U.S. Department
of Transportation

**Federal Railroad
Administration**

# RAILROAD TANK CAR RELIEF VALVE REQUIREMENTS FOR LIQUID PIH LADING

Office of Research and
Development
Washington, D.C. 20590

DOT/FRA/ORD-03/21

September 2003
Final Report

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Technical Information Service
Springfield, Virginia 22161

**1. Report No.**
DOT/FRA/ORD-03/21

**2. Government Accession No.**

**3. Recipient's Catalog No.**

**4. Title and Subtitle**
Railroad Tank Car Relief Valve Requirements for Liquid PIH Lading

**5. Report Date**
September 2003

**6. Performing Organization Code**

**7. Authors**
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**8. Performing Organization Report No.**

**9. Performing Organization Name and Address**
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P.O. Box 11130
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**10. Work Unit N o. (TRAIS)**

**11. Contract or Grant No.**
DTFR53-93-C-00001, Task Order No. 124

**12. Sponsoring Agency Name and Address**
U.S. Department of Transportation
Federal Railroad Administration
Office of Research and Development
1120 Vermont Avenue, NW MS-20
Washington, DC 20590

**13. Type of Report or Period Covered**

**14. Sponsoring Agency Code**
FRA

**15. Supplemental Notes**
,

**16. Abstract**
Analyses were performed for the Federal Railroad Administration (FRA) 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 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, surviving in 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.

**17. Key Words**
Tank Car, Hazardous Materials, Pressure Relief Valves, Poison Inhalation Hazard, PIH, Thermally Reactive Materials, Polymerizable Materials, Dangerous When Wet Materials

**18. Distribution Statement**
This document is available through National Technical Information Service Springfield, VA 22161

**19. Security Classification (of the report)**

**20. Security Classification (of this page)**

**21. No. of Pages**
50

**22. Price**

Form DOT F 1700.7 (8-72)

Metric Page Here

# EXECUTIVE SUMMARY

Analyses were performed for the Federal Railroad Administration (FRA) 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 jacketed 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 to exceed the flow rating pressure of the pressure relief 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 flows 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.

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# 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 initiated 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.
- Providing, 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 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 1966, pressure relief valve start-to-discharge (STD) requirements found in 49CFR 179.15, 179.100-1, and 179.200-1 were made much more general. The pressure relief valve (PRV) requirement that the STD pressure for tank cars be set at 75 percent of tank test pressure, were removed from §179.100-1 for each of the specific pressure car classes and from §179.200-1 for each of the non-pressure car classes. For example, a pressure car with a test pressure of 300 psi would have been equipped with a pressure relief valve having a 225 psi rating and STD pressure. Pressure relief valve requirements found in §179.15 were made much more general. This section now permits pressure relief valves with STD pressures as low as 75 psig for low vapor pressure products dependent on the tank lading pressure. Thus, it is possible that a PRV with lowered STD pressure may be used. This PRV, in turn, may be relieving pressure (by venting PIH lading) before the 100-minute guideline. While the AFFTAC fire analysis shows that a tank car would survive catastrophic failure when equipped with a higher STD pressure relief valve, no analysis has been done to indicate whether a tank will start venting at the lower pressure before the 100-minute period.

## 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 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.

The Analysis of Fire Effects on Tank Cars (AFFTAC) computer model was used to determine the behavior of tank cars loaded with these commodities when subjected to an external fire.[1] 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 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 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 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 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 | | 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. 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 | 2.1.1.1.1.1.2 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 |

