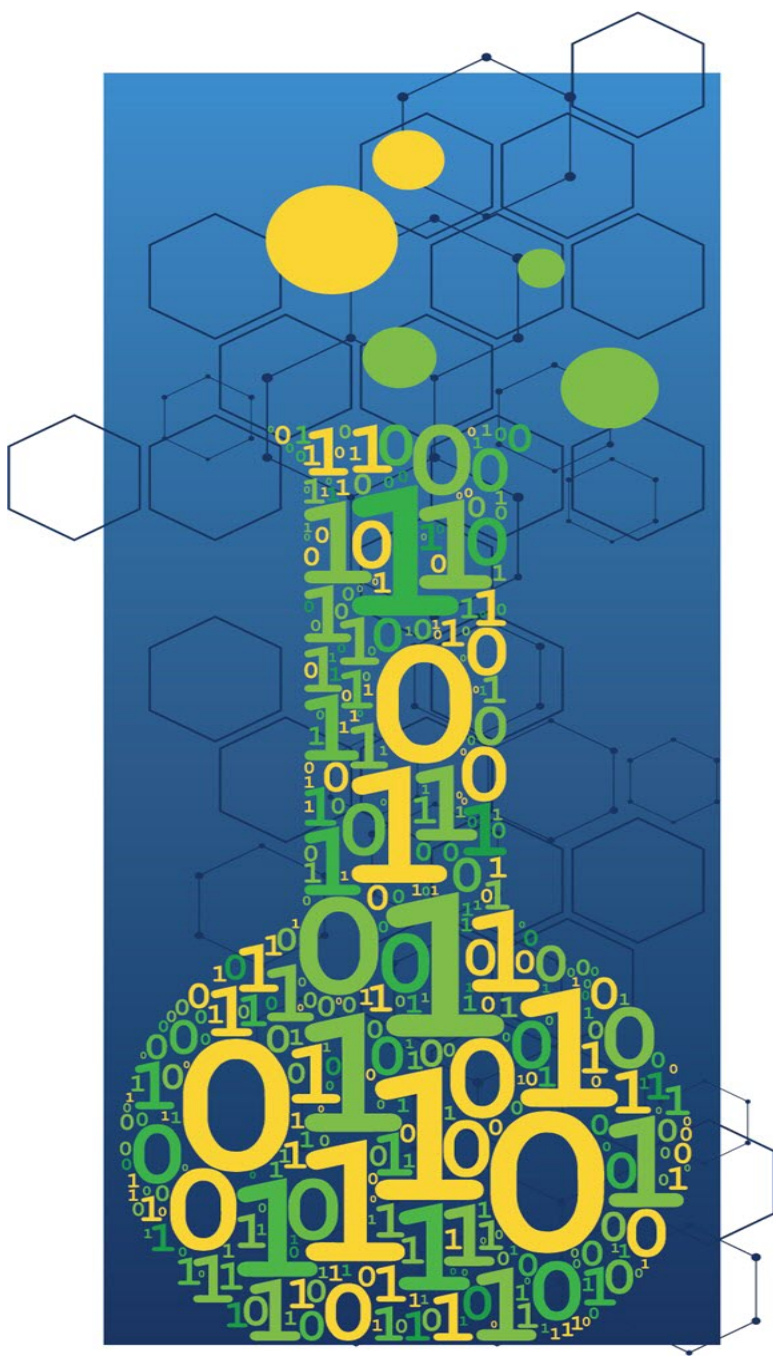


**Quickly Develop Chemical Interaction
Matrices with Process Safety Office®
SuperChems® Expert**



An **ioMosaic®** Publication

G. A. Melhem, Ph.D., FAIChE

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IOMOSAIC[®] CORPORATION

**Quickly Develop Chemical Interaction
Matrices with Process Safety Office[®]
SuperChems[®] Expert**

Process Safety and Risk Management Practices

authored by

G. A. Melhem, Ph.D., FAIChE

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1 Introduction

The development of accurate chemical interaction matrices can provide valuable information for the management of potential chemical reactivity hazards. SuperChems¹, a component of Process Safety Office², provides intuitive and easy to use utilities for the rapid development of chemical interaction matrices. These utilities were developed based on known heuristics and rules for the interaction of certain chemical groupings. SuperChems also provides additional utilities for the calculation of energy release and stoichiometry of one or more chemical reactions using detailed multiphase chemical equilibrium algorithms and reacting flow dynamics.

