Journal of Hazardous Materials, 3 (1979) 33—48

HAZARD EVALUATION OF CHEMICALS FOR BULK MARINE SHIPMENT

MICHAEL D. MORRISSETTE*

U.S. Coast Guard (G-MHM-3), Washington, D.C. 20590 (U.S.A.)

(Received July 31, 1978)

Summary

For economic reasons most chemicals used in large quantities by industry are transported in tank vessels. These chemicals range in properties from essentially harmless to highly dangerous. Although the United States and IMCO require certain minimum data before classifying a new chemical to be transported in bulk, no formal system exists to correlate these data with specific shipboard requirements such as the location of the tank within the vessel, gauging and venting systems, or cargo overfill protection.

Developing guidelines for the evaluation of chemicals is a two part problem. First, the inherent hazards of a chemical (the hazards of a product when it is released, without regard to its cargo containment system) must be investigated. In the second part of the evaluation, these hazards are then correlated with specific shipboards requirements as mentioned above. This paper outlines the essential elements for developing a comprehensive system of hazard evaluation for bulk liquid chemicals.

Introduction

During the past fifteen years the transportation of chemicals has shifted from the almost exclusive use of drums and similar sized containers to the point where a large portion of the world's chemical trade now moves by tanker. In early years these chemical vessels were for the most part converted petroleum tankers. Although many of these continue to transport the "simpler" chemical products, vessels of increasing sophistication capable of carrying many cargoes of widely differing properties and hazards are now common. Chemicals shipped in bulk quantities range in properties from essentially harmless (dioctyl phthalate) to water reactive (oleum), corrosive (caustic soda), highly toxic (allyl chloride), or unusually flammable (carbon disulfide).

Because of the risks involved in transporting the more hazardous chemicals, the United States Coast Guard began in 1965 a program of plan review and inspection of foreign vessels deemed to present potential and unusual risks to U.S. ports [1]. Later, these guidelines and instructions for the issuance of Letters of Compliance were updated and added to the U.S. regulations under

*Statements and opinions in this paper are those of the author and do not necessarily reflect the views of the U.S. Coast Guard.

Title 46 [2]. In 1967 the Maritime Safety Committee (MSC) of the Intergovernmental Maritime Consultative Organization (IMCO) established a Subcommittee on Ship Design and Equipment. Several years later the Subcommittee completed work on a Code for the Construction and Equipment of Ships Carrying Dangerous Chemicals in Bulk [3]. Both the U.S. regulations and the IMCO Chemical Code were designed to minimize risks to the ship, crew, and population at large during carriage and transfer operations involving dangerous chemicals. One of the major areas they address is the minimum requirements necessary (based on the hazards involved) for the safe transport of each of the cargoes that presents a significant risk. During the development of these requirements and subsequent additions of chemicals to both the U.S. regulations and the Code, several hazard evaluation systems were used to relate the physical properties and hazards of the various products being considered to the degree of containment needed. Although full agreement could not be reached in IMCO on a single evaluation system, the Coast Guard system using "hazard ratings" developed by the National Academy of Sciences (NAS) [4] was used extensively.

The Coast Guard is now developing a more comprehensive system for the evaluation of new chemicals based partly on more recent work done by the NAS [5]. Although still in the preliminary stages, the basic elements of the revised system are presented in this paper. It addresses products that are normally liquids at ambient temperatures and products shipped as molten liquids — liquefied and compressed gases are not considered although a number of the guidelines would still be appropriate. It is important to remember that this system or any system cannot be totally objective. A certain amount of flexibility must be available for products which in reality may present greater or lesser hazards than the evaluation system suggests. For this reason good judgment and experience are necessary.

Chemical hazards

Developing guidelines for the evaluation of chemicals is a two part problem. First the inherent hazards of a chemical (the hazards of a product when it is released, without regard to its cargo containment system) must be investigated. These hazards are then correlated with specific shipboard requirements. There are three general areas into which nearly all hazards from bulk chemical cargoes can be placed: human health, flammability, and reactivity. These hazards and their application to the marine environment are discussed below.

