8,000	296.3	100.0	480
Overturned car	30,000	269.0	100.0	457

The results show an ample margin between the burst strength of the tank and the pressure within the tank for all conditions.

The tank became shell full after 42.5 minutes in the upright car case and liquid began to be released through the valve. After 92.5 minutes, the vapor pressure of the sulfur dichloride was

high enough for vapor to be released through the valve. At the end of 100 minutes, 77.7 percent of the sulfur dichloride remained in the tank.

Liquid product began to be released after 42.5 minutes in the overturned car case with the 8,000 SCFM valve. At the end of 100 minutes, 67.1 percent of the sulfur dichloride remained in the tank. Liquid product again began to be released after 42.5 minutes in the overturned car case with the 30,000 SCFM valve. At the end of 100 minutes, only 39.0 percent of the sulfur dichloride remained in the tank.

Analyses made for a car equipped with a valve having a 75 psi start-to-discharge pressure and an 82.5 psi flow rating pressure showed that in the upright car case a valve flow capacity of 8,000 SCFM was required. If the 8,000 SCFM valve is used for the overturned car condition, the pressure exceeds the flow rating pressure by a wide margin, although the maximum pressure remains below the burst pressure of the tank. If a larger capacity valve is used the maximum pressure is reduced. However, it was found that even if a 30,000 SCFM valve were used the pressure would still exceed the flow rating pressure. The results and maximum pressures are summarized as follows:

	Valve Flow Capacity (SCFM)	Maximum Pressure (psi)	Time at Maximum Pressure (min)	Tank Burst Strength at Maximum Pressure (psi)
Upright car	8,000	80.0	82.1	550
Overturned car	8,000	254.1	90.5	393
Overturned car	30,000	110.6	73.9	436

The results show an ample margin between the burst strength of the tank and the pressure within the tank for all conditions.

The tank became shell full after 45.0 minutes in the upright car case and liquid began to be released through the valve. After 67.5 minutes, the vapor pressure of the sulfur dichloride was high enough for vapor to be released through the valve. At the end of 100 minutes, 71.7 percent of the sulfur dichloride remained in the tank.

Liquid product began to be released after 37.5 minutes in the overturned car case with the 8,000 SCFM valve. At the end of 100 minutes, 12.0 percent of the sulfur dichloride remained in the tank. Liquid product again began to be released after 37.5 minutes in the overturned car case with the 30,000 SCFM valve. At the end of 100 minutes, only 8.5 percent of the sulfur dichloride remained in the tank.

3.5.10   Sulfur Trioxide, or Sulfur Trioxide, Stabilized

49 CFR 173.244 allows sulfur trioxide to be shipped in Class 105, 109, 112, 114, or 120 tank cars. However, Note B74 to the HMT allows only Class 105S, 112J, 114J, or 120S cars with a test pressure of 300 psi or greater to be used.

Sulfur trioxide is a relatively high-density product (about 16.4 lbs/gal), thus a smaller capacity tank car would be used to transport it. A Class 105S300W tank car with the following characteristics was selected for the analyses:

- Inside diameter: 110 inches
- Wall thickness: 0.5625 inch
- Capacity: 11,000 gallons
- Tank test pressure: 300 psi
- Minimum tank burst pressure: 750 psi
- Actual burst pressure: 828.4 psi
- TC128B steel construction

The initial filled fraction of the car was 0.8945.

Analyses with a 225 psi start-to-discharge valve found that a valve flow capacity as low as 1,000 SCFM would satisfy the requirements for both the upright and overturned car conditions.

The maximum pressures are listed as follows:

	Valve Flow Capacity (SCFM)	Maximum Pressure (psi)	Time at Maximum Pressure (min)	Tank Burst Strength at Maximum Pressure (psi)
Upright car	1,000	229.7	99.5	547
Overturned car	1,000	228.1	99.4	547

The results show a wide margin between the burst strength of the tank and the pressure within the tank for both conditions.

The tank never became shell full in the upright car case. At the end of 100 minutes, all of the sulfur trioxide remained in the tank. Liquid product began to be released at about 99 minutes in the overturned car case. At the end of 100 minutes, 99.9 percent of the sulfur trioxide remained in the tank.

Analyses made for a car equipped with a valve having a 75 psi start-to-discharge pressure and an 82.5 psi flow rating pressure showed that in both the upright and overturned car cases a valve flow capacity of 1,000 SCFM was acceptable. The maximum pressures are listed as follows:

	Valve Flow Capacity (SCFM)	Maximum Pressure (psi)	Time at Maximum Pressure (min)	Tank Burst Strength at Maximum Pressure (psi)
Upright car	1,000	75.9	87.3	526
Overturned car	1,000	75.4	87.2	526

The results show a wide margin between the burst strength of the tank and the pressure within the tank for both conditions.

The tank never became shell full in the upright car case. At the end of 100 minutes, all of the sulfur trioxide remained in the tank. Liquid product began to be released at 87.5 minutes in the overturned car case. At the end of 100 minutes, 98.1 percent of the sulfur trioxide remained in the tank.

3.5.11   Sulfuric Acid, Fuming, 30 percent Sulfur Trioxide

49 CFR 173.244 allows fuming sulfuric acid to be shipped in Class 105, 109, 112, 114, or 120 tank cars. However, Note B74 to the HMT allows only Class 105S, 112J, 114J, or 120S cars with a test pressure of 300 psi or greater to be used.

Fuming sulfuric acid is a relatively high-density product (about 14.7 lbs/gal), thus a smaller capacity tank car would be used to transport it. A Class 105S300W tank car with the following characteristics was selected for the analyses:

- Inside diameter: 110 inches
- Wall thickness: 0.5625 inch
- Capacity: 12,000 gallons
- Tank test pressure: 300 psi
- Minimum tank burst pressure: 750 psi
- Actual burst pressure: 828.4 psi
- TC128B steel construction

The initial filled fraction of the car was 0.9221.

Analyses with a 225 psi start-to-discharge valve found that a valve flow capacity as low as 1,000 SCFM would satisfy the requirements for both the upright and overturned car conditions. A low capacity valve could be used because of the low vapor pressure of fuming sulfuric acid. The maximum pressures are listed as follows:

	Valve Flow Capacity (SCFM)	Maximum Pressure (psi)	Time at Maximum Pressure (min)	Tank Burst Strength at Maximum Pressure (psi)
Upright car	1,000	228.4	94.3	556
Overturned car	1,000	227.1	94.2	557

The results show a wide margin between the burst strength of the tank and the pressure within the tank for both conditions.

The tank started to release padding gas after 94.3 minutes in the upright car case. At the end of 100 minutes, all of the fuming sulfuric acid remained in the tank. Liquid product began to be released after 94.2 minutes in the overturned car case. At the end of 100 minutes, 99.4 percent of the fuming sulfuric acid remained in the tank.

Analyses made for a car equipped with a valve having a 75 psi start-to-discharge pressure and an 82.5 psi flow rating pressure showed that in both the upright and overturned car cases a valve flow capacity of 1,000 SCFM would be sufficient.

The results for this case are shown as follows:

	Valve Flow Capacity (SCFM)	Maximum Pressure (psi)	Time at Maximum Pressure (min)	Tank Burst Strength at Maximum Pressure (psi)
Upright car	1,000	75.1	82.5	526
Overturned car	1,000	75.4	82.4	529

The results show a wide margin between the burst strength of the tank and the pressure within the tank for both conditions.

The tank became shell full after 99.8 minutes in the upright car case and liquid began to be released through the valve. At the end of 100 minutes all of the fuming sulfuric acid remained in the tank. Liquid product began to be released after 82.4 minutes in the overturned car case. At the end of 100 minutes 98.2 percent of the fuming sulfuric acid remained in the tank.

3.5.12   Titanium Tetrachloride

49 CFR 173.244 allows titanium tetrachloride to be shipped in Class 105, 109, 112, 114, or 120 tank cars. However, Note B74 to the HMT allows only Class 105S, 112J, 114J, or 120S cars with a test pressure of 300 psi or greater to be used.

Titanium tetrachloride is a relatively high-density product, about 14.5 lbs/gal, so a smaller capacity tank car would be used to transport it. A Class 105S300W tank car was selected for the analyses. Its characteristics were:

- Inside diameter: 110 inches
- Wall thickness: 0.5625 inch
- Capacity: 12,000 gallons
- Tank test pressure: 300 psi
- Minimum tank burst pressure: 750 psi
- Actual burst pressure: 828.4 psi
- TC128B steel construction

The initial filled fraction of the car was 0.9271.

Analyses with a 225 psi start-to-discharge valve found that a valve flow capacity as low as 1,000 SCFM would satisfy the requirements for both the upright and overturned car conditions.

The maximum pressures are listed as follows:

	Valve Flow Capacity (SCFM)	Maximum Pressure (psi)	Time at Maximum Pressure (min)	Tank Burst Strength at Maximum Pressure (psi)
Upright car	1,000	231.8	41.4	554
Overturned car	1,000	229.3	98.4	545

The results show a wide margin between the burst strength of the tank and the pressure within the tank for both conditions.

The tank became shell full at 45.0 minutes in the upright car case. At the end of 100 minutes, 85.1 percent of the titanium tetrachloride remained in the tank. Liquid product began to be released at 42.5 minutes in the overturned car case. At the end of 100 minutes, 84.9 percent of the titanium tetrachloride remained in the tank.

Analyses made for a car equipped with a valve having a 75 psi start-to-discharge pressure and an 82.5 psi flow rating pressure showed that in both the upright and overturned car cases a valve flow capacity of 1,000 SCFM was acceptable. The maximum pressures are listed as follows:

	Valve Flow Capacity (SCFM)	Maximum Pressure (psi)	Time at Maximum Pressure (min)	Tank Burst Strength at Maximum Pressure (psi)
Upright car	1,000	76.4	35.8	550
Overturned car	1,000	82.7	100.0	492

The results show a wide margin between the burst strength of the tank and the pressure within the tank for both conditions.

The tank became shell full after 45.0 minutes in the upright car case. At the end of 100 minutes, 85.0 percent of the titanium tetrachloride remained in the tank. Liquid product began to be released at 37.5 minutes in the overturned car case. At the end of 100 minutes, 80.6 percent of the titanium tetrachloride remained in the tank.

