Standard Guide for the Preparation of a Binary Chemical Compatibility Chart[1]

INTRODUCTION

In 1982, ASTM Committee D-34 on Hazardous Waste proposed the compatibility chart PS 168 that is discussed in this standard. ASTM Committee E-27 (sponsors of this standard guide) raised several issues as to the accuracy of parts of the chart that ultimately led to the withdrawal of the proposed standard and the tacit agreement of E-27 to take over further development. As time passed, it became increasingly clear that a consensus chart, agreeable to all, and comprehensive enough to be useful to the chemical industry was and still is a difficult task. Consequently, Committee E-27 embarked on an easier but nonetheless very useful task that provides expert guidance to those who might be interested in the task of compiling compatibility information without actually dictating the answers to specific binary reactivity questions. This standard is the result of that effort. It is the Committee's belief that inter-reactivity charts will be increasingly used in industry for day-to-day operations, process hazard reviews, employee education, and emergency response. It is our hope that this standard guide can be useful in that effort.

1. Scope

1.1 A binary chemical compatibility chart also call inter-reactivity chart, compares the hazards associated with the mixing of two different materials. This guide provides an aid for the preparation these charts. It reviews a number of issues that are critical in the preparation of such charts: accurate assessment of chemical compatibility, suitable experimental techniques for gathering compatibility information, incorporation of user-friendliness, and provision for revisions.

1.2 The uses of chemical compatibility charts are summarized in this standard.

1.3 This guide also reviews existing public domain compatibility charts, the differences therein, and their advantages and disadvantages.

2. Referenced Documents

2.1 *ASTM Standards:*

E 537 Test Method for Assessing The Thermal Stability Of Chemicals By Methods Of Differential Thermal Analysis[2]

E 698 Test Method for Arrhenius Kinetic Constants for Thermally Unstable Materials[2]

E 1231 Practice for Calculation of Hazard Potential Figures-of-Merit for Thermally Unstable Materials[2]

PS 168 Proposed Guide for Estimating the Incompatibility of Selected Hazardous Wastes Based on Binary Chemical Reactions[3]

2.2 *NFPA Standard:*

NFPA 491 Guide to Hazardous Chemical Reactions[4]

3. Terminology

3.1 *Definitions:*

3.1.1 *compatibility, adj*—the ability of materials to exist in contact without specified (usually hazardous) consequences under a defined scenario.

3.1.2 *scenario, n*—a detailed physical description of the process whereby a potential inadvertent combination of materials may occur.

4. Summary of Guide

4.1 A binary chemical compatibility chart indicates whether, under a given set of conditions, that is, the scenario, combination of two materials does or does not yield a specified undesired consequence.

4.2 Determine the scenario for the determination of compatibility and the degree of reaction that constitutes incompatibility. Both should be identified in the title of the chart. Define the materials within the scope of the chart. Define the test, calculation or judgment that is used to make a decision. List the materials as both columns and rows of a grid. At the intersections of the grid note whether the materials are compatible. To avoid duplicate entries, a triangular chart is required. If a

[1] This test method is under the jurisdiction of ASTM Committee E27 on Hazard Potential of Chemicals, and is the direct responsibility of Subcommittee E27.02on Thermal Stability and Condensed Phases.

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[2] *Annual Book of ASTM Standards*, Vol 14.02.

[3] Discontinued. See 1986 *Annual Book of ASTM Standards*, Vol 11.04.

[4] Available from the National Fire Protection Association, One Batterymarch Park, PO Box 9101, Quincy, MA 02269-9101.

decision on compatibility was not by the standard means (as defined by the user) or the scenario differs, indicate by footnote the basis for the decision or the change in scenario. The chart should be dated and the author identified. See Fig. 1 for an example of a binary compatibility chart.