Human health hazards

Exposure to chemical products through inhalation, ingestion (oral intake), or skin absorption can lead to poisoning. Of these routes of exposure, inhalation is generally the most serious as the probability of exposure to vapors during routine operations (gauging, tank cleaning) and accidents involving spills is much greater than through either skin absorption or ingestion. The poison hazard from inhalation can be evaluated in several ways. The most common of these is the "Lethal Concentration Fifty" (LC_{50}). This is the concentration, usually stated in parts per million (ppm), that kills 50 percent of a group of test animals. Normally a one to four hour exposure time is followed by a 14-day observation period. Using several groups of animals at different concentration levels, an LC_{50} value can be calculated. The rat, since it is one of the least expensive animals and because it has internal organs somewhat similar to those of a human, is used most frequently. There are two basic drawbacks, however, to using the LC_{50} as a means of directly comparing inhalation hazards between chemicals:

(1) It does not take into account the vapor pressure of the chemical and

(2) Sub-lethal effects (headache, nausea, dizziness) which are important relative to a tankerman's performance or person's ability to escape a toxic vapor cloud may occur at differing concentration levels for two chemicals with the same LC_{50} value.

Therefore, chemicals with identical LC_{50}'s could present different degrees of hazard depending on the conditions involved. Another means of determining (or comparing) inhalation hazard is to subject the test animals to a saturated concentration of the vapors. This test introduces the factor of vapor pressure. Since the data represent worst possible conditions (highest vapor concentrations), they correlate best with a closed environment situation such as personnel in a cargo tank.

Up to this point the discussion of inhalation hazards has only been concerned with acute (short-term) exposures. Although of generally lesser concern, intermittent exposures to chemical vapors over a number of years should also be considered. For example, it is known that such chlorinated hydrocarbons as carbon tetrachloride and chloroform cause degradation of the liver and kidneys after prolonged exposures at concentrations less than 100 ppm. Benzene has been found to produce severe blood abnormalities and is strongly suspected of being a cancer-producing substance. Since tankermen may work for years in operations involving exposure to the vapors of various cargoes, they should be protected from this type of poisoning. The reference book *Documentation of the Threshold Limit Values* [6] is an excellent source for estimating the chronic (long-term) effects from the inhalation of chemical vapors.

A second route of exposure to chemical products is through skin absorption. Such chemicals as phenol, tetraethyl lead, and acetone cyanohydrin are rapidly absorbed through the intact skin in toxic amounts. In many cases only a tingling or irritating sensation may occur as the chemical contacts the skin. Chemicals with this property are generally systemic poisons and will produce effects or injury at a location other than the contact site. These effects will many times be delayed while the chemical is absorbed into the bloodstream. To test for skin absorption hazards, an LD_{50}, dermal (the dose that will kill 50% of a group of test animals when administered by continuous contact with the bare skin) is usually performed. Rabbits are most often used for this test. The skin absorption properties are important whenever there is a possibility of liquid contact such as in spill cleanup from an overfilled tank or a break or leak in a line.

Ingestion is another route of exposure which must be considered when evaluating the hazards of chemical products. While most ships' personnel do not "sample" the products they are carrying, this exposure route becomes important when a tanker is involved in an accident where one or more tanks have been breached and are leaking into the water. If the discharge is near to the intake of a municipal water system, the chemical could be drawn in requiring the plant be shut down if the concentration is high enough to create a poison hazard. Further, if the chemical is not detected, it may not be removed, resulting in contaminated water for those people being served by the municipal system. An experimental animal test that measures the degree of hazard under these conditions is the LD_{50}, oral (the dose that will kill 50% of a group of test animals when administered orally). Rats and mice are frequently used although other animals such as guinea pigs, cats, dogs, birds, and even frogs have been tested. Examples of bulk chemicals particularly toxic by this criterion are acetone cyanohydrin (LD_{50}, rats = 13 mg/kg) and allyl alcohol (LD_{50}, rats = 64 mg/kg). A dose of 50 mg/kg corresponds to approximately one teaspoonful of the liquid for a 70 kg (150 lb) man.

In addition to chemicals that act as poisons to the human body as discussed above, there are also products such as caustic soda solution which can produce severe corrosive effects on contact with exposed tissues (skin and eyes). These products chemically react with and destroy tissue leaving irreversible damage if not washed off immediately. Other products (for example, cashew nut shell oil) are severe skin irritants, producing rashes or blistering of the skin. During certain cargo handling operations where there is a possibility of chemicals with these properties contacting personnel, protection should be available to prevent injury.