4.0   THERMALLY REACTIVE AND POLYMERIZABLE MATERIALS

Thermally reactive and polymerizable materials are given an extended consideration in the materials cited in Reference 7. This section discusses material properties, heats of reaction, inhibitor effectiveness, and pressure relief vent size requirements.

Considerations of monomers and thermally reactive materials raises issues that are not easily resolved. For a large number of monomers, use of proper inhibitors provides satisfactory protection for fire exposure of limited duration. Other species have characteristics which render runaway reaction impractical to preclude and impractical to pressure vent. The demand for high relief set pressures to prevent spurious loss of inventory in normal operations and the benefits of low pressure relief for reactive systems represents an impediment to practical solution in the rail tank car environment.

4.1 BACKGROUND

49 CFR 173.21 (f) requires that thermally reactive and polymerizable materials contain a reaction inhibitor which stabilizes or prevents an exothermic reaction from occurring at temperatures below 54°C.[7] The regulations do not specify the stabilization time at 54°C. However, most raw material suppliers and shippers inhibit products to a level that generally provides between 20 days and 60 days stability at 54°C. Examination of literature data, where available, tends to confirm that this level of stability represents commercial practice. Inhibitor effectiveness decreases rapidly with increasing temperature (decreasing inhibitor lifetime by a factor of two for every 10°C increase temperature). For many compounds, under prolonged exposure to an external fire, a runaway exothermic polymerization reaction cannot be ruled out.

49 CFR 173.15 (b) requires that pressure relief devices for railroad tank cars have elevated activation pressures (at least 75 psig) to avoid spurious release of inventory due to slack motion in normal train operations. Reclosable relief devices are preferred. Non-reclosable devices must be set for relief at the railcar test pressure.

Since 1980, the AIChE Design Institute for Emergency Relief Systems (DIERS) has promoted the development of emergency relief system design methods for runaway exothermic chemical reactions.[8] The bulk liquid heat-up rate of the contents of a typical tank car exposed to external heat only rarely exceeds 2°C/min (without insulation). The corresponding bulk heat-up rate, due to a runaway exothermic reaction, increases at an exponential rate with increasing temperature and can reach several tens to several hundreds of °C/min, depending on relief activation pressure. In addition, DIERS technology has shown that relief vent flow at such high heating rates will likely include both liquid and vapor phases. Long experience has shown that practical emergency pressure relief design for stationary process equipment requires large relief vents (frequently as rupture disks) with relief set pressures as low as practical. These factors tend to place emergency relief vent sizing for reactive materials in conflict with the standard requirements for tank car pressure protection. Example calculations cited in Reference[7] show that even for styrene (a relatively moderate reactive monomer) impractical large relief vents would be required.

Since tank cars are not currently equipped with large diameter (> 24 inches) frangible disks set at low activation pressures, runaway reaction hazards are currently principally addressed by prevention measures.

4.1.1 Inhibitor Effectiveness

Inhibitor content of monomers shipments has been previously mentioned. Reference 6 provides a technical survey of inhibitor effectiveness beyond the temperature level of 54°C. Most acrylic monomers can survive a 100-minute fire exposure and not undergo an immediate runaway exotherm. However, the inhibitor would be nearly or completely depleted by the exposure and long-term standby at elevated temperatures and could eventually lead to a runaway exotherm occurring on a time scale of several days after the event. The role of insulation in these matters

is problematic. Insulation can be beneficial in short duration fires (<100 minutes). However, insulation can preclude rapid cool-down after a long exposure to fire heat.

4.2 SPECIAL CATEGORY CONSIDERATIONS

4.2.1 Styrene

Inhibited styrene will undergo thermal polymerization initiation at temperature levels of 100-110°C. Such temperatures can be attained in an uninsulated car in a 100-minute fire. However, the material cited in Reference 6 shows that tank car failure is not a likely consequence of runaway polymerization if the mechanical strength of the car and the vapor pressure temperature relations are considered for styrene and polystyrene mixtures. Vinyl toluene would also likely fall within this category.

4.2.2 Acrylic Acid

Acrylic Acid is known to yield both benign (little or no reaction) and explosive responses in calorimetry studies, as well as plant incidents. Contamination is a factor. Practical pressure relief for worst-case potential is not practical. In addition to proper inhibitors, proper care to avoid contamination is also a key factor in preventive measures. Severe incidents have been caused by improper thawing and freezing. When acrylic acid freezes at 13°C, the inhibitor moves out of the solid phase in such a way that when thawing is accelerated by direct heat application, heat is being applied to uninhibited acrylic acid. High rate runaway exotherms have been caused by such operations.

4.2.3 Isoprene, Chloroprene

Monomers with butadiene-like structures, such as Isoprene and Chloroprene, should be viewed as very hazardous when subjected to external heat of long duration. Data indicates that runaway reactions can occur even in inhibited samples. These products are also known to undergo secondary exothermic decomposition reactions that also would be practically unventable and would likely result in tank car failure if encountered.

4.2.4 Hydrogen Peroxide

Hydrogen peroxide is an interesting, potentially thermally reactive, compound. In commercially pure form and in clean containers, an external fire would not initiate diluted H_2O_2 mixtures. In this case, contamination (either acid or base contaminants can promote a decomposition reaction) is the key issue. In the absence of contaminants, present all-vapor venting from an external fire heat source is adequate as a pressure relief vent design strategy. There is no inhibitor requirement (nor is one possible) because the product is thermally stable at 54°C. A runaway decomposition reaction requires the double faulted conditions of (a) a long duration, external fire incident upon (b) a contaminated shipment.

5.0   CONCLUSIONS AND RECOMMENDATIONS

The start-to-discharge pressure of a pressure relief valve on a tank car used to transport PIH materials is not a significant factor in the survival of the car when subjected to a 100-minute pool fire provided a large enough flow capacity is chosen for the valve. In conducting the analyses to determine the required flow capacity of the valve it is recommended that the FRA full fire engulfment condition be used instead of the AAR fire criterion because it gives a more conservative result.

If the overturned car case is to be included in the conditions for fulfillment of 49 CFR 179.18(b), it is recommended that the criterion for the pressure in the tank not exceeding the flow rating pressure of the valve not apply because it is likely to result in an unreasonably large flow capacity requirement for the valve.

Pressure relief design methods for polymerizable and thermally reactive compounds are not considered in current standards for tank cars. However, survival of a 100-minute duration pool fire is likely for most compounds. The unresolved issues reside in the time domain beyond 100 minutes. This is discussed further in Section 6.0

6.0   RECOMMENDATIONS FOR FURTHER RESEARCH

The research described in this report illuminates additional questions about the optimal designs for pressure relief valves on tank cars transporting liquid PIH and reactive materials. Much of the previous engineering of tank car pressure reduction and relief systems was motivated by concerns related to the physical properties and hazards of flammable gasses. The hazards posed by PIH and thermally reactive materials are quite different, suggesting that over-pressure mitigation strategies may also differ. At least three questions have arisen regarding possible improved designs for tank cars transporting these types of materials.

6.1   PRESSURE RELIEF VALVES OPTIMIZED FOR PIH PHYSICAL AND TOXICOLOGICAL CHARACTERISTICS

Can the potential human exposure to PIH materials be reduced? Could the amount discharged through the pressure relief valve and emission interval be modified to reduce the hazard posed by the gaseous plume thereby altering the downwind area and/or concentration of the plume? Could these parameters be customized to take into account the toxicity and physical characteristics of the particular material?

Atmospheric dispersion and toxicological characteristics of PIH materials have not heretofore been considered in establishing valve sizing and start-to-discharge parameters for pressure relief devices. The objective is to minimize the risk of injuries and fatalities as a result of a release. Structural failure of the tank and resultant release of a large quantity of toxic material over a short time is likely to be the worst-case scenario from a hazard standpoint. However, the periodic release of smaller quantities from the pressure relief valve can also pose a hazard. By

varying the flow capacity of the pressure relief valve and the set-to-discharge setting, the amount and time interval over which that amount is released can be varied.

A combination of plume modeling and toxicological analysis could be conducted to determine the air dispersion pattern that would be least likely to cause harm to persons in the surrounding area, but still provide adequate pressure relief capacity to minimize the likelihood of structural failure of the tank car. Since the chemicals have different characteristics, the optimally designed pressure relief valve for different chemicals may also differ. However, it is likely that many materials will have similar characteristics; therefore, to enhance the practicality of implementation, materials could be categorized into a set of 'standard' groups with shared pressure relief valve characteristics.

6.2 OPTIMIZATION OF MAXIMUM DESIRABLE DURATION TO MAINTAIN TANK INTEGRITY

What is the 'optimal' or maximum practical duration to ensure that a car containing liquid PIH or reactive materials will survive in a fire?

Current practice is to ensure pressure relief and thermal protection systems to assure that in a worst-case scenario a tank will survive engulfment in a fire for at least 100 minutes. This interval was developed based on estimates of how much time it would require for emergency response authorities to evacuate people to a safe distance in the event of a catastrophic failure of a tank car containing flammable gas. The safe distance was based on past experience and calculated using engineering-based estimates of the energy that would be released, the subsequent heat and blast effects, and the destructive shrapnel travel distance.

The hazards of a PIH release are considerably different in nature from a flammable gas release. While the nearby heat and blast effects of a PIH tank failure may be less, the harmful toxic effects may be considerably greater as the plume travels and disperses following release. Consequently, it is unclear if the 100-minute criterion is appropriate for evacuation of an adequate area for PIH materials. Because PIH's have differing physical and toxicological characteristics, the minimum interval may differ for the various materials. These parameters should be accounted for in establishing the pressure relief valve and thermal protection parameters. Similar concerns exist for those materials that have the potential for runaway reactions.

As described above, plume modeling for different materials under different meteorological conditions could be conducted to determine the likely worst-case scenarios for downwind area and concentration. These results would be used in conjunction with knowledge of evacuation protocols, procedures and capacity to develop realistic estimates of the amount of time required for sufficient evacuation. These times could then be used to establish a more rational basis for the duration that a tank car must survive worst-case fire conditions in order to minimize risk to the surrounding populace.