## Table 3. Compounds Included in Physical Property Database

| Compound | Formula | Molecular Weight | Melting Temperature °F (°C) | Normal Boiling Temperature °F (°C) | Liquid Density at 77°F (25°C) | Type | Index No. |
|---|---|---|---|---|---|---|---|
| Bromine | Br2 | 159.808 | 18.95 (-7.25) | 137.75 (58.75) | 3104.33 | PIH | 1 |
| Vinylidene Chloride | C2H2C12 | 96.943 | -188.50 (-122.50) | 88.81 (31.56) | 1116.66 | TR | 2 |
| Acetaldehyde | C2H4O | 44.053 | -189.40 (-123.00) | 69.53 (20.85) | 779.91 | TR | 3 |
| Dimethyldichlorosilane | C2H6C12Si | 129.061 | -104.98 (-76.10) | 158.36 (70.20) | 1064.81 | W | 4 |
| Dimethylchlorosilane | C2H7C1Si | 94.616 | -167.80 (-111.00) | 95.90 (35.50) | 860.80 | W | 5 |
| Acrylonitrile | C3H3N | 53.064 | -118.34 (-83.52) | 171.23 (77.35) | 801.12 | P, TR | 6 |
| Acrolein | C3H4O | 56.064 | -125.86 (-87.70) | 126.84 (52.69) | 834.41 | PIH | 7 |
| Acrylic Acid | C3H4O2 | 72.064 | 56.30 (13.50) | 285.80 (141.00) | 1045.51 | P, TR | 8 |
| Epichlorohydrin | C3H5C1O | 92.525 | -70.96 (-57.20) | 245.30 (118.50) | 1173.89 | PIH | 9 |
| Acrylamide | C3H5NO | 71.079 | 184.1 (84.50) | 465.53 (240.85) | 933.25 | PIH | 10 |
| Propylene Oxide | C3H6O | 56.080 | -169.47 (-111.93) | 93.02(33.90) | 823.27 | P, TR | 11 |
| Allyl Alcohol | C3H6O | 58.080 | -200.61 (-129.23) | 206.74 (97.08) | 847.49 | PIH | 12 |
| Trimethylchlorosilane | C2H9C1Si | 108.643 | -71.86 (-57.70) | 135.68 (57.60) | 853.47 | W | 13 |
| Chloroprene | C4H5C1 | 88.536 | -202.00 (-130.00) | 138.92 (59.40) | 950.97 | P, TR | 14 |
| Vinyl Acetate | C4H6O2 | 86.090 | -135.04 (-92.80) | 162.50 (72.50) | 926.21 | TR | 15 |
| Methyl Acrylate | C4H6O2 | 86.090 | -106.29 (-76.83) | 176.36 (80.20) | 949.05 | TR | 16 |
| Methacrylic Acid | C4H6O2 | 86.090 | 59.00 (15.00) | 321.80 (161.00) | 1009.45 | P, TR | 17 |
| Acetone Cyanohydrin | C4H7NO | 85.106 | -4.00 (-20.00) | 339.53 (170.85) | 926.39 | PIH | 18 |
| Furfural | C5H4O2 | 96.086 | -33.70 (-36.50) | 323.06 (161.70) | 1154.53 | W | 19 |
| Isoprene | C5H8 | 68.118 | -230.58 (-145.88) | 93.31 (34.06) | 675.94 | P, TR | 20 |
| Ethyl Acrylate | C5H8O2 | 100.117 | -96.16 (-71.20) | 211.10 (99.50) | 918.26 | P, TR | 21 |
| Methyl Methacrylate | C5H8O2 | 100.170 | -54.76 (-48.20) | 212.54 (100.30) | 937.17 | P, TR | 22 |
| Butyl Acrylate | C7H12O2 | 128.171 | -84.28 (-64.60) | 298.13 (147.85) | 894.09 | P, TR | 23 |
| n-Butyl Methacrylate | C8H14O2 | 142.198 | -103.66 (-75.37) | 325.40 (163.00) | 890.92 | PIH | 24 |
| Styrene Monomer | C8H8 | 104.152 | -23.09 (-30.61) | 293.29 (145.16) | 900.08 | P, TR | 25 |
| 2-Vinyl Toluene | C9H10 | 118.178 | -91.43 (-68.57) | 337.66 (169.81) | 907.69 | P, TR | 26 |
| 3-Vinyl Toluene | C9H10 | 118.178 | -123.41 (-86.34) | 340.88 (171.60) | 907.57 | P, TR | 27 |
| 4-Vinyl Toluene | C9H10 | 118.178 | -29.43 (-34.13) | 343.00 (172.78) | 915.63 | P, TR | 28 |
| Methyl-trichlorosilane | CH3C13Si | 149.478 | 149.72 (65.40) | 151.52 (66.40) | 1266.30 | PIH | 29 |
| Hydrogen Cyanide | CHN | 27.026 | 8.02 (-13.32) | 78.26 (25.70) | 679.56 | PIH | 30 |
| Sulfur Chloride | C12S | 102.970 | -187.60 (-122.00) | 139.28 (59.60) | 1611.36 | PIH | 31 |
| Titanium Tetrachloride | C14Ti | 189.691 | -11.38 (-24.10) | 276.53 (135.85) | 1714.03 | PIH | 32 |
| Chlorosulfonic Acid | C1HO3S | 116.525 | -112.00 (-80.00) | 308.93 (153.85) | 1740.71 | PIH | 33 |
| Hydrogen Fluoride | FH | 20.006 | -118.05 (-83.36) | 67.14 (19.52) | 955.17 | PIH | 34 |
| Water | H2O | 18.000 | 32.00 (0.00) | 212.00 (100.00) | 1000.00 | Nr | 35 |
| Hydrogen Peroxide | H2O2 | 34.015 | 31.93 (-0.04) | 302.36 (150.20) | 1442.72 | TR | 36 |
| Sulfuric Acid (fuming) | H2SO4 | 98.079 | 50.56 (10.31) | 526.64 (274.80) | 1832.90 | PIH | 37 |
| Sodium | Na | 22.990 | 208.09 (97.83) | 1621.13 (882.85) | 921.78 | W | 38 |
| Sulfur Trioxide | O3S | 80.064 | 62.24 (16.80) | 112.55 (44.75) | 1897.48 | PIH | 39 |
| Phosphorus Trichloride | PC13 | 137.330 | -133.60 (-92.00) | 170.00 (76.10) | 1566.18 | PIH | 40 |

