Classification of Poison Inhalation Hazard Materials Into Severity Groups*

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INTRODUCTION

Approximately 1.5 billion tons of hazardous materials (hazmat) are transported in the U.S. annually, and most reach their destinations safely. However, there are infrequent transportation accidents in which hazmat is released from its packaging. These accidental releases can potentially affect the health of the exposed population and damage the surrounding environment. Although these events are rare, they cause genuine public concern. Therefore, the U. S. Department of Transportation Research & Special Programs Administration (DOT-RSPA) has sponsored a project to evaluate the protection provided by the current bulk (defined as larger than 118 gallons) packagings used to transport materials that have been classified as Poison Inhalation Hazards (PIH) and recommend performance standards for these PIH packagings. This project was limited to evaluating bulk packagings larger than 2000 gallons.

The goal of packaging performance standards is to ensure adequate public protection. One approach to setting performance standards is to select a cumulative percentage (X%) of accidents against which to protect the public, and a "protection radius (R)" around the accidental release beyond which the concentration of the released hazmat is below a chosen threshold value. The cumulative percentage of accidents correlates to specific accident conditions (i.e., X% of accidents have impact velocities less than or equal to a certain amount, thermal assault less than or equal to a certain amount, etc.) that the packaging must survive (Dennis et al. 1977). The package survives if, after experiencing the selected accident conditions, the hazmat release rate is small enough that the concentration at and beyond R is less than the chosen threshold level. This method defines a distance R beyond which people will not be exposed to concentrations in excess of the chosen threshold for (X%) of all accidents. This method does not describe the consequences of the (100 - X)% of accidents that are more severe than the performance standard. However, if X is large, then the

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remaining (100 - X)% accidents are improbable. The approach used in this project is analogous to the approach used in radioactive material transportation using Type-B packagings, with no allowable leak rate (10CFR71, 1991).

It would be extremely impractical to have a separate performance standard, and consequently a separate packaging, for each PIH. Therefore, one aspect of this project involved classifying the PIH into severity categories so that only one set of packaging performance criteria would be needed for each severity category rather than a separate set of performance criteria for each individual PIH. This paper discusses the details of the classification of the PIH into the four proposed severity categories.

CLASSIFICATION METHODOLOGY

The first step in the classification involved comparing the various PIH to determine "relative severity" with respect to each other. This was accomplished by calculating the effect of release rate and/or release amount on the distance from the release within which the concentration of the released material exceeds the threshold value for that material. From these calculations, then, the relative severity of the various PIH compounds was determined by comparing the release rates required to produce the threshold value at a given distance (i.e., the lower the maximum allowable leak rate, the more relatively severe the compound). This methodology takes into account not only the toxicity of the material but also the ease with which it disperses. This will be referred to as the TD method. The results of these comparisons indicate that the maximum allowable leak rates span five orders of magnitude for the various PIH. The dispersion calculations and the selection of appropriate threshold levels are documented in Weiner and Griego, 1995.

As general critera for defining the PIH into bulk hazard zones, we suggest that the materials with maximum allowable leak rates (per the TD method) less than 10 g/s be placed in Hazard Zone BA, those with maximum allowable leak rates between 10 and 100 g/s be placed in Hazard Zone BB, those with maximum allowable leak rates between 100 and 1000 g/s be placed in Hazard Zone BC, and those with maximum allowable leak rates larger than 1000 g/s be placed in Hazard Zone BD. However, in addition to using these TD-based criteria, we also used 49CFR173 to provide information with respect to additional hazard classes (i.e., corrosive, explosive, flammable, etc.) as an additional consideration be used to categorize the PIH into hazard zones (49CFR173, 1991).