6.3 THERMAL PROTECTION REQUIREMENTS

Can modified thermal protection systems provide greater safety for tank cars transporting PIH or thermally reactive materials?

Protection of tank cars from damaging releases of their contents due to fire-induced overpressure is really a system comprised of the pressure relief valve and the thermal protection system. The former controls when and how rapidly pressure in a tank will be relieved, and the latter helps to control the rate at which pressure increases. As discussed above, a combination of experience and engineering-based factors went into establishing the best combination of parameters to prevent or mitigate the deleterious impact due to failure of a flammable gas tank car. However, the differing requirements for PIH and thermally reactive materials may also suggest the use of different thermal protection requirements. The characteristics and impact from both the intermittent release from a pressure relief valve and a total release due to tank failure may be able to be altered using a different thermal protection requirement for tank cars containing these materials.

Thermal modeling using different thermal protection parameter values could be conducted to develop an understanding of how much alteration of these might affect tank performance. The most cost-effective means of achieving a satisfactory level of safety might entail modification of thermal protection systems alone, or in conjunction with alterations to the pressure relief valve parameters. Similar to the concepts discussed above, optimal thermal protection/pressure relief valve systems may differ for different chemical compositions.

Runaway reaction prevention through proper use and understanding of inhibitors and related thermal stability issues and control and/or prevention of contamination are the pro-active safety measures. In this regard, federal regulations could benefit from review and clarification of requirements related to these issues. Present requirements for elevated relief activation pressures are an impediment to achieving practical-sized pressure relief for most runaway reaction scenarios. Conceivably, insulation could be an effective component in runaway reaction prevention, but also has adverse effects that require consideration. It should be understood that any attempt to include runaway exothermic reactions in railcar pressure relief vent sizing standards would be a difficult undertaking with prospects for only limited success on a case-by-case basis.

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APPENDIX

SENSITIVITY OF ANALYSIS RESULTS
TO PHYSICAL PROPERTIES OF COMPOUNDS

A1.0 PHYSICAL PROPERTY SENSITIVITY ANALYSIS: TANK CAR RESPONSE TO EXTERNAL FIRE

This appendix considers all of the 40 physical property data sets included in Reference A1. Simplified, but appropriate analytical model relations are used to extract relevant physical property groups that determine a specific tank car fire response characteristic. Six specific response characteristics are considered:

- Bulk heat-up rate
- Time to bulk saturation at a relief set pressure
- Liquid Volume Expansion
- All-vapor relief vent capacity
- Two-phase flashing liquid relief vent capacity
- Two-Phase flashing mass flux

Each of above characteristics is defined by a unique property or property group, which determines the relative magnitude of various compound responses to a fixed external parameter set.

The physical response of a liquid filled tank car to an external fire is arbitrarily divided into two segments — each with three categories. The first segment is the bulk heat-up prior to reaching a bulk temperature at the relief set pressure. The second segment corresponds to product discharge in upright and overturned cars.

A.2.0 HEAT-UP PRIOR TO BULK SATURATION

This segment considers property groups affecting heat-up rate, time to reach a vapor pressure corresponding to a relief set pressure, and liquid volume expansion in this interval.

A.2.1 <u>BULK HEAT-UP RATE</u>

The bulk heat-up rate of a compound subject to a given external heat input is given by the relation,

$$\frac{dT}{dt}\ [^\circ C/min]\ =\ \frac{19.742 \times 10^6 f}{\rho C V^{0.453}} \qquad (A\text{-}1)$$

where:
dT/dt = the bulk heat-up rate, [degrees C/minute]
f = a dimensionless environmental factor
ρC = the density x heat capacity product averaged over a relevant temperature interval [J/m^{3}K]
V = the tank car volume in [m^3]

For evaluation purposes a fixed tank car volume of 77.2 m^3 (20,400 gallons) is considered in an uninsulated condition, f = 1.0. It should be noted that actual heat-up rate is strongly affected by the presence or absence of insulation. Here the aforementioned parameters are fixed to illustrate physical

property effects only. As can be observed by inspection of Equation A-1, the physical property group ρC determines the heat-up rate. Equation A-1 is consistent with API-520, [A-2] and AAR guidelines.[A-3] The dimensional constant 19.742 x 10^6 is derived in Reference A-4.

A.2.2 TIME-TO-BULK SATURATION

The time to reach a given bulk temperature from some initial temperature is simply related by:

$$t_b = \frac{(T_s - T_i)}{dT/dt} \qquad (A\text{-}2)$$

In Equation A-2, t_b [min] is the time required to heat the tank car contents from some initial temperature T_i [°C] to a final temperature, T_s [°C]. The initial temperature is arbitrarily set to T_i = 30 °C. The final temperature should correspond to a saturation temperature associated with full flow of the tank car pressure relief valve. To fix this parameter, a 75 psig relief valve is selected with full flow corresponding to 10 percent overpressure or 97.5 psia. Hence for the purposes of assessing physical property affects the final temperature $T_s = T_{sat}$ at 97.5 psia. Now, from Equations A-1 and A-2 it can be observe that in addition to the product ρC, the heat-up time also depends on the compound vapor pressure-temperature relation.

A.2.3 LIQUID THERMAL EXPANSION

The AFFTAC analysis properly considers inventory product loss due to liquid thermal expansion after shell- full conditions are attained, but prior to reaching the bulk saturation temperature at the relief set pressure. The percent volume expansion is simply given by the relation

$$vol\ [\%] = 100\ \frac{\Delta \rho}{\rho} \qquad (A\text{-}3)$$

where:

$\Delta \rho$ is the density change over the temperature interval (T_s - T_i)

ρ is the density at T_i

A.2.4 COMPARISON OF PROPERTY EFFECTS ON HEAT-UP RESPONSE

Results are presented in three Tables A-1, A-2, and A-3. A different ranking criterion is represented in each table as indicated below:

Table	Ranking Criterion
Table A-1	Bulk Heat-Up Rate in [°C/min] using Equation (A-1)
Table A-2	Time to T_{set} at 97.5 psia in [min] using Equation (A-2)
Table A-3	Liquid Volume Expansion in [%] using Equation (A-3)

Table A-1. Physical Property Effects on Bulk Heat-up Rate. A Ranking of 40 Compounds in order of Decreasing Magnitude of DT/dt, [°C/min.]