In addition to thermo-physical and transport properties databanks, SuperChems provides hazards databanks where chemical groupings and other reactivity and toxicity data are available for approximately three thousand chemicals. Of particular interest is version 8.5 of the hazards databanks, released in March of 2018.

2 Background

Details pertaining to how SuperChems constructs a chemical interaction matrix are included in the SuperChems reactivity expert framework [1]. This technical note will focus on how to best use the SuperChems utilities and on best practices for how to quickly develop accurate chemical interaction matrices. The reader is also directed to an earlier white paper on the development of chemical interaction matrices using SuperChems published by ioKinetic [2]. These two references are provided as attachments to this technical note.

Generally, three easy steps are required to develop a chemical interaction matrix.

3 Step 1 - Selecting the Hazards Databanks

First, it is important to select the updated hazards databanks. The most recent update to the ioMosaic hazards databanks is *hzdbanks_v8.5.dat*. This update was issued in March of 2018 and it includes additions/modifications to the chemical groupings as well as toxicity and hazards data for a large number of chemicals. It is a good practice to make your own copy of the hazards databanks, especially if you want to add new chemicals, or modify the attributes of any chemicals already in the databank. Suggestions for improvements or enhancements should be forwarded to support@iomosaic.com.

Figure 1 shows the existing hazards data record for ethylene oxide. The record shows that ethylene oxide reactive groups include epoxide, combustible and flammable materials, explosives, and polymerizable compounds. Up to ten reactive groups can be assigned for each chemical.

Threshold mass limits are also provided for OSHA, EPA, NJ TCPA [3], and Seveso. Toxicity data including ERPG-1, ERPG-2, ERPG-3, IDLH, TLV, and PEL are provided. A toxicity probit is also

¹SuperChems is a trademark (TM) of ioMosaic Corporation

²Process Safety Office is a trademark (TM) of ioMosaic Corporation

provided. NFPA ratings for ethylene oxide are provided as well as special designations for skin irritation and explosivity. It is always a good practice to examine the hazards data and reactive groups provided for all the mixture components of interest.

The second tab referenced in Figure 1 provides a lookup table for all the available reactive groups (142 groups) listed by group number and also alphabetically. The third tab provides description of the chemical interaction hazard codes. These codes and their descriptions appear in the chemical interaction matrix when it is constructed by SuperChems depending on the reactive groupings of each of the mixture constituents. The fourth tab provides a quick group contribution utility to estimate the heat of decomposition and/or polymerization.

The toxicity data provided in the hazards databanks can be directly accessed in the toxicity damage criteria object definition. Two utilities are provided to enable the user to apply ERPG and/or probit data to the toxicity damage criteria object.

4 Step 2 - Defining the Mixture

The second step consists of defining the mixture of interest. The user selects the mixture constituents from the thermo-physical properties databanks by typing or looking up the chemical names. An example mixture is shown in Figure 2.

5 Step 3 - Running Reactivity Expert

Once the mixture is defined and highlighted, the user clicks on the reactivity expert icon. A hazard potential report is then generated which includes the chemical interaction matrix as shown in Figure 3. The first tab referenced in Figure 3 includes a chemical hazards report which is very useful to have when conducting a reactive chemicals or general PHA/HAZOP. The report includes flammability, toxicity, and reactivity properties of each of the chemical constituents of the mixture. The third tab referenced in Figure 3 provides a listing of each binary chemical interaction shown in the matrix with a description of what is expected for each reaction involving specific binary pairs. The 4th tab shows a glossary of terms for the NFPA ratings as well as the toxicity limits definitions.

