

DEVELOPMENT OF A COMPATIBILITY GUIDE FOR THE WATER TRANSPORT OF BULK CHEMICAL CARGOES

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Summary

The United States Coast Guard in order to discharge its responsibility for safe shipment of chemical cargoes on American waterways has developed a chemical compatibility guide which designates those chemicals which are safe for adjacent loading on barges and tankers. The guide is based largely on experimental data and replaces an earlier Coast Guard publication on compatibility.

Introduction

In its function as a major operating arm of the Department of Transportation, the U.S. Coast Guard has the responsibility for the safe shipment of bulk chemicals by water. Although major mixing of bulk cargoes occurs rarely, the possibility does exist for some chemical cargoes, if mixed, to react and evolve heat and/or gases and create a hazard to personnel and property.

For economic reasons, most chemicals needed in large quantities by industry are moved whenever possible in barges or chemical tankers. Although these tank vessels have the capability of carrying a wide variety of liquid cargo at the same time, a single bulkhead (wall) is usually all that separates two liquids in adjacent tanks. If the bulkhead should develop a crack through long term stress or during a collision, the products inside these tanks will mix.

Typical designs of chemical tankers and barges permit several arrangements where the compatibility of the products being carried becomes a factor. Figure 1 is a cargo tank diagram of a relatively new chemical tank ship. The diagram shows a total of 25 tanks of various shapes and with sizes ranging from about 200 to 1,500 cubic meter capacity. If a product were being considered for carriage in tank 6C, for example, the cargoes in adjacent tanks sharing a common bulkhead (7C, 4P, and 4S) must be selected carefully to ensure they are compatible. Although tanks 5P and 5S are also adjacent, they share only a common corner which is unlikely to be a source of leakage. Tank 5C is separated from 6C by a cofferdam (empty space between bulkheads). The possibility of

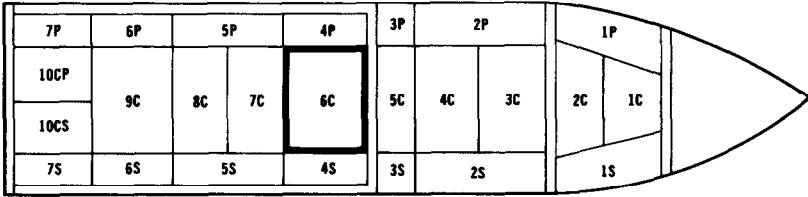


Fig. 1. Cargo tank diagram of a chemical tank ship.

cargoes on opposite sides of a cofferdam leaking and mixing are remote.

Large scale mixing would be expected only if the ship or barge were involved in a collision. In this case, additional problems may be created by chemical reactivity but it is more likely that fire and explosions will be the primary consideration. Serious destruction of tanks and framing would create adequate venting capacity for gas development or increased vapor pressure from reacting cargoes. Mixing on a more moderate scale, however, may occur if a bulkhead connecting adjacent cargo tanks cracks. 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 the 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.

In addition to compatibility considerations for adjacent tanks with common bulkheads, the use of common transfer or vent lines for cargo tanks could also lead to product mixing. Some conditions under which this might happen are: improper piping connections; incomplete cleaning of piping; overfilling a cargo tank (the excess from an overfilled tank may be forced into another tank through the vent system). Another arrangement which could result in accidental mixing is the use of pipelines which run through other cargo tanks. In some cases piping from a forward tank may run through eight or more tanks before connection with a pumproom located in the aft portion of a vessel.

Development of NVC 5-70

The U.S. Coast Guard, recognizing the need for detailed guidelines, requested the National Academy of Sciences (NAS) Committee on Hazardous Materials to study the problem. This Committee was established in 1964 at the request of the Commandant of the Coast Guard to provide continuing advisory service to the Coast Guard in the area of hazardous materials transportation by water. Members are engineers and scientists drawn from industry, government, and universities whose efforts are supplemented by experts appointed to panels working on specific tasks. Unfortunately, at the time the NAS Committee began its study of compatibility, few experimental data were available on

chemical reactivity applicable to the problems of marine transportation. Data could be found on reactions run under special conditions or with catalysts, but these were of very limited use. Since most bulk chemicals are shipped at ambient temperatures and pressures, the reactions that take place at or near these conditions are the ones that need to be considered. In developing compatibility guidelines, a number of sources of reactivity data were reviewed, including compatibility charts in use by several large chemical companies. These charts were useful to the Committee but generally covered only those chemicals manufactured by the companies that developed them. Also, there were cases where it was difficult to distinguish between combinations not recommended for adjacent stowage because of safety considerations and combinations not recommended because of product purity considerations. While the latter problem could be economically critical to some companies, the Coast Guard was interested only in the safety aspects should two cargoes mix.