5. Significance and Use

5.1 Various United States governmental regulations forbid incompatible materials to be transported together and require that chemical reactivity be considered in process hazard and risk analysis. A chemical compatibility chart is one tool to be used to satisfy these regulations. Binary compatibility charts are useful teaching tools in general education, in the chemical plant or laboratory, and for areas and operations where commonly performed tasks might lead to chemical mixtures such as might occur during co-shipment in compartmentalized containers, storage in a common area or compositing waste. Compatibility information is essential during process hazard reviews (for example, HAZOP). These charts may provide guidance to terminal operators on DOT HM-183 that requires that materials on adjacent compartments of multicompartment tank trucks are compatible. They provide documentation that the potential for inadvertent mixing as a potential source of heat and gas evolution from chemical reactions has been considered in sizing relief devices. Compatibility charts serve as check lists for use during process hazard reviews, and the preparation of the chart itself often brings attention to potential hazards that were previously unknown.

5.2 A binary chart only considers pairs of materials and therefore does not cover all possible combinations of materials in an operation. A common third component, for example, acidic or basic catalysts, may be covered by footnoting the potential for catalysis of a reaction between otherwise compatible materials, but the form of the chart does not ensure this. There may be reactive ternary systems that will escape detection in a binary chart.

6. Procedure

6.1 *Define the Scenario*—Chemical compatibility depends heavily on the mixing scenario (see Appendix X1). Consider including the following factors in the specification of the mixing scenario, as they, and other factors, may contribute to the assignment of compatibility.

6.1.1 Specific quantities of materials,

6.1.2 Storage temperatures,

6.1.3 Confinement (closed or open system),

6.1.4 Atmosphere (air, nitrogen inerted), and

6.1.5 The maximum time the materials may be in contact.

6.2 *Define Incompatibility Within the Scenario Framework*—An effective chart should clearly convey the criteria for defining two materials as incompatible. In a general sense, chemical incompatibility implies that there may be undesirable consequences of mixing these materials at a macroscopic scale. These consequences might be, in a worst case, a fast chemical reaction or an explosion, a release of toxic gas, or, in a less severe case, an undesirable temperature rise

	SUBSTANCE						
1	Hydrochloric Acid (35%)	1					
2	Sulfuric Acid (90%)	R[1]	2				
3	Acetic Acid	?[8]	R[2]	3			
4	Ethanol	NR[3]	R[4]	NR[15]	4		
5	Ethylenediamine	R[5]	R[6]	R[7]	NR[12]	5	
6	Water	R[9]	R[10]	NR[11]	NR[13]	R[14]	6

Legend:

R	Reactive under the stated scenario - **incompatible**
NR	Non-Reactive under the stated scenario - **compatible**
?	**unknown** - assume incompatible until further information is obtained

Footnotes/Information Sources:

1 Unlikely to be compatible - USCG chart NVC 4-75 indicates a hazard with non-oxidizing acids plus sulfuric acid. Heat of mixing may be significant.
2 Unlikely to be compatible - the P-168 chart indicates that gas and heat are formed; USCG chart NVC 4-75 indicates a hazard when combining sulfuric and organic acids.
3 Primary alcohols do not react with aq. HCl at ambient temperature.
4 Heat of solution followed by reaction to form ethyl hydrogen sulfate.
5 Lab experiment 980001(50/50 mix) resulted in a significant heat of neutralization.
6 Lab experiment 980002 (50/50 mix by volume) resulted in a XXX C adiabatic temperature rise.
7 Organic acids and amines are generally incompatible due to acid/base neutralization heat.
8 The P-168 and USCG charts indicate no hazard; most likely compatible, but lab testing should be performed.
9 Heat of mixing may be a concern in some circumstances. The maximum adiabatic temperature rise is XX C (see XYZ Encyclopedia of Chemical Technology).
10 Heat of mixing may be a concern in some circumstances. The maximum adiabatic temperature rise is XX C (see XYZ Encyclopedia of Chemical Technology). Violent reaction with splattering if water is added to the acid.
11 Lab experiment 98005 showed that mixing acetic acid and water is endothermic at room temperature.
12 Lab experiments 98003 and 98008 indicate that the materials do not generate heat or gases when mixed nor when heated to 100 C. Although the USCG chart NVC 4-75 indicates that some alcohols and amines are incompatible, ethylene diamine has been found to be compatible with many alcohols; see Appendix of USCG Guide.
13 Plant experience has shown materials to be compatibile.
14 Mildly exothermic hydrate formation.
15 Very slow, nearly thermoneutral, equilibrium-limited esterification at ambient temperature.