## 3.0 ANALYSES OF TANK CARS CONTAINING PIH PRODUCTS

Tank cars containing the 11 PIH materials listed in Table 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:

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

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. 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 4 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 4. 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 present regulations 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. For tank cars in PIH service, use of low start-to-discharge PRV should be investigated further as to whether venting could really occur. Should the regulations be revised to continue permitting the use of PRV with lower set pressure and lower start-to-discharge pressure. (Note to reader: AFFTAC analysis showed that tank cars containing the following ladings vent off some lading to maintain burst integrity of the tank car: acrolein, hydrogen cyanide, hydrogen fluoride, phosphorus trichloride, sulfur chloride/sulfur dichloride, and titanium tetrachloride.)

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 jacketed 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 5 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 5. 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.<br>Ovr. | 150<br>150 | 1,000<br>1,000 | 1.000<br>1.000 |
| Allyl Alcohol | 22,000 | Upr.<br>Ovr. | 225<br>225 | 1,000<br>1,000 | 1.000<br>1.000 |
| Acrolein | 20,000 | Upr.<br>Ovr. | 150<br>150 | 1,000<br>1,000 | .977<br>.968 |
| Bromine | 4,000 | Upr.<br>Ovr. | 225<br>225 | 3,000<br>7,000 | .846<br>.523 |
| Chlorosulfonic Acid | 12,000 | Upr.<br>Ovr. | 225<br>225 | 1,000<br>1,000 | 1.000<br>1.000 |
| Hydrogen Cyanide | 20,000 | Upr.<br>Ovr. | 225<br>225 | 1,000<br>1,000 | .902<br>.899 |
| Hydrogen Fluoride, Anhydrous | 20,000 | Upr.<br>Ovr. | 225<br>225 | 1,000<br>1,000 | .962<br>.961 |
| Phosphorus Trichloride | 12,000 | Upr.<br>Ovr. | 225<br>225 | 1,000<br>1,000 | .948<br>.943 |
| Sulfur Dichloride | 12,000 | Upr.<br>Ovr. | 225<br>225 | 1,000<br>1,000 | .953<br>.945 |
| Sulfur Trioxide | 11,000 | Upr.<br>Ovr. | 225<br>225 | 1,000<br>1,000 | 1.000<br>1.000 |
| Sulfuric Acid, fuming, 30 percent $SO_3$ | 12,000 | Upr.<br>Ovr. | 225<br>225 | 1,000<br>1,000 | 1.000<br>1.000 |
| Titanium Tetrachloride | 12,000 | Upr.<br>Ovr. | 225<br>225 | 1,000<br>1,000 | .970<br>.965 |

*** of initial filled fraction**

## 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 105J, 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 105J300W 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. The remaining fraction at 100 minutes was still 0.9255 for the upright car and overturned cars.

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. The remaining fraction at 100 minutes was still 0.8984 for the upright car and 0.8902 for the overturned car.

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 105J, 112J, 114J, or 120S cars with a test pressure of 300 psi or greater to be used.

A Class 105J300W 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. The remaining fraction at 100 minutes was still 0.9232 for the upright and overturned cars.

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 |

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, 96.3 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 105J300W or 105J500W 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 105J500W 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 105J, 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 105J300W 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. The remaining fraction at 100 minutes was still 0.9230 for the upright and overturned cars.

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 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 0.8954. The remaining fraction at 100 minutes was 0.8076 for the upright car and 0.0850 for the overturned car.

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 105J300W 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. The remaining fraction at 100 minutes was 0.8538 for the upright car and 0.8529 for the overturned car.

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 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 105J, 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 105J300W 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. The remaining fraction at 100 minutes was 0.8734 for the upright car and 0.8688 for the overturned car.

