

Tank Car Vent and Burn Process Study: Phase I

Office of Research and Development Washington, DC 20590

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# **Executive Summary**

Federal Railroad Administration (FRA) tasked Transportation Technology Center, Inc. (TTCI) to develop a process to safely determine when and how to employ the vent and burn emergency product removal technique in railroad tank car accidents. Vent and burn is an effective process used by emergency response personnel when dealing with serious railroad emergencies where the uncontrolled release of large amounts of hazardous materials when tank failure is imminent. This process uses two separately controlled explosive charges to cut holes in a damaged tank car to relieve internal vapor pressure and evacuate product for destruction through controlled burning. One charge is placed at the highest point on the tank over the product vapor space. This charge is designed to safely relieve internal vapor pressure. A second charge is placed at or near the lowest point of the tank to allow product to drain into a prepared containment pit where it can be disposed of through controlled burning. TTCI, a subsidiary of the Association of American Railroads (AAR), conducted this study as part of the FRA's Hazmat Transportation Safety Research and Development (R&D) Strategic Plan.

The objective of the study was to develop a checklist of items to be considered and a process map to be used as tools to aid emergency response personnel in the decision making process and help guide them through the procedure. A project advisory committee of recognized industry experts was formed to facilitate the study. TTCI reviewed and critiqued past incidents to benchmark procedures and identify process improvement opportunities. Researchers conducted computer modeling of explosive charge parameters to determine effectiveness and identify areas of concern.

The research team created a checklist of items to be considered and a process map using the information provided by the study. These are intended as tools to aid emergency response personnel in determining whether the vent and burn option is applicable and to help guide them safely through the process once the decision to use the technique has been made.

The study concludes the following:

- Vent and burn is a viable option for hazardous materials incident mitigation but only in certain instances after carefully considering all relevant information.
- A standardized post-incident reporting procedure that includes a post mortem analysis of the tank shell response to the explosive charge, as well as other pertinent details, is needed.
- A properly designed and applied charge is capable of effectively penetrating the tank shell, as well as any jacket and thermal protection/insulation present. This may eliminate the need to remove the jacket and thermal protection/insulation and can reduce the technician's time-on-target.
- Single-point venting is not a viable vent and burn option.
- Two-point venting is most effective when the proper delay between charge detonations is used.

The study makes the following recommendations:

- Additional experienced incident commanders should review the checklist of items to be considered as provided in the study.
- Validation testing to verify model results and accuracy should be performed.

- A portable electronic database containing the itemized checklist, tank car material specifications, UMLER information, and commodity characteristics should be developed in a format compatible with responders' personal digital assistants (PDAs) and laptop computers.
- A standardized, comprehensive post-incident analysis and reporting procedure should be developed and adopted.

# 1.0 Introduction

FRA tasked TTCI to develop a process to safely determine when and how to employ the vent and burn emergency product removal technique in railroad tank car accidents. Vent and burn is a method of last resort used in certain circumstances when the uncontrolled release of large amounts of hazardous materials due to tank failure is imminent. This process uses two separately controlled explosive charges to cut holes in a damaged tank car in order to relieve internal vapor pressure and evacuate product for destruction through controlled burning. TTCI, a subsidiary of AAR, conducted this study under Contract Number DTFR53-93-C-00001, Task Order No. 135, Phase I Tank Car Vent and Burn Process Study, as part of the FRA's Hazmat Transportation Safety R&D Strategic Plan.

Recommendations from this study are intended to supplement existing practices and provide additional guidelines to assist emergency response personnel in the decisionmaking process when considering the vent and burn option. These recommendations are meant as a guide only. Sound judgment on the part of the person(s) in charge is still required. The procedures are intended to supplement the incident commander's (or other personnel in charge) decisionmaking process and attempt to consider a wide range of known variables. However, individual incidents may present special, unforeseen circumstances that may not be included on the itemized checklist, and these must be carefully considered when choosing an appropriate course of action. Therefore, every incident must be evaluated independently. The research team took the following steps to develop these recommendations:

- A project advisory committee was formed to help guide the project and review results.
- Past experiences with vent and burn incidents were reviewed and evaluated.
- A process map was developed to guide emergency response personnel through the vent and burn procedure.
- Hazardous materials that are commonly transported in tank cars were evaluated and classified for applicability to the vent and burn process.
- Tank car types and construction were evaluated and classified for applicability to the vent and burn process.
- Mathematical modeling was used to evaluate type and configuration of explosive charges.
- Residual product disposition concerns were considered.
- A checklist of items to be considered was developed to determine if and when the vent and burn process is a viable option.

#### 1.1 Background

Derailments or similar accidents involving railroad tank cars containing hazardous materials often present unique challenges to emergency response personnel. Because normal recovery options are sometimes limited due to fire, severity of tank damage, or possible hidden damage, more extreme measures must sometimes be considered. One such option is the vent and burn technique.

As mentioned, the vent and burn procedure involves the use of two separate explosive charges to cut holes in the tank car. One charge is placed at the highest point on the tank, over the product vapor space. This charge is designed to safely relieve internal vapor pressure. A second charge

is placed at or near the lowest point of the tank to allow product to drain into a prepared containment pit where it can be disposed of through controlled burning. However, due to the inherent hazards associated with high-pressure vessels, hazardous commodities, and the use of explosive devices, many factors must be carefully considered before selecting this as a method of mitigation.

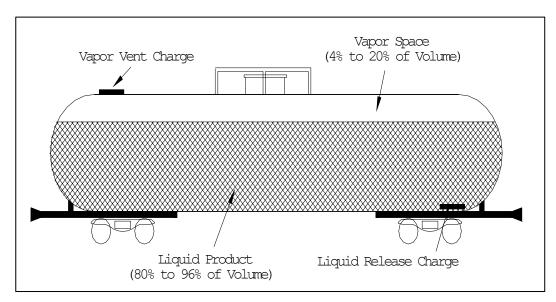


Figure 1. Schematic of Tank Car Displaying Vapor and Liquid Spaces

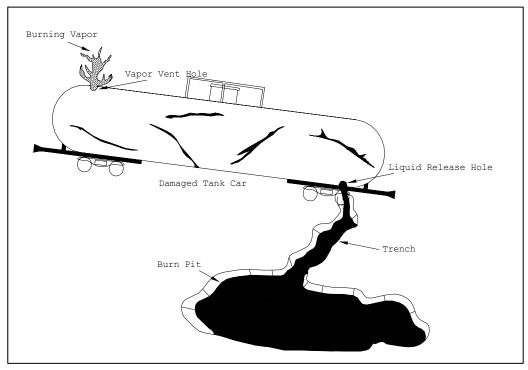


Figure 2. Application of Vent and Burn Procedure

# 2.0 Objective

The objective of this project was to develop a checklist of items to be considered when choosing the vent and burn option, as well as a process map to help obtain a predictable outcome and minimize the chances of unexpected and/or undesirable consequences when using this method. These tools are intended for use by emergency response personnel to determine if and when the vent and burn option should be used and to guide them through the procedure. The project also calls for recommendations on validating charge parameters and methodologies, as well as identifying product disposition concerns.

# 3.0 Scope

This project looked at past and present North American industry standards and practices as they apply to the vent and burn process. This study made recommendations relevant to that specific market. It did not consider or evaluate international practices. In addition, this study considered the vent and burn option only and did not address nor does it discuss other emergency mitigation options (i.e., vent and drain for noncombustible and/or cryogenic materials).

# 4.0 Approach

The approach taken in this study followed the course of action outlined in a proposal that TTCI presented to FRA and is summarized below.

# 4.1 **Project Advisory Committee**

TTCI formed a project advisory committee to receive input from recognized subject matter experts available throughout the industry. This committee guided the project, reviewed work products, provided input for modeling parameters, made necessary recommendations, and offered invaluable insight to TTCI.

#### 4.2 Review of Case Studies

Where available, the project advisory committee reviewed records of past vent and burn incidents. The committee also reviewed existing documentation on methods and recommendations. This information was used to bench mark current state-of-practice methodology and compare with past recommendations to determine where process improvements are needed.

# 4.3 Mapping Existing Vent and Burn Processes

The committee used information provided under Task 4.2 to evaluate past responses and develop a process map to guide responders through each step of the vent and burn process. The team also used this information to choose modeling parameters for Task 4.6.

#### 4.4 Classification of Hazardous Materials

The project advisory committee evaluated the hazardous materials listed in the Code of Federal Regulations under 49 CFR 172.101 for applicability to the vent and burn process and then classified them accordingly. The team focused on flammability, volatility, and environmental implications of disposal.

# 4.5 Classification of Tank Car Characteristics

The team also evaluated tank car construction for applicability to vent and burn and then classified accordingly. Because it is critical in the decision process to know construction parameters of each tank car involved in the incident, metal type and thickness were important considerations, as well as jacketing, thermal protection, and insulation.

# 4.6 Evaluation of Explosive Charge Parameters

Lawrence Livermore National Laboratories (LLNL), Livermore, CA evaluated various explosive charge parameters using computer modeling. Simulations of several combined variables, such as shaped charge diameter, charge cone angle, insulation/thermal protection thickness, and type of explosive, helped to determine effectiveness. In addition, Dr. Milton R. Johnson studied the effectiveness of single-point vent and burn, as compared to the conventional two-point method. His study also looked at expected vent times for a variety of hole diameters.

#### 4.7 Identification of Product Disposition Options

One intent of vent and burn is to dispose of the product during the burn phase of the process. However, complete product disposal is unlikely because of factors such as seepage and incomplete combustion. In addition, products of combustion may remain. Product disposal options will vary with each incident, and sound judgment of the response team is critical. The committee identified and evaluated product concerns to assist responders in choosing an appropriate cleanup method.

#### 4.8 Development of an Itemized Checklist

The team used information gathered in Tasks 4.2 through 4.7, as well as input from the project advisory committee, to develop a checklist of items to be considered pertinent to the vent and burn process. This is intended as a tool to aid emergency response personnel in safely determining the suitability of vent and burn to specific situations.

# 5.0 Results

#### 5.1 **Project Advisory Committee**

The following individuals were a part of the project advisory committee, formed of recognized subject matter experts from North American railroads, response contractors, academia, and Federal agencies:

- Mr. Mark Stehly, Assistant Vice President, Environmental and HAZMAT, Burlington Northern Santa Fe Corporation
- Mr. Jose Pena, Mechanical Engineer, FRA
- Mr. Billy Poe, President, Explosive Services International, LTD.
- Dr. David Aldist, Professional Engineer, Ph.D., LLNL
- Dr. Milt Johnson, Consultant
- Mr. Patrick Student, Director, Hazardous Materials, Union Pacific Corporation
- Mr. Skip Elliot, Assistant General Manager, Hazardous Materials Systems, CSX Transportation
- Mr. Hank Cox, Manager, Field Services, Hazardous Materials Systems, CSX Transportation
- Mr. Chet Culley, General Director, Environmental and Hazmat, Kansas City Southern Railway Company
- Mr. Patrick Brady, Assistant Director, Environmental and HAZMAT, Burlington Northern Santa Fe Corporation
- Mr. Dan Healy, Senior Inspector, Bureau of Explosives, AAR
- Mr. Doug Dibble, Transport Canada

# 5.2 Case Study Review

Review of actual incidents where the vent and burn process was used helped to determine the effectiveness of past practices. The research team reviewed and evaluated documentation of incidents that occurred from September 1982 through May 2000.

Although the number of documented incidents was not sufficient to provide statistically significant conclusions, some examples of the vent and burn process resulting in unexpected outcomes occurred. In one instance involving ambient temperatures well below freezing, the charge induced a fracture in 90 percent of the tank shell diameter. Therefore, the effects of cold temperatures (less than  $-20^{\circ}$ F) on the brittle fracture properties of the metal should be a consideration. This and other case studies reaffirm that, along with commodity and tank construction, weather conditions, such as wind speed and direction and ambient temperature, should also be considered when using vent and burn. A second unexpected outcome that occurred in a separate incident was the failure of a vent charge to penetrate the tank shell. The subsequent success of the drain charge in penetrating the shell created a pressurized release of product resulting in a blowtorch effect. The vent charge failure was attributed to the charge being placed too close to the end of the tank shell and the tank head deflecting the explosive shot. Credit must be given to Mr. William Poe for his candid assessment and self-evaluation in the post-incident review. Even with these unexpected outcomes, the response teams mitigated the effects through careful pre-planning and preparation.

Current recommendations call for a time delay between detonation of the vent charge and drain charge so that internal pressure is sufficiently reduced before draining the product. However, this guideline was not followed in the case studies reviewed.

No standardized reporting process was used, and many reports lacked satisfactory detail. Most reports included detailed information on the number and types of cars involved, the commodities contained, and the ambient temperatures. The documentation, however, did not include technician comments, including descriptions of charge configuration and placement, environmental surroundings, and resulting tank shell damage.

Because of this lack of detail in the documentation, the study highlighted the need for a standardized reporting procedure that includes detailed information about charge parameters, vent times, resulting shell failures, resulting hole sizes, and other pertinent facts. A prescribed post mortem analysis of the tank shell's response to the explosive charge is also necessary for assessing vent and burn methods in future instances.

The following lists the case studies that were reviewed:

- September 28, 1982: Illinois Central Railroad, Livingston, LA
- June 1, 1985: ICG Railroad, Aberdeen, MS
- January 31, 1987: Southern Railway, Corinth, MS
- May 24, 1990: Illinois Central Railroad, Covington, TN
- February 1996: Burlington Northern Santa Fe Railroad, Cajon Pass, CA
- March 4, 1996: Wisconsin Central Railroad, Weyauwega, WI
- July 18, 1997: Illinois Central Railroad, Flora, MS
- May 1999: CSX Railroad, Argyle, FL
- January 2000: CSX Railroad, Flint, MI
- May 2000: Union Pacific Railroad, Eunice, LA

#### 5.3 Process Map

The team used the information provided by the case studies and the project advisory committee to develop the following vent and burn process map. This process should be followed only after careful consideration has led the incident commander or other authority in charge to use the vent and burn option. Much of the information needed to follow the process will be generated when using the itemized checklist presented in Section 5.8.

#### VENT AND BURN PROCESS MAP

• Carefully consider all other options.

Use the Vent and Burn Itemized Checklist to help determine the applicability of this method. If vent and burn is the best option, proceed. Vent and burn is generally used only when a total uncontrolled release of hazardous materials because of tank car failure is imminent.

• Determine product suitability for vent and burn. Ensure that the material is flammable or combustible, and consider that the products of combustion of the material may be toxic and/or corrosive before selecting the vent and burn option. Keep in mind, however, the consequences of an uncontrolled total release of product in the event of catastrophic tank shell failure if the vent and burn option is not employed.

• Prepare site safety plan.

A site safety plan should be prepared to ensure that all eventualities are considered, and that resources are on hand to deal with them.

• Determine tank car specification.

Tank car material and construction (e.g., is the tank shell steel or aluminum; tankwithin-a-tank; what is the shell thickness; is car equipped with a jacket?) must be considered.

(Modeling indicates most insulation types do not affect charge sizing. However, some concern exists with cork insulation, but the number of cars equipped with this is small.)

- Obtain the necessary environmental permits. Virtually any jurisdiction will require burn permits or other such environmental permits before it will approve a vent and burn operation.
- Ensure that an experienced explosives expert is available.

Vent and burn is a highly specialized operation and should not be undertaken by inexperienced individuals. A sufficiently powerful, but no more powerful than necessary, explosive charge should be used to ensure that the desired hole size results and that the tank material (including jacket, if applicable) is completely cut through. Only a qualified explosives expert should determine the explosive charge size after carefully considering the pertinent circumstances related to the incident.

- *Procure the necessary explosives.* Many restrictions apply to the purchase and transportation of explosives.
- Clear the area of personnel.

Vent and burn is an inherently dangerous operation. All unnecessary personnel should be evacuated from the immediate area during implementation. Evacuation distance should be based on the worst-case scenario and the material involved (e.g., propane car explodes).

- *Clear the area of flammable materials.* At a minimum, the area around the channel and the pit should be cleared of trees, weeds, and other flammable materials to prevent an uncontrolled fire in the area.
- *Excavate a pit sufficiently large enough to contain entire contents of car.* Water capacity in gallons is stenciled on each tank car below the protective housing and on each end of the car. In the event that none of these stencils are legible, the water capacity in gallons can be obtained from the Railway Equipment Register or AAR's UMLER files. Once capacity has been determined, the following formula can be used to calculate the dimensions of the pit required to safely contain the material.

 $T_c/7.5 = Pit volume in Cu. Ft. = Pit_L x Pit_W x Pit_D$ 

Where  $T_c =$  the water capacity of the tank car in gallons

For example, the water capacity of a tank car loaded with propane is 30,000 gallons, where 30,000 gallons divided by 7.5 equals 4,000 cubic feet of earth. If a rectangular pit  $100' \times 40' \times 1'$  deep is excavated, 4,000 cubic feet of earth will be removed. The larger the surface area of the pit, the more rapidly the material will be burned. The pit should be sufficiently located so that the fire and radiant heat from the burning material in the pit will not pose a danger to personnel, property, or other railcars.

(Just before detonating charges, place an ignition source in the pit to ensure the product is ignited.)

- *Excavate a channel from the planned liquid exit hole to the pit.* The channel should be of sufficient length so that the fire and radiant heat from the burning material in the pit will not pose an inappropriate or unnecessary danger to personnel, property, or other railcars. Effort must be taken to ensure that the product does not pool under the car.
- *Have fire suppression personnel on site.* An adequate number of firefighters equipped with the appropriate apparatus and equipment should be on standby at the site before commencement of the operation in the event of an accident or uncontrolled fire.
- Ensure that wind direction and speeds are favorable for the operation. Given the large volume of material to be burned, consideration must be given to where the wind will carry the smoke and other products of combustion.
- *Place one explosive charge at the highest point of the tank over the vapor space.* Avoid head shield and other reinforcements, and ensure that the charge vertical axis is perpendicular to the tank surface.

(The technician should determine if deformation of the jacket precludes proper placement of the charge and decide if the jacket material must be removed in the area of the charge.)

The charge must be sufficient to penetrate the tank shell, as well as the jacket and the thermal protection/insulation, if applicable.

• Place a second explosive charge at the lowest point under the liquid space as near to the end of the car as possible.

Avoid head shield and other reinforcements, and ensure that the charge vertical axis is perpendicular to the tank surface.

(The technician should determine if deformation of the jacket precludes proper placement of the charge and decide if the jacket material must be removed in the area of the charge.)

The charge must be sufficient to penetrate the tank shell, as well as the jacket and the thermal protection/insulation, if applicable.

• Detonate the explosive charge over vent hole first.

The vent hole charge should be cut first, and internal pressure should be reduced to an acceptable level before cutting the liquid hole. Otherwise, the liquid flow rate will be undesirably high and may not be contained in the channel.

- Detonate the explosive charge under liquid space after pressure has been relieved. The time between the first and second detonations will vary depending on the vapor pressure in the car and the volume of the tank. It is not necessary to vent to atmospheric pressure; however, the liquid flow will be more manageable if the majority of the pressure has been relieved.
- *Monitor products of combustion downwind.* Monitoring of the products of combustion will help ensure that emergency personnel, as well as the general public, will not be exposed to any hazards. It will also serve to document, for liability purposes, that no hazardous products of combustion were spread as a result of the operation.

#### 5.4 Hazardous Material Classification

As a part of the vent and burn process, it is important to understand and consider the toxicity of the material in the tank car and toxicity of the material's products of combustion. Every product, material, or chemical is toxic; it is the dose of the material that determines if it is poisonous. Dose is considered the concentration of the exposure over a given period of time. Four primary routes of exposure exist, including inhalation, absorption, ingestion, and injection. Each chemical has its primary routes of exposure, and inhalation is the most common. Many chemicals have established safe exposure thresholds, which quantify a dose that is considered safe. Before using vent and burn, the incident command team should review the toxicity of the material and its products of combustion, the safe exposure thresholds, and the predicted plume dispersion. The incident command team should ensure that at-risk individuals are protected through evacuation and/or shelter in place. In addition to the hazards mentioned above, special consideration must be given to the safety of technicians when dealing with materials subject to polymerization.

TTCI contracted with Centaurus Technology, Inc. to analyze the applicability of hazardous materials to the vent and burn process. The following text is excerpted from their report:

Materials chemically suitable for vent and burn action generally reside in the hazards materials categories Class 2.1, (flammable gasses), and Class 3, (flammable and combustible liquids).

Among those materials falling within the above categories which should be excluded are:

(a) low molecular weight flammable gasses which have positive heats of formation, (b) flammable and combustible liquids which are monomers – which have been exposed to an incident fire of reasonably long duration, and (c) flammable gasses, liquids and/or combustible liquids which on burning would yield hazardous sulfur, chlorine, fluorine products.

Materials in hazard Classes 2.2, 2.3, 4, 5.1, 6.1, 8 and 9 should not be considered for vent and burn action for a variety of reasons related to their toxic, corrosive, or environmentally harmful characteristics.

Appendix A lists chemicals that may be considered as potential candidates for the vent and burn method. Inclusion in this list is not an endorsement of the vent and burn method as a means of mitigation. The list is intended only as a tool to be used with the sound judgment of experienced emergency response personnel when choosing the best option.

Appendix B of this report includes the entire Centaurus Technology, Inc. report.

#### 5.5 Tank Car Characteristic Classification

When choosing an explosive charge to vent a tank car, the material used in the tank car construction, as well as the construction configuration itself, must be considered. All of the materials listed as suitable for tank car construction by the Code of Federal Regulations under 49 CFR 172.101 are candidates for the vent and burn process. Construction material must be confirmed (i.e., aluminum or steel) to determine proper charge size.

Tank cars are generally constructed with a uniform circular cross section. However, some dual diameter tanks with a transition section from larger to smaller diameter exist. This transition area should be avoided when placing charges. Cars constructed as a tank within a tank where the inner tank is made of stainless steel also exist. This type of construction will require additional consideration when preparing the explosive charge.

In addition to tank configuration, insulation and thermal protection should be taken into consideration. Generally, three types are used: jacketed, low-density insulation (e.g., fiberglass); a sprayed-on coating of high-density insulation material (may or may not be jacketed); or a combination of both. Simulations suggest that, when properly applied, a single charge is capable of penetrating the thermal protection and/or insulation of any of the three types, including jacket, as well as the tank shell.

#### 5.6 Evaluation of Explosive Charges

#### 5.6.1 Modeling Parameters

TTCI used information provided by case studies and input from the project advisory committee to develop the following parameters used for modeling scenarios.

#### **Modeling Parameters**

#### Tank Material Type

- American Society for Testing and Standards (ASTM) A 516-70a, Grade 70
- Strength: 70 ksi

The material chosen is the type of steel currently used in the most common tank car types. Because of the high temperature of the cutting charge, it is assumed that the type and strength of steel used in tank car shell construction will have only a minor effect on how the charge cuts through tank shell.

#### Tank Shell Thickness

• Steel: 1 inch

Although material thickness varies among tank car types, it is assumed that, if a charge is strong enough to cut through a 1-inch thick shell, it will also be able to cut through anything that is less than 1-inch thick.

#### Insulation/Thermal Protection

- 6 inches of urethane foam
- 4 inches of glass wool compressed to 3.5 inches plus 0.65 inch of ceramic fiber

The two types of insulation that were chosen represent two differing problems for charge selection. The 6 inches of urethane foam will increase the standoff distance by 6 inches, and this effect must be better understood. The 4 inches of glass wool compressed to 3.5 inches plus 0.65 inch of ceramic fiber also increases the standoff distance by 4.15 inches.

#### Metal Jacket

• 11-gauge (0.1196-inch) ASTM A 516-70a, Grade 70

Since most pressure tank cars use a metal jacket to protect the insulation or thermal protection, the most common thickness along with the most common steel was chosen.

#### Explosive Charge

- Shape: Cone with Vertex Angles of 120 degrees and 90 degrees
- Material: Copper

The shape of the cutting medium selected was that of a cone. Two types of cones were modeled, one with a shallow vertex angle (large distance between vertex and directrix) of 120 degrees and a cone with a large vertex angle (smaller distance between vertex and directrix) of 90 degrees. The cone material was copper.