FIG. 1 Hypothetical Compatibility Chart

that might take the mixture above its flash point or cause an unacceptable pressure increase in the system. If, however, the tank where the mixing will occur is inerted with nitrogen, and the material has an acceptably low vapor pressure increase, then even this temperature rise might not pose a practical problem. Consequently, a working definition of incompatibility needs to be formulated before compatibility judgments can be effectively and accurately made.

6.2.1 Some examples of mixing scenarios and incompatibility definitions include:

6.2.1.1 Ambient temperature in summer, northern climate (approximately 25°C); (5000 gal) scale; insulated, vented storage tank; storage time 7 days maximum, nitrogen padded headspace (chemical transport scenario). Incompatible if temperature rise greater than 25°C, or grassy reaction.

6.2.1.2 Ambient temperature in a hotter, subtropical climate (approximately 40°C), drum (55 gal) storage of mixed waste for 3 months maximum. Incompatible if there could be a release from the drum.

6.2.1.3 Room temperature, _L (1 gal) bottles, loosely capped, 1 month maximum storage time (typical lab waste scenario). Incompatible if there is an evolution of flammable vapor, toxic gas, or a temperature rise greater than 10°C.

6.3 *Compile Compatibility Chart*—The following steps may be followed for constructing the compatibility chart (see Appendix X2).

6.3.1 *State the Scenario*—In the preparation of a compatibility chart, consider stating both the scenario and the scenario-based definition of incompatibility explicitly on the chart.

6.3.2 *Decide on a Hazard Rating Scheme*—Formulate the reference scale for the individual degree of mixing hazard. It may be desirable to have a simple "yes/no" (that is, compatible/incompatible) scale. In some instances, ratings that convey more information may be advantageous. For example, a numerical score of 1, 2, and 3 might be appropriate with 1 indicating a compatible mixture, 2 indicating a moderate hazard (for example, a temperature increase of 10°C or less), and 3 indicating a severe hazard, such as polymerization or spontaneous combustion. Another example of a hazard rating scheme is given in Table 1. Note that in the Table 1 example, the hazard rating scheme also conveys information about procedures for emergency response, but this information need not be included in the chart. The use of color (if available in the charting tool) may also aid in understanding the chart. For example, green could indicate safe, compatible mixtures, red could indicate reactive, incompatible mixtures. It is important to avoid making the chart too complicated.

6.3.3 *Define the Categories*—Defining categories for the chart is an important part of chart construction. For small plants and operations, each chemical may be included in the chart and the resulting chart may still be of manageable size. For more general compatibility charts, for example, for a large manufacturing site, the chart may group chemicals into natural classifications based on their chemical structure. Examples of these groupings are: mineral acids, aliphatic amines, monomers, water-based formulations, halogenated hydrocarbons, and so forth. One limitation with this manner of chart construction is that for a number of classes, certain binary combinations might be known to be compatible whereas other combinations within the same two groups may not be. It may be best to provide the worst case compatibility rating in the actual chart with a separate list of compatible exceptions. It may be prudent to include additional useful compatibility information, such as compatibility of chemicals with materials of construction, water (from process streams or from rain in diked areas), cleaning agents, sealants, and adsorbents. "Heat" might be considered as an entry to flag particularly heat sensitive materials such as polymerizable monomers. Consultation with a wide variety of personnel (management, engineers, operators, and so forth) may aid in the determination of what materials are present at a site and which ones should be included in the chart.

TABLE 1 An Example of Hazard Levels and Typical Associated Emergency Response Actions

Hazard Rating	Hazard Level	Suggested Emergency Response
0	Minimal	Report inadvertent mixing event to supervision; no further action necessary.
1	Caution	Report event to supervision; implement plan(s) to manage the situation; no emergency procedures to be initiated.
2	Danger	Report event to supervision; prepare to initiate unit emergency plan if needed; notify personnel in immediate area; consider halting normal activities until extent of situation is fully assessed.
3	Severe Danger	Report event to supervision; initiate unit emergency plan; notify all plant personnel; cease normal activities until extent of situation is fully assessed; consider need to evacuate the plant; report event to plant industrial security and other emergency response groups.
4	Extreme Danger	Initiate unit emergency plan; notify all plant personnel to evacuate the area; cease normal activities, if possible, before evacuating; report event to plant industrial security and other emergency response groups once evacuation is underway or complete.