6 Conclusions

The SuperChems chemical interaction matrix utility enables a user to generate a chemical interaction matrix in a few minutes when the chemicals are contained in the databanks already provided with SuperChems with approximately three thousand chemicals. Chemicals can also be easily added and assigned reactive groupings using additional utilities provided in the databanks manager. One should always add to the mixture components such as rust, chlorides, water, and other chemicals to be present or in proximity of the materials of interest.

Figure 1: Sample hazards databank record for ethylene oxide

| Define Hazard Data For CAS#: 75218, ETHYLENE OXIDE - C:\IOIQ\PSO84\SuperChem\BANKS\hazdbanks_v8.5.dat [Active Cell, Press F12 to Update] | | | |
|---|----------|---|--|
| Hazard Data Lookup Table Incompatibility Codes Estimate Heat of Reaction | | | |
| A | B | C | D |
| Group Name | Group # | | |
| Epoxide | 38 | Last Verified On | 03:12:50 PM, Thu Mar 15 2018 |
| Combustible and flammable materials | 134 | Last Verified By | Dona Chakra |
| Explosives | 135 | Comment A | Version 8.50 Update |
| Polymerizable compounds | 136 | Comment B | NA |
| ... | 0 | Comment C | NA |
| ... | 0 | | |
| ... | 0 | Name | ETHYLENE OXIDE |
| ... | 0 | Formula | C2H4O |
| ... | 0 | CAS # | 75218 |
| ... | 0 | Molecular Weight | 44.053 |
| ETHYLENE OXIDE OSHA mass threshold. kg | 2267.96 | | |
| ETHYLENE OXIDE EPA mass threshold. kg | 4535.92 | | |
| ETHYLENE OXIDE NJ TCPA mass threshold. kg | 1224.70 | | |
| ETHYLENE OXIDE Seveso lower mass threshold. kg | 5000.00 | | |
| ETHYLENE OXIDE Seveso upper mass threshold. kg | 50000.00 | | |
| **Toxicity Information | | | |
| | PPM | mg/m3 | |
| ERPG-1 | 0.00 | 0.00 | |
| ERPG-2 | 50.00 | 0.00 | |
| ERPG-3 | 500.00 | 0.00 | |
| IDLH | 800.00 | 0.00 | |
| TLV | 1.00 | 0.00 | |
| PEL | 1.00 | 0.00 | |
| <input checked="" type="checkbox"/> Toxicity Probit Data is Available. $Y = A + B \ln[(C/N) t] \text{ min, ppm}$ | | | |
| | | <input checked="" type="checkbox"/> Probit concentration is in mg/m3 instead of ppm | |
| Probit A | -6.80 | | |
| Probit B | 1.00 | | |
| Probit N | 1.00 | | |
| <input type="checkbox"/> ETHYLENE OXIDE is a known carcinogen <input checked="" type="checkbox"/> ETHYLENE OXIDE is a known skin irritant <input type="checkbox"/> ETHYLENE OXIDE is a peroxide former <input type="checkbox"/> ETHYLENE OXIDE is water reactive <input type="checkbox"/> ETHYLENE OXIDE is pyrophoric <input checked="" type="checkbox"/> ETHYLENE OXIDE is explosive <input type="checkbox"/> ETHYLENE OXIDE is shock sensitive | | | |
| **NFPA Rating System | | | |
| Health | 3 | | Corrosive or toxic. Avoid skin contact |
| Flammability | 4 | | Flammable gas or extremely flammable |
| Reactivity | 3 | | May be explosive if shocked, heated or |
| Special Notice | NA | | Not assigned |
| <input type="checkbox"/> Material will decompose when heated, initiated, or shocked | | | |
| Heat of decomposition. J/kg | 0.00 | | |
| Decomposition onset temperature. C | -273.15 | | |
| Data Source | NA | | |
| Data Reference | NA | | |
| <input checked="" type="checkbox"/> Material will polymerize when heated, initiated, or shocked | | | |
| Heat of polymerization. J/kg | 0.00 | | |
| Polymerization onset temperature. C | -273.15 | | |
| Data Source | NA | | |
| Data Reference | NA | | |