Finally, there are a relatively small number of chemicals which may sensitize persons who have been exposed to them (though not necessarily during the first contact). If this occurs, subsequent exposure even at very low levels will result in the same or more severe symptoms than were experienced during the exposure at which the person became sensitized. Some chemicals such as triethylenetetramine are skin sensitizers but the more hazardous cases are those that affect the respiratory tract. Exposure to high concentrations of the vapors of toluene diisocyanate (TDI) usually results in a severe asthmatic attack with marked difficulty in respiration. Once an individual has become sensitized, any later exposure even though the concentration may be below the Threshold Limit Value (TLV) established for TDI (in the U.S. the TLV is presently 0.02 ppm) is likely to provoke another attack. Exposure of personnel to sensitizing chemicals such as TDI and other isocyanates must be kept to a minimum.

Flammability hazards

The U.S. regulations for bulk hazardous liquids and the IMCO Chemical Code were not developed to protect against products that have "normal" flammability characteristics as their only significant hazard (i.e. gasoline, acetone). This does not imply these products are safe and do not require careful handling. Obviously, the number of accidents which have occurred confirm this is not the case. The U.S. has regulations [7] which address the normal flammability problems of cargoes carried on tank vessels. Certain other chemical products, however, present unusual flammability problems which put them on a higher hazard level. Products having a low autoignition temperature or wide flammable limits are more dangerous because the probability of ignition is greater. Table 1 illustrates the variance of these properties among several chemical cargoes.

TABLE 1

Flammable properties of selected bulk chemicals

Chemical	Flash point (° C)	Autoignition temperature (° C)	Limits of flammability (% in air)
Gasolines	< 0	300—450	1—8
iso-Butyraldehyde	−40	250	2—11
Acetone	−18	540	3—13
Carbon disulfide	−30	100	1—44
Ethyl ether	−45	180	2—48
Phosphorus (white)		30	

It is clear from this table that the last three cargoes present greater flammability risks during transportation and discharge operations than the first three. For example, with an upper flammable limit of 44%, even saturated concentrations of carbon disulfide would be in the flammable range at 20° C. This product would be a fire hazard both in a closed tank environment where a saturated concentration is reached and in non-confinement (open air) conditions where concentrations would be lower but still within the flammable range. In addition to its greater probability of being ignited, carbon disulfide produces sulfur dioxide, a highly irritating gas, as a product of combustion.

Special precautions such as inerting or padding and a more protective containment system to handle the hazards of these unusually flammable cargoes are necessary for their safe carriage.

Reactivity hazards

Several types of reactivity problems exist which should be considered in the hazard evaluation. These are reactivity with water, air, other chemicals, materials of construction, and self-reactivity.

Some products in bulk marine transportation react very exothermically when mixed with water. Sulfuric acid, oleum, and chlorosulfonic acid are among the most water reactive. Chemicals with this property must be stowed away from the hull of a vessel to reduce the chances of their reacting with water in the event of a collision or grounding. Large amounts of heat can be expected and under some conditions an aerosol formation leading to the generation of a toxic gas cloud is possible.

CARGO COMPATIBILITY

CARGO GROUPS \ REACTIVE GROUPS	1. NON-OXIDIZING MINERAL ACIDS	2. SULFURIC ACID	3. NITRIC ACID	4. ORGANIC ACIDS	5. CAUSTICS	6. AMMONIA	7. ALIPHATIC AMINES	8. ALKANOLAMINES	9. AROMATIC AMINES	10. AMIDES	11. ORGANIC ANHYDRIDES	12. ISOCYANATES	13. VINYL ACETATE	14. ACRYLATES	15. SUBSTITUTED ALLYLS	16. ALKYLENE OXIDES	17. EPICHLOROHYDRIN	18. KETONES	19. ALDEHYDES	20. ALCOHOLS, GLYCOLS	21. PHENOLS, CRESOLS	22. CAPROLACTAM SOLUTION	
1. NON-OXIDIZING MINERAL ACIDS		X			X	X	X	X	X	X	X	X	X			X	X		A	E			1
2. SULFURIC ACID	X		X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	2
3. NITRIC ACID		X			X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X		3
4. ORGANIC ACIDS		X			X	X	X	X	C			X				X	X			F			4
5. CAUSTICS	X	X	X	X							X	X				X	X		X	X	X	X	5
6. AMMONIA	X	X	X	X						X	X	X	X			X	X		X				6
7. ALIPHATIC AMINES	X	X	X	X							X	X	X	X	X	X	X	X	X	X	X	X	7
8. ALKANOLAMINES	X	X	X	X							X	X	X	X	X	X	X	B	X				8
9. AROMATIC AMINES	X	X	X	C							X	X							X				9
10. AMIDES	X	X	X			X						X									X		10
11. ORGANIC ANHYDRIDES	X	X	X		X	X	X	X	X														11
12. ISOCYANATES	X	X	X	X	X	X	X	X	X	X					D					X		X	12
13. VINYL ACETATE	X	X	X			X	X	X															13
14. ACRYLATES		X	X				X	X															14
15. SUBSTITUTED ALLYLS		X	X				X	X				D											15
16. ALKYLENE OXIDES	X	X	X	X	X	X	X	X															16
17. EPICHLOROHYDRIN	X	X	X	X	X	X	X	X															17
18. KETONES		X	X				X	B															18
19. ALDEHYDES	A	X	X		X	X	X	X	X														19
20. ALCOHOLS, GLYCOLS	E	X	X	F	X		X					X											20
21. PHENOLS, CRESOLS		X	X		X		X			X													21
22. CAPROLACTAM SOLUTION		X			X		X					X											22
30. OLEFINS		X	X																				30
31. PARAFFINS																							31
32. AROMATIC HYDROCARBONS			X																				32
33. MISCELLANEOUS HYDROCARBON MIXTURES			X																				33
34. ESTERS		X	X																				34
35. VINYL HALIDES			X																			X	35
36. HALOGENATED HYDROCARBONS		G			H		I																36
37. NITRILES		X																					37
38. CARBON DISULFIDE							X	X															38
39. SULFOLANE																							39
40. GLYCOL ETHERS		X										X											40
41. ETHERS		X	X																				41
42. NITROCOMPOUNDS					X	X	X	X	X														42
43. MISCELLANEOUS WATER SOLUTIONS		X										X											43
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	