Compound	Formula	Molecular Weight	Liquid Density at 30 °C [kg/m³]	Heat Capacity at 30 °C [J/kg-°K]	Density x Heat Capacity at 30 °C [J/m³-°K]	Saturation Temperature at 97.5 psia [°C]	Liquid Density at 97.5 psia sat. [kg/m³]	Heat Capacity at 97.5 psia sat. [J/kg-°K]	Density x Heat Capacity at 97.5 psia sat. [J/m³-°K]	Average of Density x Heat Capacity [J/m³-°K]	$(T_{sat\ at\ 97.5} - 30)$ x (Rho x C)avg [J/m³-°K]	Average Heat-Up Rate [$T_{sat\ at\ 97.5}^{-30\ [min]}$]	Time to $T_{sat\ at\ 97.5\ psia}$ [min]	Volume Expansion to 97.5 psia sat. [%]
Titanium tetrachloride	Cl4Ti	189.69	1706	766	1.31E+06	227	1340	775	1.04E+06	1.17E+06	2.310E+08	2.35	83.8	21.5
Sodium	Na	22.99	937	1540	1.44E+06	1135	685	1335	9.14E+05	1.18E+06	1.302E+09	2.34	472.6	26.9
Phosphorus Trichloride	PCl3	137.33	1556	844	1.31E+06	155	1287	885	1.14E+06	1.23E+06	1.533E+08	2.25	55.6	17.3
Vinylidene chloride	C2H2Cl2	96.94	1108	1157	1.28E+06	101	979	1315	1.29E+06	1.28E+06	9.121E+07	2.15	33.1	11.6
Sulfur chloride	Cl2S	102.97	1602	884	1.42E+06	133	1385	884	1.22E+06	1.32E+06	1.360E+08	2.09	49.3	13.5
Dimethylchlorosilane	C2H7ClSi	94.62	854	1687	1.44E+06	105	743	1869	1.39E+06	1.41E+06	1.061E+08	1.95	38.5	13.0
Bromine	Br2	159.81	3807	473	1.80E+06	129	2719	384	1.04E+06	1.42E+06	1.408E+08	1.94	51.1	28.6
Dimethyldichlorosilane	C2H6Cl2Si	129.06	1057	1316	1.39E+06	145	857	1715	1.47E+06	1.43E+06	1.645E+08	1.93	59.7	18.9
Methyl-trichlorosilane	CH3Cl3Si	149.48	847	1682	1.42E+06	132	687	2192	1.51E+06	1.47E+06	1.495E+08	1.88	54.2	18.9
Trimethylchlorosilane	C3H9ClSi	108.64	847	1682	1.42E+06	132	687	2192	1.51E+06	1.47E+06	1.495E+08	1.88	54.2	18.9
Chloroprene	C4H5Cl	88.54	945	1587	1.50E+06	135	795	1852	1.47E+06	1.49E+06	1.560E+08	1.85	56.6	15.9
Isoprene	C5H8	68.12	671	2264	1.52E+06	104	584	2754	1.61E+06	1.56E+06	1.157E+08	1.76	42.0	13.0
Acrylonitrile	C3H3N	53.06	795	2058	1.64E+06	153	634	2403	1.52E+06	1.58E+06	1.943E+08	1.74	70.5	20.3
4-Vinyl toluene	C9H10	118.18	910	1742	1.59E+06	267	628	2571	1.61E+06	1.60E+06	3.792E+08	1.72	137.6	31.0
n-Butyl methacrylate	C8H14O2	142.20	887	1975	1.75E+06	250	645	2360	1.52E+06	1.64E+06	3.601E+08	1.68	130.7	27.3
2-Vinyl toluene	C9H10	118.18	903	1749	1.58E+06	262	668	2596	1.73E+06	1.66E+06	3.844E+08	1.66	139.5	26.0
3-Vinyl toluene	C9H10	118.18	903	1756	1.59E+06	265	664	2614	1.74E+06	1.66E+06	3.903E+08	1.66	141.6	26.5
Hydrogen cyanide	CHN	27.03	672	2635	1.77E+06	87	578	2761	1.60E+06	1.68E+06	9.595E+07	1.64	34.8	14.0
Ethyl acrylate	C5H8O2	100.12	912	1886	1.72E+06	176	718	2323	1.67E+06	1.69E+06	2.473E+08	1.63	89.7	21.3
Styrene monomer	C8H8	104.15	896	1762	1.58E+06	237	693	2725	1.89E+06	1.73E+06	3.589E+08	1.59	130.2	22.7
Butyl acrylate	C7H12O2	128.17	889	2032	1.81E+06	234	639	2617	1.67E+06	1.74E+06	3.548E+08	1.58	128.7	28.1
Propylene oxide	C3H6O	58.08	817	2111	1.72E+06	101	716	2452	1.76E+06	1.74E+06	1.236E+08	1.58	44.8	12.4
Acrolein	C3H4O	56.06	829	2184	1.81E+06	123	713	2385	1.70E+06	1.76E+06	1.633E+08	1.57	59.2	14.0
Epichlorohydrin	C3H5ClO	92.53	1168	1439	1.68E+06	202	926	2173	2.01E+06	1.85E+06	3.176E+08	1.49	115.2	20.7
Methacrylic acid	C4H6O2	86.09	1005	1875	1.88E+06	241	770	2450	1.89E+06	1.89E+06	3.978E+08	1.46	144.3	23.4
Furfural	C5H4O2	96.09	1149	1655	1.90E+06	245	889	2139	1.90E+06	1.90E+06	4.088E+08	1.45	148.3	22.6
Vinyl acetate	C4H6O2	86.09	920	2012	1.85E+06	143	757	2587	1.96E+06	1.90E+06	2.152E+08	1.45	78.1	17.7
Methyl methacrylate	C5H8O2	100.17	932	1935	1.80E+06	183	726	2870	2.08E+06	1.94E+06	2.974E+08	1.42	107.9	22.1
Chlorosulfonic acid	ClHO3S	116.53	1734	1155	2.00E+06	242	1407	1433	2.02E+06	2.01E+06	4.260E+08	1.37	154.6	18.9
Methyl acrylate	C4H6O2	86.09	943	1903	1.79E+06	154	764	2951	2.25E+06	2.02E+06	2.510E+08	1.36	91.1	19.0
Acetaldehyde	C2H4O	44.05	768	2606	2.00E+06	86	689	3255	2.24E+06	2.12E+06	1.188E+08	1.30	43.1	10.3
Acrylic Acid	C3H4O2	72.06	1040	2029	2.11E+06	212	802	2788	2.24E+06	2.17E+06	3.955E+08	1.27	143.5	22.9
Hydrogen fluoride	HF	20.01	929	2557	2.38E+06	83	788	2773	2.19E+06	2.28E+06	1.209E+08	1.21	43.8	15.2
Acrylamide	C3H5NO	71.08	975	2454	2.39E+06	346	691	3395	2.35E+06	2.37E+06	7.487E+08	1.16	271.6	29.1
Allyl Alcohol	C3H6O	58.08	843	2624	2.21E+06	161	692	3772	2.61E+06	2.41E+06	3.159E+08	1.14	114.6	17.9
Sulfuric Acid	H2SO4	98.08	1827	1426	2.61E+06	331	1419	1713	2.43E+06	2.52E+06	7.579E+08	1.09	275.0	22.3
Acetone cyanohydrin	C4H7NO	85.11	927	2288	2.12E+06	243	670	4922	3.30E+06	2.71E+06	5.771E+08	1.02	209.4	27.7
Hydrogen peroxide	H2O2	34.02	1437	2525	3.63E+06	222	1191	2935	3.50E+06	3.56E+06	6.839E+08	0.77	248.1	17.1
Water	H2O	18.00	994	4180	4.15E+06	163	951	4346	4.13E+06	4.14E+06	5.511E+08	0.67	200.0	4.3
Sulfur trioxide	O3S	80.06	1875	3223	6.04E+06	93	1579	3223	5.09E+06	5.57E+06	3.507E+08	0.50	127.2	15.8

☐ indicates PIH compound considered in AFFTAC case evaluation.　　　　　▨ indicates ranking property group

Table A-2. Physical Property Effects on Time to a Fixed Temperature, T_{sat} at 97.5 psia. A ranking of 40 compounds in order of increasing time to T_{sat} at 97.5 psia

Compound	Formula	Molecular Weight	Liquid Density at 30 °C [kg/m³]	Heat Capacity at 30 °C [J/kg-°K]	Density x Heat Capacity at 30 °C [J/m³-°K]	Saturation Tempera-ture at 97.5 psia [°C]	Liquid Density at 97.5 psia sat. [kg/m³]	Heat Capacity at 97.5 psia sat. [J/kg-°K]	Density x Heat Capacity at 97.5 psia sat. [J/m³-°K]	Average of Density x Heat Capacity [J/m³-°K]	(T sat at 97.5 - 30) x (Rho x C)avg [J/m³-°K]	Average Heat-Up Rate [$T_{sat\ at\ 97.5}^{-30\ [min]}$]	Time to $T_{sat\ at\ 97.5\ psia}$ [min]	Volume Expansion to 97.5 psia sat. [%]
Vinylidene chloride	C2H2Cl2	96.94	1108	1157	1.28E+06	101	979	1315	1.29E+06	1.28E+06	9.121E+07	2.15	33.1	11.6
Hydrogen cyanide	CHN	27.03	672	2635	1.77E+06	87	578	2761	1.60E+06	1.68E+06	9.595E+07	1.64	34.8	14.0
Dimethylchlorosilane	C2H7ClSi	94.62	854	1687	1.44E+06	105	743	1869	1.39E+06	1.41E+06	1.061E+08	1.95	38.5	13.0
Isoprene	C5H8	68.12	671	2264	1.52E+06	104	584	2754	1.61E+06	1.56E+06	1.157E+08	1.76	42.0	13.0
Acetaldehyde	C2H4O	44.05	768	2606	2.00E+06	86	689	3255	2.24E+06	2.12E+06	1.188E+08	1.30	43.1	10.3
Hydrogen fluoride	HF	20.01	929	2557	2.38E+06	83	788	2773	2.19E+06	2.28E+06	1.209E+08	1.21	43.8	15.2
Propylene oxide	C3H6O	58.08	817	2111	1.72E+06	101	716	2452	1.76E+06	1.74E+06	1.236E+08	1.58	44.8	12.4
Sulfur chloride	Cl2S	102.97	1602	884	1.42E+06	133	1385	884	1.22E+06	1.32E+06	1.360E+08	2.09	49.3	13.5
Bromine	Br2	159.81	3807	473	1.80E+06	129	2719	384	1.04E+06	1.42E+06	1.408E+08	1.94	51.1	28.6
Methyl-trichlorosilane	CH3Cl3Si	149.48	847	1682	1.42E+06	132	687	2192	1.51E+06	1.47E+06	1.495E+08	1.88	54.2	18.9
Trimethylchlorosilane	C3H9ClSi	108.64	847	1682	1.42E+06	132	687	2192	1.51E+06	1.47E+06	1.495E+08	1.88	54.2	18.9
Phosphorus Trichloride	PCl3	137.33	1556	844	1.31E+06	155	1287	885	1.14E+06	1.23E+06	1.533E+08	2.25	55.6	17.3
Chloroprene	C4H5Cl	88.54	945	1587	1.50E+06	135	795	1852	1.47E+06	1.49E+06	1.560E+08	1.85	56.6	15.9
Acrolein	C3H4O	56.06	829	2184	1.81E+06	123	713	2385	1.70E+06	1.76E+06	1.633E+08	1.57	59.2	14.0
Dimethyldichlorosilane	C2H6Cl2Si	129.06	1057	1316	1.39E+06	145	857	1715	1.47E+06	1.43E+06	1.645E+08	1.93	59.7	18.9
Acrylonitrile	C3H3N	53.06	795	2058	1.64E+06	153	634	2403	1.52E+06	1.58E+06	1.943E+08	1.74	70.5	20.3
Vinyl acetate	C4H6O2	86.09	920	2012	1.85E+06	143	757	2587	1.96E+06	1.90E+06	2.152E+08	1.45	78.1	17.7
Titanium tetrachloride	Cl4Ti	189.69	1706	766	1.31E+06	227	1340	775	1.04E+06	1.17E+06	2.310E+08	2.35	83.8	21.5
Ethyl acrylate	C5H8O2	100.12	912	1886	1.72E+06	176	718	2323	1.67E+06	1.69E+06	2.473E+08	1.63	89.7	21.3
Methyl acrylate	C4H6O2	86.09	943	1903	1.79E+06	154	764	2951	2.25E+06	2.02E+06	2.510E+08	1.36	91.1	19.0
Methyl methacrylate	C5H8O2	100.17	932	1935	1.80E+06	183	726	2870	2.08E+06	1.94E+06	2.974E+08	1.42	107.9	22.1
Allyl Alcohol	C3H6O	58.08	843	2624	2.21E+06	161	692	3772	2.61E+06	2.41E+06	3.159E+08	1.14	114.6	17.9
Epichlorohydrin	C3H5ClO	92.53	1168	1439	1.68E+06	202	926	2173	2.01E+06	1.85E+06	3.176E+08	1.49	115.2	20.7
Sulfur trioxide	O3S	80.06	1875	3223	6.04E+06	93	1579	3223	5.09E+06	5.57E+06	3.507E+08	0.50	127.2	15.8
Butyl acrylate	C7H12O2	128.17	889	2032	1.81E+06	234	639	2617	1.67E+06	1.74E+06	3.548E+08	1.58	128.7	28.1
Styrene monomer	C8H8	104.15	896	1762	1.58E+06	237	693	2725	1.89E+06	1.73E+06	3.589E+08	1.59	130.2	22.7
n-Butyl methacrylate	C8H14O2	142.20	887	1975	1.75E+06	250	645	2360	1.52E+06	1.64E+06	3.601E+08	1.68	130.7	27.3
4-Vinyl toluene	C9H10	118.18	910	1742	1.59E+06	267	628	2571	1.61E+06	1.60E+06	3.792E+08	1.72	137.6	31.0
2-Vinyl toluene	C9H10	118.18	903	1749	1.58E+06	262	668	2596	1.73E+06	1.66E+06	3.844E+08	1.66	139.5	26.0
3-Vinyl toluene	C9H10	118.18	903	1756	1.59E+06	265	664	2614	1.74E+06	1.66E+06	3.903E+08	1.66	141.6	26.5
Acrylic Acid	C3H4O2	72.06	1040	2029	2.11E+06	212	802	2788	2.24E+06	2.17E+06	3.955E+08	1.27	143.5	22.9
Methacrylic acid	C4H6O2	86.09	1005	1875	1.88E+06	241	770	2450	1.89E+06	1.89E+06	3.978E+08	1.46	144.3	23.4
Furfural	C5H4O2	96.09	1149	1655	1.90E+06	245	889	2139	1.90E+06	1.90E+06	4.088E+08	1.45	148.3	22.6
Chlorosulfonic acid	ClHO3S	116.53	1734	1155	2.00E+06	242	1407	1433	2.02E+06	2.01E+06	4.260E+08	1.37	154.6	18.9
Water	H2O	18.00	994	4180	4.15E+06	163	951	4346	4.13E+06	4.14E+06	5.511E+08	0.67	200.0	4.3
Acetone cyanohydrin	C4H7NO	85.11	927	2288	2.12E+06	243	670	4922	3.30E+06	2.71E+06	5.771E+08	1.02	209.4	27.7
Hydrogen peroxide	H2O2	34.02	1437	2525	3.63E+06	222	1191	2935	3.50E+06	3.56E+06	6.839E+08	0.77	248.1	17.1
Acrylamide	C3H5NO	71.08	975	2454	2.39E+06	346	691	3395	2.35E+06	2.37E+06	7.487E+08	1.16	271.6	29.1
Sulfuric Acid	H2SO4	98.08	1827	1426	2.61E+06	331	1419	1713	2.43E+06	2.52E+06	7.579E+08	1.09	275.0	22.3
Sodium	Na	22.99	937	1540	1.44E+06	1135	685	1335	9.14E+05	1.18E+06	1.302E+09	2.34	472.6	26.9