- Outside Diameter of Tube: 4 inches, 8 inches
- Standoff-Distance: 4 inches, 8 inches

The standoff-distance is typically equal to the outside diameter of the tube that is being used. The three common sizes used are 4, 6, and 8 inches. It was assumed that the results for a 6-inch tube would be able to be interpolated from the 4-inch and 8-inch size tube; thus, only these 2 sizes were modeled.

Charge (Weight): Enough of each charge was applied to have the charge height 2 inches above the vertex of the cone. This factor determined weight.

Type of Charges: C-4 (a mixture of 91 percent cyclonite (RDX), 2.1 percent polyisobutylene, 5.3 percent diethylhexyl sebacate, and 1.6 percent motor oil).

Composition B3 (a mixture of 64 percent RDX and 36 percent trinitrotoluene(TNT)).

The two charges modeled were C-4 and Composition B3.

#### 5.6.2 Simulations by LLNL

LLNL performed computer simulations using various combinations of parameters specified in Section 5.6.1. Appendix C includes the entire LLNL report. The following text is excerpted from the "Discussion of Results" and "Conclusion" sections of the report:

Two parameters appear to dominate the response, the shaped charge diameter and the shaped charge cone angle. The other parameters in the design do not appear, in this analysis, to play a significant role. One concern at the beginning of the study was whether the additional stand off provided by the insulation between the railroad car jacket and tank-shell would cause the shaped charge jets to stretch and fragment. This analysis appears to indicate that the additional stand off does not appear to appreciably affect the hole penetration capability of the shaped charges studied.

Table 1 lists the expected hole diameter for various parameter combinations and is also excerpted from the LLNL report.

Shape Charge Diameter	Cone Angle Degrees	High Explosive	Insulation	Tank Shell Hole Diameter	Tank Shell Hole Radius	Jacket Hole Radius
4 in	90 degrees	C-4	4 in	1.57 in	2.0 cm	2.5 cm
8 in	90 degrees	C-4	4 in	2.36 in	3.0 cm	3.9 cm
4 in	90 degrees	C-4	6 in	1.42 in	1.8 cm	1.6 cm
8 in	90 degrees	C-4	6 in	2.36 in	3.0 cm	4.1 cm
4 in	120 degrees	C-4	4 in	1.42 in	1.8 cm	2.8 cm
8 in	120 degrees	C-4	4 in	2.91 in	3.7 cm	3.8 cm
4 in	120 degrees	C-4	6 in	1.42 in	1.8 cm	2.7 cm
8 in	120 degrees	C-4	6 in	3.15 in	4.0 cm	4.9 cm
4 in	90 degrees	Comp-B	4 in	1.18 in	1.5 cm	1.6 cm
8 in	90 degrees	Comp-B	4 in	2.68 in	3.4 cm	2.3 cm
4 in	90 degrees	Comp-B	6 in	1.02 in	1.3 cm	1.5 cm
8 in	90 degrees	Comp-B	6 in	2.52 in	3.2 cm	2.5 cm
4 in	120 degrees	Comp-B	4 in	1.18 in	1.5 cm	3.6 cm
8 in	120 degrees	Comp-B	4 in	2.91 in	3.7 cm	5.8 cm
4 in	120 degrees	Comp-B	6 in	1.02 in	1.3 cm	4.4 cm
8 in	120 degrees	Comp-B	6 in	2.68 in	3.4 cm	5.7 cm

# Table 1. Results of Parameter Study on the Response ofRailroad Car Tanks to Shaped Charges

#### 5.6.3 Simulations by Dr. Milton R. Johnson

In addition to work done by LLNL, Dr. Milton R. Johnson conducted independent research analyzing single-point venting of tank cars using Analysis of Fire Effects on Tank Cars (AFFTAC), a computer program developed for FRA. In single-point venting, only one hole is used to relieve internal vapor pressure and release product for incineration. Johnson's model used two typical commodities to illustrate various effects, including butane, a moderate vapor pressure product, and propane, a high vapor pressure product. A typical pressure tank car design was assumed for the examples. The AFFTAC model predicted vent times for 2-, 4- and 6-inch diameter vent holes. Previous recommendations call for 7 1/2-inch diameter for vent and drain holes. Johnson concludes, "Single-point venting can be used for high vapor pressure products, but it results in a large variation in the rate of product outflow from the tank." The committee concluded that single-point venting is not a viable option and should not be used. Johnson also modeled two-point venting of both butane and propane.

Table 2 shows the results of a simulation of two-point venting of a propane-filled tank. The vent diameter at the top of the tank was 5.375 inches, and the drain diameter at the bottom of the tank was 3.5 inches. Time delay between charges was 32.0 minutes.

Table 2. Results from Analysis of 1 wo-1 ont venting of 1 topane-r med 1 ank						
Time	Temperature	Vapor Pressure	Fraction of Product Remaining	Rate of Product Release		
0.0 min	70.0°F	110.2 psig	1.000	2,506 lb/min		
3.0 min	57.2°F	88.5 psig	.946	2,199 lb/min		
6.0 min	45.5°F	71.1 psig	.901	1,818 lb/min		
9.0 min	34.8°F	57.4 psig	.864	1,521 lb/min		
12.0 min	25.1°F	46.3 psig	.832	1,287 lb/min		
15.0 min	16.2°F	37.4 psig	.806	1,098 lb/min		
18.0 min	8.3°F	30.2 psig	.783	945 lb/min		
21.0 min	1.0°F	24.3 psig	.763	822 lb/min		
24.0 min	-5.7°F	19.6 psig	.746	722 lb/min		
27.0 min	-11.7°F	15.6 psig	.730	639 lb/min		
30.0 min	-17.3°F	12.2 psig	.717	568 lb/min		
33.0 min	-21.9°F	9.7 psig	.696	2,586 lb/min		
36.0 min	-25.3°F	7.8 psig	.658	2,533 lb/min		
39.0 min	-28.1°F	6.5 psig	.624	2,483 lb/min		
42.0 min	-30.4°F	5.4 psig	.591	2,434 lb/min		
45.0 min	-32.3°F	4.5 psig	.559	2,384 lb/min		
48.0 min	-33.9°F	3.8 psig	.529	2,337 lb/min		
51.0 min	-35.2°F	3.3 psig	.500	2,288 lb/min		

 Table 2. Results from Analysis of Two-Point Venting of Propane-Filled Tank

#### 5.7 **Product Disposition Considerations**

Disposing of products not entirely consumed by the vent and burn process, as well as dealing with residual products, of combustion, must be given careful consideration before choosing the this option. Before any vent and burn operation, the responder(s) must notify State, local, and Federal authorities of the operation and determine what permits are required to burn any released material.

The majority of the Class 3 flammable liquids and combustible liquids are made up of various types of alcohols and petroleum distillates (fuels). This report does not discuss environmental considerations of those materials, which are identified specifically by name, but can be found in most common reference books.

The one composition requirement common to all petroleum fuels is that they are predominately made up of hydrocarbon molecules (hydrogen and carbon) with small amounts of impurities and/or additives.

The refining of crude oil, also known as fractional distillation, produces a range of petroleum compounds that are primarily characterized by their boiling points and molecular weights. Short-chain, single-ring, light hydrocarbons are more volatile, less viscous, and have lower boiling points than long-chain, multiple-ring, heavy hydrocarbons. Denoting the number of carbon atoms (CX) in a hydrocarbon molecule is a way to describe its weight relative to other hydrocarbon molecules. Natural gas is composed primarily of the light hydrocarbons methane (C1), ethane (C2), propane (C3), and butane (C4). Gasoline typically contains hydrocarbons in the C4–C10 range. Kerosene and aviation fuels fall primarily into the C4–C19 range. Diesel fuels are composed primarily of hydrocarbons in the C8–C21 range. Heating oils, the most common being Fuel Oil No. 2, are similar to diesel fuels but are less refined and fall into the heavier C15–C22 range. Lubricating oils, hydraulic fluids, tars, and other heavy residual petroleum compounds are made up of hydrocarbon molecules in the C20–C60 range and larger.

Most petroleum fuels are mixtures of hundreds of different hydrocarbon compounds. The exact number and proportions of these compounds in a particular fuel may vary. Thus, most fuels are formulated to meet general property limits rather than a specified chemical composition.

Volatility is a property of fuels that affects its ability to vaporize and form a combustible mixture with air. This property results in a quantifiable characteristic called vapor pressure. Vapor pressure and volatility are important properties to be considered by emergency responders who may be considering vent and burn. Lighter fuels, such as gasoline and aviation fuel, tend to be more volatile and have higher vapor pressures than heavier fuels, such as diesel and heating oil, at the same temperature and pressure.

#### 5.7.1 Products

#### 5.7.1.1 Diesel Fuels

Diesel fuel is formulated for engines used in buses, trucks, ships, and locomotives, which are commonly heavier and more powerful than gasoline engines. Diesel fuel is generally classified into the following three grades.

Diesel No. 1 is relatively volatile (C8–C19) when compared to other diesel fuels. It is used in high-speed diesel engines that vary in speeds and loads and was originally formulated to meet the specifications for Detroit Diesel Series 71 engines used in city buses.

Diesel No. 2 is composed of lower volatility and heavier (C9–C21) petroleum compounds than Diesel No. 1. It is used in high-speed diesel engines involving high loads and uniform speeds, such as automobiles, trucks, and locomotives.

Diesel No. 4 is the most viscous and least volatile diesel blend and is a mixture of heavy diesel distillates and residual (C25+) fuel oils. It is for use in low- and medium-speed services involving sustained loads and constant speeds. Large stationary power generators and ships mainly use this type of fuel.

#### 5.7.1.2 Heating Oils

Heating oils are a clean burning, nonexplosive, highly efficient fuel that produce negligible amounts of smoke and soot emissions. Heating oils are graded 1 through 6, with Fuel Oil No. 2 (C15–C22) being one of the most common. Fuel Oil No. 6 (Bunker C) is composed entirely of heavy residual hydrocarbons and is a black viscous fuel that must be heated before it can be pumped and burned. Heavier fuel oils are sometimes blended with used lubricating oil or waste oils, which can contain elevated levels of cadmium, lead, and other metals.

#### 5.7.1.3 Gasoline

Automotive gasoline is a very sophisticated fuel and is often a blend of separately distilled petroleum products. Gasoline is very volatile and produces large amounts of vapor at ordinary temperatures. Gasoline contains hydrocarbon compounds in the C4–C10 range. The major component (60–80 percent) of gasoline consists of the alkanes, which are stable and burn cleanly. Aromatic compounds comprise about 20–40 percent of gasoline formulations; however, these compounds are gradually being replaced with other less polluting octane boosters, such as methyl tertiary butyl ether (MTBE) and ethanol.

Several toxic compounds exist in gasoline and other lighter petroleum distillates; the most notable of which are lead and benzene, which is a confirmed carcinogen. Other suspected carcinogens in gasoline include other aromatics, ethylene dibromide, and oxygenating additives.

#### 5.7.1.4 Flammable Gases

Most of the Division 2.1 (Flammable Gases) materials are liquefied gases shipped under their own vapor pressure. Once released, these products will rapidly expand and mix with air to form a flammable mixture. The liquefied gas released will pool in the burn pit, boil, and continue to rapidly evolve vapors, which will burn above the pool. Low ambient temperatures will reduce the rate at which this material boils and evolves vapors. Because of the low boiling point, it is unlikely that much liquid material will penetrate the soil deeply and mix with groundwater. The most common Division 2.1 material shipped is Liquefied Petroleum Gas (LPG). The products of combustion of some Division 2.1 materials are not well defined but include carbon dioxide, carbon monoxide, and, depending upon the product, may contain other toxic constituents. Large amounts of incompletely burned material may be released as soot. Provisions must be made for environmental cleanup of any contaminated soils, which result from vent and burn operations.

#### 5.7.1.5 Alcohols

The alcohols shipped in bulk by rail are primarily butyl, ethyl, and methyl alcohols. These are used as industrial solvents and gasoline additives in pharmaceuticals, antifreeze, foods, perfumes, and alcoholic beverages. They generally have a low flash point, moderate vapor pressure, and are easily ignited. The alcohols are also generally completely soluble in water.

Ethyl alcohol may be shipped denatured to render it unfit for human consumption. The materials used to denature ethyl alcohol can be gasoline, heptane, methyl isobutyl ketone, kerosene, methanol, or ethyl acetate. When burned, the products of combustion include carbon monoxide and possible contaminants from the denaturing additives.

Butyl alcohol is shipped as various isomers (e.g., normal, secondary, and tertiary). All are lighter than water and water-soluble. The flash point varies from 52°F to 84°F. Products of combustion are not well defined but may include toxic constituents.

Methyl alcohol is lighter than water and has a flash point of around 54°F. The products of combustion include toxic formaldehyde, carbon monoxide, and possibly unburned methanol.

The release of large amounts of alcohol into the soil has effects similar to the petroleum distillates, as they may permeate the soil and enter groundwater. Because alcohol is soluble in water, it is difficult to remove once it mixes with groundwater. The materials used to denature ethyl alcohol may be a greater threat to contaminate groundwater than the alcohol itself. This can be addressed by proper sizing and confinement (of the burn pit), insuring proper and prompt ignition, and the presence of emergency response personnel and heavy earth moving equipment. Provisions must be made for the environmental cleanup of any contaminated soils, which result from vent and burn operations.

#### 5.7.2 Additives

Fuel additives are contained in many of the petroleum distillates shipped in tank cars and are intended to help improve fuel economy, lower maintenance costs, reduce impurities and harmful deposits, reduce exhaust emissions, and improve the overall performance and reliability of the fuel. Different fuels may be formulated with different packages of fuel additives. Often the precise chemical composition of many fuel additives and additive packages is proprietary to the manufacturer. Common fuel additives include the following:

- Alkyl lead is used in aviation gasoline at levels typically greater than 1,000 parts per million.
- Antioxidants are primarily used to prevent gum formation in gasoline and aviation fuels.
- Biocides may be added to any type of fuel to kill microbes when their growth becomes a recurring problem.
- Conductivity additives increase the electrical conductivity of gasoline, aviation, and diesel fuels, thereby reducing the buildup of static charges during mixing, transfer, and shipment.
- Corrosion inhibitors protect against corrosion during pipeline transfer and storage of fuels. They have also been found to improve the lubricity or capacity to reduce friction of fuels. Corrosion inhibitors are used primarily in gasoline, aviation fuels, and diesel fuels.
- Detergent additives prevent the buildup of gum deposits in engines and extend fuel injector life. They also help keep fuel filters clean. Detergent additives are primarily found in diesel fuels and automotive gasoline.
- Icing inhibitors are used primarily in aviation fuels to prevent the formation of ice crystals from entrapped water in the fuel at freezing temperatures. Diethylene glycol monomethyl ether is specified for most military aviation fuels as an icing inhibitor.
- Metal deactivators prevent metal contaminants in any type of fuel from oxidizing with hydrocarbons and other compounds to form gums or precipitates.
- Oxygenates are oxygen-containing hydrocarbons that are added to automotive gasoline to boost the octane rating, reduce the smog-forming tendencies of exhaust gases, and suppress engine knock. The increased oxygen content promotes more complete combustion, thereby reducing tailpipe emissions. Common oxygenating additives are MTBE and ethanol.

#### 5.7.3 Effects of Combustion

Before the release of large amounts of products through vent and burn, consideration must be given to the material and hazardous products of combustion. The hazardous products of combustion are often hard to define but typically include carbon, carbon monoxide, carbon dioxide, hydrochloric acid, benzene, xylene, toluene, and other various hydrocarbons. Other compounds formed or released during combustion may result from additives, such as lead compounds and other toxic constituents. In addition to the products of combustion, consideration must be given to black soot and other particulates that may be released as a result of incomplete combustion. The intent of vent and burn is to shorten exposure times and keep contact below less than established limits through predictable and controlled release as opposed to sudden and total uncontrolled release.

#### 5.7.4 Fuel Releases to the Subsurface

A material spill caused as the result of a vent and burn operation can pose health and explosion risks. These can be addressed by proper sizing and confinement (of the burn pit), insuring proper and prompt ignition, and the presence of emergency response personnel and heavy earth moving equipment. For these reasons, a large spill from a vent and burn operation should not produce the same level of environmental damage that can result from long-term leaks from underground fuel system components or a total uncontrolled release in the event of sudden and catastrophic tank shell failure.

A large number of interrelated factors determine the fate of fuel products once they are released into the environment. The major factors include the following:

- Type of fuel released
- Rate of the release
- Characteristics of subsurface soils
- Vertical distance to groundwater surface
- Characteristics of the groundwater formation
- Proximity to surface water bodies

The vent and burn process attempts to control some of these factors in an effort to provide a predictable outcome. The moment a fuel release occurs, it is subject to a variety of physical and chemical changes. Volatile components begin to vaporize, indigenous microbial action will begin to break down the fuel into less harmful components, and hydrocarbons will begin to be adsorbed into/by organic matter in the environment. In the unsaturated soils lying above the groundwater zone, fuel migrates downward under the force of gravity and may spread horizontally under other mechanical forces. In some cases, the release may migrate through fractured bedrock formations where it can move quickly and be difficult to characterize. Once the fuel reaches the groundwater, it will dissolve to a minor degree and may accumulate as a thin light non-aqueous phase liquid lens at the groundwater surface, where it will continue to volatilize into the dry soils above and dissolve in the groundwater below.

Although hydrocarbons are not very soluble in water, very small dissolved concentrations (1 part per million) can give water a very strong fuel smell. Some of the more toxic components of fuels are considered harmful to human health and the environment when dissolved in drinking

water at concentrations as low as one part per billion. A small amount of fuel can contaminate a very large quantity of water. Groundwater migrates horizontally in the subsurface at a rate typically ranging between a few inches to a few feet per day. Coupled with the fact that the groundwater surface can also rise and fall, this can bring undissolved fuel in continuous contact with previously uncontaminated groundwater. Since groundwater usually migrates in one general direction (with minor seasonal fluctuations), the contaminated portion of the groundwater frequently takes on a three-dimensional elongated shape that may widen and disperse with distance from the source. Thus, the term plume is frequently used to describe contaminated groundwater zones.

Fuel additives pose the most serious threat of groundwater contamination. For example, MTBE is very persistent in the environment and is used as a marker for plume definition. Provisions must be made for environmental cleanup of any contaminated soils that may result from vent and burn operations.

#### 5.8 Items Checklist

Researchers developed a checklist of items to be considered that takes into account variables, such as tank car structure and damage, environmental concerns, location, commodity considerations, and available resources to help response personnel evaluate the applicability of the vent and burn method. The rating terms used in the checklist refer to the desirability of vent and burn as a viable option and are defined as follows. High implies that the condition is favorable to the vent and burn process and/or a positive predictable outcome is supported. Medium suggests that, although the condition does not exclude the vent and burn process, a predictable result is less likely. Low means that the condition does not support the vent and burn process may not be available or may be less desirable (i.e., a total uncontrolled release due to shell failure).

Again, this checklist (see Table 3) is intended as an aid only and is not meant to be a substitute for the sound judgment of the incident commander or other person(s) in charge.

Structure/Damage Assessment:	High	Medium	Low
Is tank car being impinged upon by fire?	Yes	Close to Fire	No
Are contents of subject tank car burning?	No		Yes
Is tank car venting continuously?	No		Yes
Is shell rupture imminent?	Yes	Possible	No
Is there a possibility of product polymerization?	Yes		No
Is the tank damaged?	Yes	Somewhat	No
Has tank construction material been determined?	Yes		No
Will the ambient temperature affect ductile/brittle transition point of tank?	Yes	Possible	No
_ocation/Environment/Site Assessment:			·
Is the subject tank close to other tanks?	No	Somewhat	Yes
Is the subject tank near buildings or structures?	No	Somewhat	Yes
Is the subject tank near habitation?	No	~0.5 mile	~0.25 mile
Is the accident scene among swales/marshes where excavation of a burn pit is impossible?	No	~0.5 mile	~0.25 mile
Is the accident scene close to water sources?	No	~0.5 mile	~0.25 mile
Will the current wind speed and direction produce dangerous product fallout?	No	Somewhat	Yes
If near habitation, have people been evacuated?	Yes	In Process	No
Product Considerations:			
Is product combustible?	Yes		No
Will controlled release of the product exceed toxicity levels?	No		Yes
Will the products of combustion exceed toxicity levels?	No		Yes
What is the type and permeability of the soil? (How much of the liquid product will absorb into ground	Small Perme-	Somewhat	Very

#### Table 3. Checklist of Items to be Considered by Responders

# What is the type and permeability of the soil?Small<br/>Perme-<br/>abilitySomewhat<br/>Perme-<br/>abilityVery<br/>Permeable(How much of the liquid product will absorb into ground<br/>before burn-off?)Wery<br/>PermeabilityVery<br/>PermeabilityWhat is the viscosity of product?<br/>(Will product seep into ground quickly or not?)High<br/>ViscosityMedium ViscosityLow Viscosity

#### **Resources/Containment of Product:**

In case of unforeseen problems, are local fire suppression personnel present?	Yes	On Call	No
Is the proper equipment available to dig a burn pit and a trench from the pit to the tank car?	Yes	Enroute	No
Is an explosives expert available?	Yes	Enroute	No
Are the proper explosives available?	Yes	Enroute	No

## 6.0 Conclusions

The vent and burn process should only be employed after all other options have been considered and after careful evaluation and input from all parties involved in a hazardous materials incident. A qualified incident commander must use sound judgment when considering and choosing this option. When carefully planned for and properly applied, vent and burn can be an effective method of mitigating a serious incident.

In reviewing past incident documentation, it is evident that a standardized reporting system is necessary to track all pertinent details. Additional information provided from standardized reporting of future incidents is needed for continued process improvement. Postmortem analysis of the tank shell to determine shell response to the explosive charge is needed to fully understand the cause and effect relationships involved.

Modeling has suggested that a properly designed and applied charge is capable of penetrating both the insulation and/or thermal protection (including jacket) and the tank shell. This may eliminate the need to remove the insulation/thermal protection and jacket before setting the charge and could help minimize time-on-target for response personnel.

Modeling also indicates that single-point tank car venting is not a viable vent and burn option and should not be considered or used. The two-point configuration using an appropriate time delay between charge detonations is the optimum method.

# 7.0 Recommendations

The following are recommendations for continued improvement of the vent and burn process:

#### 7.1 Review of Itemized Checklist by Incident Commanders

Further review of the itemized checklist by additional experienced incident commanders and other key emergency response personnel who will be using it is recommended to critique and refine the tool.

#### 7.2 Validation Testing

In order to corroborate modeling results, a test plan should be drafted, and validation tests should be carried out. The test plan should specify the use of full-scale pressure and non-pressure tank cars, as well as tank shell coupons of various tank materials and configurations of thermal protection/insulation. It should evaluate various charge design parameters, such as cone angles, tube materials, standoff distances, and differential detonation times. A study of vent and drain times for various hole diameters should be included. Future testing should also seek to identify the dynamics of the explosive charge shock wave and its effects on the process.

#### 7.3 **Portable Electronic Database**

Pertinent information, such as the itemized checklist contained in this report, tank car material specifications, UMLER information, and commodity characteristics, should be compiled into a format compatible with in-field, personal computing tools, such as laptop computers. This would allow emergency response personnel immediate access to valuable information and aid in the decisionmaking process at the incident.

# 7.4 Standardized Report and Post-Incident Analysis

A detailed standardized reporting procedure is needed to learn more from actual applications of the vent and burn process. Along with information reported, detailed charge parameters, including specific placement location, actual venting times, environmental conditions (temperature, humidity), tank shell condition, and other mitigating circumstances, as well as technician comments, should also be recorded. When possible, a close inspection and postmortem analysis of the response of the tank shell in the area of the charge should be conducted. This additional information is crucial to gaining further insight into the actual mechanics of the process.

# 7.5 Dual Charge Time Delayed Detonation

Single-point venting is not recommended as a viable option for the vent and burn process. Experience and modeling indicate that the most effective vent and burn method is the use of two separate charges detonated one after the other. Although this method is most effective, it is seldom followed. Additional research is needed to determine optimum delay times and to develop feasible methods of implementation.