Figure 2: Ethylene oxide sample mixture

Define Mixture - MY MIXTURE, 5 Components

| | A | B | C | D | E | F | G | H | I |
|----|---|---------------------------------|---|------|----------|---|---------------|---------|---------------|
| 1 | COMPOUND | FORMULA | CAS# | ID | Mw | MASS | MASS FRACTION | MOLE | MOLE FRACTION |
| 2 | WATER | H ₂ O | 7732185 | 1013 | 18.015 | 1.00000 | 1.00000 | 0.05551 | 1.00000 |
| 3 | ETHYLENE OXIDE | C ₂ H ₄ O | 75218 | 524 | 44.053 | 0.00000 | 0.00000 | 0.00000 | 0.00000 |
| 4 | AMMONIA | H ₃ N | 7664417 | 923 | 17.031 | 0.00000 | 0.00000 | 0.00000 | 0.00000 |
| 5 | SODIUM HYDROXIDE | HNaO | 1310732 | 922 | 39.997 | 0.00000 | 0.00000 | 0.00000 | 0.00000 |
| 6 | SULFURIC ACID | H ₂ O ₄ S | 7664939 | 915 | 98.079 | 0.00000 | 0.00000 | 0.00000 | 0.00000 |
| 7 | | | | | 18.01530 | 1.00000 | 1.00000 | 0.05551 | 1.00000 |
| 8 | SHORT DESCRIPTION | | | | | | | | |
| 9 | Enter a short description here | | | | | | | | |
| 10 | | | | | | | | | |
| 11 | OPTIONS | | | | | | | | |
| 12 | | | | | | | | | |
| 13 | <input checked="" type="checkbox"/> Use mass basis data to compute fractions | | | | | C:\ioiq\PS08.4\SuperChems\BANKS\SC6.ID | | | |
| 14 | <input checked="" type="checkbox"/> Perform data quality and consistency checks | | | | | C:\ioiq\PS08.4\SuperChems\BANKS\SC6.TPP | | | |
| 15 | <input type="checkbox"/> Sort by normal boiling point | | | | | <input type="checkbox"/> Decreasing | | | |
| 16 | <input type="checkbox"/> Sort by molecular weight | | | | | <input type="checkbox"/> Decreasing | | | |
| 17 | <input type="checkbox"/> Mixture is soluble in water at this rate >>> | | | | | 0.00000 kg/kg-water | | | |
| 18 | | | | | | | | | |
| 19 | BIP8 System Pressure Basis. barg | | 0.00 | | | | | | |
| 20 | BIP8 System Temperature Basis. C | | 25.00 | | | | | | |
| 21 | | | | | | | | | |
| 22 | Group ID | | 0 << Use 0 for default or a non-zero value for grouping and consolidation | | | | | | |
| 23 | | | | | | | | | |

Figure 3: Ethylene oxide sample mixture chemical interaction matrix

Reactivity Expert >> MY MIXTURE Mixture Summary - C:\IOIQ\PS08.4\SuperChems\BANKS\hzbanks_v8.5.dat

Chemical Hazard Report | Chemical Interaction Matrix | Chemical Interaction Listing | Glossary