6.3.4 *Consider the Hazards for all Binary Combinations*—The potential hazard for each and every binary mixture needs to be carefully considered. Avoid using blanks (empty cells) in compatibility charts since blanks may indicate that there is no hazard, or, simply that the hazard is unknown. Clearly distinguishing between a non-hazard and an unknown hazard is an important consideration. See Appendix X2 for sources of compatibility information.

6.3.5 *Document How the Decisions Are Made*—Backup and supporting data should be easily accessible for chart users and to allow for easier chart updates. If testing was performed to make a decision about a particular binary combination in a chart, then a reference to this test should be included in the chart.

6.3.6 *Label the Chart*—Date the chart and ensure that title clearly states the purpose of the chart such as "Chemical Compatibility Chart for the Styrene Polymerization Plant A-104, last updated 9/98." Scenarios may differ from process to process and if the chart is not specifically labeled with the intended use, the chart may be used in a process for which it was not intended, with possible undesired consequences. Since a large plant often has distinct areas, consider including only those materials in each area in the chart, to avoid making the chart needlessly large and complicated.

7. Experimental Tools for the Determination of Compatibility

7.1 In certain cases, an experimental determination of the compatibility is the most prudent approach. This may be necessary if the compounds or molecular types cannot be found in one of the published charts, if the data are not provided by the manufacturer, or if the scale and scenario of mixing warrant, an actual verification of the hazards involved. It is beyond the scope of this guide to provide standard test methods and details for the experimental determination of chemical compatibility. However, some general considerations are given that may assist in the design of an appropriate experiment.

7.2 Scale is one key consideration in the accurate design of an experimental compatibility test. Start the testing at small enough scale to minimize the potential dangers to the test operator. Also, in order to apply the results of compatibility tests to various scenarios, quantitative data suitable for scaleup are needed. One such quantitative testing scheme using 2 to 200-mg quantities is described. This experimental technique involves differential scanning calorimetry (DSC) testing of the individual components and the mixture and also mixing calorimetry. A summary of this approach is as follows:

7.2.1 Determine some measure of the inherent thermal stability of the individual components using DSC.

7.2.2 Determine the instantaneous energy release (heat and gas evolution) upon mixing of the two components using heat-of-mixing calorimetry. (Use an appropriate mixing ratio that adequately quantifies the hazard; see 7.3).

7.2.3 Determine the relative thermal stability of the mixture (as compared and contrasted to the individual components) by DSC.

7.3 This experimental formalism allows an evaluation of materials that might react very quickly upon mixing and also materials that require more elevated temperature or an induction period to react. Neither mixing calorimetry nor DSC alone are adequate to fully evaluate the reactivity hazards associated with a mixture. For example, a DSC on a mixture of HCl(aq) and NaOH(aq) would show no exothermic activity (to approximately 400°C) since the acid-base neutralization takes place virtually instantaneously and the resultant solution is simply NaCl(aq). A mixing calorimetry test could quantify the heat of neutralization and thus more accurately define the hazards associated with this mixture. If a reaction is autocatalytic, the mixing calorimetry might not detect any heat due to the characteristic induction times for this type of process. The DSC test would probably be able to detect the reaction since it subjects the sample to a continuous temperature ramp.

7.4 The choice of mixing ratio may be important. If the reaction stoichiometry is known, then the maximum heat release will occur with a stoichiometric mixture. The maximum adiabatic temperature rise will also occur near the stoichiometric point unless the heat capacities of the constituents are widely different. If the stoichiometry is unknown, then experiments at several ratios may be necessary. The details of the mixing scenario may also affect the choice of mixing ratio (for example, it may not be possible to get a stoichiometric mixture). In the case of heat generation by dilution, the heat capacities of constituents play a major role in defining the optimum ratio.