The consideration of 49CFR173 affects the PIH materials that are categorized in more stringent hazard zones for non-bulk shipments in 49CFR173 than those indicated by the TD criteria discussed above. For example, even though the maximum leak rates calculated by the TD method for the PIH listed in Packaging Group I (per 49CFR173) range from 0.15 g/s (Hazard Zone BA) to 1500 g/s (Hazard Zone BD), we recommend that they not be placed in Hazard Zones BC or BD because that is less stringent than the 49CFR173 classification which placed these materials in Packaging Group I (which is the most stringent group). Similarly, even though the maximum leak rates calculated for the Packaging Group II materials range from 12 g/s (Hazard Zone BB) to 3000 g/s (Hazard Zone BD), we recommend that they not be placed in Hazard Zone BD. We are making these recommendations because many of these materials have hazards in addition to their toxicity and the analyses supporting the categorization of materials into Packaging Groups I, II, and III in 49CFR173 takes these additional hazards into account.

For example, ethylene oxide/propylene (maximum leak rate of 300 g/s) and acrylonitrile (maximum leak rate of 820 g/s) are in Packaging Group I yet have higher maximum leak rates than crotonaldehyde (maximum leak rate of 94 g/s) and chlorine dioxide (maximum leak rate of 200 g/s) which are in Packaging Group II. Thus, although ethylene oxide/propylene and acrylonitrile are less relatively severe according to the TD based criteria than crotonaldehyde and chlorine dioxide, they are required to satisfy more stringent packaging performance standards because of the severity of their primary hazard (in this case, flammability). For all four of these PIH compounds, toxicity is only the secondary hazard.

We treated chlorine as an exception to our method of giving priority to 49CFR173. For chlorine, which is normally transported as a compressed gas, we recommend that it be in Hazard Zone BD. This is actually less stringent than recommended for non-bulk transport in 49CFR173, which classifies chlorine in Hazard Zone B. The TD calculations in Weiner and Griego, 1995, are based on the assumption that released chlorine would quickly react with moisture in the air to become hydrogen chloride. Hence, the airborne toxicant in a chlorine release would actually be hydrogen chloride. The calculations for chlorine, therefore, are based on the toxicity and dispersibility of hydrogen chloride. However, the authors recognize that there could be potential, though less likely, incidences where the relative humidity is low and the chlorine does not release as hydrogen chloride. The hazard zone used in 49CFR173 appears to assume that chlorine is released as Cl_2 rather than as hydrogen chloride.

An additional PIH worthy of specific mention is hydrogen sulfide. Because hydrogen sulfide has a vapor density that is 120% of the vapor density of air, it is not clear whether hydrogen sulfide would behave as an ideal gas or as a dense gas in the event of a release. Therefore, it was modeled both as an ideal gas and as a dense gas. In the absence of further guidance on the true (or most probable) behavior of hydrogen sulfide, we used the model which produced the lower maximum allowable leak rate. This was the ideal gas model.

Dispersion calculations were not performed for the PIH materials that are classified to behave as liquids in the event of a release. For those that are in Packaging Group I, we recommend that they also be placed in Hazard Zone BB, and for those that are in Packaging Group II, we recommend that they also be placed in Hazard Zone BC. Again, this is intended to be consistent with the treatment of the other Packaging Group I and II materials. In general, since a released liquid must evaporate before dispersing as a gas, liquids are less likely than gasses to disperse in high concentrations as far away from the release.

CLASSIFICATION RESULTS

The analysis performed according to the classification methodology described above resulted in a recommended scheme which classifies the PIH into four severity groups. The recommended categorization of the PIH materials into Hazard Zones BA, BB, BC, and BD, is shown in Table 1. Thus, Hazard Zones A, B, C, and D pertain to shipments smaller than 118 gallons, and Hazard Zones BA, BB, BC, and BD will pertain to shipments larger than 2000 gallons. Hazard Zone BA represents the more hazardous materials (as does Hazard Zone A for non-bulk transport), and Hazard Zone BD represents the relatively less hazardous materials (as does Hazard Zone D for non-bulk transport).

DISCUSSION

To set performance standards, it is necessary to select a cumulative percentage (X%) of accidents against which to protect the public. The cumulative percentage of accidents, then, correlates to specific accident conditions (i.e., X% of accidents have impact velocities less than or equal to a certain amount, thermal assault less than or equal to a certain amount, etc.) that the packaging must survive (Dennis et al. 1977). Survival can be defined as enduring these accident conditions without leaking more than the limit set for that performance category.