| | A | B | C | D | E | F | G | H | I | J | K | L | M | N |
|----|--|--|-------------------|---------------|---------------------|------------------------|---|---|---|---|---|---|---|---|
| 1 | Chemical Incompatibility Matrix For Mixture MY MIXTURE | | | | | | | | | | | | | |
| 2 | | | | | | | | | | | | | | |
| 3 | | WATER | ETHYLENE OXIDE | AMMONIA | SODIUM HYDROXIDE | SULFURIC ACID | | | | | | | | |
| 4 | | | | | | | | | | | | | | |
| 5 | | A | B | C | D | E | | | | | | | | |
| 6 | WATER | A | 300, 204 | 300 | | 300 | | | | | | | | |
| 7 | | | | | | 300, 400, 200, 403, | | | | | | | | |
| 8 | ETHYLENE OXIDE | B | 109, 400 | 300, 400, 105 | 300, 400, 105 | 402, 105 | | | | | | | | |
| 9 | AMMONIA | C | | 302 | 300 | 300, 302 | | | | | | | | |
| 10 | SODIUM HYDROXIDE | D | | | | 300 | | | | | | | | |
| 11 | SULFURIC ACID | E | | | | 302 | | | | | | | | |
| 12 | | | | | | | | | | | | | | |
| 13 | 105 | May form explosive peroxides | | | | | | | | | | | | |
| 14 | 109 | Explosive | | | | | | | | | | | | |
| 15 | 200 | May cause fire | | | | | | | | | | | | |
| 16 | 204 | Flammable gas generation | | | | | | | | | | | | |
| 17 | 300 | Heat generation by chemical reaction | | | | | | | | | | | | |
| 18 | 302 | Water reactive | | | | | | | | | | | | |
| 19 | 400 | May cause violent polymerization, possibly with heat/toxic or flammable gas generation or with explosive reaction, causes pressurization | | | | | | | | | | | | |
| 20 | 402 | Contact with substances liberate toxic gas; causes pressurization | | | | | | | | | | | | |
| 21 | 403 | Innocuous and non-flammable gas generation; causes pressurization | | | | | | | | | | | | |
| 22 | 900 | Materials are compatible | | | | | | | | | | | | |

References

- [1] S. Saraf and G. A. Melhem. SuperChems Reactivity Expert System for screening chemical reactivity hazards. In *3rd International Symposium on Runaway reactions, Pressure Relief Design and Effluent Handling*. DIERS, AIChE, 2005.
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Dr. Melhem is an internationally known pressure relief and flare systems, chemical reaction systems, process safety, and risk analysis expert. In this regard he has provided consulting, design services, expert testimony, incident investigation, and incident reconstruction for a large number of clients. Since 1988, he has conducted and participated in numerous studies focused on the risks associated with process industries fixed facilities, facility siting, business interruption, and transportation.

Prior to founding [ioMosaic®](#) Corporation, Dr. Melhem was president of Pyxsys Corporation; a technology subsidiary of Arthur D. Little Inc. Prior to Pyxsys and during his twelve years tenure at Arthur D. Little, Dr. Melhem was a vice president of Arthur D. Little and managing director of its Global Safety and Risk Management Practice and Process Safety and Reaction Engineering Laboratories.

Dr. Melhem holds a Ph.D. and an M.S. in Chemical Engineering, as well as a B.S. in Chemical Engineering with a minor in Industrial Engineering, all from Northeastern University. In addition, he has completed executive training in the areas of Finance and Strategic Sales Management at the Harvard Business School. Dr. Melhem is a Fellow of the American Institute of Chemical Engineers (AIChE) and Vice Chair of the AIChE Design Institute for Emergency Relief Systems (DiERS).

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Appendices

This document includes one or more Appendices that provide additional insight, context, and/or deeper analysis for interested readers.

A SuperChems Reactivity Expert System for Screening Chemical Reactivity Hazards Publication

SuperChems Reactivity Expert System for Screening Chemical Reactivity Hazards

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ABSTRACT

Recognizing reactivity hazards posed by pure chemicals and mixtures is critical for managing risks in processing industries, waste-treatment facilities, and emergency response activities. A binary interaction matrix is a simple but effective technique for summarizing chemical reactivity information. The construction of such an interaction matrix is a complex task and may involve several man-hours. A variety of data sources have to be consulted to generate a good quality chemical interaction matrix.

This paper discusses the development of the SuperChems Reactivity Expert system - a computerized algorithm that utilizes several databases of chemical interactions to generate a binary compatibility matrix along with a hazard report. The reactivity expert system also displays available regulatory and toxicity information for a chemical, if available.