# References

- 1. 49 CFR 172.101, Code of Federal Regulations.
- 2. "Material Property Considerations for Vent and Burn Emergency Recovery Operations," Centaurus Technology Inc., December 2002.
- 3. Aldis, David F., "Railroad Tank Car Vent and Burn Process Study: Analysis of a Shaped Charge Impact on a Jacket and Shell," Lawrence Livermore National Laboratory.
- 4. Johnson, Milton R., "Temperatures, Pressures and Liquid Levels of Tank Cars Engulfed in Fires," DOT/FRA/OR&D-84/08.II, Federal Railroad Administration, Washington, DC, June 1984.

# Appendix A.

# Railcar Shipment in 2001 Sorted by Hazardous Material Classification and Relative Number of Shipments in Category

Materials considered less suitable for VENT AND BURN action relative to propane for reasons related to chemical characteristics are indicated in blue italics. For black and white print copies, the same information is indicated by the last column VENT AND BURN code.

#### Code Description

- (ok) No intrinsic chemical property reason for not employing VENT AND BURN action. Operational risk is viewed comparable to propane.
- (sr) Potentially self-reactive if exposed to fire of long duration.
- (phf) Potentially shock sensitive because of positive heat of formation.
- (env) Potential elevated environmental risk on burning due to presence of amine or halogen groups or other toxic elements or reaction products.

Rank in Class	Rank in Total	Haz Mat Code	Tank Car (only) for Year 2001 Hazard Class 2.1 Flammable Gas Description	VB Code
1	1	4905752	PETROLEUM GASES, LIQUEFIED	OK
2	8	4905421	PROPANE	OK
4	19	4905423	BUTANE	OK
6	25	4905430	ISOBUTANE	OK
8	91	4905715	BUTYLENE	OK
12	107	4905707	PETROLEUM GASES, LIQUEFIED	OK
13	108	4905791	PROPANE	OK
14	109	4905457	PETROLEUM GASES, LIQUEFIED	OK
15	115	4905749	HYDROCARBON GAS MIXTURE, LIQUEFIED, N.O.S.	OK
16	126	4905759	ISOBUTANE	OK
18	144	4905417	PETROLEUM GASES, LIQUEFIED	OK
19	158	4905788	BUTANE	OK
20	160	4905748	ISOBUTYLENE	OK
21	163	4905753	ISOBUTANE	OK
23	166	4905711	PETROLEUM GASES, LIQUEFIED	OK
24	178	4905789	BUTANE	OK
28	292	4905763	LIQUEFIED GAS, FLAMMABLE, N.O.S.	OK
30	327	4905742	DIMETHYL ETHER	OK
31	329	4905781	PROPANE	OK
33	368	4905762	PETROLEUM GASES, LIQUEFIED	OK
35	383	4905747	ISOBUTANE	OK
39	486	4905706	BUTANE	OK
40	493	4905702	BUTANE	OK
41	522	4905780	PETROLEUM GASES, LIQUEFIED	OK
42	698	4905725	DIMETHYL ETHER	OK
43	739	4905428	BUTYLENE	OK
44	756	4905757	ISOBUTYLENE	OK
Notes:	(ok)	No intrinsic cl	nemical property reason for not employing V&B action.	

Table A-1(a). Hazard Material Class 2.1, Flammable Gas. Suitable for V&B Action.(Ranked per relative frequency of shipments in 2001)

#### Table A-1(b). Hazardous Material Class 2.1, Flammable Gas. V&B Action Would Carry Increased Risk Relative to Propane. (Ranked per relative frequency of shipments in 2001)

Rank in Class	Rank in Total	Haz Mat Code	Tank Car (only) for Year 2001 Hazard Class 2.1 Flammable Gas Description	VB Code
3	10	4905792	VINYL CHLORIDE, STABILIZED	sr/phf
7	27	4905704	BUTADIENES, STABILIZED	sr/phf
11	102	4905703	BUTADIENES, STABILIZED	sr/phf
22	164	4905705	BUTADIENES, STABILIZED	sr/phf
37	403	4905795	VINYL METHYL ETHER, STABILIZED	sr
5	22	4905784	PROPYLENE	phf
9	97	4905782	PROPYLENE	phf
26	202	4905735	ETHYLENE, REFRIGERATED LIQUID	phf
38	476	4905758	METHYLACETYLENE AND PROPADIENE MIXTURES	phf
10	99	4905761	METHYL CHLORIDE	env
17	137	4905510	DIMETHYLAMINE, ANHYDROUS	env
25	184	4905414	METHYLAMINE, ANHYDROUS	env
27	215	4905540	TRIMETHYLAMINE, ANHYDROUS	env
29	308	4905716	1,1-DIFLUOROETHANE	env
32	343	4905787	1,1,1-TRIFLUOROETHANE, COMPRESSED	env
34	371	4905720	1-CHLORO-1,1-DIFLUOROETHANE	env
36	400	4905712	ETHYL CHLORIDE	env
45	780	4905444	DIFLUOROMETHANE	env
Notes:	(ok)	No intrinsic ch	emical property reason for not employing V&B action.	-
	(sr)	Potentially sel	f-reactive if exposed to fire.	,
	(phf)	Potentially sho	ock sensitive because of positive heat of formation.	
	(env)	Potential high	environmental risk due to presence of amine or halogen co	mpounds.

# Table A-2. Hazard Material Class 2.2, Non-Flammable Gas. Compounds Where V&BAction Would Carry Increased Risk Relative to Propane Are Indicated by VB Code.(Ranked per relative frequency of shipments in 2001)

Rank in Class	Rank in Total	Haz Mat Code	Tank Car (only) for Year 2001 Hazard Class 2.2 Non-Flammable Gas Description	VB Code
2	16	4904509	CARBON DIOXIDE, REFRIGERATED LIQUID	ОК
3	122	4904503	ARGON, REFRIGERATED LIQUID	OK
8	447	4904360	OXYGEN, REFRIGERATED LIQUID	OK
1	5	4904210	AMMONIA, ANHYDROUS	ENV
4	141	4904520	CHLORODIFLUOROMETHANE	ENV
5	183	4904304	1,1,1,2-TETRAFLUOROETHANE	ENV
6	282	4904552	CHLORODIFLUOROMETHANE	ENV
7	337	4904318	PENTAFLUOROETHANE	ENV
9	511	4904879	AMMONIA, ANHYDROUS	ENV
10	581	4904523	1-CHLORO-1,2,2,2-TETRAFLUOROETHANE	ENV
11	611	4904526	1,2-DICHLORO-1,1,2,2-TETRAFLUOROETHANE	ENV
12	658	4904558	1-CHLORO-1,2,2,2-TETRAFLUOROETHANE	ENV
Notes:	(ok)	No intrinsic	chemical property reason for not employing V&B action.	
	(sr)	Potentially	self-reactive if exposed to fire.	
	(phf)	Potentially	shock sensitive because of positive heat of formation.	
	(env)	Potential hi compounds	gh environmental risk due to presence of amine or halogen	

# Table A-3. Hazard Material Class 2.3, Poisonous Gas. For All Compounds, V&B Action Would Carry Increased Risk Relative to Propane as Indicated by VB Code. (Ranked per relative frequency of shipments in 2001)

Rank in Class	Rank in Total	Haz Mat Code	Tank Car (only) for Year 2001 Hazard Class 2.3 Poisonous Gas Description	VB Code
1	6	4920523	CHLORINE	env
2	28	4920353	ETHYLENE OXIDE	*env
3	68	4920508	SULFUR DIOXIDE	env
4	112	4920355	METHYL MERCAPTAN	env
5	170	4920504	HYDROGEN CHLORIDE, REFRIGERATED LIQUID	env
6	339	4920518	METHYL BROMIDE	env
7	463	4920513	HYDROGEN SULFIDE	env
8	751	4920359	AMMONIA, ANHYDROUS	env
Notes:	(ok)	No intrinsic ch	emical property reason for not employing V&B action.	•
	(sr)	Potentially sel	f-reactive if exposed to fire.	
	(phf)	Potentially she	ock sensitive because of positive heat of formation.	
	(env)	Potential high	environmental risk due to presence of amine or halogen co	ompounds.

\* Ethylene Oxide is a special risk category due to its susceptibility of internal tank explosion. UFL = 100 percent and AIT = 429 oC. V&B charge explosion can potentially ignite EO in tank.

Rank in Class	Rank in Total	Haz Mat Code	Tank Car (only) for Year 2001 Hazard Class 3(a) Flammable Liquids Description	VB Code
1	12	4909230	METHANOL	OK
2	13	4908175	GASOLINE	OK
4	20	4912217	FUEL OIL	OK
5	23	4908177	GASOLINE	OK
6	29	4909215	FUEL, AVIATION, TURBINE ENGINE	OK
7	30	4908224	METHYL TERT BUTYL ETHER	OK
9	34	4909351	XYLENES	OK
10	38	4909159	ETHANOL	OK
12	40	4906620	PROPYLENE OXIDE	OK
13	46	4910165	PETROLEUM CRUDE OIL	OK
14	47	4908132	CYCLOHEXANE	OK
16	54	4912216	FUEL OIL	OK
17	56	4912247	COMPOUNDS, CLEANING LIQUID	OK
18	59	4908105	ACETONE	OK
19	60	4910256	PETROLEUM DISTILLATES, N.O.S.	OK
20	61	4909305	TOLUENE	OK
22	64	4912511	ELEVATED TEMPERATURE LIQUID, FLAMMABLE	OK
24	73	4909205	ISOPROPANOL	OK
25	74	4810560	WASTE FLAMMABLE LIQUIDS	OK
26	76	4908110	BENZENE	OK
27	77	4909382	PETROLEUM DISTILLATES, N.O.S.	OK
28	79	4909381	METHANOL	OK
29	82	4909103	ALCOHOLS, N.O.S.	OK
30	84	4909130	BUTANOLS	OK
31	86	4907428	HYDROCARBONS, LIQUID, N.O.S.	OK
32	98	4912590	FLAMMABLE LIQUIDS, N.O.S.	OK
33	104	4912812	ELEVATED TEMPERATURE, LIQUID, FLAMMABLE	OK
34	105	4910102	ALCOHOLIC BEVERAGES	OK
35	110	4909160	ETHYL ACETATE	OK
36	111	4908183	HEXANES	OK
37	114	4912271	KEROSENE	OK
39	117	4909243	ETHYL METHYL KETONE	OK
40	119	4907210	ACETALDEHYDE	OK
41	120	4909249	TRIPROPYLENE	OK
42	124	4908176	GASOLINE	OK
43	127	4912280	HYDROCARBONS, LIQUID, N.O.S.	OK
45	131	4908255	PENTANES	OK
46	133	4910444	FLAMMABLE LIQUIDS, N.O.S.	OK
47	134	4909348	XYLENES	OK
48	135	4908182	1-HEXENE	OK

# Table A-4(a). Hazard Material Class 3(a), Flammable Liquids. Suitable for V&B Action.(Ranked per relative frequency of shipments in 2001)

Rank in Class	Rank in Total	Haz Mat Code	Tank Car (only) for Year 2001 Hazard Class 3(a) Flammable Liquids Description	VB Code
49	136	4909128	BUTYL ACETATES	OK
50	138	4908119	BUTYRALDEHYDE	OK
51	143	4910185	FLAMMABLE LIQUIDS, N.O.S.	OK
52	146	4909363	ALCOHOLS, N.O.S.	OK
53	147	4907219	DICYCLOPENTADIENE	OK
54	148	4909198	XYLENES	OK
55	149	4909267	N-PROPANOL	OK
56	152	4908112	FLAMMABLE LIQUIDS, N.O.S.	OK
58	159	4908125	CARBON DISULFIDE	OK
59	161	4909201	FLAMMABLE LIQUIDS, N.O.S.	OK
60	168	4909237	METHANOL	OK
61	176	4909190	HEPTANES	OK
62	177	4907872	HEXAMETHYLENEIMINE	OK
63	180	4910320	FLAMMABLE LIQUIDS, N.O.S.	OK
64	181	4910282	RESIN SOLUTION	OK
65	185	4912620	FUEL OIL	OK
67	188	4910445	1-HEXENE	OK
69	195	4912675	PROPYLENE TETRAMER	OK
70	201	4809188	WASTE FLAMMABLE LIQUIDS	OK
71	203	4912505	ELEVATED TEMPERATURE LIQUID, FLAMMABLE	OK
73	205	4912631	ISOPROPENYLBENZENE	OK
75	213	4910242	PETROLEUM DISTILLATES, N.O.S.	OK
76	217	4910240	ETHANOL	OK
77	220	4909244	METHYL ISOBUTYL KETONE	OK
78	225	4908270	PROPIONALDEHYDE	OK
79	228	4909124	ISOBUTANOL	OK
80	229	4909163	ETHYLBENZENE	OK
81	230	4910115	FLAMMABLE LIQUIDS, N.O.S.	OK
82	231	4912498	DIESEL FUEL	OK
83	232	4910290	ALCOHOLS, N.O.S.	OK
84	233	4912211	FUEL OIL	OK
85	242	4912186	DIESEL FUEL	OK
86	244	4912079	CYCLOHEXANONE	OK
87	247	4810185	WASTE FLAMMABLE LIQUIDS	OK
88	249	4910324	FLAMMABLE LIQUIDS, N.O.S.	OK
89	253	4908290	TETRAHYDROFURAN	OK
90	255	4909268	N-PROPYL ACETATE	OK
91	260	4912015	FORMALDEHYDE, SOLUTIONS, FLAMMABLE	OK
92	264	4908185	ISOBUTYRALDEHYDE	OK
93	269	4810118	WASTE FLAMMABLE LIQUIDS	OK
94	271	4908178	GASOLINE	OK
95	279	4910280	RESIN SOLUTION	OK

Rank in Class	Rank in Total	Haz Mat Code	Tank Car (only) for Year 2001 Hazard Class 3(a) Flammable Liquids Description	VB Code
97	281	4912285	HYDROCARBONS, LIQUID, N.O.S.	OK
98	284	4909313	1-METHOXY-2-PROPANOL	OK
100	291	4910135	COAL TAR DISTILLATES, FLAMMABLE	OK
101	293	4912187	GAS OIL	OK
103	295	4910196	FLAMMABLE LIQUIDS, N.O.S.	OK
104	299	4909207	ISOBUTYL ACETATE	OK
105	301	4912540	ELEVATED TEMPERATURE LIQUID, FLAMMABLE	OK
106	305	4910167	FLAMMABLE LIQUIDS, N.O.S.	OK
107	314	4910534	FLAMMABLE LIQUIDS, N.O.S.	OK
108	316	4909210	ISOPROPYL ACETATE	OK
109	317	4912219	FUEL OIL	OK
110	318	4910489	FLAMMABLE LIQUIDS, N.O.S.	OK
111	320	4910139	COAL TAR DISTILLATES, FLAMMABLE	OK
112	323	4910111	ALCOHOLS, N.O.S.	OK
113	324	4912043	METHYL ISOBUTYL CARBINOL	OK
114	333	4909178	TOLUENE	OK
116	335	4907419	FLAMMABLE LIQUIDS, TOXIC, N.O.S.	OK
117	341	4909225	2-METHYL-2-BUTENE	OK
118	347	4807419	WASTE FLAMMABLE LIQUIDS, TOXIC, N.O.S.	OK
120	349	4912550	ELEVATED TEMPERATURE, LIQUID, FLAMMABLE	OK
121	351	4912507	ELEVATED TEMPERATURE LIQUID, FLAMMABLE	OK
122	353	4910132	COAL TAR DISTILLATES, FLAMMABLE	OK
123	360	4910306	FLAMMABLE LIQUIDS, N.O.S.	OK
129	372	4907875	FLAMMABLE LIQUIDS, N.O.S.	OK
130	374	4912044	FORMALDEHYDE, SOLUTIONS, FLAMMABLE	OK
131	376	4909383	PETROLEUM DISTILLATES, N.O.S.	OK
132	386	4912032	N-AMYL METHYL KETONE	OK
133	388	4908156	DIETHYL ETHER	OK
135	392	4912298	PETROLEUM DISTILLATES, N.O.S.	OK
137	396	4912811	ELEVATED TEMPERATURE, LIQUID, FLAMMABLE	OK
138	399	4912045	FORMALDEHYDE, SOLUTIONS, FLAMMABLE	OK
140	405	4909219	FLAMMABLE LIQUIDS, N.O.S.	OK
141	408	4909328	FLAMMABLE LIQUIDS, N.O.S.	OK
142	412	4909349	XYLENES	OK
143	414	4910410	FLAMMABLE LIQUIDS, N.O.S.	OK
144	417	4912213	FUEL OIL	OK
145	418	4907614	ESTERS, N.O.S.	OK
147	420	4909277	PYRIDINE	OK
148	426	4910171	FLAMMABLE LIQUIDS, N.O.S.	OK
149	428	4810119	WASTE FLAMMABLE LIQUIDS	OK
150	430	4909150	DIETHYL KETONE	OK
151	432	4912035	DIETHYLBENZENE	OK

Rank in Class	Rank in Total	Haz Mat Code	Tank Car (only) for Year 2001 Hazard Class 3(a) Flammable Liquids Description	VB Code
152	439	4909149	DIACETONE ALCOHOL	ОК
153	440	4909251	FLAMMABLE LIQUIDS, N.O.S.	OK
154	443	4907241	FLAMMABLE LIQUIDS, N.O.S.	OK
155	449	4912233	COAL TAR DISTILLATES, FLAMMABLE	OK
156	451	4909135	N,N-DIMETHYLFORMAMIDE	OK
158	453	4910488	FLAMMABLE LIQUIDS, N.O.S.	OK
159	460	4909356	TOLUENE	OK
160	462	4912646	ALCOHOLS, N.O.S.	OK
161	480	4910225	ALCOHOLIC BEVERAGES	OK
162	481	4909179	PICOLINES	OK
163	483	4909111	AMYL ACETATES	OK
164	491	4909301	PENTANOLS	OK
166	498	4908285	TETRAHYDROFURAN	OK
167	499	4909158	DIOXOLANE	OK
169	505	4910485	FLAMMABLE LIQUIDS, N.O.S.	OK
170	510	4910326	TURPENTINE	OK
171	515	4909208	ISOBUTYRONITRILE	OK
172	529	4909366	ISOBUTYRIC ACID	OK
173	531	4907846	MORPHOLINE	OK
174	532	4912120	BUTYL BENZENES	OK
175	534	4910186	FLAMMABLE LIQUIDS, N.O.S.	OK
176	537	4907878	FLAMMABLE LIQUIDS, N.O.S.	OK
177	539	4908195	DIISOPROPYL ETHER	OK
180	546	4909211	ISOPROPYLBENZENE	OK
181	552	4912813	ELEVATED TEMPERATURE, LIQUID, FLAMMABLE	OK
182	554	4912539	ISOBUTYL ISOBUTYRATE	OK
183	557	4910313	TURPENTINE	OK
184	573	4912662	5-METHYLHEXAN-2-ONE	OK
185	582	4910224	FLAMMABLE LIQUIDS, N.O.S.	OK
186	584	4912361	TARS, LIQUID	OK
187	588	4912040	DIISOBUTYL KETONE	OK
188	590	4909281	PROPIONITRILE	OK
189	591	4912244	PINE OIL	OK
190	592	4910179	KETONES, LIQUID, N.O.S.	OK
191	593	4907690	SODIUM METHYLATE SOLUTIONS	OK
192	594	4912273	FLAMMABLE LIQUIDS, N.O.S.	OK
193	599	4908160	PROPANETHIOLS	OK
194	600	4909133	BUTYL MERCAPTANS	OK
195	601	4910201	FLAMMABLE LIQUIDS, N.O.S.	OK
196	604	4909239	FLAMMABLE LIQUIDS, N.O.S.	OK
197	606	4909266	ALPHA-PINENE	OK
198	616	4809230	WASTE METHANOL	OK

Rank in Class	Rank in Total	Haz Mat Code	Tank Car (only) for Year 2001 Hazard Class 3(a) Flammable Liquids Description	VB Code
200	622	4908225	METHYL FORMATE	OK
201	625	4909377	METHANOL	OK
202	626	4909101	ACETALDEHYDE OXIME	OK
203	629	4909378	METHANOL	OK
204	639	4910209	FLAMMABLE LIQUIDS, N.O.S.	OK
205	641	4912290	FLAMMABLE LIQUIDS, N.O.S.	OK
206	645	4909343	TERPENE HYDROCARBONS, N.O.S.	OK
207	648	4910234	FLAMMABLE LIQUIDS, CORROSIVE, N.O.S.	OK
208	650	4909193	NITROPROPANES	OK
209	653	4912236	COAL TAR DISTILLATES, FLAMMABLE	OK
210	655	4909227	ISOPROPANOL	OK
211	656	4910316	FLAMMABLE LIQUIDS, N.O.S.	OK
212	659	4909380	METHANOL	OK
213	660	4910480	FLAMMABLE LIQUIDS, N.O.S.	OK
215	669	4910130	FLAMMABLE LIQUIDS, N.O.S.	OK
216	672	4912414	TURPENTINE	OK
217	673	4910113	FLAMMABLE LIQUIDS, N.O.S.	OK
218	675	4909395	XYLENES	OK
219	676	4910318	FLAMMABLE LIQUIDS, N.O.S.	OK
220	677	4912335	FUEL OIL	OK
222	680	4910309	ALCOHOLIC BEVERAGES	OK
223	684	4907885	FLAMMABLE LIQUIDS, N.O.S.	OK
224	685	4912286	HYDROCARBONS, LIQUID, N.O.S.	OK
225	692	4810242	WASTE PETROLEUM DISTILLATES, N.O.S.	OK
226	693	4910431	ALCOHOLS, FLAMMABLE, TOXIC, N.O.S.	OK
227	694	4909216	METHYL PROPYL KETONE	OK
228	699	4908135	CYCLOPENTANE	OK
229	700	4909391	XYLENES	OK
231	708	4910414	COMPOUNDS, CLEANING LIQUID	OK
232	709	4912525	FLAMMABLE LIQUIDS, N.O.S.	OK
233	710	4912816	ELEVATED TEMPERATURE, LIQUID, FLAMMABLE	OK
234	718	4910105	FLAMMABLE LIQUIDS, N.O.S.	OK
235	723	4909196	N-PROPANOL	OK
236	724	4912017	ETHYLENE GLYCOL MONOETHYL ETHER ACETATE	OK
238	726	4912380	FLAMMABLE LIQUIDS, N.O.S.	OK
239	730	4910175	FLAMMABLE LIQUIDS, N.O.S.	OK
240	736	4809195	WASTE FLAMMABLE LIQUIDS	OK
241	737	4910405	ALCOHOLS, N.O.S.	OK
242	738	4909229	ISOPROPANOL	OK
243	741	4910184	FLAMMABLE LIQUIDS, N.O.S.	OK
244	744	4907891	FLAMMABLE LIQUIDS, N.O.S.	OK

Rank in Class	Rank in Total	Haz Mat Code	Tank Car (only) for Year 2001 Hazard Class 3(a) Flammable Liquids Description	VB Code
245	745	4909261	ALCOHOLS, N.O.S.	OK
246	746	4909284	WOOD PRESERVATIVES, LIQUID	OK
247	747	4912310	FLAMMABLE LIQUIDS, N.O.S.	OK
248	753	4912815	ELEVATED TEMPERATURE, LIQUID, FLAMMABLE	ОК
249	757	4907255	FLAMMABLE LIQUIDS, N.O.S.	OK
250	758	4910168	FLAMMABLE LIQUIDS, N.O.S.	OK
251	759	4910220	TARS, LIQUID	OK
252	760	4910395	FLAMMABLE LIQUIDS, N.O.S.	OK
253	761	4912062	ETHYLENE GLYCOL MONOMETHYL ETHER	OK
254	762	4912336	FUEL OIL	OK
255	774	4807241	WASTE FLAMMABLE LIQUIDS	OK
256	775	4912660	FLAMMABLE LIQUIDS, N.O.S.	OK
257	776	4912185	HEATING OIL, LIGHT	OK
126	365	4910535	FLAMMABLE LIQUIDS, N.O.S.	OK
Notes:	(ok)	No intrinsic c	hemical property reason for not employing V&B action.	