☐ indicates PIH compound considered in AFFTAC case evaluation.   ▨ indicates ranking property group

Table A-3. Physical property effects on liquid volume expansion from 30°C to T $_{sat}$ at 97.5 psia. A ranking of 40 compounds in order of decreasing liquid volume expansion

Compound	Formula	Molecular Weight	Liquid Density at 30 °C [kg/m³]	Heat Capacity at 30 °C [J/kg-°K]	Density x Heat Capacity at 30 °C [J/m³-°K]	Saturation Temperature at 97.5 psia [°C]	Liquid Density at 97.5 psia sat. [kg/m³]	Heat Capacity at 97.5 psia sat. [J/kg-°K]	Density x Heat Capacity at 97.5 psia sat. [J/m³-°K]	Average of Density x Heat Capacity [J/m³-°K]	(T sat at 97.5 - 30) x (Rho x C)$_{avg}$ [J/m³-°K]	Average Heat-Up Rate [T$_{sat\ at\ 97.5}$ $^{-30\ [min]}$]	Time to T$_{sat\ at\ 97.5\ psia}$ [min]	Volume Expansion to 97.5 psia sat. [%]
4-Vinyl toluene	C9H10	118.18	910	1742	1.59E+06	267	628	2571	1.61E+06	1.60E+06	3.792E+08	1.72	137.6	31.0
Acrylamide	C3H5NO	71.08	975	2454	2.39E+06	346	691	3395	2.35E+06	2.37E+06	7.487E+08	1.16	271.6	29.1
Bromine	Br2	159.81	3807	473	1.80E+06	129	2719	384	1.04E+06	1.42E+06	1.408E+08	1.94	51.1	28.6
Butyl acrylate	C7H12O2	128.17	889	2032	1.81E+06	234	639	2617	1.67E+06	1.74E+06	3.548E+08	1.58	128.7	28.1
Acetone cyanohydrin	C4H7NO	85.11	927	2288	2.12E+06	243	670	4922	3.30E+06	2.71E+06	5.771E+08	1.02	209.4	27.7
n-Butyl methacrylate	C8H14O2	142.20	887	1975	1.75E+06	250	645	2360	1.52E+06	1.64E+06	3.601E+08	1.68	130.7	27.3
Sodium	Na	22.99	937	1540	1.44E+06	1135	685	1335	9.14E+05	1.18E+06	1.302E+09	2.34	472.6	26.9
3-Vinyl toluene	C9H10	118.18	903	1756	1.59E+06	265	664	2614	1.74E+06	1.66E+06	3.903E+08	1.66	141.6	26.5
2-Vinyl toluene	C9H10	118.18	903	1749	1.58E+06	262	668	2596	1.73E+06	1.66E+06	3.844E+08	1.66	139.5	26.0
Methacrylic acid	C4H6O2	86.09	1005	1875	1.88E+06	241	770	2450	1.89E+06	1.89E+06	3.978E+08	1.46	144.3	23.4
Acrylic Acid	C3H4O2	72.06	1040	2029	2.11E+06	212	802	2788	2.24E+06	2.17E+06	3.955E+08	1.27	143.5	22.9
Styrene monomer	C8H8	104.15	896	1762	1.58E+06	237	693	2725	1.89E+06	1.73E+06	3.589E+08	1.59	130.2	22.7
Furfural	C5H4O2	96.09	1149	1655	1.90E+06	245	889	2139	1.90E+06	1.90E+06	4.088E+08	1.45	148.3	22.6
Sulfuric Acid	H2SO4	98.08	1827	1426	2.61E+06	331	1419	1713	2.43E+06	2.52E+06	7.579E+08	1.09	275.0	22.3
Methyl methacrylate	C5H8O2	100.17	932	1935	1.80E+06	183	726	2870	2.08E+06	1.94E+06	2.974E+08	1.42	107.9	22.1
Titanium tetrachloride	Cl4Ti	189.69	1706	766	1.31E+06	227	1340	775	1.04E+06	1.17E+06	2.310E+08	2.35	83.8	21.5
Ethyl acrylate	C5H8O2	100.12	912	1886	1.72E+06	176	718	2323	1.67E+06	1.69E+06	2.473E+08	1.63	89.7	21.3
Epichlorohydrin	C3H5ClO	92.53	1168	1439	1.68E+06	202	926	2173	2.01E+06	1.85E+06	3.176E+08	1.49	115.2	20.7
Acrylonitrile	C3H3N	53.06	795	2058	1.64E+06	153	634	2403	1.52E+06	1.58E+06	1.943E+08	1.74	70.5	20.3
Methyl acrylate	C4H6O2	86.09	943	1903	1.79E+06	154	764	2951	2.25E+06	2.02E+06	2.510E+08	1.36	91.1	19.0
Dimethyldichlorosilane	C2H6Cl2Si	129.06	1057	1316	1.39E+06	145	857	1715	1.47E+06	1.43E+06	1.645E+08	1.93	59.7	18.9
Methyl-trichlorosilane	CH3Cl3Si	149.48	847	1682	1.42E+06	132	687	2192	1.51E+06	1.47E+06	1.495E+08	1.88	54.2	18.9
Trimethylchlorosilane	C3H9ClSi	108.64	847	1682	1.42E+06	132	687	2192	1.51E+06	1.47E+06	1.495E+08	1.88	54.2	18.9
Chlorosulfonic acid	ClHO3S	116.53	1734	1155	2.00E+06	242	1407	1433	2.02E+06	2.01E+06	4.260E+08	1.37	154.6	18.9
Allyl Alcohol	C3H6O	58.08	843	2624	2.21E+06	161	692	3772	2.61E+06	2.41E+06	3.159E+08	1.14	114.6	17.9
Vinyl acetate	C4H6O2	86.09	920	2012	1.85E+06	143	757	2587	1.96E+06	1.90E+06	2.152E+08	1.45	78.1	17.7
Phosphorus Trichloride	PCl3	137.33	1556	844	1.31E+06	155	1287	885	1.14E+06	1.23E+06	1.533E+08	2.25	55.6	17.3
Hydrogen peroxide	H2O2	34.02	1437	2525	3.63E+06	222	1191	2935	3.50E+06	3.56E+06	6.839E+08	0.77	248.1	17.1
Chloroprene	C4H5Cl	88.54	945	1587	1.50E+06	135	795	1852	1.47E+06	1.49E+06	1.560E+08	1.85	56.6	15.9
Sulfur trioxide	O3S	80.06	1875	3223	6.04E+06	93	1579	3223	5.09E+06	5.57E+06	3.507E+08	0.50	127.2	15.8
Hydrogen fluoride	HF	20.01	929	2557	2.38E+06	83	788	2773	2.19E+06	2.28E+06	1.209E+08	1.21	43.8	15.2
Acrolein	C3H4O	56.06	829	2184	1.81E+06	123	713	2385	1.70E+06	1.76E+06	1.633E+08	1.57	59.2	14.0
Hydrogen cyanide	CHN	27.03	672	2635	1.77E+06	87	578	2761	1.60E+06	1.68E+06	9.595E+07	1.64	34.8	14.0
Sulfur chloride	Cl2S	102.97	1602	884	1.42E+06	133	1385	884	1.22E+06	1.32E+06	1.360E+08	2.09	49.3	13.5
Dimethylchlorosilane	C2H7ClSi	94.62	854	1687	1.44E+06	105	743	1869	1.39E+06	1.41E+06	1.061E+08	1.95	38.5	13.0
Isoprene	C5H8	68.12	671	2264	1.52E+06	104	584	2754	1.61E+06	1.56E+06	1.157E+08	1.76	42.0	13.0
Propylene oxide	C3H6O	58.08	817	2111	1.72E+06	101	716	2452	1.76E+06	1.74E+06	1.236E+08	1.58	44.8	12.4
Vinylidene chloride	C2H2Cl2	96.94	1108	1157	1.28E+06	101	979	1315	1.29E+06	1.28E+06	9.121E+07	2.15	33.1	11.6
Acetaldehyde	C2H4O	44.05	768	2606	2.00E+06	86	689	3255	2.24E+06	2.12E+06	1.188E+08	1.30	43.1	10.3
Water	H2O	18.00	994	4180	4.15E+06	163	951	4346	4.13E+06	4.14E+06	5.511E+08	0.67	200.0	4.3

indicates PIH compound considered in AFFTAC case evaluation.

indicates ranking property group

In each table, the compounds considered in an AFFTAC analysis case are shown as shaded table row entries and the parameter being ranked is indicated as a shaded column. In this way one may readily observe both the relative ranking of the PIH compounds included in the AFFTAC analysis cases, as well as the relative ranking of all 40 products included in the Reference. A.1 database. It is satisfying to note that the PIH compound cases considered in the AFFTAC analysis also reflect the same range of property effects variation contained in the full 40 compound data base.