We applied the reactivity expert system for screening the 167 CSB incidents and were successful in screening 126 of 127 incidents where the chemicals involved were specified.

1. INTRODUCTION

Understanding the compatibility of chemicals is necessary for their safe handling and processing. A chemical reactivity interaction matrix is a simple, but effective means of consolidating and documenting chemical compatibility information along with toxicity and flammability hazards. The significance of the binary interaction matrix has led to the establishment of an ASTM standard – E-2012¹.

A chemical interaction chart usually indicates if two materials are reactive under given conditions. Although conceptually straightforward, it is not always easy to construct a binary interaction matrix. One of the difficulties lies in gathering the information necessary to construct such a matrix. This information can generally be obtained from Material Safety Data Sheets (MSDS), literature sources, and/or experiments. It is a common notion that the MSDS has all the required hazard information. However, some of the MSDSs are not updated, and a few chemicals, especially in waste processing, do not have a MSDS. A literature search may require

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significant man-hours and there is no single data source for all the requisite information. Experimentation is a costlier option and contains an inherent risk when the potential reactivity of chemicals is unknown. In lieu of the above problems we have developed the ***SuperChems Reactivity Expert System*** - a computer algorithm that utilizes a variety of literature sources and databases and displays information as a compatibility chart.

Literature pertaining to reactive hazard assessment has grown over the years and is available in the form of test data, functional group characterizations, and heuristics/rules of thumb. Due to a lack of standardization there is no single reference that integrates chemical reactivity data. Our aim was to develop a platform to integrate the disparate pieces of information on chemicals related to reactivity, flammability, and toxicity.

We first performed an exhaustive survey of available literature. We then created a unique database structure to consolidate the different forms of data. We also added certain rules of thumbs / heuristics to aid in hazard evaluation. This data was assembled in specialized Hazard databanks in ioMosaic's SuperChems Expert software. Finally, a computer program was developed capable of analyzing this information and generating an interaction matrix for any mixture. The next section discusses the various sources from which we assembled our hazard information.

2. DATA SOURCES

In this section, we have listed the data sources containing reactivity information that form the basis of the Reactivity Expert System. The reactivity information is available as compatibility charts, lists of reactive chemicals, and experimental data. In addition, we have included toxicity information for chemicals, if available.

2.1 Compatibility Information

2.1.1 EPA Chemical Compatibility Chart

The U.S. Environmental Protection Agency (EPA) has developed the Computer-Aided Management of Emergency Operations (CAMEO) suite of software for performing consequence analysis. CAMEO has a database of chemicals containing a variety of information such as chemical name, identification number, regulatory information, labeling conventions, and Response Information Data Sheets (RIDS). Each substance in the CAMEO library is assigned to one or more reactive groups based on the chemical structure. To predict the reactivity of a mixture of chemicals, CAMEO first identifies the reactive groups to which each of the chemicals belong, and then predicts the type of chemical reactions likely to occur when members of these groups are mixed together. The EPA has published a matrix that summarizes reactivity between different functional groups.² The interactions between the functional groups are assigned one the following reactivity potential in the EPA matrix.

The EPA interaction matrix is utilized by the SuperChems Reactivity Expert System as one of the sources of chemical compatibility information:

| | |
|----|--|
| H | Heat generation |
| F | Fire |
| G | Innocuous and non-flammable gas generation |
| GT | Toxic gas formation |
| GF | Flammable gas formation |
| E | Explosion |
| P | Violent polymerization |
| S | Solubilization of toxic substances |
| U | May be hazardous, but unknown. |

2.1.2 United States Coast Guard

The U.S. Coast Guard (USCG) has published a Cargo Compatibility Chart for identifying incompatible hazardous materials.³ The USCG chart specifies rules for carrying materials in bulk as cargo in permanently attached tanks or in tanks that are loaded or discharged while aboard the vessel. It covers an extensive list of chemicals and materials. The pairs of chemicals appearing in the chart are classified as reactive or non-reactive based on experimental results. The two cargos are considered hazardous or reactive if under the specified conditions the temperature rise of the mixture exceeds 25 °C or gases are evolved. The following experimental procedures were observed to determine reactivity between two cargos:

- **Step 1:** 0.5 ml of chemical A and B are mixed in a test tube. If a violent reaction, such as sputtering or boiling of reactants or release of fumes occurs, the mixture is classified as hazardous and the experiment is terminated. Else one needs to perform Step 2.
- **Step 2:** 20 ml combinations of binary mixture are taken in a definite proportion such as 2 ml : 18 ml, 10 ml : 10 ml, and 18 ml : 2 ml in a Dewar flask to see if there is an exothermic reaction. If the observed temperature rise is greater than 25 °C or if gases are evolved, the mixture is classified as hazardous and one does not need to perform Step 3.
- **Step 3:** A 10 ml mixture of chemicals is immersed in an oil bath maintained at 50 °C and rise in temperature or gaseous evolution is observed to determine reactive hazards.

The USCG compatibility chart for cargo forms another source of compatibility information for the SuperChems Reactivity Expert System.

2.1.3 TCPA List Of Functional Groups

The New Jersey Department of Environmental Protection (NJ DEP) recently broadened its Toxic Catastrophe Prevention Act (TCPA)⁴ to include reactive chemicals. In order to recognize reactive chemicals, TCPA provides a list of 43 functional groups believed to be inherently unstable and having high potential of a catastrophic accident when mixed or blended with other chemicals. These functional groups are shown in

Table 1. A chemical that contains one of the TCPA functional groups is shown as reactive when the SuperChems Reactivity Expert System generates an interaction matrix.

Table 1. TCPA Reactive Functional Groups

| Groups Containing Carbon | | |
|--------------------------|---|---|
| 1. | $\text{-C}\equiv\text{C-}$ | Acetylenic compounds |
| 2. | $\text{-C}\equiv\text{C-M}$ | Metal acetylides |
| 3. | $\text{-C}\equiv\text{C-X}$ $\text{N}=\text{N}$ $\begin{array}{c} \diagdown \diagup \\ \text{C} \end{array}$ | Haloacetylene derivatives Diazirines |
| 4. | -CN_2 | Diazo compounds |
| 5. | -C-N=O , -N-N=O | Nitroso compounds |
| 6. | -C-NO_2 Ar-NO_2 , $\text{Ar(NO}_2)_n$ $\text{C(NO}_2)_n$ $\text{O}_2\text{NC-CNO}_2$ $\text{HC[OCH}_2\text{C(NO}_2)_3]_3$, $\text{C[OCH}_2\text{(NO}_2)_3]_4$ | Nitroalkanes, C-nitro and Nitroaryl and Polynitroaryl compounds Polynitroalkyl compounds Trinitroethyl orthoesters |
| 7. | -C-O-N=O | Acyl or alkyl nitrites |
| 8. | -C-O-NO_2 | Acyl or alkyl nitrates |
| 9. | $>\text{C}-\text{C}<$ $\begin{array}{c} \diagdown \diagup \\ \text{O} \end{array}$ | 1,2-Epoxides |
| 10. | $\text{MC=N}\rightarrow\text{O}$ C=N-O-M | Metal fulminates or aci-nitro salts, oximates |
| 40. | $\text{-(CH-CH-)}_n\text{-}$ | Polymerization alkene monomers |