# Table A-4(b). Hazard Material Class 3(a), Flammable Liquids. V&B Action Would Carry Increased Risk Relative to Propane. (Ranked per relative frequency of shipments in 2001)

Rank in Class	Rank in Total	Haz Mat Code	For Year 2001 Hazard Class 3(a) Flammable Liquids Description	VB Code
134	391	4907829	FLAMMABLE LIQUIDS, CORROSIVE, N.O.S.	?
99	288	4907630	METHYLTRICHLOROSILANE	ENV
124	361	4909265	1,2-DICHLOROPROPANE	ENV
125	364	4907680	TRIMETHYLCHLOROSILANE	ENV
139	402	4907820	DIMETHYLAMINE, SOLUTION	ENV
146	419	4907877	TRIETHYLAMINE	ENV
157	452	4907815	DIETHYLAMINE	ENV
165	496	4909157	DIPROPYLAMINE	ENV
214	668	4907610	DIMETHYLDICHLOROSILANE	ENV
221	679	4908169	ETHYL MERCAPTAN	ENV
230	704	4908151	DIMETHYL SULFIDE	ENV
237	725	4912353	ETHYLAMINE, AQUEOUS SOLUTION	ENV
68	189	4908194	ISOPROPYLAMINE	ENV
74	210	4907412	ALLYL CHLORIDE	ENV
102	294	4909255	DICHLOROPROPENES	ENV
115	334	4909153	CHLOROBENZENE	ENV
119	348	4907840	METHYLAMINE, AQUEOUS SOLUTION	ENV
178	544	4907801	AMINES, FLAMMABLE, CORROSIVE, N.O.S.	ENV
23	70	4909166	ETHYLENE DICHLORIDE	ENV
3	17	4907265	STYRENE MONOMER, STABILIZED	SR
8	33	4907270	VINYL ACETATE, STABILIZED	SR
11	39	4907250	METHYL METHACRYLATE MONOMER, STABILIZED	SR
15	50	4912215	BUTYL ACRYLATES, STABILIZED	SR
21	62	4906420	ACRYLONITRILE, STABILIZED	SR
38	116	4907215	ETHYL ACRYLATE, STABILIZED	SR
72	204	4907245	METHYL ACRYLATE, STABILIZED	SR
96	280	4909209	DIISOBUTYLENE, ISOMERIC COMPOUNDS	SR
127	367	4907251	METHYL METHACRYLATE MONOMER, STABILIZED	SR
128	370	4907235	STYRENE MONOMER, STABILIZED	SR
136	395	4912235	N-BUTYL METHACRYLATE, STABILIZED	SR
168	500	4912275	VINYLTOLUENES, STABILIZED	SR
199	617	4908144	1,2-BUTYLENE OXIDE, STABILIZED	SR
57	153	4907280	VINYLIDENE CHLORIDE, STABILIZED	SR/ENV
44	128	4907230	ISOPRENE, STABILIZED	SR/PHF/ENV
66	186	4907223	CHLOROPRENE, STABILIZED	SR/PHF/ENV
179	545	4908128	2-CHLOROPROPENE	SR/PHF/ENV
Notes:	(ok)	•	hemical property reason for not employing V&B action.	·
	(sr)		If-reactive if exposed to fire.	
	(phf)		ock sensitive because of positive heat of formation.	
	(env)		n environmental risk due to presence of amine or halogen o	ompounds.

Rank in Class	Rank in Total	Haz Mat Code	For Year 2001 Hazard Class 3(b) Combustible Liquids Description	VB Code
108	688	4914275	VINYL TOLUENE, STABILIZED	SR
1	11	4912210		OK
2	21	4914166	DIESEL FUEL	OK
3	31	4914164	FUEL OIL	OK
4	37	4905424		OK
5	42	4915165	PETROLEUM CRUDE OIL	OK
6	53	4914168	FUEL OIL	OK
7	55	4905439		OK
8	57	4914256	PETROLEUM DISTILLATES, N.O.S.	OK
9	81	4905437		OK
10	83	4914848	FUEL OIL	OK
11	92	4913250	COMBUSTIBLE LIQUID, N.O.S.	OK
12	96	4915399	COMBUSTIBLE LIQUID, N.O.S.	OK
13	100	4914170	DIESEL FUEL	OK
14	113	4915185	COMBUSTIBLE LIQUID, N.O.S.	OK
15	118	4905427		OK
16	121	4914108	COMBUSTIBLE LIQUID, N.O.S.	OK
17	125	4914247	PETROLEUM DISTILLATES, N.O.S.	OK
18	139	4914851	FUEL OIL	OK
19	167	4950110	FAK-HAZARDOUS MATERIALS	OK
20	192	4915407	COMBUSTIBLE LIQUID, N.O.S.	OK
21	207	4914009	COMBUSTIBLE LIQUID, N.O.S.	OK
22	211	4914109	COMBUSTIBLE LIQUID, N.O.S.	OK
23	226	4912082		OK
24	239	4913262	PROPYLENE TETRAMER	OK
25	238	4914135	N,N-DIMETHYLFORMAMIDE	OK
26	241	4913273	COMBUSTIBLE LIQUID, N.O.S.	OK
27	254	4914215	FUEL, AVIATION, TURBINE ENGINE	OK
28	256	4914001	COMBUSTIBLE LIQUID, N.O.S.	OK
29	257	4915590	COMBUSTIBLE LIQUID, N.O.S.	OK
30	262	4950150	FAK-HAZARDOUS MATERIALS	OK
31	261	4913128	ALCOHOLS, N.O.S.	OK
32	267	4915776	COMBUSTIBLE LIQUID, N.O.S.	OK
33	270	4950130	FAK-HAZARDOUS MATERIALS	OK
34	272	4913101	COMBUSTIBLE LIQUID, N.O.S.	OK
35	286	4905419		OK
36	296	4914110	GAS OIL	OK
37	300	4914014	OCTYL ALDEHYDES	OK
38	303	4914026	HYDROCARBONS, LIQUID, N.O.S.	OK
39	304	4914172	COMBUSTIBLE LIQUID, N.O.S.	OK
40	307	4914250	PETROLEUM OIL	OK

# Table A-5. Hazard Material Class 3(b), Combustible Liquids. Compounds Where V&BAction Would Carry Increased Risk Relative to Propane Are Indicated by VB Code.<br/>(Ranked per relative frequency of shipments in 2001)

Rank in Class	Rank in Total	Haz Mat Code	For Year 2001 Hazard Class 3(b) Combustible Liquids Description	VB Code
41	328	4914246	PETROLEUM DISTILLATES, N.O.S.	OK
42	326	4913270	ESTERS, N.O.S.	OK
43	340	4914854	ALCOHOLS, N.O.S.	OK
44	357	4940364		OK
45	363	4915378	COMBUSTIBLE LIQUID, N.O.S.	OK
46	379	4913271	HYDROCARBONS, LIQUID, N.O.S.	OK
47	389	4913158	ALCOHOLS, N.O.S.	OK
48	407	4915473	COMBUSTIBLE LIQUID, N.O.S.	OK
49	409	4913263	ALCOHOLS, N.O.S.	OK
50	410	4914041	COMBUSTIBLE LIQUID, N.O.S.	OK
51	421	4914852	KEROSENE	OK
52	422	4915777	COMBUSTIBLE LIQUID, N.O.S.	OK
53	424	4913230	COMBUSTIBLE LIQUID, N.O.S.	OK
54	427	4915276	COMBUSTIBLE LIQUID, N.O.S.	OK
55	431	4914013	HEXANOLS	OK
56	437	4915209	COMBUSTIBLE LIQUID, N.O.S.	OK
57	438	4905438		OK
58	441	4913102	COMBUSTIBLE LIQUID, N.O.S.	OK
59	442	4914211	ISOPROPYLBENZENE	OK
60	454	4908101		OK
61	457	4914251	PAINT	OK
62	465	4909278		OK
63	464	4913111	COMBUSTIBLE LIQUID, N.O.S.	OK
64	473	4860105		OK
65	484	4914050	COMBUSTIBLE LIQUID, N.O.S.	OK
66	495	4950120	FAK-HAZARDOUS MATERIALS	OK
67	497	4909151		OK
68	504	4914016	COMBUSTIBLE LIQUID, N.O.S.	OK
69	501	4913150	COMBUSTIBLE LIQUID, N.O.S.	OK
70	509	4860124		OK
71	507	4914165	KEROSENE	OK
72	520	4914005	COMBUSTIBLE LIQUID, N.O.S.	OK
73	518	4914849	COMBUSTIBLE LIQUID, N.O.S.	OK
74	523	4915289	COMBUSTIBLE LIQUID, N.O.S.	OK
75	536	4915582	COMBUSTIBLE LIQUID, N.O.S.	OK
76	541	4915382	COMBUSTIBLE LIQUID, N.O.S.	OK
77	542	4915505	COMBUSTIBLE LIQUID, N.O.S.	OK
78	547	4914042	COMBUSTIBLE LIQUID, N.O.S.	OK
79	548	4914119	ALCOHOLS, N.O.S.	OK
80	553	4914007	ALCOHOLS, N.O.S.	OK
81	558	4913246	COMBUSTIBLE LIQUID,N.O.S.	OK
82	568	4904290		OK
83	569	4915111		OK
84	565	4915392	COMBUSTIBLE LIQUID, N.O.S.	OK
85	572	4914121	COMBUSTIBLE LIQUID, N.O.S.	OK

Rank in Class	Rank in Total	Haz Mat Code	For Year 2001 Hazard Class 3(b) Combustible Liquids Description	VB Code
86	578	4913256	COMBUSTIBLE LIQUID, N.O.S.	OK
87	579	4915291	COMBUSTIBLE LIQUID, N.O.S.	OK
88	585	4914134	N-AMYL METHYL KETONE	OK
89	589	4914051	ISOPROPENYLBENZENE	OK
90	595	4915101	ALCOHOLS, N.O.S.	OK
91	596	4915471	COMBUSTIBLE LIQUID, N.O.S.	OK
92	597	4915497	COMBUSTIBLE LIQUID, N.O.S.	OK
93	602	4914120	FORMALDEHYDE SOLUTIONS, FLAMMABLE	OK
94	609	4914855	ALCOHOLS, N.O.S.	OK
95	610	4915301	COMBUSTIBLE LIQUID, N.O.S.	OK
96	614	4914011	COMBUSTIBLE LIQUID, N.O.S.	OK
97	615	4932359		OK
98	627	4913232	COMBUSTIBLE LIQUID, N.O.S.	OK
99	636	4914264	PETROLEUM DISTILLATES, N.O.S.	OK
100	631	4813103	WASTE COMBUSTIBLE LIQUID	OK
101	632	4915148	COMBUSTIBLE LIQUID, N.O.S.	OK
102	633	4915389	COMBUSTIBLE LIQUID, N.O.S.	OK
103	651	4914122	COMBUSTIBLE LIQUID, N.O.S.	OK
104	661	4913105	COMBUSTIBLE LIQUID, N.O.S.	OK
105	678	4915747	COMBUSTIBLE LIQUID, N.O.S.	OK
106	686	4913260	COMBUSTIBLE LIQUID, N.O.S.	OK
107	687	4914208	COMBUSTIBLE LIQUID, N.O.S.	OK
109	711	4915121	COMBUSTIBLE LIQUID, N.O.S.	OK
110	740	4904120		OK
111	731	4913104	COMBUSTIBLE LIQUID, N.O.S.	OK
112	720	4850130	FREIGHT ALL KINDS, HAZARDOUS WASTES	OK
113	748	4815185	WASTE COMBUSTIBLE LIQUID	OK
114	749	4913253	COMBUSTIBLE LIQUID, N.O.S.	OK
115	750	4915349	COMBUSTIBLE LIQUID, N.O.S.	OK
116	754	4913106	COMBUSTIBLE LIQUID, N.O.S.	OK
117	755	4815130	WASTE COMBUSTIBLE LIQUID	OK
118	763	4914040	COMBUSTIBLE LIQUID, N.O.S.	OK
119	764	4914147	COMPOUNDS, CLEANING,LIQUID	OK
120	765	4914220	TARS, LIQUID	OK
121	781	4807251		OK
Notes:	(ok)		chemical property reason for not employing V&B action	
110163.	(sr)		elf-reactive if exposed to fire.	
	(phf)	Potentially s	hock sensitive because of positive heat of formation.	
	(env)	Potential hig compounds.	h environmental risk due to presence of amine or halog	gen

# Table A-6. Hazard Material Class 4 Flammable Solid. For All Compounds, V&B Action Would Carry Increased Risk Relative to Propane as Indicated by VB Code. (Ranked per relative frequency of shipments in 2001)

Rank in Class	Rank in Total	Haz Mat Code	For Year 2001 Hazard Class 4 Flammable Solid Description	VB Code
1	18	4917403	SULFUR, MOLTEN -(4.1)	ENV
2	103	4916141	PHOSPHORUS, WHITE, DRY -(4.2)	ENV
3	182	4917473	NAPHTHALENE, MOLTEN -(4.1)	ENV
4	214	4917459	NAPHTHALENE, MOLTEN -(4.1)	ENV
5	274	4916456	SODIUM -(4.3)	ENV
6	394	4916127	ALUMINUM ALKYLS -(4.2)	ENV
7	398	4916365	METHYLDICHLOROSILANE -(4.3)	ENV
8	435	4916323	TRICHLOROSILANE -(4.3)	ENV
9	512	4916490	ORGANOMETALLIC COMPOUND, WATER-REACTIVE, -(4.3)	ENV
10	640	4816300	WASTE CHLOROSILANES, WATER-REACTIVE, -(4.3)	ENV
11	732	4916302	CHLOROSILANES, WATER-REACTIVE, -(4.3)	ENV
12	742	4916205	PYROPHORIC ORGANOMETALLIC COMPOUND, -(4.2)	ENV
Notes:	(ok)	No intrinsic ch	nemical property reason for not employing V&B action.	
	(sr)	Potentially se	f-reactive if exposed to fire.	
	(phf)	Potentially sh	ock sensitive because of positive heat of formation.	
	(env)		environmental risk due to presence of amine or halogen compounds dous combustion products.	

# Table A-7. Hazard Material Class 5.1, Oxidizers. For All Compounds, V&B Action Would Carry Increased Risk Relative to Propane as Indicated by VB Code. (Ranked per relative frequency of shipments in 2001)

Rank in Class	Rank in Total	Haz Mat Code	For Year 2001 Hazard Class 5.1 Oxidizers Description	VB Code
1	36	4918335	HYDROGEN PEROXIDE, STABILIZED	SR
2	71	4918765	SODIUM CHLORATE, AQUEOUS SOLUTION	ENV
3	89	4918774	AMMONIUM NITRATE, LIQUID	SR
4	129	4918775	HYDROGEN PEROXIDE, AQUEOUS SOLUTIONS	SR
5	196	4918510	CHROMIUM TRIOXIDE, ANHYDROUS	ENV
6	384	4918531	NITRITES, INORGANIC, AQUEOUS SOLUTION,	SR
7	517	4918311	AMMONIUM NITRATE	ENV
8	664	4918761	OXIDIZING SOLID, N.O.S.	SR
9	702	4918746	SODIUM NITRATE	ENV
10	654	4918723	SODIUM CHLORATE	ENV
Notes:	(ok)	No intrinsic	chemical property reason for not employing V&B action.	
	(sr)	Potentially s	elf reactive if exposed to fire.	
	(phf)	Potentially s	hock sensitive because of positive heat of formation.	
	(env)		h environmental risk due to presence of amine or halogen or very hazardous combustion products.	

# Table A-8. Hazard Material Class 6.1, Poisonous. For all Compounds, V&B Action Would<br/>Carry a Special Increased Risk Relative to Propane due to Toxic Characteristic.<br/>(Ranked per relative frequency of shipments in 2001)

Rank in Class	Rank in Total	Haz Mat Code	For Year 2001 Hazard Class 6.1 Poisonous Description	VB Code
1	24	4921598	PHENOL, MOLTEN	ENV-TOX
2	51	4921575	TOLUENE DIISOCYANATE	ENV-TOX
3	132	4925206	4-THIAPENTANAL	ENV-TOX
4	140	4925182	1,1,1-TRICHLOROETHANE	ENV-TOX
5	156	4921005	EPICHLOROHYDRIN	ENV-TOX
6	157	4921410	ANILINE	ENV-TOX
7	169	4925225	CHLOROFORM	ENV-TOX
8	171	4925212	ADIPONITRILE	ENV-TOX
9	175	4925202	TETRACHLOROETHYLENE	ENV-TOX
10	191	4921401	ACETONE CYANOHYDRIN, STABILIZED	ENV-TOX
11	199	4925123	ACRYLAMIDE	ENV-TOX
12	212	4921455	NITROBENZENE	ENV-TOX
13	222	4925312	TOXIC LIQUID, INORGANIC, N.O.S.	ENV-TOX
14	224	4925175	2,4-TOLUYLENEDIAMINE	ENV-TOX
15	227	4925131	DICHLOROMETHANE	ENV-TOX
16	235	4923227	SODIUM CYANIDE	ENV-TOX
17	251	4927014	HYDROGEN CYANIDE, STABILIZED	ENV-TOX
18	259	4921475	TOXIC LIQUIDS, ORGANIC, N.O.S.	ENV-TOX
19	275	4921016	PHOSPHORUS TRICHLORIDE	ENV-TOX
20	278	4925275	TOXIC LIQUIDS, ORGANIC, N.O.S.	ENV-TOX
21	310	4921496	SILICON TETRACHLORIDE	ENV-TOX
22	315	4925233	TOXIC LIQUIDS, INORGANIC, N.O.S.	ENV-TOX
23	325	4921047	FURALDEHYDES	ENV-TOX
24	332	4925121	TRICHLOROBENZENES, LIQUID	ENV-TOX
25	354	4925005	NITRILES, TOXIC, N.O.S.	ENV-TOX
26	355	4923106	ARSENIC ACID, LIQUID	ENV-TOX
27	358	4825021	WASTE PHENOL SOLUTIONS	ENV-TOX
28	366	4921485	TOLUIDINES	ENV-TOX
29	369	4925176	PHENYLENEDIAMINES	ENV-TOX
30	373	4921210	PHENOL SOLUTIONS	ENV-TOX
31	375	4927016	TOXIC LIQUIDS, FLAMMABLE, ORGANIC, N.O.S.	ENV-TOX
32	387	4921831	CARBON TETRACHLORIDE	ENV-TOX
33	390	4921706	CRESOLS	ENV-TOX

Rank in Class	Rank in Total	Haz Mat Code	For Year 2001 Hazard Class 6.1 Poisonous Description	VB Code
34	404	4921278	TOXIC LIQUID, CORROSIVE, INORGANIC, N.O.S.	ENV-TOX
35	415	4925203	O-DICHLOROBENZENE	ENV-TOX
36	416	4921060	TOXIC LIQUIDS, FLAMMABLE, ORGANIC, N.O.S.	ENV-TOX
37	423	4925262	TOXIC, LIQUIDS, ORGANIC, N.O.S.	ENV-TOX
38	429	4925181	TRICHLOROETHYLENE	ENV-TOX
39	434	4921457	CHLORONITROBENZENES	ENV-TOX
40	436	4921019	ALLYL ALCOHOL	ENV-TOX
41	444	4925208	FURFURYL ALCOHOL	ENV-TOX
42	445	4925126	4,4'-DIAMINODIPHENYL METHANE	ENV-TOX
43	450	4921459	CHLORONITROBENZENE	ENV-TOX
44	469	4921405	DIMETHYL SULFATE	ENV-TOX
45	477	4921414	CHLOROPICRIN	ENV-TOX
46	487	4925302	TOXIC, LIQUIDS, ORGANIC, N.O.S.	ENV-TOX
47	506	4921579	HEXAMETHYLENE DIISOCYANATE	ENV-TOX
48	513	4921203	TOXIC LIQUIDS, CORROSIVE, ORGANIC, N.O.S.	ENV-TOX
49	514	4921606	CRESYLIC ACID	ENV-TOX
50	533	4923114	CHLOROACETIC ACID, SOLUTION	ENV-TOX
51	549	4921237	TOXIC LIQUID, CORROSIVE, INORGANIC, N.O.S.	ENV-TOX
52	567	4923945	TOXIC, LIQUIDS, ORGANIC, N.O.S.	ENV-TOX
53	570	4925107	ISOPHORONE DIISOCYANATE	ENV-TOX
54	586	4925148	PHENETIDINES	ENV-TOX
55	598	4821210	WASTE PHENOL SOLUTIONS	ENV-TOX
56	618	4921064	TOXIC LIQUIDS, FLAMMABLE, ORGANIC, N.O.S.	ENV-TOX
57	621	4921638	CHLORONITROBENZENE	ENV-TOX
58	628	4925081	ARSENICAL PESTICIDES, LIQUID, TOXIC	ENV-TOX
59	634	4925193	AMMONIUM FLUORIDE	ENV-TOX
60	637	4921483	TOLUIDINES	ENV-TOX
61	644	4921722	HEXACHLOROCYCLOPENTADIENE	ENV-TOX
62	646	4921466	NITROANILINES	ENV-TOX
63	662	4921264	TOXIC LIQUID, CORROSIVE, INORGANIC, N.O.S.	ENV-TOX
64	681	4921231	METAL CARBONYLS, N.O.S.	ENV-TOX
65	683	4821236	WASTE TOXIC LIQUID, CORROSIVE, INORGANIC	ENV-TOX
66	703	4921648	THIOGLYCOL	ENV-TOX
67	705	4921306	2-ETHYLHEXYL CHLOROFORMATE	ENV-TOX
68	712	4921020	ETHYL CHLOROFORMATE	ENV-TOX
69	743	4921032	MOTOR FUEL ANTI-KNOCK MIXTURES	ENV-TOX

Rank in Class	Rank in Total	Haz Mat Code	For Year 2001 Hazard Class 6.1 Poisonous Description	VB Code			
70	766	4921233	TOXIC LIQUID, INORGANIC, N.O.S.	ENV-TOX			
71	767	4927008	METHYL CHLOROFORMATE	ENV-TOX			
72	777	4921787	XYLENOLS	ENV-TOX			
73	779	4921656	ORGANOPHOSPHORUS PESTICIDES, LIQUID	ENV-TOX			
Notes:							

# Table A-9. Hazard Material Class 8, Corrosive Materials. For All Compounds, V&B ActionWould Carry a Special Increased Risk Relative to Propane due to Corrosive Characteristics.See notes at bottom of table. (Ranked per relative frequency of shipments in 2001)

Rank in Class	Rank in Total	Haz Mat Code	For Year 2001 Hazard Class 8 Corrosive Description	VB Code
1	2	4935240	SODIUM HYDROXIDE SOLUTION	ENV-COR
2	3	4930040	SULFURIC ACID	ENV-COR
3	14	4930228	HYDROCHLORIC ACID	ENV-COR
4	15	4930247	PHOSPHORIC ACID	ENV-COR
5	32	4930042	SULFURIC ACID, SPENT	ENV-COR
6	35	4930248	PHOSPHORIC ACID	ENV-COR
7	41	4931405	ACRYLIC ACID, STABILIZED	SR/ENV- COR
8	43	4935230	POTASSIUM HYDROXIDE, SOLUTION	ENV-COR
9	45	4935640	HEXAMETHYLENEDIAMINE, SOLID	ENV-COR
10	49	4931303	ACETIC ACID, GLACIAL	ENV-COR
11	58	4932059	FORMALDEHYDE SOLUTIONS	ENV-COR
12	66	4932342	FERRIC CHLORIDE, SOLUTION	ENV-COR
13	69	4930024	HYDROGEN FLUORIDE, ANHYDROUS	ENV-COR
14	78	4932329	FERROUS CHLORIDE, SOLUTION	ENV-COR
15	80	4931304	ACETIC ANHYDRIDE	ENV-COR
16	88	4930030	SULFURIC ACID, FUMING	ENV-COR
17	90	4936330	MALEIC ANHYDRIDE	ENV-COR
18	94	4930026	FLUOROSILICIC ACID	ENV-COR
19	95	4930223	NITRIC ACID	ENV-COR
20	106	4935645	HEXAMETHYLENEDIAMINE SOLUTION	ENV-COR
21	142	4935268	SODIUM HYDROSULFIDE SOLUTION	ENV-COR
22	154	4936653	CORROSIVE LIQUIDS, N.O.S.	ENV-COR
23	155	4931702	CORROSIVE LIQUID, ACIDIC, ORGANIC, N.O.S.	ENV-COR
24	162	4930050	SULFUR TRIOXIDE, STABILIZED	ENV-COR
25	173	4935665	ETHANOLAMINE	ENV-COR
26	174	4935260	SODIUM ALUMINATE, SOLUTION	ENV-COR
27	190	4932376	BISULFITES, AQUEOUS SOLUTIONS, N.O.S.	ENV-COR
28	193	4936015	CORROSIVE LIQUIDS, TOXIC, N.O.S.	ENV-COR
29	209	4931463	CORROSIVE LIQUID, ACIDIC, INORGANIC, N.O.S.	ENV-COR
30	218	4931447	PROPIONIC ACID	ENV-COR
31	219	4931485	ALKYLPHENOLS, SOLID, N.O.S.	ENV-COR
32	221	4935263	CORROSIVE LIQUID, BASIC, ORGANIC, N.O.S.	ENV-COR
33	223	4935219	CAUSTIC ALKALI LIQUIDS, N.O.S.	ENV-COR
34	234	4936606	ALUMINUM CHLORIDE, SOLUTION	ENV-COR
35	237	4935603	CAUSTIC ALKALI LIQUIDS, N.O.S.	ENV-COR
36	240	4935258	CORROSIVE LIQUID, BASIC, INORGANIC, N.O.S.	ENV-COR
37	243	4931486	ALKYLPHENOLS, LIQUID, N.O.S.	ENV-COR
38	245	4930066	SULFURIC ACID, FUMING	ENV-COR
39	246	4931401	ACETIC ACID SOLUTION	ENV-COR
40	248	4935220	CAUSTIC ALKALI LIQUIDS, N.O.S.	ENV-COR