A.3.0 RELIEF VENTING CONSIDERATIONS

The next set of response characteristics are related to relief device vent flow.

A.3.1 ALL-VAPOR VENTING

Based on the normal relations for all-vapor venting it can be shown that for a fixed heat input and for comparisons made at a fixed venting pressure, the relative size of required relief vent area, (or standard relief flow capacity rating) scales with the physical property group

$$VI_V = \frac{\sqrt{zRT/Mw}}{P\lambda} \qquad (A\text{-}4)$$

where:
VI_v = vent capacity index given in units [cm^2/100 kw]
z = compressibility factor at the normal boiling temperature
R = gas constant, 8,314 [J/kg mol K]
T = normal boiling temperature [K]
Mw = molecular weight
P = normal atmospheric pressure [101,325 N/m^2]
λ = latent heat of evaporation at the normal boiling temperature [J/kg]

Note that Equation A-4 does not represent the actual required vent flow area. Reference A-5 provides details which illustrate the derivation of Equation A-4 and show that the required vent area can be obtained from Equation A-4 and a universal scaling law with only absolute pressure as the independent variable. Hence, only the property group represented by Equation A-4 is required, evaluated at the normal boiling temperature, to determine relative property dependent ranking of various compounds.

It is also noted that all-vapor vent flow is the standard relief vent assumption for upright rail cars. See project reference (A-4) for confirmation of the validity of this assumption.

A.3.2 FLASHING LIQUID FLOW

Under accident conditions, in addition to eternal fire exposure, a rail tank car may be in an overturned condition with the relief vent flow having the characteristics of a two-phase flashing flow.

A valid expression for two-phase flashing mass flux of a pure compound is given by

$$G_{2\phi} = \frac{\lambda P Mw}{zR T\sqrt{C T}} \qquad (A\text{-}5)$$

In Equation A-5, $G_{2\phi}$ is a two-phase mass flux [kg/m^2.sec], and the only new term is C, the liquid heat capacity. A relative comparison of various compounds can be based on properties evaluated at the normal boiling point. The relative ranking remains the same at any other fixed pressure, (less than the thermodynamic critical pressure).

The relevance of the two-phase flashing mass flux, is that along with a given vent flow area, the rate of inventory discharge as a flashing liquid will be determined by this characteristic.

A.3.3 VENT AREA FOR TWO-PHASE FLASHING LIQUID DISCHARGE

In the extreme case of a completely overturned railroad tank car, the product discharge can be conservatively characterized as a flashing two- phase flow. A steady state vent area index based on all two-phase flashing flow would involve the following property grouping.

$$VI_{2\phi} = 10^9 \, \rho_I \sqrt{C T} \left[\frac{zR T}{\lambda P Mw} \right]^2 \qquad (A\text{-}6)$$

where:
$VI_{2\phi}$ = property grouping vent index for flashing liquid flow [cm^2/100 kw]
ρ_1 = liquid density [kg/m^3]

All other parameters in Equation A-6 have been previously defined. Again, as in Section A.3.1, Equation A-6 does not represent the actual flow area. Flow area at a selected pressure is also based on a universal correlation with only absolute pressure as an independent variable. Therefore, it is only necessary to evaluate Equation A-6 at the normal boiling point to provide a comparative ranking of various compounds.

A.3.4 <u>COMPARISON OF PROPERTY EFFECTS ON VENT FLOW RESPONSE</u>

Results are presented in three Tables A.4, A.5, and A.6. A different ranking criterion is represented in each table as indicated below:

Table	Ranking Criterion
Table A-4	Vent Area Required for All-Vapor Flow, [cm^2/100 kw]
Table A-5	Flashing Liquid Mass Flux, [cm^2/100 kw] at 1 atmosphere
Table A-6	Vent Area Required for Flashing-Liquid Flow, [cm^2/100 kw]

In each table, the compounds considered in an AFFTAC analysis case are shown as shaded table row entries and the parameter being ranked is indicated as a shaded column. In this way one may readily observe both the relative ranking of the PIH compounds included in the AFFTAC analysis cases, as well as the relative ranking of all 40 compounds included in the Reference A-1 data base. It is satisfying to note that the PIH compound cases considered in the AFFTAC analysis also reflect the same range of property effects variation contained in the full 40 compound data base.

Table A.4 Physical Property Effects on Required Relief Vent Capacity for All-vapor Venting. A Ranking of 40 Compounds in order of Decreasing Vent Index for All-vapor Flow

Compound	Formula	Molecular Weight	Melting Temp. [°C]	Normal Boiling Temp.[°C]	Liquid Density at 25 °C	Latent Heat at T_{nbt} [J/kg]	Compressibility at T_{nbt} [-]	Heat Capacity at T_{nbt} [J/kg-°K]	Liquid Density at T_{nbt} [kg/m³]	All-Vapor Vent Index [cm²/100 kw]	Flashing Liquid Vent Index [cm²/100 kw]	2-Phase Mass Flux at T_{nbt} [kg/m²-sec]
Hydrogen fluoride	HF	20.01	-83.36	19.52	955.17	433.4	0.964	2508.1	955.18	7.80	5834	437.2
Titanium tetrachloride	Cl4Ti	189.69	-24.10	135.85	1714.03	183.9	0.957	770.9	1528.30	7.03	727	1934.4
Methyl-trichlorosilane	CH3Cl3Si	149.48	65.40	66.40	1266.30	188.02	0.947	1138.1	1192.72	7.02	653	1713.6
Bromine	Br2	159.81	-7.25	58.75	3104.33	187.5	0.972	455.5	2985.34	6.82	906	2911.3
Phosphorus Trichloride	PCl3	137.33	-92.00	76.10	1566.18	214.2	0.961	854.6	1464.72	6.57	701	1955.0
Dimethyldichlorosilane	C2H6Cl2Si	129.06	-76.10	70.20	1064.81	227.9	0.948	1439.7	994.19	6.27	576	1566.4
Dimethylchlorosilane	C2H7ClSi	94.62	-111.00	35.50	860.80	262.27	0.948	1699.9	847.24	6.03	574	1426.9
Trimethylchlorosilane	C3H9ClSi	108.64	-57.70	57.60	853.47	256.52	0.945	1804.3	807.90	5.95	529	1406.7
Vinylidene chloride	C2H2Cl2	96.94	-122.50	31.56	1116.66	274.46	0.959	1159.9	1105.88	5.69	534	1866.6
Sulfur chloride	Cl2S	102.97	-122.00	59.60	1611.36	291.6	0.964	883.9	1545.98	5.45	644	2103.5
n-Butyl methacrylate	C8H14O2	142.20	-75.37	163.00	890.92	280.1	0.935	2207.6	756.36	5.44	524	1213.1
Chloroprene	C4H5Cl	88.54	-130.00	59.40	950.97	314.93	0.953	1646.2	906.82	5.41	584	1449.2
Butyl acrylate	C7H12O2	128.17	-64.60	147.85	894.09	292.3	0.933	2370.7	758.75	5.39	561	1163.5
4-Vinyl toluene	C9H10	118.18	-34.13	172.78	915.63	334.0	0.945	2240.9	751.82	5.09	577	1142.0
3-Vinyl toluene	C9H10	118.18	-86.34	171.60	907.57	333.8	0.943	2272.5	772.59	5.08	591	1140.2
Ethyl acrylate	C5H8O2	100.12	-71.20	99.50	918.26	336.9	0.948	2093.8	828.74	5.02	541	1317.3
Styrene monomer	C8H8	104.15	-30.61	145.16	900.08	351.6	0.951	2190.6	792.89	5.00	603	1172.0
2-Vinyl toluene	C9H10	118.18	-68.57	169.81	907.69	339.0	0.946	2259.4	774.19	5.00	571	1164.7
Isoprene	C5H8	68.12	-145.88	34.06	675.94	376.14	0.949	2286.5	666.74	4.95	487	1277.9
Methyl methacrylate	C5H8O2	100.17	-48.20	100.30	937.17	342.7	0.948	1992.9	847.61	4.94	524	1369.8
Chlorosulfonic acid	ClHO3S	116.53	-80.00	153.85	1740.71	348.0	0.969	1317.4	1556.34	4.87	818	1592.5
Vinyl acetate	C4H6O2	86.09	-92.80	72.50	926.21	366.7	0.949	2200.2	864.79	4.79	548	1345.0
Methyl acrylate	C4H6O2	86.09	-76.83	80.20	949.05	374.2	0.952	2216.7	877.26	4.75	570	1318.7
Methacrylic acid	C4H6O2	86.09	15.00	161.00	1009.45	417.4	0.955	2188.7	869.54	4.73	760	1083.6
Epichlorohydrin	C3H5ClO	92.53	-57.20	118.50	1173.89	385.5	0.954	1775.3	1053.36	4.69	649	1395.3
Furfural	C5H4O2	96.09	-36.50	161.70	1154.53	433.6	0.959	1950.9	1001.62	4.32	622	1321.9
Propylene oxide	C3H6O	58.08	-111.93	33.90	823.27	477.52	0.955	2126.3	811.82	4.23	494	1426.6
Acrolein	C3H4O	56.06	-87.70	52.69	834.41	517.9	0.955	2233.6	803.61	4.09	530	1332.9
Sulfuric Acid	H2SO4	98.08	10.31	274.80	1832.90	511.0	0.963	1712.8	1419.17	4.08	1026	1194.9
Acetaldehyde	C2H4O	44.05	-123.00	20.85	779.91	563.73	0.957	2519.0	779.91	4.03	580	1250.0
Acrylonitrile	C3H3N	53.06	-83.52	77.35	801.12	585.33	0.951	2166.7	738.69	3.85	499	1303.2
Acrylic Acid	C3H4O2	72.06	13.50	141.00	1045.51	590.03	0.957	2491.5	905.06	3.58	538	1287.1
Sulfur trioxide	O3S	80.06	16.80	44.75	1897.48	508.5	0.968	3223.6	1807.26	3.47	704	1592.8
Acetone cyanohydrin	C4H7NO	85.11	-20.00	170.85	926.39	589.0	0.953	3783.0	769.71	3.41	479	1114.0
Allyl Alcohol	C3H6O	58.08	-129.23	97.08	847.49	687.9	0.960	3134.4	772.54	3.24	443	1271.7
Acrylamide	C3H5NO	71.08	84.50	240.85	933.25	755.93	0.958	3081.5	800.28	3.13	570	1056.7
Hydrogen cyanide	CHN	27.03	-13.32	25.70	679.56	995.1	0.959	2628.9	678.51	2.94	460	1290.2
Hydrogen peroxide	H2O2	34.02	-0.04	150.20	1442.72	1374.	0.982	7782.3	1289.92	2.29	1247	754.8
Water	H2O	18.00	0.00	100.00	1000.00	2265.	0.982	4219.5	973.44	1.79	664	1080.6
Sodium	Na	22.99	97.83	882.85	921.78	3888.	0.986	1317.9	745.18	1.63	1007	774.3