This early work by the NAS Committee culminated in a report [1] to the Coast Guard in September 1969. Based on this report, the Coast Guard's first guide, NVC 5-70 [2], was published in 1970 and later adopted by a number of countries and ports. Although as much experimental information as possible was used, a large part of the input was based on the judgment of Committee members*. The compatibility chart from NVC 5-70 is shown in Fig. 2. Since it provided a rapid and straight-forward means of determining whether two chemicals might be dangerously reactive, the guide found wide acceptance among shipping interests.

Establishment of an experimental basis for a new compatibility guide

During the development of NVC 5-70 the Committee recognized that there were many compatibility questions that could not be resolved without experimental data. The uncertainties resulted in conservative ratings on the chart. The Committee recommended experimental studies to fill these data gaps and the Coast Guard, through the National Academy of Sciences, funded Contract CCT-40-69-15 to The Dow Chemical Company to examine 202 bulk chemicals of commerce for possible hazards from self-reactivity and binary incompatibility [3].

1. Principle of chemical grouping

The large number of chemicals, particularly the number of binary systems (20,301), necessitated a separation of the 202 chemicals into groups based on chemical structure such that group members might be expected to have similar chemical reactivity. Chemicals having only the hydroxyl group were placed in one group and chemicals having only the amino group in another; but chemicals having both the hydroxyl and amino groups were placed in still another group. The remaining chemicals were treated similarly until all

*The principle contributors were W.W. Crouch, G.H. Damon, J.H. Paden, and M.A. Paul.

202 bulk chemicals on the Coast Guard list were placed into 53 groups. Group sizes varied from a single member to as many as 25.

A representative or "working chemical" was chosen for each of the 53 groups. Selection of the working chemical was based upon an expected high level of reactivity for its group and, in a few cases, the ease with which it could be handled at ambient conditions. The 53 working chemicals and list of bulk chemicals are given in Table 1.

The result of the chemical grouping was to reduce for experimentation the number of single chemicals from 202 to 53 and the binary possibilities from 20,301 to 1,378.

Samples of all working chemicals were acquired in "practical" or "technical" grade, similar or identical to the quality of the as-shipped material.

2. *Experimental method*

Since the most important consideration of chemical incompatibility is the overpressurization of a cargo tank or pipe, the experimental program for determining reactivity hazards required a procedure which would determine:

- Whether an exothermic reaction occurred when two working chemicals were mixed.
- A good approximation of the maximum temperature rise.
- Whether a gas was a product of reaction.

The procedure used in the Dow investigation consisted of three steps: In the first step, the two working chemicals were mixed together by simultaneous delivery from graduated syringes into a 300 ml silvered Dewar flask. The working chemicals were delivered in a 1:1 molar ratio and the volumes of each calculated so that the final volume was 10 ml. A No. 30 iron-constantan thermocouple, sheathed in a 2 mm O.D. glass capillary, sensed any temperature change. Temperature was recorded continuously on a strip-chart recorder. When an exothermic reaction occurred, the maximum temperature reached was noted and the change in temperature (ΔT) was calculated.

If no exothermic reaction occurred in the initial mixing experiment, or if only a small exotherm was observed and a liquid mixture remained, a sample of the mixture was taken for differential thermal analysis. The sample was heated at a rate of 20°C/min to 200°C or until an exothermic reaction took place.

In the last step of the experimental procedure, measurements of pressure and temperature increases were made on those binaries found reactive between room temperature and 46°C (115°F). For the measurements, the Dewar flask was instrumented.

Using the above techniques, data were generated on the 1378 possible binaries of the 53 working chemicals.