7.5 Perhaps the easiest part of the experimental procedure is the actual testing. The hardest part sometimes is an unambiguous interpretation of the results. If there is no substantial mixing heat (or gas generation) and the DSC trace of the mixture is ostensibly a superposition of the DSC traces of the individual components, no incompatibilities may exist regardless of the scenario. If substantial incompatibility exists between the substances, however, a large mixing heat will be observed or the DSC trace will show a large exotherm detected at a lower temperature (with respect to the individual component DSC traces), or both. Unfortunately, both these behaviors are rare in practice and, often, the results fall in between the two extreme cases. The analyst then may have a more difficult time in assessing the results. For these reasons, it may be desirable to estimate the thermokinetics of the incompatibility reaction and from these data, predict the conditions (temperature, volume, and so forth) whereby a mixture might become a large scale hazard using heat gain - heat loss models. This technique has been described in Ref. **(1)**.[5] Additional information regarding use of DSC for determination of thermal stability may be found in Test Methods E 537 and E 698, and Practice E 1231.

8. Report

8.1 An example binary compatibility chart is shown in Fig. 1. The important features of a compatibility chart are:

8.1.1 A clearly defined process or area for which the chart is applicable (given in the title in this example),

8.1.2 The date that the chart is published,

8.1.3 A grid showing hazards resulting from binary combinations,

8.1.4 A clearly defined hazards rating scheme (explained by a legend in this example); the scheme may be as simple as using an R (reactive) for incompatible combinations, a NR (non-reactive) for compatible combinations, and "?" for unknown. Other schemes are yes/no, and numerical schemes such as 0, 1, 2 (compatible, caution, danger, resp.), and

8.1.5 Documentation of information sources (given by footnotes in this example but may be included in the "notes/comments" cell background of standard spreadsheets).

8.2 In the example chart in Fig. 1, much of the data comes from literature and little of it comes from actual testing. This chart can be considered representative of a chart in its early stages. Ideally, all information is based on tests or experience and no information is unknown.

8.3 It is recommended to define the scenarios in which materials are incompatible. Materials may create a hazard when combined in certain scenarios within a process while not creating a hazard when combined in others. The temperature

[5] The boldface numbers in parentheses refer to the list of references at the end of this standard.

under which materials are in combination is a good example of a variable that can drastically affect compatibility. It is dangerous to assume materials are compatible at higher temperatures just because they are known to be compatible at lower temperatures. Use of plant experience may be legitimate, but it may be dangerous to extrapolate this information to other conditions (for example, larger scale, longer storage times, higher temperatures).

9. Keywords

9.1 chemical compatibility chart; inter-reactivity chart; mixing hazards

APPENDIXES

(Nonmandatory Information)

X1. THE SCENARIO DEPENDENCE OF MIXING

X1.1 There is a great difference in combining relatively reactive materials, such as strong oxidizers with strong reducing agents, on a small scale (for example, 0.05 ml) under controlled laboratory conditions, as compared to pumping a tank-truck full of the oxidizer into a large storage tank of reducing agent. However, it is important to recognize the potential time and temperature dependency of chemical reactions. Size of the mixture affects both the total amount of energy and the rates at which that energy can be given off to the environment. A small flask may be able to lose heat fast enough to its environment relative to the amount of heat it is giving off, while a rail car of the same mixture will lose heat proportionately at a much slower rate and possibly self-heat to thermal explosion. Chemical reaction rates increase exponentially with temperature. For a typical reaction with an activation energy of 84 kJ/mol (20 kcal/mol), this translates into a >6000-fold increase in rate for a temperature increase from 20 to 120°C. For a reaction with an activation energy of 145 kJ/mol (35 kcal/mol), as is not uncommon in peroxide decomposition, the rate increase is over 4 million for the same temperature increase. These rates translate into changing half-lives from months and days at lower temperatures to minutes and seconds at higher temperatures. For the same reasons, one cannot define incompatibility in terms of a specific temperature at which two materials react. Response, contact time, and cleanup time impact the consideration of compatibility. The answer to many questions depends partly on the confidence placed in the reliability of operating discipline.