indicates PIH compound considered in AFFTAC case evaluation.

indicates ranking property group

Table A.5 Physical Property Effects on Two-phase Flashing Mass Flux. A Ranking of 40 Compounds in order of Decreasing Two-Phase Mass Flux Evaluated at Normal Boiling Point Properties

Compound	Formula	Molecular Weight	Melting Temp.[°C]	Normal Boiling Temp. [°C]	Liquid Density at 25 °C [kg/m³]	Latent Heat at T_{nbt} [J/kg]	Compressibility at T_{nbt} [-]	Heat Capacity at T_{nbt} [J/kg-°K]	Liquid Density at T_{nbt} [kg/m³]	All-Vapor Vent Index [cm²/100 kw]	Flashing Liquid Vent Index [cm²/100 kw]	2-Phase Mass Flux at T_{nbt} [kg/m²-sec]
Bromine	Br2	159.81	-7.25	58.75	3104.33	187.5	0.972	455.5	2985.34	6.82	906	2911.3
Sulfur chloride	Cl2S	102.97	-122.00	59.60	1611.36	291.6	0.964	883.9	1545.98	5.45	644	2103.5
Phosphorus	PCl3	137.33	-92.00	76.10	1566.18	214.2	0.961	854.6	1464.72	6.57	701	1955.0
Titanium	Cl4Ti	189.69	-24.10	135.85	1714.03	183.9	0.957	770.9	1528.30	7.03	727	1934.4
Vinylidene	C2H2Cl2	96.94	-122.50	31.56	1116.66	274.46	0.959	1159.9	1105.88	5.69	534	1866.6
Methyl-	CH3Cl3Si	149.48	65.40	66.40	1266.30	188.02	0.947	1138.1	1192.72	7.02	653	1713.6
Sulfur trioxide	O3S	80.06	16.80	44.75	1897.48	508.5	0.968	3223.6	1807.26	3.47	704	1592.8
Chlorosulfonic	ClHO3S	116.53	-80.00	153.85	1740.71	348.0	0.969	1317.4	1556.34	4.87	818	1592.5
Dimethyldichlo	C2H6Cl2Si	129.06	-76.10	70.20	1064.81	227.9	0.948	1439.7	994.19	6.27	576	1566.4
Chloroprene	C4H5Cl	88.54	-130.00	59.40	950.97	314.93	0.953	1646.2	906.82	5.41	584	1449.2
Dimethylchloro	C2H7ClSi	94.62	-111.00	35.50	860.80	262.27	0.948	1699.9	847.24	6.03	574	1426.9
Propylene	C3H6O	58.08	-111.93	33.90	823.27	477.52	0.955	2126.3	811.82	4.23	494	1426.6
Trimethylchlor	C3H9ClSi	108.64	-57.70	57.60	853.47	256.52	0.945	1804.3	807.90	5.95	529	1406.7
Epichlorohydri	C3H5ClO	92.53	-57.20	118.50	1173.89	385.5	0.954	1775.3	1053.36	4.69	649	1395.3
Methyl	C5H8O2	100.17	-48.20	100.30	937.17	342.7	0.948	1992.9	847.61	4.94	524	1369.8
Vinyl acetate	C4H6O2	86.09	-92.80	72.50	926.21	366.7	0.949	2200.2	864.79	4.79	548	1345.0
Acrolein	C3H4O	56.06	-87.70	52.69	834.41	517.9	0.955	2233.6	803.61	4.09	530	1332.9
Furfural	C5H4O2	96.09	-36.50	161.70	1154.53	433.6	0.959	1950.9	1001.62	4.32	622	1321.9
Methyl	C4H6O2	86.09	-76.83	80.20	949.05	374.2	0.952	2216.7	877.26	4.75	570	1318.7
Ethyl acrylate	C5H8O2	100.12	-71.20	99.50	918.26	336.9	0.948	2093.8	828.74	5.02	541	1317.3
Acrylonitrile	C3H3N	53.06	-83.52	77.35	801.12	585.33	0.951	2166.7	738.69	3.85	499	1303.2
Hydrogen	CHN	27.03	-13.32	25.70	679.56	995.1	0.959	2628.9	678.51	2.94	460	1290.2
Acrylic Acid	C3H4O2	72.06	13.50	141.00	1045.51	590.03	0.957	2491.5	905.06	3.58	538	1287.1
Isoprene	C5H8	68.12	-145.88	34.06	675.94	376.14	0.949	2286.5	666.74	4.95	487	1277.9
Allyl Alcohol	C3H6O	58.08	-129.23	97.08	847.49	687.9	0.960	3134.4	772.54	3.24	443	1271.7
Acetaldehyde	C2H4O	44.05	-123.00	20.85	779.91	563.73	0.957	2519.0	779.91	4.03	580	1250.0
n-Butyl	C8H14O2	142.20	-75.37	163.00	890.92	280.1	0.935	2207.6	756.36	5.44	524	1213.1
Sulfuric Acid	H2SO4	98.08	10.31	274.80	1832.90	511.0	0.963	1712.8	1419.17	4.08	1026	1194.9
Styrene	C8H8	104.15	-30.61	145.16	900.08	351.6	0.951	2190.6	792.89	5.00	603	1172.0
2-Vinyl toluene	C9H10	118.18	-68.57	169.81	907.69	339.0	0.946	2259.4	774.19	5.00	571	1164.7
Butyl acrylate	C7H12O2	128.17	-64.60	147.85	894.09	292.3	0.933	2370.7	758.75	5.39	561	1163.5
4-Vinyl toluene	C9H10	118.18	-34.13	172.78	915.63	334.0	0.945	2240.9	751.82	5.09	577	1142.0
3-Vinyl toluene	C9H10	118.18	-86.34	171.60	907.57	333.8	0.943	2272.5	772.59	5.08	591	1140.2
Acetone	C4H7NO	85.11	-20.00	170.85	926.39	589.0	0.953	3783.0	769.71	3.41	479	1114.0
Methacrylic	C4H6O2	86.09	15.00	161.00	1009.45	417.4	0.955	2188.7	869.54	4.73	760	1083.6
Water	H2O	18.00	0.00	100.00	1000.00	2265.	0.982	4219.5	973.44	1.79	664	1080.6
Acrylamide	C3H5NO	71.08	84.50	240.85	933.25	755.93	0.958	3081.5	800.28	3.13	570	1056.7
Sodium	Na	22.99	97.83	882.85	921.78	3888.	0.986	1317.9	745.18	1.63	1007	774.3
Hydrogen peroxide	H2O2	34.02	-0.04	150.20	1442.72	1374.	0.982	7782.3	1289.92	2.29	1247	754.8
Hydrogen fluoride	HF	20.01	-83.36	19.52	955.17	433.4	0.964	2508.1	955.18	7.80	5834	437.2

indicates PIH compound considered in AFFTAC case evaluation.　　　　indicates ranking property group

Table A.6 Physical Property Effects On Required Vent Area For Two-Phase Flashing Relief Vent Flow. A Ranking Of 40 Compounds in Order of Decreasing Two-Phase Mass Flux Evaluated at Normal Boiling Point Properties.