3. *Norwegian data*

Steenland et al. [4] used similar techniques to obtain compatibility data on an additional 350 binary systems. The differential thermal analysis

(continued on p. 338)

TABLE 1

List of bulk products considered in the Dow study, separated by chemical groups (working chemical for each group indicated by *)

<i>Group No. 1</i>	1,2-Dichloropropane	Diethylbenzene
* Aniline	Ethyl chloride	Ethyl benzene
<i>Group No. 2</i>	* Ethylene dichloride	Tetrahydronaphthalene
Asphalt	Ethylene dibromide	Toluene
Butane	Methyl bromide	Triethylbenzene
Casinghead gasoline	Methyl chloride	Xylenes
Crude oil (petroleum)	Monochlorodifluoro-	* Cumene (isopropylbenzene)
Cyclohexane	methane	Dodecylbenzene,
Gasoline, commercial	1,1,1-Trichloroethane	commercial
Heptane	Dichlorodifluoro-	<i>Group No. 15</i>
* Hexane (n-)	methane	Butadiene (inhibited)
Jet fuel, JP-3	Dichlorobenzene	* Isoprene (inhibited)
Jet fuel, JP-4	1,2,4-Trichlorobenzene	<i>Group No. 16</i>
Jet fuel, JP-5	Chlorobenzene	* Carbon disulfide
Kerosene	<i>Group No. 7</i>	<i>Group No. 17</i>
Methane	* Ethylene chlorohydrin	Acetaldehyde
Pentane	<i>Group No. 8</i>	* Butyraldehyde (n-)
Petroleum ether	* Creosote oil	Isobutyraldehyde
Propane	Creosote, coal tar	Isodecaldehyde
Nonane	<i>Group No. 9</i>	Isooctyl aldehyde
<i>Group No. 3</i>	* Acetonitrile	Propionaldehyde
* Glyoxal (40% soln.)	Adiponitrile	Valeraldehyde
Formaldehyde (37-50%	<i>Group No. 10</i>	Furfural
soln.)	* Acrolein	Methyl formal
<i>Group No. 4</i>	Crotonaldehyde	Methyl butyraldehyde
Caustic potash solution	2-Ethyl-3-propyl-acrolein	<i>Group No. 18</i>
Caustic soda solution	<i>Group No. 11</i>	Cyclohexanone
* Caustic soda (50%)	* Acrylonitrile	Acetone
<i>Group No. 5</i>	<i>Group No. 12</i>	Camphor oil
Amyl acetate	* Allyl alcohol	* Methyleneethyl ketone
Butyl acetate	<i>Group No. 13</i>	Methylisobutyl ketone
* Ethyl acetate	* Allyl chloride	Diisobutyl ketone
Isobutyl acetate	Dichloropropene	<i>Group No. 19</i>
Isopropyl acetate	<i>Group No. 14</i>	* Acetic acid, glacial
Propyl acetate	Benzene	Formic acid
Methyl acetate	Naphthalene, molten	Propionic acid
Methyl amyl acetate	Cymene	Butyric acid
Dibutyl phthalate	<i>Group No. 20</i>	* Acetic anhydride
<i>Group No. 6</i>	Carbon tetrachloride	Propionic anhydride
Chloroform		

continued

TABLE 1 (continued)