If the packaging groups are defined according to the classification scheme presented in this report, then the maximum allowable leak rates corresponding to the classification criteria can be used as the leak limits for proposed performance-oriented packaging standards. By definition, then, a maximum allowable leak rate of 0.10 g/s for Hazard Zone BA would prevent the ground-level concentrations of any of the released materials in Hazard Zone BA from exceeding their threshold levels beyond a one-km radius. Similarly, a maximum allowable leak rate of 10 g/s for Hazard Zone BB, 100 g/s for Hazard Zone BC, and 1000 g/s for Hazard Zone BD would prevent the ground-level concentrations of any of the materials in those hazard zones from exceeding their threshold levels at one kilometer from the release. In reality, for Hazard Zone BA with a maximum allowable leak rate of 0.10 g/s, the packaging manufacturers may opt for a zero leak rate since 0.10 g/s is already so small.

CONCLUSIONS

This project involved classifying the PIH into severity categories so that only one set of packaging performance criteria would be needed for each severity category rather than a separate set of performance criteria for each individual PIH.

With the PIH grouped into hazard zones, Packaging Groups and performance standards for these hazard zones can be defined. Each hazard zone can correspond to a Packaging Group or, as in 49CFR173 for non-bulk packagings, one Packaging Group may cover more than one hazard zone. If the packaging groups are chosen to

Table 1. Recommended Hazard Zones for PIH Transport in Packages Larger than 2000 Gallons

Name of Compound	Hazard Zone	Name of Compound	Hazard Zone
Acrylonitrile	BB	Hydrogen Fluoride	BB
Allyl Alcohol	BB	Hydrogen Selenide	BA
Ammonia; ammonium hydroxide	BC	Hydrogen Sulfide	BC
Arsine	BB	Iron Pentacarbonyl	BB
Bromine	BB	Methyl Bromide	BB
Bromine Chloride	BC	Methyl Isocyanate	BB
Bromine Pentafluoride	BA	Methyl Mercaptan	BC
Bromine Trifluoride	BB	Methylhydrazine	BB
Carbon Monoxide		Nickel Carbonyl	BB
Carbon Monoxide/Hydrogen		Nitric Acid, Nitrating Acid	BB
Carbonyl Fluoride	BC	Nitric Oxide	BB
Carbonyl Sulfide	BB	Nitrogen Dioxide	BB
Chlorine	BD	Nitrogen Fluoride Oxide	BB
Chlorine Dioxide	BC	Nitrogen Trifluoride	BB
Chlorine Trifluoride	BB	Oxygen Difluoride	BA
Crotonaldehyde	BC	Pentaborane	
Cyanogen	BB	Perchloromethyl Mercaptan	BB
Cyanogen Bromide	BB	Perchloryl Fluoride	BC
Cyanogen Chloride	BA	Phenyl Mercaptan	BC
Diborane	BA	Phosgene	BC
2,2-Dichlorodiethyl Ether	BC	Phosphine	BB
Dichlorodifluoromethane	BC	Phosphorus Oxychloride	BC
Dichlorosilane	BD	Phosphorus Pentafluoride	
Ethylene Chlorohydrin	BC	Phosphorus Pentachloride	
Ethylene Dibromide	BC	Phosphorus Trichloride	BC
Ethylene Oxide	BC	Selenium Hexafluoride	BB
Ethylene Oxide/Propylene	BB	Silicon Tetrafluoride	BC
Ethyleneimine	BB	Sulfur Chloride	BB
Fluorine	BB	Sulfur Dioxide	BB
Germane	BA	Sulfuric Acid, fuming	BB
Hexachlorocyclopentadiene	BB	Sulfuryl Fluoride	BC
Hydrazine	BA	Tetranitromethane	BB
Hydrogen Bromide	BB	Thiophosgene	BC
Hydrogen Chloride	BB		

correspond to the classification categories presented in this report, then the maximum allowable leak rates used to define these categories could be used as the maximum allowable leak rates for the performance-oriented packaging standards. The results discussed in this report are intended to provide quantitative guidance for the appropriate authorities to use in making these decisions.

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