Rank in Class	Rank in Total	Haz Mat Code	For Year 2001 Hazard Class 8 Corrosive Description	VB Code
41	252	4936526	CORROSIVE LIQUIDS, N.O.S.	ENV-COR
42	258	4930251	METHACRYLIC ACID, STABILIZED	SR/ENV- COR
43	265	4935601	AMINES, LIQUID, CORROSIVE, N.O.S.	ENV-COR
44	268	4931320	FORMIC ACID	ENV-COR
45	273	4931466	CORROSIVE LIQUID, ACIDIC, ORGANIC, N.O.S.	ENV-COR
46	276	4932022	CORROSIVE LIQUID, ACIDIC INORGANIC, N.O.S.	ENV-COR
47	277	4936655	CORROSIVE LIQUIDS, N.O.S	ENV-COR
48	283	4935206	SODIUM HYDROXIDE SOLUTION	ENV-COR
49	287	4936601	CORROSIVE LIQUIDS, FLAMMABLE, N.O.S.	ENV-COR
50	290	4935226	CAUSTIC ALKALI LIQUIDS, N.O.S.	ENV-COR
51	297	4935274	SODIUM ALUMINATE, SOLUTION	ENV-COR
52	298	4932031	CORROSIVE LIQUID, BASIC, INORGANIC, N.O.S.	ENV-COR
53	302	4932348	BISULFITES, AQUEOUS SOLUTIONS, N.O.S.	ENV-COR
54	306	4931484	2-DIMETHYLAMINOETHANOL	ENV-COR
55	311	4930201	CORROSIVE LIQUIDS, N.O.S.	ENV-COR
56	312	4932030	CORROSIVE LIQUID, ACIDIC, ORGANIC, N.O.S.	ENV-COR
57	313	4935208	CAUSTIC ALKALI LIQUIDS, N.O.S.	ENV-COR
58	319	4932332	CORROSIVE LIQUIDS, N.O.S.	ENV-COR
59	321	4936076	CORROSIVE LIQUIDS, TOXIC, N.O.S.	ENV-COR
60	322	4932309	ALKYL SULFONIC ACIDS, LIQUID	ENV-COR
61	330	4935211	AMINES, LIQUID, CORROSIVE, FLAMMABLE	ENV-COR
62	331	4930204	CHLOROSULFONIC ACID	ENV-COR
63	336	4936351	CORROSIVE LIQUIDS, N.O.S.	ENV-COR
64	346	4931421	AMINES, LIQUID, CORROSIVE, N.O.S.	ENV-COR
65	352	4931490	CORROSIVE LIQUID, ACIDIC, INORGANIC, N.O.S.	ENV-COR
66	356	4830221	WASTE CORROSIVE LIQUIDS, N.O.S.	ENV-COR
67	382	4935248	CORROSIVE LIQUIDS, N.O.S.	ENV-COR
68	385	4935609	BISULFITES, AQUEOUS SOLUTION, N.O.S.	ENV-COR
69	393	4935284	SODIUM BOROHYDRIDE AND SODIUM HYDROXIDE	ENV-COR
70	397	4935608	CORROSIVE LIQUIDS, N.O.S.	ENV-COR
71	401	4930231	HYDROCHLORIC ACID	ENV-COR
72	406	4931492	2-DIMETHYLAMINOETHANOL	ENV-COR
73	411	4930218	NITRATING ACID MIXTURES	ENV-COR
74	425	4932385	TITANIUM TETRACHLORIDE	ENV-COR
75	433	4930221	CORROSIVE LIQUIDS, N.O.S.	ENV-COR
76	446	4930017	CORROSIVE LIQUID, ACIDIC, INORGANIC, N.O.S.	ENV-COR
77	448	4936110	BROMINE	ENV-COR
78	455	4935280	AMMONIA SOLUTIONS	ENV-COR
79	458	4932370	SILICON TETRACHLORIDE	ENV-COR
80	459	4931487	ALKYLPHENOLS, LIQUID, N.O.S.	ENV-COR
81	461	4935234	AMMONIA SOLUTIONS	ENV-COR
82	466	4835240	WASTE SODIUM HYDROXIDE	ENV-COR
83	467	4936343	AMMONIUM SULFIDE SOLUTION	ENV-COR
84	468	4932384	ZINC CHLORIDE, SOLUTION	ENV-COR

Rank in Class	Rank in Total	Haz Mat Code	For Year 2001 Hazard Class 8 Corrosive Description	VB Code
85	472	4936219	AMINES, SOLID, CORROSIVE, N.O.S.	ENV-COR
86	479	4935628	ETHYLENEDIAMINE	ENV-COR
87	482	4935221	CAUSTIC ALKALI LIQUIDS, N.O.S.	ENV-COR
88	485	4931431	CORROSIVE LIQUIDS, N.O.S.	ENV-COR
89	492	4935276	SODIUM HYDROSULFIDE SOLUTION	ENV-COR
90	489	4932050	CORROSIVE LIQUID, BASIC, INORGANIC, N.O.S.	ENV-COR
91	490	4932055	CORROSIVE LIQUID, ACIDIC, ORGANIC, N.O.S.	ENV-COR
92	494	4932040	CORROSIVE LIQUID, ACIDIC, ORGANIC, N.O.S.	ENV-COR
93	508	4932004	FORMALDEHYDE SOLUTIONS	ENV-COR
94	516	4932021	CORROSIVE LIQUIDS, BASIC, INORGANIC	ENV-COR
95	524	4936339	BISULFITES, AQUEOUS SOLUTIONS, N.O.S.	ENV-COR
96	521	4931310	ALKYL SULFONIC ACIDS, LIQUID	ENV-COR
97	527	4935235	SODIUM HYDROXIDE, SOLID	ENV-COR
98	525	4931445	CORROSIVE LIQUIDS, N.O.S.	ENV-COR
99	526	4932042	CORROSIVE LIQUID, ACIDIC, ORGANIC, N.O.S.	ENV-COR
100	528	4935614	DIETHYLENETRIAMINE	ENV-COR
101	530	4935212	CYCLOHEXYLAMINE	ENV-COR
102	535	4935261	HYDROXYLAMINE SULPHATE	ENV-COR
103	538	4935245	SODIUM HYDROXIDE SOLUTION	ENV-COR
104	540	4935201	AMINES, LIQUID, CORROSIVE, N.O.S.	ENV-COR
105	550	4931313	CORROSIVE LIQUIDS, FLAMMABLE, N.O.S.	ENV-COR
106	551	4935655	SODIUM HYDROXIDE SOLUTION	ENV-COR
107	556	4930270	CORROSIVE LIQUIDS, N.O.S.	ENV-COR
108	559	4935202	CAUSTIC ALKALI LIQUIDS, N.O.S.	ENV-COR
109	562	4936540	CORROSIVE LIQUIDS, N.O.S.	ENV-COR
110	563	4935632	TRIETHYLENETETRAMINE	ENV-COR
111	564	4935209	CAUSTIC ALKALI LIQUIDS, N.O.S.	ENV-COR
112	571	4936602	CORROSIVE LIQUIDS, FLAMMABLE, N.O.S.	ENV-COR
113	574	4932393	ZINC CHLORIDE, SOLUTION	ENV-COR
114	575	4935243	CORROSIVE LIQUIDS, N.O.S.	ENV-COR
115	577	4935216	TETRAETHYLENEPENTAMINE	ENV-COR
116	580	4932044	CORROSIVE LIQUID, ACIDIC, ORGANIC, N.O.S.	ENV-COR
117	587	4931414	BUTYRIC ACID	ENV-COR
118	603	4932028	CORROSIVE LIQUID, ACIDIC, INORGANIC, N.O.S.	ENV-COR
119	612	4836540	WASTE CORROSIVE LIQUIDS	ENV-COR
120	605	4835258	WASTE CORROSIVE LIQUID, BASIC, INORGANIC	ENV-COR
121	607	4932315	CORROSIVE LIQUIDS, N.O.S.	ENV-COR
122	608	4936555	DYES, LIQUID, CORROSIVE, N.O.S.	ENV-COR
123	613	4935030	HYDRAZINE HYDRATE	ENV-COR
124	620	4831463	WASTE CORROSIVE LIQUID, ACIDIC, INORGANIC	ENV-COR
125	623	4931419	DODECYLBENZENESULFONIC ACID	ENV-COR
126	630	4935605	2-(2-AMINOETHOXY) ETHANOL	ENV-COR
127	643	4930010	FLUOROSULFONIC ACID	ENV-COR
128	647	4930022	HYDROFLUORIC ACID	ENV-COR

Rank in Class	Rank in Total	Haz Mat Code	For Year 2001 Hazard Class 8 Corrosive Description	VB Code
129	652	4936533	COMPOUNDS, WEEDKILLING, LIQUID	ENV-COR
130	670	4931435	CORROSIVE LIQUIDS, N.O.S.	ENV-COR
131	666	4930002	2-DIETHYLAMINOETHANOL	ENV-COR
132	671	4931426	DODECYLBENZENESULFONIC ACID	ENV-COR
133	674	4932060	CORROSIVE LIQUID, BASIC, INORGANIC, N.O.S.	ENV-COR
134	690	4931202	CORROSIVE LIQUID, TOXIC, N.O.S.	ENV-COR
135	691	4932026	CORROSIVE LIQUID, ACIDIC, INORGANIC, N.O.S.	ENV-COR
136	682	4931725	BENZOYL CHLORIDE	ENV-COR
137	695	4934221	CORROSIVE LIQUIDS, N.O.S.	ENV-COR
138	696	4936539	CORROSIVE LIQUIDS, N.O.S.	ENV-COR
139	719	4936360	CHLORITE SOLUTION	ENV-COR
140	706	4932020	CORROSIVE LIQUIDS, ACIDIC, ORGANIC, N.O.S.	ENV-COR
141	707	4935652	SODIUM HYDROXIDE SOLUTION	ENV-COR
142	713	4935267	SODIUM HYDROSULFIDE	ENV-COR
143	714	4935273	SODIUM HYDROXIDE SOLUTION	ENV-COR
144	721	4932035	CORROSIVE LIQUID, ACIDIC, ORGANIC, N.O.S.	ENV-COR
145	722	4930229	CORROSIVE LIQUID, ACIDIC, ORGANIC, N.O.S.	ENV-COR
146	727	4931258	CORROSIVE LIQUIDS, N.O.S.	ENV-COR
147	728	4832342	WASTE FERRIC CHLORIDE	ENV-COR
148	733	4935213	CAUSTIC ALKALI LIQUIDS, N.O.S.	ENV-COR
149	734	4935228	CAUSTIC ALKALI LIQUIDS, N.O.S.	ENV-COR
150	768	4931240	CORROSIVE LIQUID, ACIDIC, ORGANIC, N.O.S.	ENV-COR
151	769	4932025	CORROSIVE LIQUID, ACIDIC, INORGANIC, N.O.S.	ENV-COR
152	778	4931425	CORROSIVE LIQUIDS, FLAMMABLE, N.O.S.	ENV-COR
Notes: (env-cor) Many compounds in this category are non-flammable but yield toxic reaction products with water. Some may be flammable but have been designated in this corrosive category for other reasons.				

Rank	Rank in	Haz Mat	For Year 2001	VB
in Class	Total	Code	Hazard Class 9 Miscellaneous Description	Code
1	4	4961605	ELEVATED TEMPERATURE LIQUID, N.O.S.	?
2	7	4945770	SULFUR, MOLTEN	ENV-TOX
3	26	4960196	ENVIRONMENTALLY HAZARDOUS SUBSTANCES, LIQUID	?
4	44	4962137	OTHER REGULATED SUBSTANCES, LIQUID	?
5	48	4966109	OTHER REGULATED SUBSTANCES	?
6	52	4961619	ELEVATED TEMPERATURE LIQUID, N.O.S.	?
7	63	4941104	OTHER REGULATED SUBSTANCES, LIQUID	?
8	65	4961614	ELEVATED TEMPERATURE LIQUID, N.O.S.	?
9	67	4960131	ENVIRONMENTALLY HAZARDOUS SUBSTANCES, LIQUID	?
10	72	4961606	ELEVATED TEMPERATURE LIQUID, N.O.S.	?
11	75	4961384	ENVIRONMENTALLY HAZARDOUS SUBSTANCES, LIQUID	?
12	85	4961602	ELEVATED TEMPERATURE LIQUID, N.O.S.	?
13	87	4962136	OTHER REGULATED SUBSTANCES, LIQUID	?
14	93	4960156	ELEVATED TEMPERATURE LIQUID, N.O.S.	?
15	101	4961387	ENVIRONMENTALLY HAZARDOUS SUBSTANCES, LIQUID	?
16	123	4960149	ELEVATED TEMPERATURE LIQUID, N.O.S.	?
17	130	4962131	ELEVATED TEMPERATURE LIQUID, N.O.S.	?
18	145		ENVIRONMENTALLY HAZARDOUS SUBSTANCES, LIQUID	?
19	150		ELEVATED TEMPERATURE LIQUID, N.O.S.	?
20	151		ELEVATED TEMPERATURE LIQUID, N.O.S.	?
21	165		ELEVATED TEMPERATURE LIQUID, N.O.S.	?
22	172		ELEVATED TEMPERATURE LIQUID, N.O.S.	?
23	179		ENVIRONMENTALLY HAZARDOUS SUBSTANCES, LIQUID	?
24	187	4961607	ELEVATED TEMPERATURE LIQUID, N.O.S.	?
25	194		ENVIRONMENTALLY HAZARDOUS SUBSTANCES, LIQUID	?
26	197		ENVIRONMENTALLY HAZARDOUS SUBSTANCES, LIQUID	?
27	198	4960206	ENVIRONMENTALLY HAZARDOUS SUBSTANCES, LIQUID	?
28	200	4960187	ENVIRONMENTALLY HAZARDOUS SUBSTANCES, LIQUID	?
29	206	4960186	ENVIRONMENTALLY HAZARDOUS SUBSTANCES, LIQUID	?
30	208	4941202	OTHER REGULATED SUBSTANCES	?
31	216		ENVIRONMENTALLY HAZARDOUS SUBSTANCES, LIQUID	?
32	236		ENVIRONMENTALLY HAZARDOUS SUBSTANCES, SOLID	?
33	250		ELEVATED TEMPERATURE LIQUID, N.O.S.	?
34	263		ELEVATED TEMPERATURE LIQUID, N.O.S.	?
35	266		ENVIRONMENTALLY HAZARDOUS SUBSTANCES, LIQUID	?
36	285		ELEVATED TEMPERATURE LIQUID, N.O.S.	?
37	289		ENVIRONMENTALLY HAZARDOUS SUBSTANCES, LIQUID	?
38	309		OTHER REGULATED SUBSTANCES	?
39	338		ENVIRONMENTALLY HAZARDOUS SUBSTANCES, LIQUID	?
40	344		ELEVATED TEMPERATURE LIQUID, N.O.S.	?
41	342		HAZARDOUS WASTE, LIQUID, N.O.S.	?

Table A-10. Hazardous Material Class 9, Miscellaneous.See notes at bottom of table. (Ranked per relative frequency of shipments in 2001)

Rank in Class	Rank in Total	Haz Mat Code	For Year 2001 Hazard Class 9 Miscellaneous Description	VB Code
42	345	4961182	ENVIRONMENTALLY HAZARDOUS SUBSTANCES, LIQUID	?
43	350	4961615	ELEVATED TEMPERATURE LIQUID, N.O.S.	?
44	359	4960141	ENVIRONMENTALLY HAZARDOUS SUBSTANCES, LIQUID	?
45	362	4960148	ELEVATED TEMPERATURE LIQUID, N.O.S.	?
46	377	4961101	ENVIRONMENTALLY HAZARDOUS SUBSTANCES, LIQUID	?
47	378	4960159	ENVIRONMENTALLY HAZARDOUS SUBSTANCES, LIQUID	?
48	381		ENVIRONMENTALLY HAZARDOUS SUBSTANCES, LIQUID	?
49	380	4875506	HAZARDOUS WASTE, LIQUID, N.O.S.	?
50	413	4960137	ENVIRONMENTALLY HAZARDOUS SUBSTANCES, LIQUID	?
51	456	4960114	ENVIRONMENTALLY HAZARDOUS SUBSTANCES, LIQUID	?
52	471	4941204	OTHER REGULATED SUBSTANCES	?
53	470		ENVIRONMENTALLY HAZARDOUS SUBSTANCES, LIQUID	?
54	474		ENVIRONMENTALLY HAZARDOUS SUBSTANCES, LIQUID	?
55	475		ENVIRONMENTALLY HAZARDOUS SUBSTANCES, LIQUID	?
56	478	4960181	ENVIRONMENTALLY HAZARDOUS SUBSTANCES, LIQUID	?
57	488	1	ENVIRONMENTALLY HAZARDOUS SUBSTANCES, LIQUID	?
58	503		WASTE ENVIRONMENTALLY HAZARDOUS SUBSTANCE	?
59	502	1	ENVIRONMENTALLY HAZARDOUS SUBSTANCES, LIQUID	?
60	519	4860132	HAZARDOUS WASTE, LIQUID, N.O.S.	?
61	543	4963336	ENVIRONMENTALLY HAZARDOUS SUBSTANCES, LIQUID	?
62	555	4963104	ENVIRONMENTALLY HAZARDOUS SUBSTANCES, LIQUID	?
63	560	4961610	ELEVATED TEMPERATURE LIQUID, N.O.S.	?
64	561	4962110	ENVIRONMENTALLY HAZARDOUS SUBSTANCES, LIQUID	?
65	566	4961622	SULFUR, MOLTEN	ENV-TOX
66	576	4962108	ENVIRONMENTALLY HAZARDOUS SUBSTANCES, LIQUID	?
67	583	4963335	ENVIRONMENTALLY HAZARDOUS SUBSTANCES, LIQUID	?
68	619	4960140	ENVIRONMENTALLY HAZARDOUS SUBSTANCES, LIQUID	?
69	624	4961380	ENVIRONMENTALLY HAZARDOUS SUBSTANCES, LIQUID	?
70	635	4963361	ENVIRONMENTALLY HAZARDOUS SUBSTANCES, LIQUID	?
71	638	4960135	ENVIRONMENTALLY HAZARDOUS SUBSTANCES, SOLID	?
72	642	4960203	ENVIRONMENTALLY HAZARDOUS SUBSTANCES, LIQUID	?
73	649	4875631	HAZARDOUS WASTE, LIQUID, N.O.S.	?
74	657	4875602	HAZARDOUS WASTE, LIQUID, N.O.S.	?
75	663	4966317	ENVIRONMENTALLY HAZARDOUS SUBSTANCES, LIQUID	?
76	665	4960168	ENVIRONMENTALLY HAZARDOUS SUBSTANCES, LIQUID	?
77	667	4875633	HAZARDOUS WASTE, LIQUID, N.O.S.	?
78	689	4963333	ENVIRONMENTALLY HAZARDOUS SUBSTANCES	?
79	697	4962120	ENVIRONMENTALLY HAZARDOUS SUBSTANCES, LIQUID	?
80	701	4960161	ENVIRONMENTALLY HAZARDOUS SUBSTANCES, SOLID, N.O.S.	?
81	715	4940322	OTHER REGULATED SUBSTANCES, LIQUID	?
82	716		ENVIRONMENTALLY HAZARDOUS SUBSTANCES, LIQUID	?
83	717		ENVIRONMENTALLY HAZARDOUS SUBSTANCES, LIQUID	?

Rank in Class	Rank in Total	Haz Mat Code	For Year 2001 Hazard Class 9 Miscellaneous Description	VB Code
84	729	4875626	HAZARDOUS WASTE, LIQUID, N.O.S.	?
85	735	4966303	ENVIRONMENTALLY HAZARDOUS SUBSTANCES, LIQUID	?
86	752	4960136	ENVIRONMENTALLY HAZARDOUS SUBSTANCES, LIQUID	?
87	770	4960162	ENVIRONMENTALLY HAZARDOUS SUBSTANCES, LIQUID	?
88	771	4960179	ENVIRONMENTALLY HAZARDOUS SUBSTANCE, LIQUID	?
89	772	4961612	ELEVATED TEMPERATURE LIQUID, N.O.S.	?
90	773	4962135	ENVIRONMENTALLY HAZARDOUS SUBSTANCES, LIQUID	?
Notes:	(env-tox)		npounds in this category have special toxic characteristics ter reaction products.	
	?	Cannot ch	naracterize due to lack of information.	

# Appendix B.

#### CTI 02-319 (Revised)

Material Property Considerations for Vent & Burn Emergency Recovery Operations

Work Performed for

Transportation Technology Center, Inc. 55500 DOT Road Pueblo, CO 81001

Under Work Authorization No. 13108

Work Performed by

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December 2002

# **DISCLAIMER**

Analysis, results, conclusions and recommendations in this report are based on specific data, materials and methods stated, and may not be applicable to circumstances not identical to those considered. While best efforts are extended to use sound engineering judgment and evaluation methods, it is also possible that new information or different analysis may lead to different results.

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APPENDIX A – Rail Car Shipments in 2001 Sorted by Hazardous Material Classification and Number of Shipments in Category

6.0 Glossary

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#### 1

#### 1.0 INTRODUCTION AND SUMMARY

#### 1.1 Introduction

Vent and Burn (V & B) is an emergency recovery strategy whereby explosive charges are used to open a top and a bottom located vent hole in a damaged or disabled railroad tank car. This procedure is described in detail in Ref. [1]. As described in Ref. [1], the procedure is inherently dangerous and is intended as a last resort effort with the expected outcome of a net reduction in the overall risk associated with rail car accident recovery operations involving tank cars with hazardous material contents. As the name implies, V & B, results in both venting and burning of the hazardous contents. This technique has been applied successfully to rail tank cars carrying propane and a limited number of other flammable gases.

The issues addressed in this document relate to material properties or characteristics, which can lead to an informed judgment as to the suitability of other hazardous rail tank car products for a V & B recovery operation. Section 2 of this report outlines the approach and methodology. Section 3 provides details regarding various hazardous material classification categories. Overall results and recommendations are summarized below.

#### 1.2 <u>Summary</u>

A record of tank car shipments for the year 2001, compiled by TTCI has been used as a basis for material identification. This list is separated by hazardous material category and is included in Appendix A. In a review draft of this document certain materials were designated as <u>not</u> appropriate for V & B action. Discussions in review of this draft (with special acknowledgement to Patrick Brady) were helpful in clarifying this concept. Since V & B is a "last resort" action in rail car incident recovery virtually all decisions are based on incident specific considerations. Included in such considerations is the prospect that a tank car may likely explode with some certainty if no action is taken. Therefore, judgments as to suitability for V & B action based on material properties alone are likely to flawed or incomplete without the corresponding site-specific judgments.