<i>Group No. 21</i>	Tetraethylene glycol	<i>Group No. 33</i>
Isophorone		* Phosphorus, elemental, white
* Mesityl oxide	<i>Group No. 26</i>	
	* Ethylene glycol monoethyl ether acetate	<i>Group No. 34</i>
<i>Group No. 22</i>		* Styrene (inhibited)
* Dichloroethyl ether	<i>Group No. 27</i>	Vinyl toluene (inhibited)
	* Cresols	
<i>Group No. 23</i>	Nonyl phenol	<i>Group No. 35</i>
Amyl alcohol	Phenol	* Sulfur, molten
Butyl alcohol		
Decyl alcohol	<i>Group No. 28</i>	<i>Group No. 36</i>
Diethylene glycol	Diethylene triamine	Sulfuric acid (77 to 98%)
Dipropylene glycol	Dimethylamine	* Sulfuric acid (96%)
Ethyl alcohol	* Ethylene diamine	
Butylene glycol	Diethylamine	<i>Group No. 37</i>
* Ethylene glycol	Triethylene tetramine	Vinyl chloride (inhibited)
Furfuryl alcohol	Morpholine	* Vinylidene chloride (inhibited)
Glycerine		
Hexylene glycol	<i>Group No. 29</i>	<i>Group No. 38</i>
Isopropyl alcohol	Diethanolamine	* Ethyl acrylate (inhibited)
Isooctanol	* Monoethanolamine	Methyl acrylate (inhibited)
Methylamyl alcohol	Monoisopropanolamine	Methyl methacrylate (inhibited)
Methyl alcohol	Triethanolamine	n-Butyl acrylate (inhibited)
Propyl alcohol	Aminoethyl ethanolamine	2-Ethylhexyl acrylate (inhibited)
Propylene glycol	Diisopropanolamine	
Tridecanol		<i>Group No. 39</i>
2-Ethyl-1-hexanol	<i>Group No. 30</i>	Ethyl ether
Isodecanol	* Diisobutylene	* Isopropyl ether
Nonyl alcohol	Ethylene	
Cyclohexanol	Propylene	<i>Group No. 40</i>
	Tetrapropylene	* Ethylene cyanohydrin
<i>Group No. 24</i>	Tripropylene	Acetone cyanohydrin (stabilized)
* Acrylic acid	Dipentene	
	Heptene	<i>Group No. 41</i>
<i>Group No. 25</i>	Nonene	* Vinyl acetate (inhibited)
Ethylene glycol mono-butyl ether	Turpentine	
Diethylene glycol mono-butyl ether	Dicyclopentadiene	<i>Group No. 42</i>
Ethylene glycol monoethyl ether		* Chlorosulfonic acid
* Diethylene glycol monoethyl ether	<i>Group No. 31</i>	
Ethylene glycol monomethyl ether	* Epichlorohydrin	<i>Group No. 43</i>
Diethylene glycol monomethyl ether		* 2-Nitropropane
Triethylene glycol	<i>Group No. 32</i>	
Ethoxytriglycol	Oleum	
	* Oleum (15—18% free sulfur trioxide)	

continued

TABLE 1 (continued)

1-Nitropropane	Group No. 47	Group No. 50
Group No. 44	Hydrochloric acid	★ Pyridine
★ Sulfolane	★ Hydrochloric acid (36%)	2-Methyl-5-ethyl pyridine
	Phosphoric acid	
Group No. 45	Group No. 48	Group No. 51
Ethylene oxide	Hydrofluoric acid	★ Ammonia (28% aqueous)
★ Propylene oxide	★ Hydrofluoric acid (48%)	
Butylene oxide		Group No. 52
	Group No. 49	Tetrachloroethylene
Group No. 46	Nitric acid (70% or less)	★ Trichloroethylene
★ Ethylenimine	★ Nitric acid (70%)	Group No. 53
		★ Propiolactone

experiments were taken to 100°C. The Norwegian data added considerably to the body of data on binary compatibility since much of their work was based on working chemicals other than those of the Dow study.

Revision of the compatibility guide

The NAS Committee of Hazardous Materials again was asked for advice on cargo compatibility and, as a result, a Panel* was established to review and consolidate all existing compatibility data and develop recommendations for a revision to the Coast Guard Compatibility Guide. The Panel was also requested to develop an experimental procedure for testing new binary combinations. Their study on compatibility [5] was completed in 1975.

1. Definition of a hazardous reaction

After reviewing the Dow and Norwegian data, a major area of concern to Panel members was the possible risk in extrapolating from laboratory data to shipping conditions. Although the laboratory data were obtained in a manner to minimize heat loss, the procedure could not be termed adiabatic. Wehman [6] examined this aspect of the experimental procedure and concluded that, for ΔT values up to 50°C, the procedure was about 80–90% adiabatic. This study further supported the Panel's position that a temperature rise of 25°C with no gas generation on mixing in the laboratory procedure was the maximum allowable for adjacent loading of cargoes. For its definition of a hazardous incompatibility, the Panel decided on: A binary mixture is considered hazardous

*Panel members: Howard L. Smith, Chm; Lyle F. Albright; James P. Flynn; Joseph L. Franklin; Michael Morrisette, Jerry J. O'Driscoll; Richard F. Schwab; and Anthony T. Wehman.

when the materials are mixed under specified conditions and the temperature rise exceeds 25° C or a gas is evolved.

This definition of a hazardous binary is a conservative one. However, a study of the data showed that the definition would impose little, if any, penalty on a shipper or ship operator because most combinations were found to be either unreactive or highly reactive.