REACTIVITY DIFFERENCES (DEVIATIONS) WITHIN CHEMICAL GROUPS

A	Acrolein (19), Crotonaldehyde (19), and 2–Ethyl–3–propyl acrolein (19) are not compatible with Group 1, Non–Oxidizing Mineral Acids.
B	Isophorone (18), and Mesityl Oxide (18) are not compatible with Group 8, Alkanolamines.
C	Acrylic Acid (4) is not compatible with Group 9, Aromatic Amines.
D	Allyl Alcohol (15) is not compatible with Group 12, Isocyanates.
E	Furfuryl Alcohol (20) is not compatible with Group 1, Non–oxidizing Mineral Acids.
F	Furfuryl Alcohol (20) is not compatible with Group 4, Organic Acids.
G	Dichloroethyl Ether (36) is not compatible with Group 2, Sulfuric Acid.
H	Trichloroethylene (36) is not compatible with Group 5, Caustics.
I	Ethylenediamine (7) is not compatible with Ethylene Dichloride (36).

Fig.1. Revised compatability chart with list of deviations.

Reactivity towards other chemicals being carried is also important. Although tank vessels have the capability of carrying a wide variety of liquid cargo at the same time, a single bulkhead is usually all that separates two liquids in adjacent tanks. If the bulkhead develops a crack through long term stress or a collision, the products inside these tanks will mix. The rate of mixing will depend on the size of the crack, the difference in level between the two liquids, and the densities of the liquids. Pressure may increase in the cargo tank either as a result of the rapid heating of cargoes during a strongly exothermic reaction or the evolution of a gaseous reaction product. If the capacity of the relief valve is insufficient, the increasing pressure will lead to a rupture of the cargo tank which could be violent. Because of the complexity of evaluating the possible hazardous reactivity of one chemical with all others, this problem has been addressed in the U.S. by a separate publication, *Guide to Compatibility of Chemicals* (NVC 4-75) [8]. Products are assigned to groups based on their chemical structure. These groups have been arranged in the form of a chart with an "x" indicating hazardous reactivity (temperature increase greater than 25° C or evolution of gas) and a letter other than an "x" directing the user to another listing for specific compatibility data. The chart and listing of reactivity differences are shown in Fig.1.

Oxygen present in the air can in certain cases react with the cargo being carried. During loading and unloading operations and as the tank breathes during transit, air will normally be in the ullage (vapor) space. Many of the ethers (for example, ethyl ether) react with available oxygen to form peroxides. If the peroxides of ethyl ether become concentrated, they can present an explosion hazard, particularly in cases where a relatively small amount of ether remains in a tank or line and is evaporating, leaving the less volatile peroxides behind. To prevent buildup of peroxides, inhibition or inertion with nitrogen gas is necessary.