Compound	Formula	Molecular Weight	Melting Temp.[°C]	Normal Boiling Temp.[°C]	Liquid Density at T_{nbt} [kg/m³]	Latent Heat at T_{nbt} [J/kg]	Compressibility at T_{nbt} [-]	Heat Capacity at T_{nbt} [J/kg-°K]	Liquid Density at T_{nbt} [kg/m³]	All-Vapor Vent Index [cm²/100 kw]	Flashing Liquid Vent Index [cm²/100 kw]	2-Phase Mass Flux at Tnbp [kg/m²-sec]
Hydrogen fluoride	HF	20.01	-83.36	19.52	955.17	433.4	0.964	2508.1	955.18	7.80	5834	437.2
Hydrogen peroxide	H2O2	34.02	-0.04	150.20	1442.72	1374.	0.982	7782.3	1289.92	2.29	1247	754.8
Sulfuric Acid	H2SO4	98.08	10.31	274.80	1832.90	511.0	0.963	1712.8	1419.17	4.08	1026	1194.9
Sodium	Na	22.99	97.83	882.85	921.78	3888.	0.986	1317.9	745.18	1.63	1007	774.3
Bromine	Br2	159.81	-7.25	58.75	3104.33	187.5	0.972	455.5	2985.34	6.82	906	2911.3
Chlorosulfonic acid	ClHO3S	116.53	-80.00	153.85	1740.71	348.0	0.969	1317.4	1556.34	4.87	818	1592.5
Methacrylic acid	C4H6O2	86.09	15.00	161.00	1009.45	417.4	0.955	2188.7	869.54	4.73	760	1083.6
Titanium tetrachloride	Cl4Ti	189.69	-24.10	135.85	1714.03	183.9	0.957	770.9	1528.30	7.03	727	1934.4
Sulfur trioxide	O3S	80.06	16.80	44.75	1897.48	508.5	0.968	3223.6	1807.26	3.47	704	1592.8
Phosphorus Trichloride	PCl3	137.33	-92.00	76.10	1566.18	214.2	0.961	854.6	1464.72	6.57	701	1955.0
Water	H2O	18.00	0.00	100.00	1000.00	2265.	0.982	4219.5	973.44	1.79	664	1080.6
Methyl-trichlorosilane	CH3Cl3Si	149.48	65.40	66.40	1266.30	188.02	0.947	1138.1	1192.72	7.02	653	1713.6
Epichlorohydrin	C3H5ClO	92.53	-57.20	118.50	1173.89	385.5	0.954	1775.3	1053.36	4.69	649	1395.3
Sulfur chloride	Cl2S	102.97	-122.00	59.60	1611.36	291.6	0.964	883.9	1545.98	5.45	644	2103.5
Furfural	C5H4O2	96.09	-36.50	161.70	1154.53	433.6	0.959	1950.9	1001.62	4.32	622	1321.9
Styrene monomer	C8H8	104.15	-30.61	145.16	900.08	351.6	0.951	2190.6	792.89	5.00	603	1172.0
3-Vinyl toluene	C9H10	118.18	-86.34	171.60	907.57	333.8	0.943	2272.5	772.59	5.08	591	1140.2
Chloroprene	C4H5Cl	88.54	-130.00	59.40	950.97	314.93	0.953	1646.2	906.82	5.41	584	1449.2
Acetaldehyde	C2H4O	44.05	-123.00	20.85	779.91	563.73	0.957	2519.0	779.91	4.03	580	1250.0
4-Vinyl toluene	C9H10	118.18	-34.13	172.78	915.63	334.0	0.945	2240.9	751.82	5.09	577	1142.0
Dimethyldichlorosilane	C2H6Cl2Si	129.06	-76.10	70.20	1064.81	227.9	0.948	1439.7	994.19	6.27	576	1566.4
Dimethylchlorosilane	C2H7ClSi	94.62	-111.00	35.50	860.80	262.27	0.948	1699.9	847.24	6.03	574	1426.9
2-Vinyl toluene	C9H10	118.18	-68.57	169.81	907.69	339.0	0.946	2259.4	774.19	5.00	571	1164.7
Methyl acrylate	C4H6O2	86.09	-76.83	80.20	949.05	374.2	0.952	2216.7	877.26	4.75	570	1318.7
Acrylamide	C3H5NO	71.08	84.50	240.85	933.25	755.93	0.958	3081.5	800.28	3.13	570	1056.7
Butyl acrylate	C7H12O2	128.17	-64.60	147.85	894.09	292.3	0.933	2370.7	758.75	5.39	561	1163.5
Vinyl acetate	C4H6O2	86.09	-92.80	72.50	926.21	366.7	0.949	2200.2	864.79	4.79	548	1345.0
Ethyl acrylate	C5H8O2	100.12	-71.20	99.50	918.26	336.9	0.948	2093.8	828.74	5.02	541	1317.3
Acrylic Acid	C3H4O2	72.06	13.50	141.00	1045.51	590.03	0.957	2491.5	905.06	3.58	538	1287.1
Vinylidene chloride	C2H2Cl2	96.94	-122.50	31.56	1116.66	274.46	0.959	1159.9	1105.88	5.69	534	1866.6
Acrolein	C3H4O	56.06	-87.70	52.69	834.41	517.9	0.955	2233.6	803.61	4.09	530	1332.9
Trimethylchlorosilane	C3H9ClSi	108.64	-57.70	57.60	853.47	256.52	0.945	1804.3	807.90	5.95	529	1406.7
n-Butyl methacrylate	C8H14O2	142.20	-75.37	163.00	890.92	280.1	0.935	2207.6	756.36	5.44	524	1213.1
Methyl methacrylate	C5H8O2	100.17	-48.20	100.30	937.17	342.7	0.948	1992.9	847.61	4.94	524	1369.8
Acrylonitrile	C3H3N	53.06	-83.52	77.35	801.12	585.33	0.951	2166.7	738.69	3.85	499	1303.2
Propylene oxide	C3H6O	58.08	-111.93	33.90	823.27	477.52	0.955	2126.3	811.82	4.23	494	1426.6
Isoprene	C5H8	68.12	-145.88	34.06	675.94	376.14	0.949	2286.5	666.74	4.95	487	1277.9
Acetone cyanohydrin	C4H7NO	85.11	-20.00	170.85	926.39	589.0	0.953	3783.0	769.71	3.41	479	1114.0
Hydrogen cyanide	CHN	27.03	-13.32	25.70	679.56	995.1	0.959	2628.9	678.51	2.94	460	1290.2
Allyl Alcohol	C3H6O	58.08	-129.23	97.08	847.49	687.9	0.960	3134.4	772.54	3.24	443	1271.7

indicates PIH compound considered in AFFTAC case evaluation.   indicates ranking property group

A.4.0 SUMMARY OF FINDINGS

Within each response characteristic, the 40 compounds are always ranked in order of decreasing severity of the response property group. The significance for the most part is self evident. Once again, it must be emphasized that the tabulated data in Tables A-1 through A-6, do not represent actual implementation results, but only represent the relative order of implementation results obtained using consistent analysis parameters which would be determined by physical property data considerations only. In this project study the AFFTAC evaluation model was used for a specially selected group of compounds.

Table A.7 provides a summary of the three most severe compounds in each response category. Compounds entered in bold type in Table A.7 are compounds considered in an AFFTAC analysis. Table A-7 shows that AFFTAC analysis cases are well represented in each of the response categories. Furthermore, examination of Tables A-1 through A-6, clearly indicates that the AFFTAC case studies are representative of the property variations that exist in the full 40 compound data base.

Not all response characteristics are of equal relevance.

Table A-7. Summary of Compounds with Highest Values for Property Dependent Response Characteristics

Response Characteristic	Top Three Compounds	Parameter Value
Bulk heat-up Rate [°C/min] (Table A-1)	**Titanium Tetrachloride**	2.35
	Sodium	2.34
	Phosphorus Trichloride	2.25
Time to T_{sat} at 95 psia [min] (Table A-2)	Vinylidene Chloride	33
	Hydrogen Cyanide	35
	Dimethylchlorosilane	39
Liquid thermal expansion to T_{sat} at 95 psia [%] (Table A-3)	4-Vinyl Toluene	37
	Acrylamide	34
	Bromine	33
Relief vent capacity for all-vapor cenitng [cm^2/100 kw] (Table A-4)	**Hydrogen Fluoride**	7.8
	Titanium tetrachloride	7.0
	Methyl-trichlorosilane	7.0
Two-phase mass flux evaluated at normal boiling point, [kg/m2 sec] (Table A-5)	**Bromine**	2911
	Sulfur Chloride	2104
	Phosphorous trichloride	1955
Relief vent capacity for two-phase flashing liquid flow, [cm^2/100 kw] (Table A-6)	**Hydrogen Fluoride**	5834
	Hydrogen Peroxide	1247
	Sulfuric Acid	1036
Bold entries designate PIH compounds covered as an AFFTAC evaluation case study.		

Heat-Up Rate: Property variations give rise to only a factor of two variations in heat-up rate. External effects such as insulation and size of the fire have a much more significant effect.

Time to Relief Full Flow: This response characteristic is one of the most significant to be considered. The variation among the 40 compounds is approximately a factor of 10 and is principally determined by variations in vapor pressure-temperature relations. Over one half of the compounds would require over 100 minutes to full relief flow as determined by a conventional AAR heat input without insulation. Variations in insulation and relief set pressure will have a significant effect on actual case evaluations.

Volume Expansion: Excluding water, there is about a factor of three variation in liquid volume expansion (10 percent to 30 percent) prior to reaching full relief flow. For some compounds, the full magnitude of liquid volume expansion would be outside the 100-minute fire duration.

All-Vapor Vent Index: This parameter group is the most significant of the second set of response characteristics. Here it is shown that the AFFTAC case studies include those compounds requiring the largest relief flow capacities, as well as a well distributed representation of all other compounds.

Flashing Liquid Mass Flux: This ranking property group provides an indication of which compounds would have the largest rate of discharge in an overturned condition. Actual case studies provide guidance with respect to relief vent size, event duration and other considerations.

Flashing Liquid Vent Index: This index is included only for completeness. Flashing liquid flow considerations are unnecessary for upright tank cars subject to fire heat input.

In specific cases it would be impractical to size a relief device for two-phase relief flow with 10 percent overpressure limitations. Reference A.4 shows, however, that relief devices correctly sized for all-vapor flow can accommodate two-phase flashing flow discharge in overturned rail cars without failure, in most instances.

References

A1. T. E. Daubert, et.al., Editors, CTI 00-230, "Physical Property Data for Compounds Transported in American Rail Cars," Centaurus Technology, Inc., Report - Project Support Document, *Data Base*: Physical and Thermodynamic Properties of Pure Chemicals, *Design Institute for Physical Property Data, AIChE*, Taylor and Francis Publishers, 1999.

A2. API-RP-520, Sizing, Selection, and Installation of Pressure Relieving Devices in Refineries, Part 1-"Sizing and Selection," American Petroleum Institute.

A3. Association of American Railroads, *Manual of Standards and Recommended Practices, Section C-Part III Specifications for Tank Cars,* Specification M-1002, December 2000

A4. CTI00-247, "Two-Phase Relief Vent Flow and Self-Reactive Material Considerations in Rail Car Transportation," September 2000.

A5. Grolmes, M. A., "Some Useful Considerations in Pressure Relief Vent Sizing for Non-Reactive Systems Subject to Fire Exposure," Presentation DIERS User Group Meeting, Phoenix, Arizona, 1999.