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 105J300W 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. The remaining fraction at 100 minutes was 0.8795 for the upright car and 0.8722 for the overturned car.

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 105J, 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 105J300W 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. The remaining fraction at 100 minutes was still 0.8945 for the upright and overturned cars.

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 105J, 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 105J300W 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. The remaining fraction at 100 minutes was still 0.9221 for the upright car and overturned cars.

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 | 75.7 | 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 105J, 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 105J300W 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. The remaining fraction at 100 minutes was 0.8992 for the upright car and 0.8946 for the overturned car

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.

Consideration 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 129°F.[7] The regulations do not specify the stabilization time at 129°F. However, most raw material suppliers and shippers inhibit products to a level that generally provides between 20 days and 60 days stability at 129°F. 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 50°F 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 37°F/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 °F/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 129°F. 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 212-230°F. 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 55°F, 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 129°F. 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 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.

## 6.3 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 thermally reactive (TR) materials will survive in a fire?

Current practice is to equip all tank cars in hazardous materials service with a pressure relief system, or combination pressure relief valve/thermal protection system, to ensure that a tank will survive engulfment in a fire for at least 100 minutes either through controlled release of vaporized lading through the PRV or by thermal insulation protection. This 100-minute interval was developed based on estimates of how much time it would require for emergency response authorities to respond to an incident/accident and prevent a catastrophic failure of a tank car containing flammable gas.

The hazards of a PIH release are considerably different in nature from a flammable gas release. Because of PIH's have differing physical and toxicological characteristics, the minimum interval may differ for the various materials. Venting PIH lading (to relieve pressure and maintain tank car integrity) should be avoided because of the toxicological effects of the released lading.) 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.

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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 Bulk Heat-Up Rate

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

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

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 [$J/m^3K$]

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:

Δρ 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/m$^3$] | Heat Capacity at 30°C [J/kg-°K] | Density × Heat Capacity at 30°C [J/m$^3$-°K] | Saturation Temperature at 97.5 psia [°C ] | Liquid Density at 97.5 psia sat. [kg/m$^3$] | Heat Capacity at 97.5 psia sat. [J/kg-°K] | Density x Heat Capacity at 97.5 psia sat. [J/m$^3$-°K] | Average of Density x Heat Capacity [J/m$^3$-°K] | $(T_{sat\ at\ 97.5} - 30)$ x $(Rho\ x\ C)_{avg}$ [J/m$^3$-°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 |

(black) indicates PIH compound considered in AFFTAC case evaluation.

(grey) 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 × 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 |

(black) indicates PIH compound considered in AFFTAC case evaluation.

(grey) 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 [$kg/m^3$] | Heat Capacity at 30 °C [J/kg-°K] | Density x Heat Capacity at 30°C [$J/m^3$-°K] | Saturation Temperature at 97.5 psia [ °C ] | Liquid Density at 97.5 psia sat. [$kg/m^3$] | Heat Capacity at 97.5 psia sat. [J/kg-°K] | Density x Heat Capacity at 97.5 psia sat. [$J/m^3$-°K] | Average of Density x Heat Capacity [$J/m^3$-°K] | (T sat at 97.5 - 30) x (Rho x C)$_{avg}$ [$J/m^3$-°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 | C2H6Cl2 Si | 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

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

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 $N/m^2$]
$\lambda$ = 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 illustrating 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.

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

where:

$VI_{2\phi}$ = property grouping vent index for flashing liquid flow [$cm^2$/100 kw]

$\rho_l$ = 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 Comparison of Property Effects on Vent Flow Response

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] 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.

**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/m$^3$] | All-Vapor Vent Index [cm$^2$/100 kw] | Flashing Liquid Vent Index [cm$^2$/100 kw] | 2-Phase Mass Flux at $T_{nbt}$ [kg/m$^2$-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 | C2H6Cl2 Si | 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 |

[black box] indicates PIH compound considered in AFFTAC case evaluation.

[grey box] 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 / m$^3$ ] | 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/m$^3$] | All-Vapor Vent Index [cm$^2$/100 kw] | Flashing Liquid Vent Index [cm$^2$/100 kw] | 2-Phase Mass Flux at $T_{nbt}$ [kg/m$^2$-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/m$^3$] | 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/m$^3$] | All-Vapor Vent Index [cm$^2$/100 kw] | Flashing Liquid Vent Index [cm$^2$/100 kw] | 2-Phase Mass Flux at Tnbp [kg/m$^2$-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 |

(black box) 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 venting [$cm^2$/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, Washington, D.C., 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.