Another form of reactivity that has potential for serious problems is the tendency of some chemicals, usually monomers, to undergo a hazardous self-reaction. Products which will polymerize (the most common type of self-reaction for bulk chemicals) include styrene, ethyl acrylate, acrylic acid, and vinyl acetate. The process of polymerization creates heat and sometimes gas as the single molecules join up to form long chains. The heat released, if not lost to the tank walls, further accelerates the reaction, creating more heat. In time the reaction becomes self-sustaining and proceeds past the point of requiring outside stimulus to continue. The pressure generated as the liquid heats up to high temperatures can lead to a violent rupture of the tank. Polymerization is usually initiated by other chemical cargoes which may act as catalysts or from heat from an adjacent tank carrying an elevated temperature cargo. To help prevent the reaction from starting, inhibitors must be added to these monomers which should be stowed away from cargoes that are heated.

The last type of reactivity that will be discussed is chemical corrosion. Products that are severely corrosive to common materials of construction, particularly steel, should not be used in the cargo containment system. Corrosion in excess of approximately 0.1 inch (2.54 mm) per year would result in leaking tanks and structural problems within a few years if carried regularly. Also, chemicals which liberate significant amounts of hydrogen during the corrosion process (dilute concentrations of sulfuric acid) will create the additional problem of flammable vapors in the tank or surrounding spaces such as a double bottom or void. Since special electrical equipment is necessary for hydrogen atmospheres, the standard equipment adequate for the vapors of the pure product could be a source of ignition for hydrogen. With flammable limits between 4 and 75% in air, this gas presents a very severe explosion hazard when confined.

Minimum hazard criteria and evaluation of new products

To determine whether a bulk chemical possesses properties dangerous enough to require special precautions during handling and transport, criteria establishing significant (minimum) hazards are necessary. These guidelines would be used to screen new chemicals, with products falling within the guidelines considered hazardous. Using the discussion of the various hazards in the preceeding section as a basis, the criteria outlined below have been developed to identify chemicals which appear to require special precautions. They should not be used as absolutes, however. For a number of products the suggested numerical values will need adjustment to account for such physical properties as vapor pressure, solubility, and density. For example, in estimating the inhalation hazard, the LC_{50} will provide a relative idea of the vapor toxicity but the chemical's volatility and odor characteristics also need to be considered for a realistic hazard assessment. Products which are volatile and offer little warning that their vapors are harmful (chloroform, benzene) are more dangerous than those having a low vapor pressure at ambient temperatures and a distinct odor (propionic acid, ethanolamine). Similarly, the LD_{50} (oral) cannot be used as the sole criterion for judging the hazard from ingestion: products which are soluble in water and do not have a pronounced taste or odor are more likely to be ingested in larger doses.

Minimum hazard criteria

Chemicals which fall into one or more of the following categories should be considered hazardous:

(a) Significantly toxic by inhalation — LC_{50} less than or equal to 2000 ppm (1 h exposure to rats). Products that have higher LC_{50}'s but correspondingly high vapor pressures should be included, particularly if the vapors have poor warning properties. Products with higher LC_{50}'s should also be considered if they are less dense than water since they will float if spilled from a damaged tank and present a much greater inhalation hazard than those which are more dense and sink. Non-volatile products should not be included unless they have low LC_{50}'s.

(b) Significantly toxic by oral ingestion — LD_{50} less than or equal to 1000 mg/kg (rats). Products with somewhat lower LD_{50}'s but which have a very low solubility in water or a distinct taste should not be included.

(c) Significantly toxic by skin absorption — LD_{50} less than or equal to 1200 mg/kg (rabbits). Products with somewhat higher LD_{50}'s but which are absorbed with very little or no irritation should be included.

(d) Inhalation of vapors can cause allergic sensitization.

(e) Intermittent exposure to vapors over an extended period of time can cause moderate to severe injury.

(f) Liquids that are severely irritating or corrosive to skin or are skin sensitizers.

(g) Reactive with water producing gas, aerosols, or large amounts of heat.

(h) Inhibition, stabilization, or inertion required to prevent hazardous reactivity.

(i) Autoignition temperature below 200° C (392° F).

(j) Difference between upper and lower limits of flammability (expressed in percent by volume in air) exceeds 20. If most of the flammable range occurs above ambient temperatures (approximately 25° C), the product should not be included (for example, methyl alcohol).

(k) Severely corrosive to steel (in excess of 0.1 inch per year) or significant hydrogen gas generation.

As mentioned earlier, both the U.S. regulations and the IMCO Chemical Code are designed to minimize risks to the ship, crew, and population at large during carriage and transfer operations involving dangerous chemicals. Different degrees of containment are specified for the various products carried depending upon the hazards they possess.