It is however entirely possible to provide a relative indication of V & B action as a process risk, where the normalizing standard is <u>propane</u>. Propane is a flammable gas, transported under pressure, is not self-reactive, and is clean burning with no hazardous combustion products. Propane has been tested in V & B action at both small and large scale.

Materials chemically suitable for V & B action with a materials risk factor comparable to propane generally reside in the hazardous materials (HazMat) Class 2.1, (flammable gases), and Class 3, (flammable and combustible liquids).

The following classes of compounds have material property characteristics, which result in a V & B process risk, which exceeds that of propane.

<u>Positive Heat of Formation (phf)</u> – Certain low molecular weight flammable gasses and liquids have positive heats of formation, which is primarily the result of the presence double and triple carbon bonds. A positive heat of formation is a first order screening criterion for the possibility of a shock triggered exothermic decomposition. The worst case result would be a tank car explosion in response to V & B action. This is by no means a certain response but the potential increases with the magnitude of the phf. There is also at present an absence of empirical data to clarify the concern.

<u>Self Reaction on Exposure to Heat (sr)</u> – Monomers are stabilized against self-reaction during normal transport. Long term exposure to an external fire or heat source can deplete or eliminate the stabilizing agent. Polymerization is an exothermic process, which with certain species can result in catastrophic rail tank car failure. The increased risk factor relative to propane is that assumed by the explosives technicians and team making preparation for the V & B action. This risk is inversely proportional to the molecular weight of the monomer. Self-reactive materials are usually found in the HazMat Class 3, but are also found included in flammable gasses, and corrosives (acrylic acid).

<u>Environmental (env)</u> – Effects resulting from materials release or combustion, which would cause greater concern for the inhabitants of the area surrounding a V & B action, are included in the category of increased environmental risk. Compounds in this category are highly varied but generally have the following identifiable characteristics:

- (a) contain halogens (chlorine, fluorine etc. in their molecular structure)
- (b) amine compounds
- (c) other transportation code classifications as toxics
- (d) most corrosive materials, which may not be flammable but yield toxic reaction products with water.

With the above noted, the characteristics of materials having a V & B risk comparable to propane on a material property basis would generally be classified as hydrocarbons having fuel or fuel-like properties. This includes many hydrocarbon solvents as well.

# 2.0 MATERIAL PROPERTY HAZARDS AND APPROACH

#### 2.1 <u>Background</u>

V & B action has been used successfully with rail tank cars carrying propane in actual incident recovery operations. However, high expectations of success with propane are supported by actual full scale tests, Ref. [1], and small scale tests Ref. [2]. It is understood as noted in Ref. [1], that V & B is considered as a last resort strategy to be considered for example when mechanical damage to the rail car or its pressure relieving or drain equipment precludes conventional recovery procedures. In the same context, propane may be considered as the ideal candidate material. It is a clean burning fuel with an above ambient boiling temperature. Hence, it has little or no residual environmental impact. It is not shock sensitive and will not detonate in response to the external explosive charge. Concerns for boiling liquid expanding vapor explosives (BLEVE) have been studied in Ref. [2] and found to be absent in the context of V & B activities.

A skeleton list of propane properties is given below.

Critical Pressure	616.12 psia
Critical Temperature	96.68°C
Critical Compressibility Factor	0.276
Normal Boiling Temperature	- 42.04°C
Vapor Pressure @ 25°C	138.3 psia
Latent Heat @ 25°C	335.8 kJ/kg
Liquid Density @ 25°C	491 kg/m <sup>3</sup>
Liquid Heat Capacity @ 25°C	2723 J/kg K
Liquid Thermal Conductivity @ 25°C	0.094 w/m K
Heat of Formation	- 1.0468 E8 J/kmol
Heat of Combustion	- 46.3 MJ/kg
Lower Flammable Limit	2 v%
Upper Flammable Limit	9.5 v%
Autoignition Temperature	450°C

Table 2.1Skeleton Propane Properties, Mw 44.096.

# 2.2 <u>Material Properties and Hazard Characteristics</u>

Material properties and composition effects can yield some insight regarding the suitability of a given specie for V & B action.

<u>Shock Instability</u> – Some liquid and solid materials will undergo a high rate decomposition reaction in response to a strong (energetic) initiating event. Here one is concerned with the explosive charge used in a V & B action, being the trigger for an internal explosive decomposition of the tank car product. The strength of the charge used in a V & B event far exceeds the energy levels used in some UN standard tests to screen hazardous materials, Ref. [3]. Material response to energetic shock events is typically the subject of empirical tests. However, heat of formation is one useful guide. Materials with negative heat of formation can be presumed not to decompose (with release of energy) in response to a V & B shock. On the other hand a positive heat of formation indicates such a potential may exist. Organic compounds with double and triple carbon bonds may have a positive heat of formation. This criterion is particularly applicable to some low molecular weight compounds in hazard class 2.1 (flammable gases). Note that propane has a highly negative heat of formation and hence is very satisfactory in this regard.

<u>BLEVE</u> – Much has been written regarding boiling liquid, expanding vapor explosions. There as yet remains no fundamental criterion for its occurrence or non-occurrence. Both propane and butadiene, Refs. [4, 5] have undergone large scale BLEVE events. Some relate to BLEVE events as the resulting vapor cloud explosion following a catastrophic vessel failure induced by an external heat source applied to an unwetted surface of the liquid container. Other studies in particular Ref. [6] have focused more closely on the requirements for catastrophic failure of the container and have shown that in principle even non-flammable superheated (relative to the one atmosphere boiling temperature) liquids can produce catastrophic vessel failure after heating in the manner typical of a BLEVE event sequence. Therefore, one must conclude that many of the liquids in hazard category 2.1 and 2.2 could BLEVE under the right circumstances.

However, Ref. [2] has shown by direct experiments that an explosive charge induced vessel failure (with propane at various uniform temperatures up to 50°C) does not lead to a classic BLEVE, with follow-on catastrophic vessel failure. While at the same bulk propane temperatures it is shown in Ref. [4] that failure induced by a jet flame impingement resulted in catastrophic failure and classic BLEVE response.

Therefore it is provisionally concluded that (a) there are no material properties (including spontaneous nucleation or limit of superheat thresholds) which provide a screen for BLEVE potential, and (b) so long as a target rail car is not in direct exposure to a fire heat source, a BLEVE is not expected to result from the V & B explosive charge. An alternative statement is that V & B action should not be applied to a rail car under the immediate influence of an external fire.

<u>Exothermic Polymerization</u> - Many compounds in hazard class 2.1, and 3 are shipped in a "stabilized" form but under certain circumstances may undergo an exothermic polymerization. These materials are easily identified. For the shock instability and BLEVE hazards previously discussed, the issue of concern is an unintended and undesirable response to the V & B explosive charge. Runaway polymerization represents an undesirable hazard, which can jeopardize the set up protocol for V & B activity. The nature of these hazards are discussed in detail in Section 4.

<u>Environmental Hazards</u> - Some compounds are unsuitable for V & B action due to one or more environmental factors including toxicity, corrosivity and or hazardous combustion products. There are considered in the context of the various hazardous material classification categories.

#### 2.3 <u>Approach</u>

This study takes as a starting point, a list of rail shipments in CY 2001 with loadings identified by car type, compound and hazardous material classification code. This list was compiled by P. Williams of TTCI. This master list was reduced by eliminating entries having less than 10 car loadings in the year. This action alone reduced the size of the original 2001 tabulation from approximately 2000 entries to 780. This reduced tabulation was separated by hazardous material classification and included only tank car shipments. The separated categories include

Category	Category Description	Number of Entries
2.1	Flammable Gas	45
2.2	Non-Flammable Compressed Gas	12
2.3	Poisonous (toxic) Gas and Asphyxiants	8
3	Flammable/Combustible Liquid	378
4	Flammable Solids	12
5.1	Oxidizers	10
6.1	Poisonous Material	73
8	Corrosives	152
9	Other (environmentally offensive) materials	
	not falling into other classification categories.	90

The separated tables have been reordered by number of specific commodity shipments and included in appendix A to this document.

In the next Section 3, commodities and compounds in these hazardous material categories are reviewed for suitability to a V & B emergency recovery action. As indicated in Section 1.2, the concept of suitability is placed in a relative position with respect to propane. In this review a very conservative approach is adopted. This is believed to be warranted because of the intrinsic operational hazards of V & B action, but also due to

lack of empirical test experience with most of the materials. This initial assessment does not preclude later differing assessments based on a better understanding of presently unknown response characteristics.

# 3.0 <u>EVALUATION OF MATERIAL SUITABILITY BY HAZARDOUS</u> <u>MATERIAL CLASSIFICATION</u>

# 3.1 Hazardous Material Class 2.1 Flammable Gasses

Appendix Tables A-1a and A-1b provide a selection of compounds in this category taken from the 2001 tank car shipment summary. Products are ranked in decreasing order according to relative number of shipments. Propane is in this category. A large number of products in this hazard class would be candidates for V & B action. At first glance the list of likely candidates would include; all saturated hydrocarbon fuels and liquefied petroleum gasses. These are indicated in Table A-1a.

Caution should be exercised in assessing V & B action for the following subcategories in this class.

<u>Compounds Containing Double and Triple Bonds with Positive Heat of Formation</u> – Heat of formation is a good guide to decomposition hazard. See Ref. [6] for additional considerations. However, Table 3.1 provides a ranking of compounds selected from appendix Table A-1 according to heat of formation.

Specie (Mw)	$\Delta H_{ m f}$	$\Delta H_{decomp}$	T <sub>bp</sub>
	[kcal/gmol]	[kJ/kg	[°C]
Acetylene (26.04) CH≡H	+ 54.5	8764	
Methylacetylene (40-07) CH <sub>3</sub> C≡CH	+ 44.2	4615	- 23.2
Butadiene (54.09) CH <sub>2</sub> =CH–CH=CH <sub>2</sub>	+ 26.3	2037	- 4.4
Chloroprene (88.54) $CH_2 = CHCl = CH_2$	+ 17.4	825	59
Ethylene (28) $CH_2 = CH_2$	+12.5	1875	-103
Vinyl Chloride (62.50) CH <sub>2</sub> =CH-Cl	+ 6.8	455	- 13.9
Propylene (42.08) $CH_2=CH-CH_3$	+ 4.71	468	- 47.6
Butylene (56.11) CH <sub>2</sub> =CH–CH=CH <sub>2</sub>	- 0.13	- 9.6	- 6.25
Iso Butylene (56.11) $CH_2=C-(CH_3)_2$	- 4.04	- 301	- 6.9
Dimethyl Amine (45.08) ( $CH_3$ ) <sub>2</sub> N H	- 4.4	- 4.09	6.88
Propane (44.096) $C_3H_8$	- 25.02	- 2374	- 42.0
Dimethyl ether (46.07) $(CH_3)_2O$	- 44	- 3996	-24.8

# Table 3.1Representative heats of formation.

The following interpretation of Table 3.1 is offered. Acetylene, while not a rail car transport commodity is included as a standard because of its known instability. Methyl acetylene, a constituent of MAAP gas is close to acetylene in thermal parameter values.

Butadiene, chloroprene, ethylene, vinyl chloride and propylene follow in order with decreasing heat of formation values.

It would be provisionally recommended that those flammable gas commodities with a positive heat of formation should be placed in a significantly higher risk category relative to propane, when considering V & B action. This is a conservative position. It is recognized that V & B has been applied to tank cars with a butadiene and vinyl chloride lading. However, one success does not rule out the possibility of a future unsafe result, unless or until more studies such as found in Refs. [1 & 2] can be undertaken. Ethylene has been shown to decompose rapidly in response to an explosive shock, Ref. [18]. However, scale effects are significant in interpretation of such results.

It is to be noted that the energy of decomposition in Table 3.1 designated as  $\Delta H_{decomp}$  is given on a per kilogram mass basis on the assumption that decomposition yields elemental components. Here one should note another reference value that the energy of decomposition TNT is 4500 kJ/kg. In this regard, one would be more cautious regarding butadiene versus vinyl chloride.

Any Class 2.1 compound having a double carbon bond but with a negative heat of formation should be considered an acceptable candidate for V & B.

<u>Polymerization</u> – Butadiene and vinyl chloride are stabilized with inhibitors – discussed in Section 4.0. Here an additional caution is required. Prolonged exposure to fire can lead to depletion of the inhibitor and subsequently lead to a runaway polymerization. Should this occur, rail car rupture due to excess internal pressure can be expected. However, short-term exposure to fire (of the order of one to two hours) should not be a cause for concern.

<u>Hazardous Combustion Products</u> - Compounds containing chlorine and fluorine in Table A-1b have the potential for yielding chlorine gas  $(Cl_2)$  hydrochloric acid gas (HCl) or similar fluorine compounds on combustion. This is an additional consideration related to application of V & B action to compounds in Class 2.1. The list of compounds in Table A-1b are judged to have one or more of the above characteristics, which place them in a higher risk category relative to propane.

# 3.2 <u>Hazardous Material Class 2.2 – Non-Flammable Nonpoisonous</u> <u>Compressed Gas</u>

See Appendix A Table A-2. This category includes a short list of compressed gas liquids;  $O_2$ ,  $CO_2$ , argon, anhydrous ammonia and various chloro-fluoro carbon refrigerants. One would expect the latter refrigerant gasses not to be V & B candidates on environmental grounds. Nominally V & B is considered only for flammable or combustible materials. However, V & B action (the explosive relief part) might be usefully considered for  $O_2$ ,  $CO_2$ , and argon provided due consideration is given to down

wind dispersal. It should be noted that relief valves for cryogenic vessels have been known to fail due to icing on repeated actuation. Ref. [7] describes one particularly catastrophic failure of a  $CO_2$  tank, (not a rail car) after an overheating condition with a subsequent relief valve failure. In summary it is proposed that select non-flammable and non-toxic gasses in this category could be considered as candidates for explosive charge venting.

#### 3.3 Hazardous Material Class 2.3 – Poisonous by Inhalation

By virtue of previous considerations it is proposed that none of the materials in this hazard classification be considered for V & B action. See Appendix A Table A-3. Ethylene oxide is a special case in this category with added risk factors relative to propane. See notes in Appendix A Table A-3.

# 3.4 <u>Hazardous Material Class 3 – Flammable Liquids/Combustible</u> <u>Liquids</u>

See Appendix A Tables A-4a, A-4b and A-5. These tables contain an extensive list of organic liquids, a large number of which are in the general category of fuels. Most of the materials in these tables would be candidates for V & B action. However, due to vapor pressure considerations one should anticipate relatively little loss of inventory due to venting and most of the inventory loss due to draining. It correspondingly follows that any burning action would be expected to be very sooty ground pool fires, which should be planned for. It is easier to discuss the smaller group of materials in this category, which are not suitable for V & B action.

<u>Monomers</u> – As previously stated, V & B action for monomers carries a risk for site technicians that is greater than propane or other non-sr materials. Section 4 provides an extended discussion of these materials. An exception to this general preclusion would be as follows. V & B action considered for an incident damaged tank car, which has <u>not</u> been exposed to a fire heat source associated with the incident, would not carry an increased risk attributable to self reactivity.

<u>Sulfur and Hologenated Compound</u> - Caution should be exercised in considering V & B action for materials such as dimethyl sulfide where incomplete combustion will result in an obnoxious sulfur order with perhaps evacuation or exclusion precautions required. Chloride compounds can produce  $Cl_2$  or HCl gas on burning as previously noted. Hence use of V & B with these compounds may be highly site specific where such action is only appropriate in remote incidents.

Appendix Tables A-4a and A-5 contain an extensive list of flammable and combustible liquids, which have fuel – like characteristics. Some will have additives that may pose a slight elevation in environmental risk relative to propane. Ref. [19] provides some useful estimates of pool fire burning rates for various compounds.

9

Examples are:

Fuel	Large Pool Burn Rate
LNG/LPG	10 mm/min
Gasoline	4 mm/min
Methyl Alcohol	2 mm/min

If an incident burn pit is 12 inches or 305 mm deep, then one can estimate the burn duration as between 30 minutes and 3 hours depending on fuel type. For minor offensive additives in fuels, (in trace quantities) the duration of the environmental concern is short enough to be insignificant. Therefore, one places emphasis on compounds with halogens in their make up as having a higher risk factor than trace additives in fuels.

Appendix Table A-4b lists virtually all of the materials having a higher risk for V & B action relative to propane.

### 3.5 <u>Hazardous Material Class 4.1 – Flammable Solids</u>

See Appendix A Table A-6. This list of materials would be less likely candidates for V & B action due to environmental factors. These materials have low vapor pressure, react exothermically with air and water and most have hazardous combustion or oxidation products.

### 3.6 <u>Hazardous Material Class 5.1 – Oxidizers</u>

See Appendix A Table A-7. This list includes hydrogen peroxide, which is also included in the Section 4 discussion of self-reactive materials. However in general these compounds are not flammable and not likely to be serious candidates for V & B action.

### 3.7 <u>Hazardous Material Class 6.1 – Poisonous by Inhalation</u>

See Appendix A Table A-8. This hazard classification will most likely not be seriously considered for V & B action, due to environmental considerations.

### 3.8 <u>Hazardous Material Class 8 – Corrosives</u>

See Appendix A Table A-9. the material list includes highly acidic and basic compounds – most of which do not easily burn. While some materials in this category are flammable, the environmental and toxicity risk is high.

### 3.9 <u>Hazardous Material Class 9 – Other Environmentally Hazardous</u> <u>Materials</u>

See Appendix A Table A-10. The material description given in Table A-10 is an indication of the difficulty in assessing these materials. Hence because of suspected environmental impact with this class of materials, they are not considered desirable for V & B action.

### 4.0 <u>SELF-REACTIVE MATERIALS</u>

Various compounds – notably monomers and hydrogen peroxide which are shipped in rail cars also have potentially exothermic self-reactive characteristics. Note that in accord with Ref. [8] monomers must be inhibited (stabilized) so as to preclude polymerization in transport. However, inhibitor depletion both in transit and under incident conditions with fire with a resulting runaway polymerization. This section describes some of the characteristics of such compounds.

### 4.1 <u>Relevant Properties</u>

Inhibitor depletion in tank cars carrying self-reactive materials introduce the following additional hazards.

- 1. If a reaction is initiated in a self-reactive material the compound can be taken to significant excess temperature at high rates of temperature increase.
- 2. A pressure relief vent based on all-vapor flow and heat-up rates driven by an external fire only will be too small owing to two main factors; (a) a heat-up rates can be greater than those related to external fire heat input only, by one to several orders of magnitude and (b) under volume heating two-phase flow is likely for up to 50% of the inventory even for upright cars.
- 3. Some materials such as isoprene and chloroprene may undergo secondary explosive gas generating decomposition reactions at temperatures in the 300°C range.

		Molecular	Boiling	Heat of	Heat of	Liquid	Adiabatic	Sat.	Sat.	Sat.
						Heat		Temp at	Temp at	Temp at
Self-Reactive	Formula	Weight	Temperature	Reaction	Reaction	Capacity	Temperature	89.7	239.7	514.7
Compound							Increase	psia	psia	psia
			[°C]	[kcal/gmol]	[kJ/kg]	[kJ/kgK]	[°C]	[°C]	[°C]	[°C]
Hydrogen Peroxide	H2O2	34.0	105*	24	2953*	3.2	922			
Acetaldehyde	C2H4O	44.0	20.8	20	1902	2.5	761	83	127	167
Acrylonitrile	C3H3N	53.1	77.4	20	1576	2.2	716	149	200	247
Propylene Oxide	C3H6O	58.1	33.9	20	1440	2.4	600	97	144	188
Butadiene	C4H6	54.1	-4.4	18	1392	2.7	515	59	100	142
Vinylidene	C2H2Cl2	96.9	31.6	16.5	712	1.4	508	97	146	188
Chloroprene	C4H5Cl	88.5	59.4	16.5	780	1.8	433	131	185	238
Vinyl Acetate	C4H6O2	86.1	72.5	21	1021	2.4	425	139	190	239
Acrylic Acid	C3H4O2	72.1	141.0	18	1044	2.5	418	208	259	308
Isoprene	C5H8	68.1	34.1	16.5	1014	2.6	390	100	152	204
Methyl Acrylate	C4H6O3	86.1	80.2	18	875	2.4	364	150	201	250
Methacrylic Acid	C4H6O2	86.1	161.0	18	875	2.4	364	237	296	359
Methyl-	C5H8O3	100.1	100.3	18	752	2.1	358	179	236	287
Methacrylate										
Ethyl Acrylate	C5H8O2	100.1	99.5	18	752	2.3	327	177	226	277
Styrene	C8H8	104.1	145.2	18	725	2.5	290	232	289	364
2-Vinyl toluene	C9H10	118.2	169.8	18	637	2.3	277	257	323	388
Butyl Acrylate	C7H12O2	128.2	147.8	18	587	2.4	245	229	290	350
* Shipped as 30% or	: 50 %									
assay in water.										

Table 4.1 Energy content of potentially self-reactive materials listed in order of decreasing adiabatic temperature increase.

One begins with an initial assessment of properties of self-reactive materials. Table 4.1 provides a summary of the heat of reaction, the adiabatic temperature increase and the temperature corresponding to various relief device set pressures. Here adiabatic temperature increase is defined as

$$\Delta T_a = \frac{H_{Rx}}{C} \tag{4-1}$$

where

 $\begin{array}{ll} \Delta T_{a} & \text{is the adiabatic temperature increase } [^{o}C] \\ H_{Rx} & \text{is the mass specific heat of reaction } [J/kg] \\ C & \text{is the liquid heat capacity } [J/kg K] \end{array}$ 

Most monomers have heats of reaction in the range of 18 to 20 kcal/gmole, Ref. [9]. Therefore those compounds in Table 4.1 having the lowest molecular weight have the largest energy per unit mass. Reference will be made to Table 4.1 in the following discussion. Temperatures corresponding to various pressure conditions are based on properties of the pure compound Ref. [10].

### 4.2 <u>Role of Inhibitors</u>

Table 4.2 shows typical polymerization inhibitors used in the transport of monomers.

Inhibitor	Acronym	Formula	Molecular	T <sub>mp</sub>	T <sub>bp</sub>
			Weight		_
			[kg/kg-mol]	[°C]	[°C]
Monomethyl ether of hydroquinoine;					
para-methoxy phenol	MEHQ	$C_7H_8O_2$	124.14	56.00	243.00
Hydroquinoine	HQ	$C_6H_6O_2$	110.11	173	285
4-tert butyl catechol	TBC	$C_{10}H_{14}O_2$	166.22	52	285
Phenothiazine	PTZ	C <sub>12</sub> H <sub>9</sub> NS	199.28	185	371

Table 4.2	Typical inhibitor	properties.

T<sub>mp</sub> – Melting Temperature

T<sub>bp</sub> – Boiling Temperature

Table 4.3 shows typical inhibitor monomer combinations.

Monomer	Inhibitor	Typical Con.	Additional Requirements		
		Level [ppm]			
Acrylic Acid	MEHQ	200	Requires presence of dissolved $O_2$ to be effective		
Acrylonitrile	MEHQ	35-50	Requires presence of dissolved $O_2$ to be effective		
Butadiene	TBC	100-150	Requires presence of dissolved $O_2$ to be effective		
Butyl Acrylate	MEHQ	10-20	Requires presence of dissolved $O_2$ to be effective		
Ethyl Acrylate	MEHQ	10-20	Requires presence of dissolved $O_2$ to be effective		
Methyl	MEHQ	10-20	Requires presence of dissolved $O_2$ to be effective		
Methacrylate					
Styrene	TBC	12-15 or	Requires presence of dissolved $O_2$ to be effective		
-		50-100			
Vinyl Acetate	HQ	3-5	Does not require presence of dissolved O <sub>2</sub> to be		
			effective		
	PTZ		Does not require presence of dissolved O <sub>2</sub> to be		
			effective		

Table 4.3Selected monomers with typical inhibitor and concentration.

### 4.2.1 Inhibitor Effectiveness

Inhibitor effectiveness is measured by the concept of the isotherm induction period. Refs. [11 & 12] have shown that various scarce information in this regard may be correlated by an Arrhenius expression of the form

$$\tau = \left[c\right]^{n} A \exp\left[\frac{\left(Ea\right)}{RT}\right]$$
(4-2)

In Equation (4-2),

- $\tau$  is the induction time in days
- c is the inhibitor concentration in [ppm]
- n is a dimensionless exponent
- A is the pre-exponential factor [day]
- Ea is the activation energy [cal/gmole K]
- R is the gas constant, 1.9872 cal/gmole K
- T is the absolute temperature [K]

Table 4.4 provides a summary of monomer/inhibitor combinations for which correlating parameter values for Equation (4-2) are obtainable.