X1.2 It is imperative, when making a decision about the compatibility of two chemicals, that a scenario be defined. The scenario should contain the essential information of temperature, quantities, heat transfer characteristics, and the length of time the materials will remain mixed. Other elements that could be included in the scenario are discussed in 6.1.

X2. RESOURCES FOR COMPATIBILITY INFORMATION

X2.1 *Tools for Preparation of Compatibility Charts*—Standard and commonly available software can be quite useful in the preparation of a compatibility chart. Commercially available spreadsheets are useful, allowing the chart to then be made accessible via a network server to all those involved in a common operation. See Refs. **(2-3)** for more information on available software tools.

X2.2 *Sources of Compatibility Information*:

X2.2.1 *Public Literature*:

X2.2.1.1 The public scientific literature may be useful to find compatibility information but sometimes these data are relatively obscure. An excellent source of such data is Ref. **(4)**, which has been in print for at least 20 years and is still published in book form, and has recently been made available for PC searches and now is also available in a format that allows for logical searches (for example, chlorine AND amine). Reference **(4)** summarizes the data for individual compounds, mixtures, and certain classes of materials (such as nitro aromatics, and so forth). There is also an extensive discussion of the general field of reactive chemicals hazards, including the basics of hazard evaluation, kinetic factors, adiabatic systems, reactivity versus composition and structure, reaction mixtures, and protective measures. This work covers 4800 elements or compounds with an additional 5000 secondary entries involving two or more materials, with 30000 cross-references.

X2.2.1.2 If the material is a pure substance, as opposed to a chemically complex process stream, a good source for compatibility information in the United States is the Material Safety Data Sheet (MSDS). These data sheets are compiled by the manufacturers and may present detailed, known incompatibility problems that might be otherwise difficult to find.

X2.2.1.3 Other good sources of chemical reactivity and compatibility information include NFPA 491 and Refs. **(5-9)**. Finally, do not overlook the myriad of college text books on organic and inorganic chemistry that provide valuable information about chemical synthesis.

X2.2.2 *Organic and Inorganic Synthesis Chemists*—These individuals are trained to know what chemicals react under defined conditions. For those unfamiliar with synthesis chemistry, these experts should be consulted.

X2.2.3 *Knowledgeable Process Personnel*—There is no substitute for experience in a complicated chemical process. Those who have practical plant experience may be a good source of historical compatibility information. Capturing this information in a compatibility chart will help ensure this information is not lost.

X2.2.4 *NOAA Chemical Reactivity Worksheet*—The Chemical Reactivity Worksheet **(10)** is a free program one may use to assess the binary reactivity of substances or mixtures of substances. It includes a database of reactivity information for more than 4000 common hazardous chemicals. The database also includes information about the special hazards of each chemical and about whether a chemical reacts with air, water, or other materials. One advantage of this tool is its categorization not only be individual chemical names but also by functional group (such as alcohols, ethers, and so forth). The reactivity decisions were made by a number of chemists using chemical knowledge and a variety of standard references, many of which have already been described in this guide.

X2.2.5 *Public Compatibility Charts*—Several published charts are available for consultation in the preparation of a specific chart **(11, 12)**. Ref. **(12)** covers a large number of materials, but was superseded by Ref. **(11)**, which includes the information in Ref. **(12)** as well as additional information. Although it was never adopted as a full consensus ASTM standard, ASTM PS 168 is still widely used. Use public domain charts carefully as they may have missing or inaccurate information. See Ref. **(13)** for a review of known errors and pitfalls in these charts. In spite of some errors, these charts can provide helpful insights, and usually reference supporting compatibility information. The charts in Refs. **(11-12)** and in PS 168 have similarities in their approach, including:

X2.2.5.1 Reactivity groups are used,

X2.2.5.2 Charts are displayed as a matrix showing consequences of binary mixtures,

X2.2.5.3 Charts consider only binary mixtures,

X2.2.5.4 Scenarios are limited to near room temperature (less than 55°C) and ambient pressure conditions,

X2.2.5.5 Charts attempt to be conservative, in that the most reactive materials are considered for each binary mixture, and

X2.2.5.6 Charts contain warnings regarding application.

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