In the system presented in this paper, products being considered for bulk shipment would be initially reviewed to determine whether they meet one or more of the minimum hazard criteria outlined above. Those that do are further evaluated using the guidelines suggested below. These guidelines have been developed to relate the chemical hazards of a product to a ship's cargo containment system, venting, gauging, and other requirements necessary for safe transport. The qualifying remarks under some of the minimum hazard criteria, although not restated, are equally valid. Except where otherwise indicated, products which meet one or more of the criteria under each requirement would be assigned that requirement.

Cargo containment

Type I (highest standard of protection; requires cargo to be located inboard from the side and above the bottom of the ship; damage stability standards for ship also prescribed):

(a) Extremely toxic products (meets one or more).

(1) LD_{50} (oral, rats) less than 25 mg/kg.

(2) LD_{50} (dermal, rabbits) less than 100 mg/kg.

(3) LC_{50} (1h exp., rats) less than 200 ppm.

(b) Extremely reactive with water producing large quantities of toxic gas or aerosols.

(c) Very severe flammability characteristics:

(1) Autoignition temperature below 75° C (167° F), or

* (2) Difference between the limits of flammability (percent by volume in air) exceeds 50.

Type II (intermediate standard of protection; requires cargo to be located inboard from the side (but a lesser distance than type I) and above the bottom of the ship; damage stability standards also prescribed):

* (a) Moderately to highly toxic products (meets one or more):

(1) LD_{50} (oral, rats) between 25 and 500 mg/kg.

(2) LD_{50} (dermal, rabbits) between 100 and 600 mg/kg.

(3) LC_{50} (1 h exp., rats) between 200 and 1200 ppm.

(b) Highly reactive with water producing toxic gas or aerosols.

(c) Severe flammability characteristics:

(1) Autoignition temperature below 200° C (392° F), or

* (2) Difference between the limits of flammability exceeds 20.

Type III (significant standard of protection for cargoes of lesser hazards): All other bulk products meeting the minimum hazard criteria guidelines.

Tanks

Independent gravity (a cargo tank that does not incorporate a part of the vessel's hull and is not essential to the integrity of the hull; this type of tank is less likely to develop a leak than an integral gravity tank (normal tank) after long term hull stress, collision or grounding):

(a) Volatile liquids which are highly to severely toxic by inhalation — LC_{50} (1 h exp., rats) less than 800 ppm.

* (b) Highly to severely toxic by more than one mode of administration:

(1) LC_{50} (1h exp., rats) less than 800 ppm.

(2) LD_{50} (dermal, rabbits) less than 350 mg/kg.

(3) LD_{50} (oral, rats) less than 250 mg/kg.

(c) Autoignition temperature below 75° C (167° F).

* (d) Difference between the limits of flammability exceeds 20.

(e) Required because of structural considerations (i.e. sulfur).

Integral gravity (a cargo tank that is part of the vessel's hull structure so that the tank and hull may be stressed by the same loads): All other bulk products meeting the minimum hazard criteria guidelines.

Venting device

Pressure vacuum valve (fitted to each tank with vent exits extending to a minimum of four meters above the deck; vent exits are located away from air intake or opening into accommodation or other service spaces):

*(a) Significantly to extremely toxic by inhalation (acute) — LC_{50} (1h exp, rats) less than 2,000 ppm.

(b) Moderate to severe injury expected from intermittent, long term exposure to vapors.

---

*See footnote p. 45.

(c) Exposure to vapors may cause allergic sensitization.
(d) Inerted cargo.
(e) Flash point at or below 27° C (80° F).
(f) Inhibited cargo where oxygen depletes the inhibitor.
Open (allows vapor to flow freely to and from the tank; permitted for cargoes of lesser hazards): All other bulk products meeting the minimum hazard criteria guidelines.

Gauging device
Closed (an arrangement for gauging the amount of cargo in a tank that does not have any opening through which cargo vapor or liquid can escape):
*(a) Highly to severely toxic by inhalation (acute) — LC_{50} (1 h exp., rats) less than 800 ppm.
(b) Severe injury expected from intermittent, long term exposure to vapors.
(c) Exposure to vapors may cause allergic sensitization and subsequent severe injury.
*(d) Highly to severely toxic by skin absorption — LD_{50} (rabbits) less than 350 mg/kg.
Restricted (an arrangement of gauging through an opening of limited size that does not vent the tank's vapor space):
*(a) Significantly to moderately toxic by inhalation (acute) — LC_{50} (1 h exp., rats) between 800 and 2000 ppm.
(b) Moderate injury expected from intermittent, long term exposure to vapors.
(c) Exposure to vapors may cause allergic sensitization.
(d) Inerted cargo.
Open: All other bulk products meeting the minimum hazard criteria guidelines.