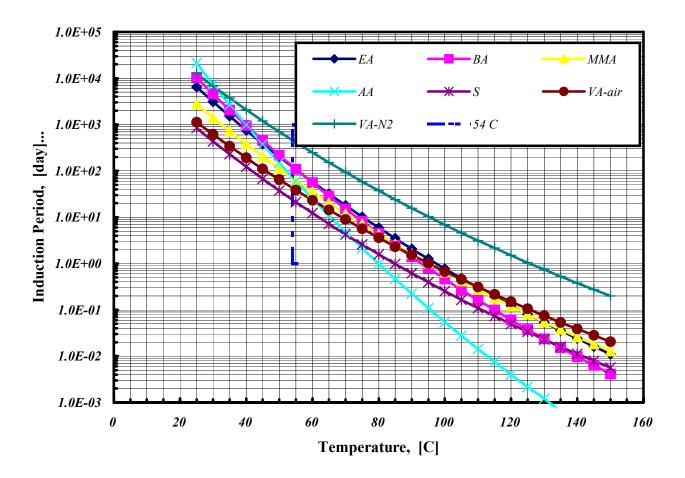
Monomer/Inhibitor		Add.	Ν	А	Ea	В
System		Requirements	[-]	[day]	[kcal/gmole]	[K]
Acrylic Acid	MEHQ	Air	1.185	5.9763E-27	37.955	19099.7
Vinyl Acetate	HQ	Air	1.2000	1.4609E-14	21.896	11018.4
Vinyl Acetate	HQ	No Oxygen	1.2000	1.0376E-13	22.163	11152.9
Ethyl Acrylate	MEHQ	Air	0.5500	5.4681E-17	26.635	13403.3
Methyl Methacrylate	MEHQ	Air	0.8840	1.4073E-16	24.640	12399.3559
Butyl Acrylate	MEHQ	Air	0.4500	7.8242E-19	29.570	14880.2335
Styrene	TBC	Air	1.2000	2.3026E-17	23.909	12031.7029
Butadiene	TBC	Air				
Acrylonitrile	TBC	Air				
Methacrylic Acid	MEHQ	Air				

Table 4.4Parameters for induction time Equation (4-2).

The information in Table 4.4 is represented in graphic form in Fig. 4.1 for the following monomer and inhibitor concentration levels.

Monomer	Inhibitor	Concentration
Acrylic Acid	MEHQ	200 ppm (w O <sub>2</sub> )
Vinyl Acetate	HQ	5 ppm (no O <sub>2</sub> )
Vinyl Acetate	HQ	5 ppm (w O <sub>2</sub> )
Ethyl Acrylate	MEHQ	10 ppm (w O <sub>2</sub> )
Methyl Methacrylate	MEHQ	15 ppm (w O <sub>2</sub> )
Butyl Acrylate	MEHQ	10 ppm (w O <sub>2</sub> )
Styrene	TBC	50 ppm (w O <sub>2</sub> )

For the most part trends are similar are similar suggesting that various monomer inhibitor combinations are selected to provide similar stability for monomers in transport. Finally, Table 4.5 indicates the induction time measure of stability at 54°C, and at the monomer boiling temperature, as well as the temperature corresponding to a 30 minute induction time.



15 Induction Period for Inhibited Monomers

Fig 4.1 Graphic illustration of induction period for inhibitors.

Monomer/Inhibitor	Induction	Monomer	Induction Time @	Temp. Corresponding
	Time @	Boiling	Monomer Boiling	to 30 min Induction
	54°C	Temp.	Temp.	Time
Acrylate Acid w 200 ppm	72.5 day	141°C	0.5 min	107 °C
MEHQ (air)				
Vinyl Acetate w 5 ppm HQ	459 day	72.5 °C	74 day	190 °C
(low oxygen)				
Vinyl Acetate w 5 ppm HQ	43 day	72.5 °C	7 day	150 °C
(air)				
Ethyl Acrylate w 10 ppm	121	99.5 °C	19.5 hr	142 °C
MEHQ (air)				
Methyl Methacrylate w 15	45 day	100.3 °C	10 hr	137 °C
ppm MEHQ (air)	-			
Butyl Acrylate w 10 ppm	125	147.9 °C	7 min	138 °C
MEHQ (air)				
Styrene w 50 ppm TBC (air)	24 day	145.2 °C	11 min	131 °C

### Table 4.5Typical monomer properties.

From the Table 4.5 evaluation one can observe that monomer stability at the 54°C Ref. [8], requirement is quite adequate but decreases rapidly at elevated temperature. By comparison with Table 4.1 values for temperatures corresponding to pressure relief activation, say 177°C for ethyl Acrylate, there is less than 30 minutes inhibitor effectiveness at 142°C so that with heat-up rates of 1 to 2°C/minute can no longer guarantee that the inhibitor will prevent self-heating at the relief activation temperature. However, note that with insulation reducing the heat-up rate due to fire to 0.1 to 0.3°C per minute after 100 minutes the temperature would be only of the order of 40°C to 60°C with  $\approx$  36 hr of inhibitor effectiveness remaining.

It is this uncertainty regarding inhibitor status, which superposes the added risk of runaway polymerization during V & B preparation activities.

### 4.3 <u>Case Examples</u>

The effectiveness of inhibitors under sustained heating which carries monomers and other self-reactive materials above 54°C is mixed. Here we review experience with a selection of materials.

<u>Styrene</u> – Styrene monomer is known to undergo thermal initiated polymerization with measurable rates of temperature increase at the temperature level of  $\approx 100^{\circ}$ C ± 10°C. the polymerization kinetics are well known, Ref. [13] and its reproducible reactivity have made it a standard specimen in calorimetry studies Ref. [14]. An interesting aspect of adiabatic styrene polymerization of significance to rail car transport is that the maximum reaction pressure is within the bounds of rail car pressure containment. Figs. 4.2 and 4.3 illustrate an adiabatic runaway polymerization of 100% styrene monomer. Fig. 4.3 shows the maximum pressure to be of the order of 250 psig. This is a result of the polymer effect on monomer vapor pressure. With external heating of the order of

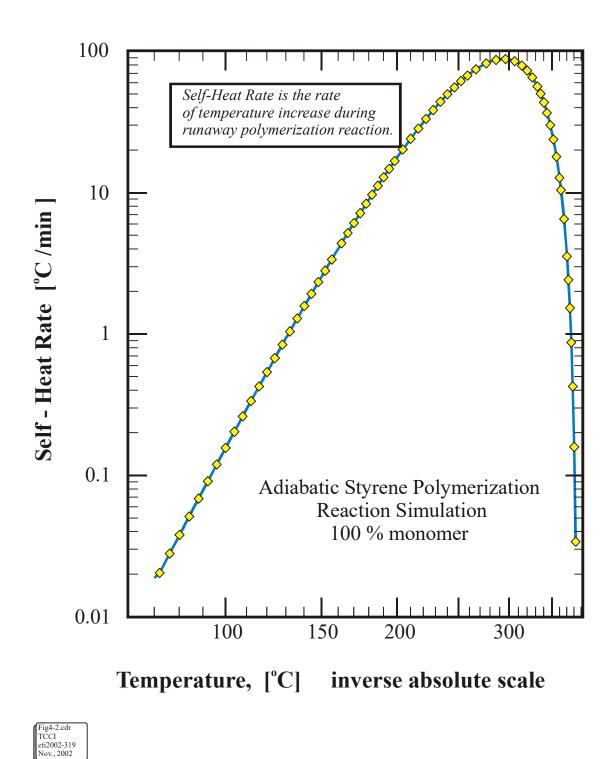


Fig. 4.2 Reaction self-heat rate vs inverse absolute temperature for adiabatic runaway reaction of 100% styrene monomer.

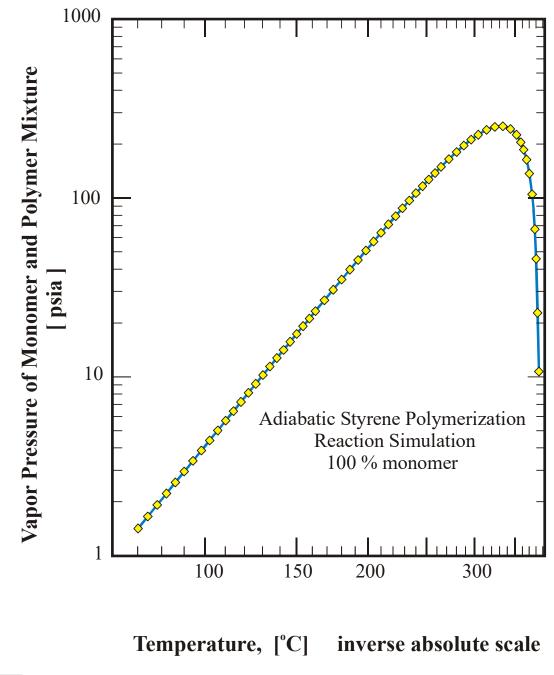




Fig. 4.3 Mixture vapor pressure vs inverse absolute temperature for adiabatic runaway reaction of 100% styrene monomer.

 $2^{\circ}$ C/min, the maximum reaction pressure would be estimated to be of the order of 400 psig, which is still within the pressure containment capacity of rail cars. Note that at a relief set pressure of 75 psig or 225 psig the reaction self-heat rate would be of the order of 60°C/min and 100°C/min respectively. We will comment on the significance of these heat rates relative to pressure relief vents sized for vapor flow only at external driven heat-up rates of 1°C/min to 2°C/min, or less.

<u>2-Vinyl Toluene</u> – No known runaway reaction data for this compound is known. However, because of its structural similarity with styrene one can expect similar behavior. Further, because of its higher molecular weight, lower adiabatic temperature increase and lower monomer vapor pressure, (See Table 4.1) one can reasonably expect maximum reaction pressures to be less than that of styrene.

<u>Acrylic Monomers</u> – Monomers such as acrylic acid, vinyl acetate, methyl-, ethyl- and butyl Acrylate, methyl methacrylate and methacrylic acid show interesting results when subjected to adiabatic calorimetry tests attempting to initiate a runaway reaction. Predictable results are always obtained with the presence of a free radical initiator (any organic peroxide). However, most acrylates without an initiator or catalysts will survive a one time heat-up to elevated temperature approaching 300°C without initiating selfheating polymerization. Hence, boil off may occur without a runaway reaction in the immediate time scale of the event. However, long term stand by at elevated temperatures without an effective inhibitor can be expected to eventually lead to reactive self-heating.

Acrylic acid is also interesting because of its high freezing temperature  $\approx 14^{\circ}$ C. Freezing displaces the inhibitor such that if heat is applied to a frozen shell, a runaway reaction is likely.

<u>Isoprene</u> – Isoprene, chloroprene and Vinylidene are monomers structurally similar to butadiene. Ref. [15] shows that butadiene can undergo thermal initiated polymerization in the absence of inhibitor at temperatures as low as 70°C. Studies with chloroprene, Ref. [16] have shown similar results. These materials are particularly dangerous because of the known potential for a second high rate (explosive) decomposition reaction to follow the initial runaway polymerization. Ref. [15] also produced a runaway polymerization in initially inhibited butadiene at  $\approx 80^{\circ}$ C.

<u>*Hydrogen Peroxide*</u> – Hydrogen peroxide is transported in bulk at 35% and 50% assay in water. Hydrogen peroxide will under go decomposition at elevated temperature with a small concentration of a catalytic agent. In the absence of such agents,  $H_2O_2$  is stable to high temperatures and may not self-react. So long as  $H_2O_2$  is shipped in 60 psi rail cars with 35 psig relief vents, safe vapor venting is possible so long as catalytic contamination can be ruled out.

### 4.4 <u>Possibility for Safe Venting of Runaway Reactions in Rail Cars</u>

The possibility for safe venting of runaway reaction in rail cars where high relief set pressure is a safety imperative for other valid reasons, is essentially beyond practical consideration. Ref. [17] provides analytical details for this conclusion using AIChE DIERS methods. The AIChE DIERS methodology has been widely accepted by the chemical industry as a state of the art protocol for reactive vent sizing. This methodology is based on use of the runaway reaction self-heat rate at relief set pressure and allowance for two-phase flow.

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### 6.0 GLOSSARY OF CHEMICAL AND MATERIAL TERMS

**Monomer** - A chemical compound typically used in industry to manufacture polymers. It is a chemical species usually characterized by at least one carbon-to-carbon double bond. The reaction in which a monomers combine to make long chain polymers is exothermic and in the absence of heat removal can be self-accelerating.

<u>Halogenated Compound</u> – A compound containing a halogen atom or group in its chemical structure. Halogens are Fluorine, Chlorine, Bromine and Iodine.

 $\underline{Oxidizer}$  – A compound, which is an oxygen donor. The oxidation reaction is usually exothermic.

<u>Self-Reactive</u> – A specie which can undergo a chemical change without a second reactant. Examples would include polymerization and decomposition.

<u>Self-Accelerating</u> – A reaction which is both exothermic and which reaction rate increases with temperature is potentially self-accelerating.

**Exothermic** – A chemical reaction which releases heat in the reaction process.

<u>**Heat of Reaction**</u> – The amount of heat released per unit mass of reacting specie in a reaction process.

<u>**Heat of Formation**</u> – A thermodynamic measure of the amount of heat liberated or which must be provided to assemble a molecule from its elemental components. This heat effect may be reversed on disassembly.

<u>Inhibitor or Stabilizer</u> – An additive that prevents an undesired chemical reaction by means of an alternative chemical blocking reaction.

<u>Induction Period</u> – The time required to deplete an inhibitor or stabilizer compound, or produce some other effect, which results in a self-accelerating reaction.

Appendix C.

# Railroad Tank Car Vent and Burn Process Study: Analysis of a Shaped Charge Impact on a Jacket and Shell

Submitted to the Transportation Technology Center Inc. Pueblo, CO.

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NTED New Technologies Engineering Division



### Introduction

The vent and burn process uses high-explosive-shaped charges to cut holes in a railroad tank car during extreme transportation-accident emergencies. In this report, estimates of the response of the railcar exterior jacket and tank-shell to several shaped charge designs are presented.

Several design parameters of the shaped charges, the railroad car jacket, and the railroad car tank-shell were evaluated. For this present analysis the railroad car tank-shell thickness was assumed to be 1 inch and the railroad car jacket thickness was assumed to be 0.1196 inch. The shaped charge standoff was assumed to be equal to the diameter of the shaped charge. The effects of differences in several design parameters were evaluated. The design parameters included the shaped charge diameter (4 and 8 inches); the shaped charge cone angle (90 and 120°); the thickness (type) of insulation between the railroad car jacket and tank-shell (4 and 6 inches); and the type of high explosive (C-4 and Comp-B) used in the shaped charge.

### Approach

The response of the railroad car jacket and tank-shell to shaped charges was evaluated computationally. A two dimensional, axi-symmetric analysis was performed. In Figs. 1 through 14, 17, and 18 the vertical axis is the radial coordinate and the horizontal axis is in the direction perpendicular to the face of the tank car and parallel to the axis of the cone of the shaped charge. The spatial units used in the figures are centimeters and the time units are microseconds. The computer program used for the analysis was CALE (Tipton, 1997). The project committee provided the railroad car jacket and shaped charge parameters used in the analysis. The equation of state and detonation parameters for the explosive C-4 were obtained from the LLNL Explosives Reference Guide (2002). The equation of state and detonation parameters for the explosive Comp-B were obtained from the handbook by Dobratz and Crawford (1985). The project committee provided the yield strength of railroad car jacket and shell, 70 ksi. An example of the computational mesh for a shaped charge analysis is shown in Fig. 1. The location of detonation initiation and charge stand off are illustrated in Fig. 2. The zoning used for the railroad car jacket and shell is illustrated in a later figure (Fig. 10).

#### Results

A shaped charge works by using a detonating high explosive to both accelerate and to compress metal (copper in this case) into a slug or a jet. The metal jet, which has been accelerated to super sonic velocity, then hits the target, the railroad car jacket and shell. The momentum of metal jet is so great that it causes the target to fail.

Figures 3 through 14 illustrate the progress of the shaped charge from the initial detonation of the high explosive (Figs. 3-7), to jet formation (Figs. 8-9), to impact with the railroad car jacket (Figs. 10-11), to impact with the railroad car shell and passage

through the railroad car tank shell (Figs. 12-14). The specific responses of concern to the vent burn process investigation are the hole-sizes of the railroad car jacket and tank-shell caused by the various shaped charges designs. This is illustrated in Fig. 14. The accuracy of this approach is estimated at be about 0.25 cm.

The responses of the railroad car jacket and tank-shell for all of the cases studied are given in Table 1 and in Figs. 15, and 16. The specific responses of concern to the vent burn process investigation are the hole-sizes of the railroad car jacket and tank-shell caused by the various shaped charges designs. The values of the parameters used in the calculations and the results are given for all cases in Table 1. In Fig. 15, the effects on the hole diameter produced in the railroad car tank-shell for different values of the shaped charge cone angle, shaped charge diameter and, type and thickness of the insulation located between the railroad car jacket and tank-shell are shown for shaped charge diameter and, type and the railroad car tank-shell for different values of the shaped charge cone angle, shaped charge the shaped charge cone angle, shaped charges using the explosive C-4. In Fig. 16, the effects on the hole diameter produced in the railroad car tank-shell are shown for shaped charge diameter and, type and of the insulation located between the railroad car jacket and tank-shell are shown for shaped charge diameter and, type and of the insulation located between the railroad car jacket and tank-shell are shown for shaped charge diameter and, type and of the insulation located between the railroad car jacket and tank-shell are shown for shaped charge diameter and, type and of the insulation located between the railroad car jacket and tank-shell are shown for shaped charges using the explosive Comp-B.

Figures 17 and 18 illustrate the influence of the cone angle on railroad car jacket deformation. The results are for simulations using C-4, an insulation thickness of 6 inches, and a shaped charge diameter of 8 inches. A cone angle of  $90^{\circ}$  is simulated in Fig. 17 and a cone angle of  $120^{\circ}$  is simulated in Fig. 18.

### **Discussion of Results**

Two parameters appear to dominate the response of the parameters shown in Figs. 15 and 16, the shaped charge diameter and the shaped charge cone angle. The other parameters in the design do not appear, in this analysis, to play a significant role. One concern at the beginning of the study was whether the additional stand off provided by the insulation between the railroad car jacket and tank-shell would cause the shaped charge jets to stretch and fragment. This analysis appears to indicate that the additional stand off does not appear to appreciably affect the hole penetration capability of the shaped charge studied.

An additional issue is the railroad car jacket deformation caused by a  $120^{\circ}$  charge vs. a  $90^{\circ}$  charge. It appears that the explosive gas pressure from the  $120^{\circ}$  charge causes a wider range of damage. A trade off exists between the increased hole size possible with the  $120^{\circ}$  charge and the increased potential damage to the jacket.

The steel casing containing the high explosive may also be a concern because of possible collateral damage. If a thermally insulated plastic cased charge were used to contain the high explosive, this possible collateral damage might be minimized. It is not believed, at this time that the confinement provided by the steel casing is required.

Another concern, during the initial project discussions, was how to minimize tank tearing or cracking, after the shaped charge penetrated the tank shell. Tank tearing or

cracking should be minimized by allowing adequate high explosive standoff. Adequate standoff allows the shaped charge jet to impact the tank shell yet keeps the high pressure explosive gas away, as far as possible, from the tank shell. One earlier design was a circular-ring shaped charge. It is now believed that a ring charge might aggravate tank tarring or cracking. The circular-ring shaped charge will not be studied further.

### Conclusion

The computational results of the report indicate that all of the designs proposed would cut acceptable holes in the railroad car tank jackets and shells. The largest hole is produced using an 8-inch diameter shaped charge with a 120° cone angle. The type of high explosive does not appear to be extremely important, but C-4 seems to perform slightly better than Comp-B. The affect of the differences in the thickness of insulation do not appear to be significant.

### Acknowledgements

Several people have assisted with his effort. Randy Jackson, Peter Conlon, Rich Couch, Ray Pierce, and Dennis Baum worked for several years in developing the project. Julie Fone and Gary Kleinheim fought through piles of paper to set up the LLNL project. Mike Murphy, Phil Pincosy, Robert Kuklo, and Nick Collier provided guidance early in the analysis. Randy Jackson, Bill Poe, and the project steering provided the design matrix and years of valuable experience in safe railroad transportation and shaped charge design and use. And with out CALE, Robert Tipton's code, this effort would not have been possible within the existing constraints. To those above and to all the others should be acknowledged who I have missed, thank you.