2. Compatibility chart development

In its study of the compatibility data, the Panel recognized that chemical cargoes can be separated into three major groups from the standpoint of chemical reactivity. Many cargoes are relatively non-reactive (aromatic hydrocarbons, paraffins) while others form hazardous combinations with many groups (inorganic acids). The Panel separated the revised chart, Fig. 3, into two sections, Reactive groups (1 through 22) and Cargo groups (30 through 43). A third group, not included in the chart, can be distinguished by an extreme reactivity or, because of product nature, must be shipped in special containment systems. A listing of products both alphabetically and by chemical group follows the chart. Reactive groups contain products which are chemically the most reactive; dangerous combinations may result between members of different Reactive groups and between members of Reactive and Cargo groups. Products assigned to Cargo groups, however, are much less reactive and dangerous combinations can be formed only with members of certain Reactive groups. Because of the differences in reactivity, the Panel was able to eliminate a significant part of the usual two-dimensional chart.

3. Integrity of chemical groups and deviations within groups

In forming chemical groups it is essential that members of the group have similar reactivity. If some group members have significant reactivity differences from the working chemical, the shipper or ship operator may be unnecessarily penalized or hazards may be unknowingly introduced by permitting adjacent loading. The chemical groups selected by the Advisory Panel are believed to be on the conservative side. However, in reviewing the Dow, Norwegian, and Wehman data where different working chemicals were chosen for a number of groups, several problems of group integrity were uncovered. For example, the Norwegians observed an exothermic reaction between furfuryl alcohol and hydrochloric and formic acids. Ethylene glycol, the working chemical of the Dow group in which furfuryl alcohol was placed, is nonreactive to these acids.

Letters other than an "X" appear on the chart where deviations in reactivity have been found. These letters refer to the listing presented below the chart. Chemicals displaying reactivity differences were handled in this manner as opposed to splitting them into separate groups because, with other products, they followed the reactivity of the working chemical closely.

4. Recommended experimental procedure for testing binary combinations

The hazard ratings in the chart are based largely upon direct experimental data using one of the more reactive members of the group. Combinations of other group members may display considerably less reactivity. The experimental procedure adopted by the Panel allows a shipper to test product combinations he believes non-hazardous even though an "X" appears in the chart for their respective groups. It may also be used for testing new products which cannot be assigned to one of the groups listed on the chart. The procedure and data sheet, along with the chart in Fig. 3, are included in the Coast Guard's revised Compatibility Guide, NVC 4-75 [7]. Briefly, the approved method involves mixing experiments at ambient temperature and at 50° C. Three separate mixes of a proposed binary combination are tested at the two temperature levels. The mixtures of components A and B taken for test are: 2 ml A to 18 ml B, 10 ml A to 10 ml B, and 18 ml A to 2 ml B at ambient temperature. These ratios were selected to simulate minor leaks of one component into the other and the failure of a wall separating two tanks allowing approximately equal volumes of components to mix. Another consideration was that the maximum temperature rise on other combinations was not found to occur at any specific molar or volume ratio. Using more than one ratio, therefore, increases the probability of generating temperatures near the maximum.

The components are mixed as specified in the test procedure and the temperature is observed for at least 30 minutes to check for delayed reaction. If a reaction occurs from which gases are evolved or the rise in temperature exceeds 25° C, the test at 50° C is omitted. If no reaction occurs, or the temperature rise is 25° C or less, the binary is tested at 50° C. The ratio of chemicals that resulted in the largest temperature rise in the previous stop is used for this test. Where no temperature rise was measured, a mixture of 5 ml A and 5 ml B is tested.

The above procedure is simpler than that used in the Dow and Norwegian studies. Wehman, in his work, found the procedure to give good to excellent comparisons with the Dow and Norwegian work on similar binaries. Wehman also generated data on an additional 132 binary combinations.

Conclusion

Although recent shipping trends are toward the construction of more cofferdams and independent piping and venting arrangements for each tank, questions of compatibility on new vessels may be reduced but not eliminated. An accurate and easy to use compatibility system is needed for these newer vessels as well as for the many existing barges and ships which generally have a lower degree of cargo separation. The revised compatibility guide, NVC 4-75, should fill this need. It has been designed to accommodate new chemicals and, as necessary, new chemical groups. In its present form the guide represents 335 bulk chemicals of commerce.

Acknowledgement

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Note. The National Technical Information Center (NTIS) of the U.S. Department of Commerce is the central source for the public sale of Government-sponsored research, development, and engineering reports. Reports can be ordered at modest cost through NTIS, Springfield, Virginia, 22161 (U.S.A.).