Other requirements and special requirements
Inertion of space above the cargo:
(a) Cargo is air-reactive resulting in dangerous peroxide formation.
(b) Autoignition temperature below 200° C (392° F).
*(c) Difference between the limits of flammability exceeds 20.
Toxic vapor detection instrumentation (required onboard the vessel): *Products which are significantly to extremely toxic by inhalation (acute) — LC_{50} (1 h exp., rats) less than 2000 ppm.
Cargo tank overfill protection (high level alarm and a tank overfill control system that automatically closes the filling line):
*(a) Highly to severely toxic products (meets one or more):
(1) LD_{50} (oral, rats) less than 250 mg/kg.
(2) LD_{50} (dermal, rabbits) less than 350 mg/kg.
(3) LC_{50} (1 h exp., rats) less than 800 ppm.
(b) Exposure to vapors may cause allergic sensitization and subsequent severe injury.
(c) Autoignition temperature below 200° C (392° F).

*See footnote p. 45.

*(d) Difference between limits of flammability exceeds 20.

Protective clothing (required for persons involved in transfer operations):

(a) Corrosive liquids.

*(b) Highly to severely toxic by skin absorption — LD_{50} (dermal, rabbits) less than 350 mg/kg.

(c) Severe skin sensitizers.

Unusually toxic products (increased vent heights with the vent systems further away from openings or air intake to accomodation or service spaces; vapor return line connections on the tank vent systems; additional segregation restrictions from products not assigned this special requirement):

*(a) Moderately to severely toxic products (meets one or more):

(1) LD_{50} (oral, rats) less than 500 mg/kg.

(2) LD_{50} (dermal, rabbits) less than 600 mg/kg.

(3) LC_{50} (1 h exp., rats) less than 1200 ppm.

(b) Moderate to severe injury expected from intermittent, long term exposure to vapors.

(c) Exposure to vapors may cause allergic sensitization and subsequent severe injury.

Increased pumproom ventilation (changes the air in the cargo pumproom 45 times per hour):

*(a) Highly to severely toxic by inhalation — LC_{50} (1 h exp., rats) less than 800 ppm.

(b) Severe injury expected from intermittent, long term exposure to vapors.

(c) Exposure to vapors may cause allergic sensitization and subsequent severe injury.

Limitations

To use this evaluation system, certain data must be available in the areas of toxicology, reactivity and flammability. Additionally, basic physical properties such as vapor pressure, solubility and density must be known. These input data were selected because it was felt they could be found for most new products and would be sufficient if used properly to estimate a chemical's hazard in the marine environment. If data are not available, the system is useless. Therefore, in developing criteria for hazard evaluation it is usually necessary to select testing techniques that are fairly standard even though they may not fully reflect the actual hazards. For example, when developing a new product, a chemical manufacturer will frequently run LD_{50} (oral and dermal) and LC_{50} tests. Although these tests are not designed to investigate effects other than death, they can be used as an indication of a chemical's ability to produce serious effects at lower concentrations. In an ideal sense, when evaluating a new

---

*The numerical values suggested are not intended as absolutes. Because of the effects various physical properties may have on the actual hazard, the qualifying remarks discussed in the listing of Minimum Hazard Criteria must be consulted.

chemical for bulk shipment, it would be better to have data which could be more closely correlated to the tankerman's actual exposure; that is, human or animal data to indicate what harmful effects he could expect from, for example, breathing the vapors for 10 to 15 minutes during a topping off operation. Sub-lethal data of this nature, however, are not readily available and requiring animal studies can be costly and the results subject to interpretation. Because of this limitation it must be kept in mind that the guidelines presented in this paper cannot take into account all conditions and possible hazards. Requirements for products which appear to possess greater or lesser hazards than the system suggests (such as in cases where accidental human exposure data differs from experimental animal data or the chemical possesses properties not addressed in this system) should be upgraded or downgraded accordingly.