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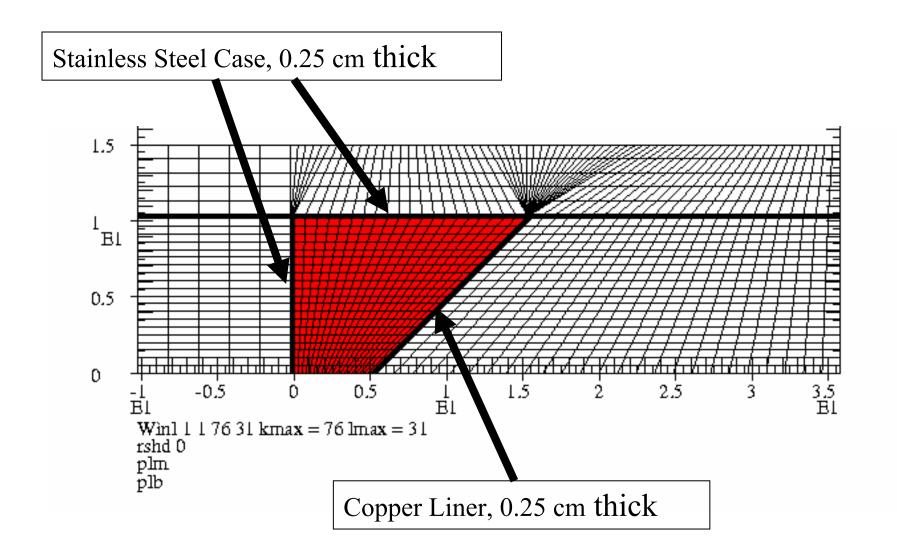
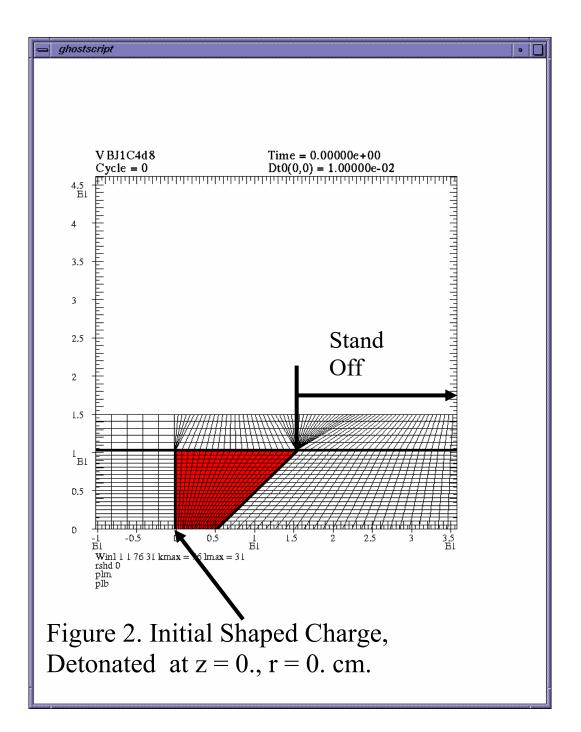
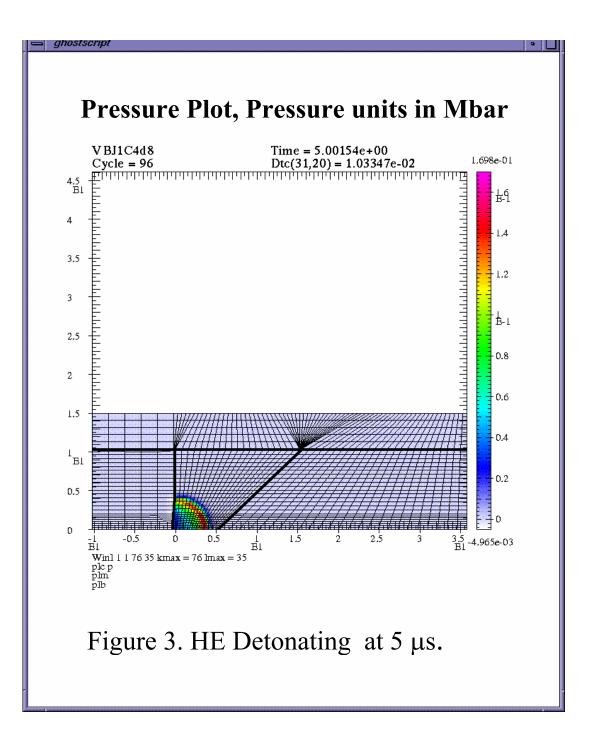
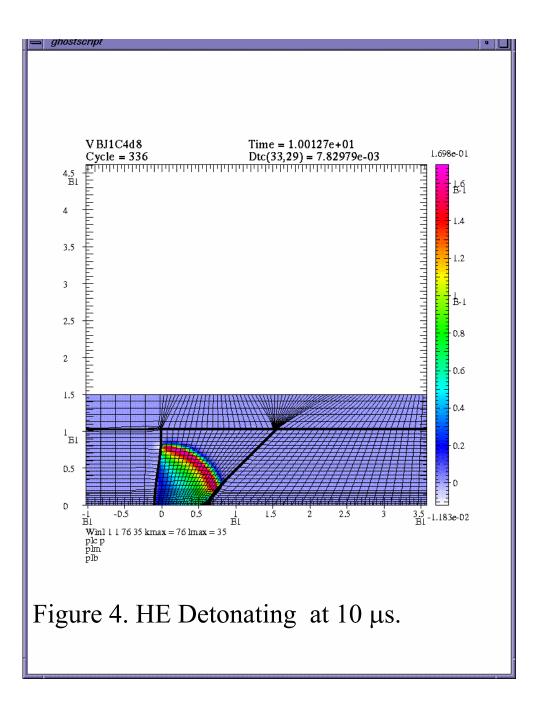
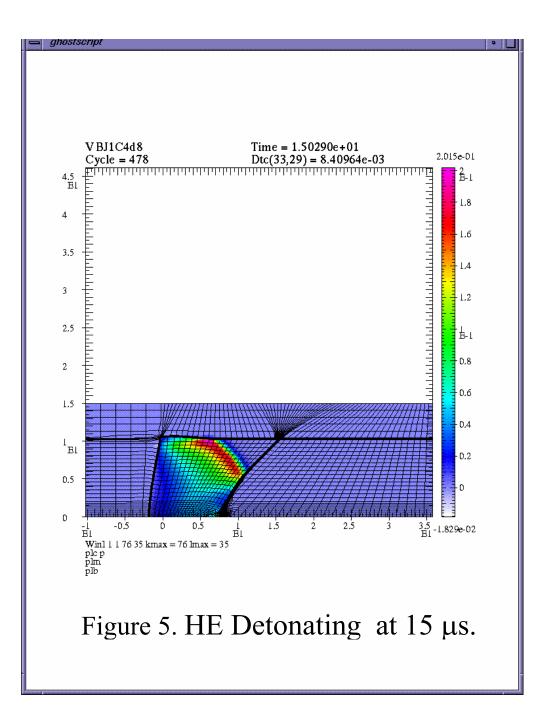


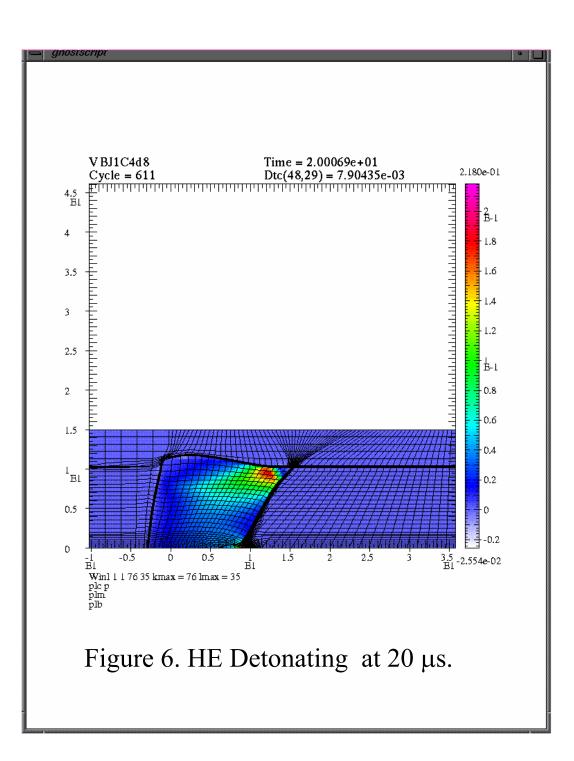
Figure 1.Charge Radius (4") 10.16 cm, Stand Off 20.32 cm, with 90° Cone.

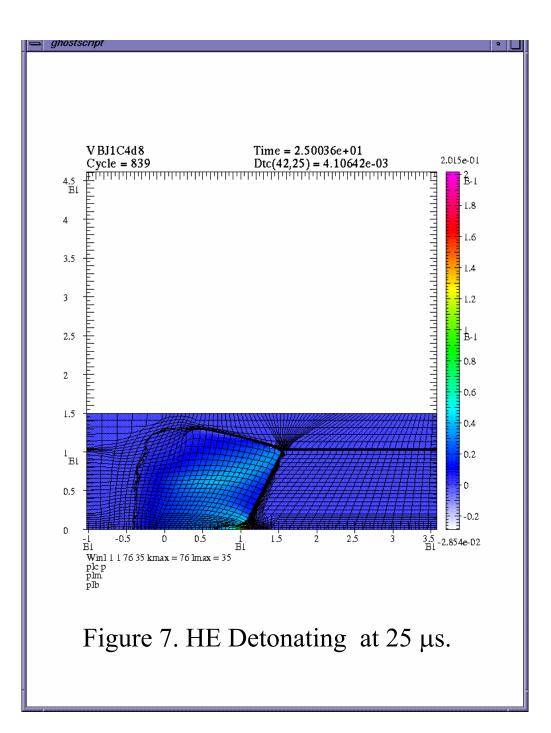


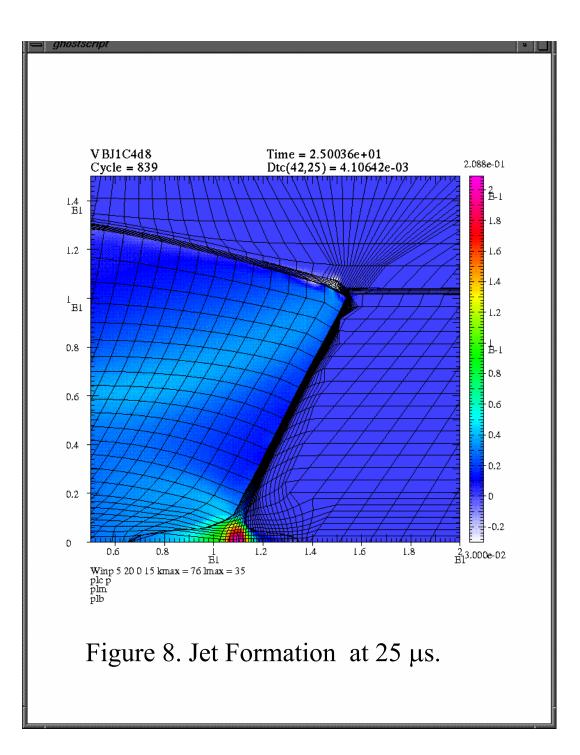


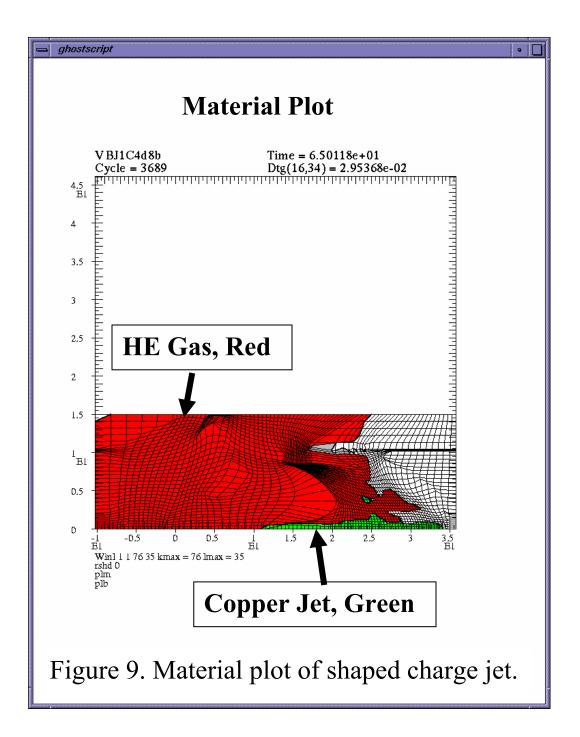


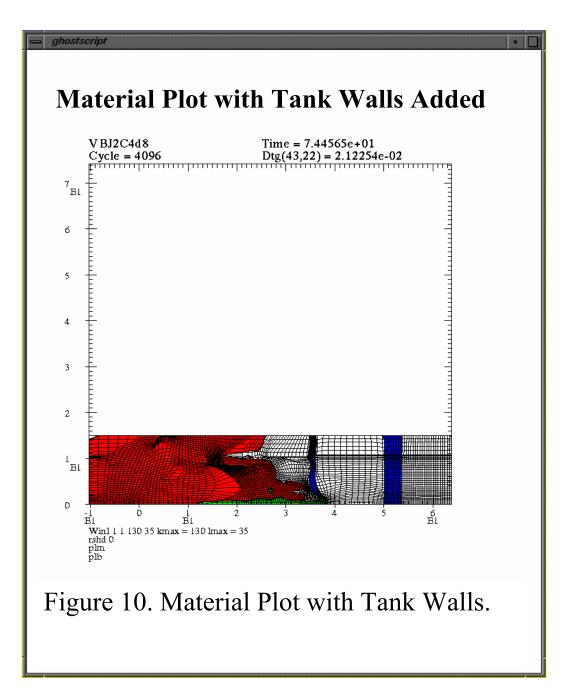


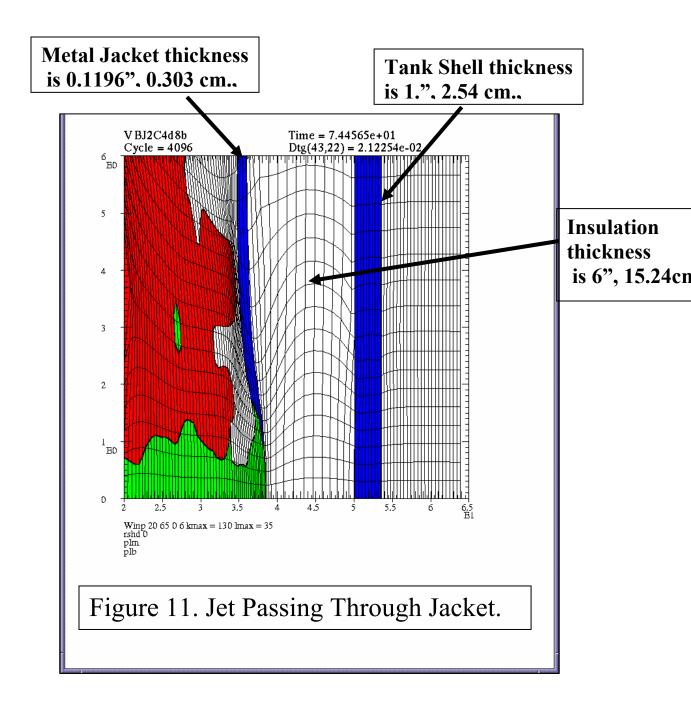


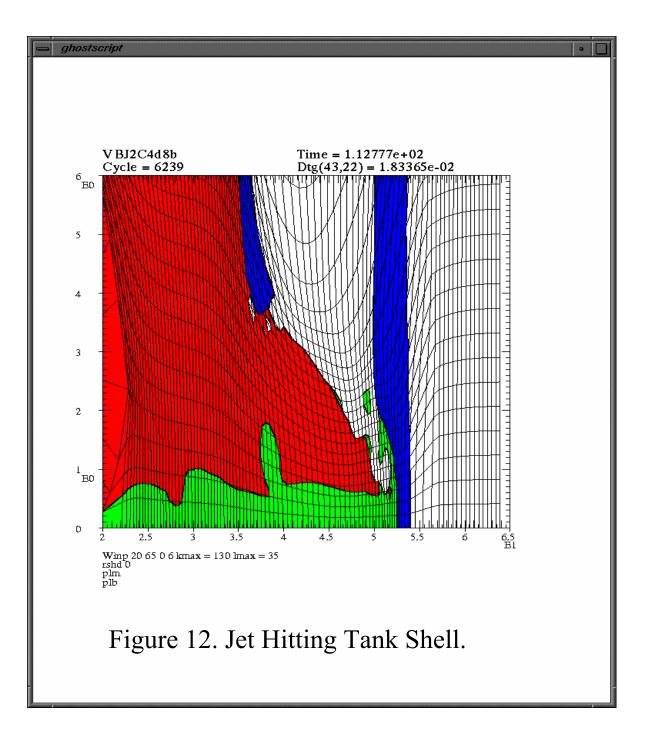


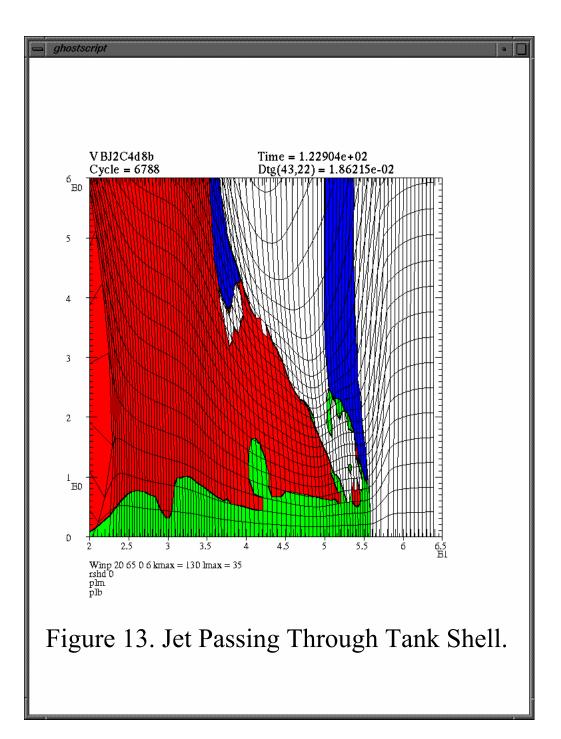


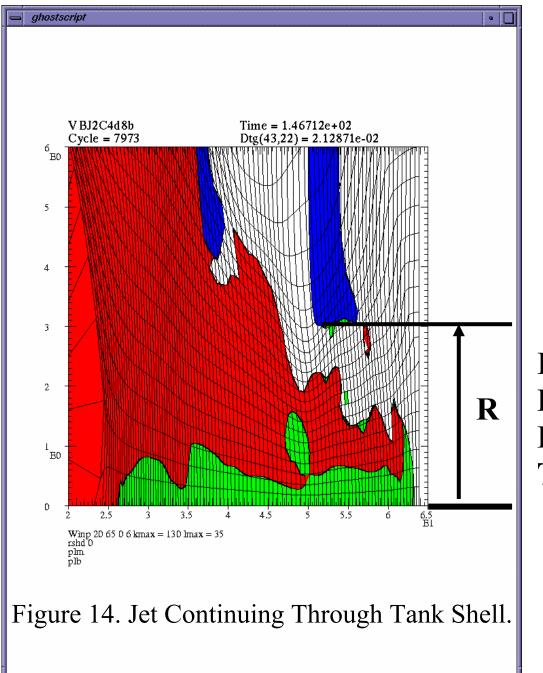












Predicted Radius of Hole in Tank (cm)

Diameter	Cone Angle	HE	Insulation	Hole Diameter	Tank-shell Hole Radius	Jacket Hole Radius
inches	Degrees		inches	inches	cm	cm
4	90	C-4	4	1.57	2.0	2.5
8	90	C-4	4	2.36	3.0	3.9
4	90	C-4	6	1.42	1.8	1.6
8	90	C-4	6	2.36	3.0	4.1
4	120	C-4	4	1.42	1.8	2.8
8	120	C-4	4	2.91	3.7	3.8
4	120	C-4	6	1.42	1.8	2.7
8	120	C-4	6	3.15	4.0	4.9
4	90	Comp-B	4	1.18	1.5	1.6
8	90	Comp-B	4	2.68	3.4	2.3
4	90	Comp-B	6	1.02	1.3	1.5
8	90	Comp-B	6	2.52	3.2	2.5
4	120	Comp-B	4	1.18	1.5	3.6
8	120	Comp-B	4	2.91	3.7	5.8
4	120	Comp-B	6	1.02	1.3	4.4
8	120	Comp-B	6	2.68	3.4	5.7

Table 1. Results of parameter study on the response of railroad car tanks to shaped charges.

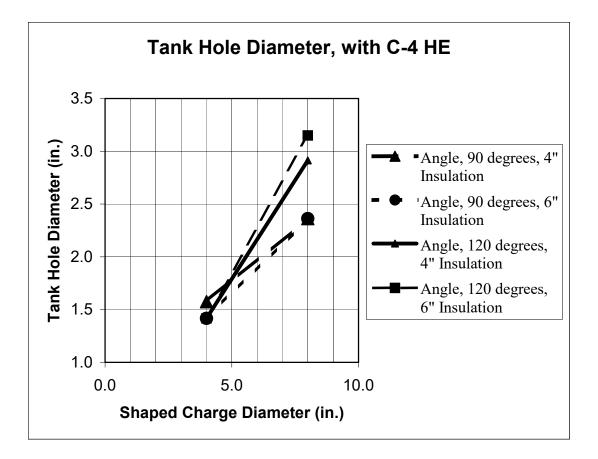


Figure 15. Estimated hole size in tank shell for shaped charges using high explosive C-4 for differing values of shaped charge diameter, cone angle, and insulation thickness.

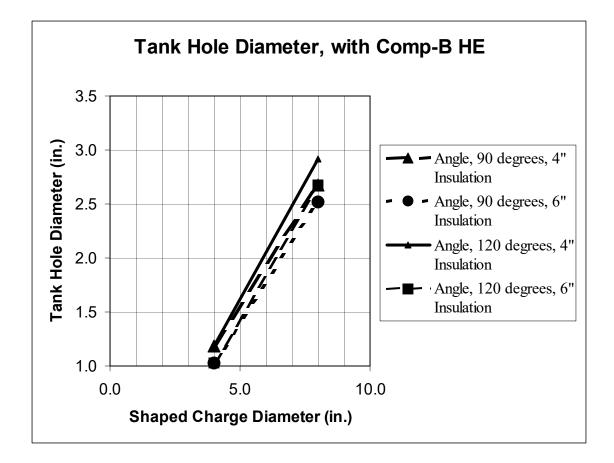
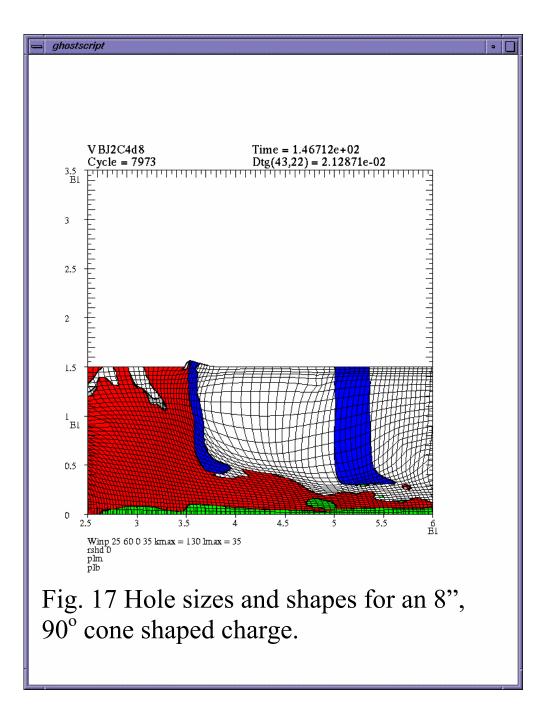
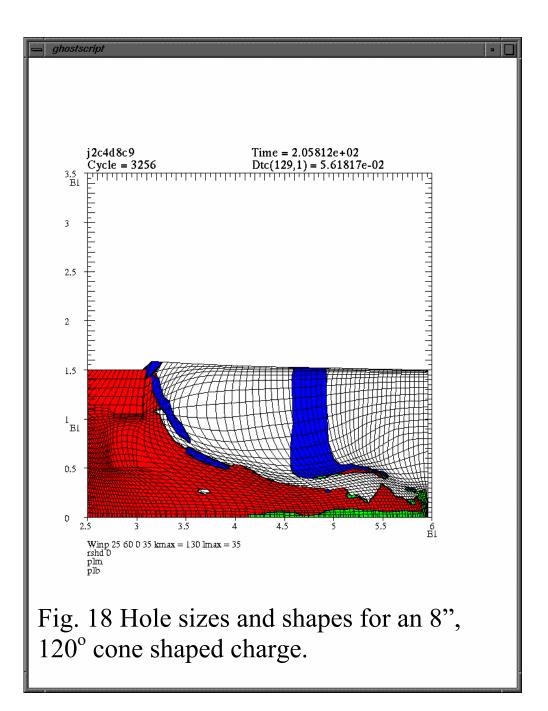


Figure 16. Estimated hole size in tank shell for shaped charges using high explosive C-4 for differing values of shaped charge diameter, cone angle, and insulation thickness.





### Glossary

- 1. **Head shield:** A 1/2-inch steel shield contoured to the shape of the tank head and designed to protect the head from being punctured in a derailment.
- **2.** Hot Zone: The area at a hazardous materials incident assumed to be contaminated requiring restricted access and appropriate personal protective equipment.
- 3. **Insulation:** The material that is wrapped around or sprayed on a tank car tank to maintain the temperature of the product in the tank within a given range.
- 4. Liquid space: The space in the tank car tank occupied by liquid.
- 5. **Single-point vent and burn:** The use of one explosive charge to cut a hole in the tank car tank vapor space to relieve pressure and allow the product to burn off.
- 6. **Standoff distance:** The distance between the bottom of the explosive charge and the tank car tank.
- 7. **Tank car jacket:** The 1/8-inch sheet metal covering a tank car tank that holds the thermal protection/insulation in place and protects it from the elements.
- 8. **Tank car specification:** An alphanumeric classification that designates the type of tank car, tank shell thickness, material of construction, and other important construction features.
- 9. Thermal protection: A material, which remains effective at high temperature, that is wrapped around or sprayed on a tank car tank to protect the tank in the event of a fire.
- 10. **Time-on-Target:** The amount of time a technician(s) spends preparing the tank shell and placing the explosive charge.
- 11. **Two-point vent and burn:** The use of two separate explosive charges, one at the highest point in the vapor space to relieve pressure and the other at the lowest point in the liquid space to allow liquid product to exit the tank.
- 12. Universal machine language equipment register (UMLER): A computer database maintained by the Association of American Railroads.
- 13. Vapor space: The space in the tank car tank not occupied by liquid.

### Acronyms

AAR	Association of American Railroads
AFFTAC	Analysis of Fire Effects on Tank Cars
ASTM	American Society for Testing and Standards
CFR	Code of Federal Regulations
CX	carbon atoms
FRA	Federal Railroad Administration
LLNL	Lawrence Livermore National Laboratories
LPG	liquefied petroleum gas
MTBE	methyl tertiary butyl ether
R&D	research and development
RDX	cyclonite
TNT	tri-nitrotoluene
TTCI	Transportation Technology Center, Inc.