In many instances toxicological data may be located on a product for tests which are different than those specified in the criteria used in the guidelines. Numerous experimental animal studies have been performed using different animal species (guinea pig rather than a rat) or a different mode of administration (subcutaneus injection instead of an oral dose). While data from these animal studies are valid and have specific uses, they are difficult to correlate with data generated from the specified tests. Since metabolism rates and biological mechanisms may vary depending upon the type of test and animal used, the resulting dosages (for example, for an LD_{50}) are likely to be quite different. To remain as consistent as possible in the evaluation of new chemicals, the use of data from animal studies other than those described should be avoided. Data from studies involving different exposure times, however, can usually be extrapolated when the difference in time is not too great. If a four hour exposure to rats of some chemical's vapor results in an LC_{50} of 50 ppm, a one hour exposure could be expected to yield an LC_{50} of approximately 200 ppm.

Products too hazardous for bulk shipment

A number of products possess characteristics which appear to be too hazardous for their safe shipment in large quantities. Products capable of detonations (nitromethane) or very powerful oxidizing agents (nitrogen tetroxide) should obviously not be considered for bulk shipments. Certain other chemicals however, possess properties which are borderline between the assignment of the most restrictive containment requirements and not permitting bulk carriage. Any product with properties dangerous enough to qualify for a Type I cargo containment system should be further evaluated to determine whether it may be too hazardous for bulk shipment. In general, chemicals with more than one extremely hazardous property (or in some cases just one) should not be permitted in bulk. For example, the very volatile chemical acrolein has an LC_{50} (1 h exposure to rats) of 8 ppm and is known to be lethal to man in ten minutes at a concentration of 153 ppm [9]. These data indicate acrolein to be a very severe inhalation problem and it should not be authorized for bulk shipment. Another volatile product, ethylenimine, has an LD_{50} (oral, rats) of 15 mg/kg, an LD_{50} (dermal, guinea pigs) of 14 mg/kg, and an LC_{50} (1h exposure to rats) of 250 ppm [10]. This combination of extremely hazardous properties precludes ethylenimine from being carried in large quantities. Although it may be possible to safely ship acrolein, ethylenimine and other similar products using the most stringent containment system, the consequences from an accident releasing one of these would be very severe.

Conclusion

The purpose of this paper has been to review the various hazards of chemicals being shipped in bulk and to present guidelines for an evaluation system which can be used to relate these hazards to design and operational requirements for ships. These guidelines are in the preliminary stages and do not represent an official U.S. Coast Guard evaluation system. They are subject to further review and modification before being adopted, particularly in the area of aquatic toxicity where such criteria as bioaccumulation, persistence, and TL_m values would influence cargo containment requirements. Accident review and a more detailed analysis of operational procedures and equipment should provide additional insight, resulting in a more refined evaluation system.

The suggested guidelines will be submitted in the near future to IMCO's Subcommittee on Bulk Chemicals for consideration. If the products presently in the Chemical Code were re-evaluated under the proposed system, most would be assigned similar minimum requirements. Since several hazard evaluation systems were used to evaluate these chemicals, however, it would not be possible to construct a system which would duplicate the requirements given the properties of the various products. Some inconsistencies presently exist in both the Code and U.S. regulations. A standard means of evaluating new chemicals proposed for bulk water movement would be a definite step forward in maintaining consistency between transport requirements and chemical hazards.

References

1 United States Coast Guard, Navigation and Vessel Inspection Circular No. 13-65, September, 1965.

2 United States, Code of Federal Regulations, Title 46, Shipping, Part 154, Special Interim Regulations for Issuance of Letters of Compliance, October 1976.

3 IMCO Resolution A. 212 (VII), Code for the Construction and Equipment of Ships Carrying Dangerous Chemicals in Bulk, adopted October 1971.

4 National Academy of Sciences — National Research Council, Evaluation of the Hazard of Bulk Water Transportation of Industrial Chemicals, Washington, D.C., 1970.

5 National Academy of Sciences — National Research Council, System for Evaluation of the Hazards of Bulk Water Transportation of Industrial Chemicals, Washington, D.C., February, 1974.

6 American Conference of Governmental Industrial Hygienists, Documentation of the Threshold Limit Value, Third Edition, American Conference of Governmental Industrial Hygienists, 1971, Cincinnati, Ohio.

7 United States, Code of Federal Regulations, Title 46, Shipping, Parts 30—40, Rules and Regulations for Tank Vessels, October 1976.

8 United States Coast Guard, Navigation and Vessel Inspection Circular No. 4—75, December 1975.
9 K.C. Back, A.A. Thomas and J.D. MacEwen, Reclassification of Materials Listed as Transportation Health Hazards, p. A-164, Aerospace Medical Research Laboratory, Wright-Patterson Air Force Base, Ohio, August 1972.
10 Ref. 9, p. A-206.