| Groups Containing Nitrogen | | |
|----------------------------|--|---|
| 11. | F-C- (NO ₂) ₂ | Fluorodinitromethyl compounds |
| 12. | -N-M | N-metal derivatives |
| 13. | -N=Hg+=N- | Poly(dimercuryimmonium salts) |
| 14. | -N-NO ₂ | N-nitro compounds |
| 15. | =N+-N-NO ₂ | N-Azolium nitroimidates |
| 16. | -C-N=N-C- | Azo compounds |
| 17. | Ar-N=N-O-R | Arenediazoates |
| 18. | ArN=N-S-Ar | Arenediazo aryl sulfides |
| 19. | Ar-N=N-O-N=N-Ar | Bis(arenediazo) oxides |
| 20. | Ar-N=N-S-N=N-Ar | Bis(arenediazo) sulfides |
| 21. | -C-N=N-N-C- R (R=H, CN, OH, NO) | Trizenes |
| 22. | -N=N-N=N- -N=N-N=C- | High-nitrogen compounds Tetrazoles |
| 28. | -N ₃ | Azides (acyl, halogen, nonmetal, organic) |
| 29. | C-N ₂ ±O- | Arenediazonium oxides |
| 30. | -C-N ₂ +S- | Diazonium sulfides and derivatives, Xanthates |
| 31. | N+-HZ-, N+EO- | Hydrazinium salts, Oxosalts of nitrogenous bases |
| 32. | -N+-OH Z- | Hydroxylaminium salts |
| 33. | -C-N ₂ +Z- | Diazonium carboxylates or salts |
| 34. | [N→Metal]+ Z- | Amminemetal oxosalts |
| 35. | Ar-Metal-X X-Ar-Metal | Halo-arylmets, Haloarenemetal p-complexes |
| 36. | -N-X XN ₃ -C-N-C- O X O | Halogen azides N-halogen compounds N-haloamides |
| 37. | -N-F ₂ -C(NF)NF ₂ | Difluoroamino compounds N,N,N-trifluoroalkylamidines |
| 38. | N-O- | N-O compounds |

| Groups Containing Oxygen | |
|---|---|
| 23. -C-O-O-H, R-CO-OOH | Alkylhydroperoxides, Peroxyacids |
| 24. -C-O-O-C-, -CO-OOR | Peroxides (cyclic, diacyl, dialkyl,), peroxyesters |
| 25. -O-O-M, EOO-, MOO- | Metal peroxides, peroxyacid salts |
| 26. -O-O-E | Peroxoacids, peroxyesters |
| 27. H3N.Cr-OO- | Amminechromium peroxocomplexes |
| 39. -O-X XOn -Cl-O3 ClO2- R-O-Cl-O3 RN+H3ClO4 | Hypohalites Halogen oxides Perchloryl compounds Chlorite salts Alkyl perchlorates Aminium perchlorates |
| 43. S2O4 | Dithionites |
| 42. $\begin{array}{c} \text{-(C-C-O-)}_n \\ \\ \text{O} \end{array}$ | Polymerization ester monomers |
| 41. $\begin{array}{c} \text{-(C-C-N-)}_n \\ \\ \text{O} \end{array}$ | Polymerization amide monomers |

Abbreviations: Ar = aromatic (benzene); M = metal; R = organic chain; X = halogen; E = nonmetal; Z = anion; n = integer variable; all other abbreviations are for the element symbols from the periodic table of elements. Note: Not all chemical bond symbols are shown.

2.1.4 Spill Prevention Guidance Document

Naval Facilities Engineering Service Center (NFESC) has published a spill prevention guidance document⁵ that serves as a guide to the Navy in developing and implementing their Spill Prevention, Control, and Countermeasure Plan for oil and hazardous substances (HS). In Appendix E, the spill prevention guidance document contains a chemical/material compatibility matrix on various chemicals and common materials of construction. The compatibility information is used to ensure that spill control structures and liners are compatible with the contained material. This information is utilized by the Reactivity Expert System when constructing an interaction matrix.

2.2 List Of Chemicals

The Reactivity Expert System contains lists of reactive chemicals and functional groups indicative of reactive hazards.

2.2.1 Peroxide Formers

Many liquid organic compounds, a few solid and gaseous organic compounds, and a few inorganic solids form peroxides when stored for extended durations. Most organic peroxides are sensitive to shock, heat, or friction to varying degrees. The peroxides are formed by the reaction of the chemical with oxygen allowed in the headspace of the chemical containers. Some peroxides quickly build up to an explosive level, and some are only explosive on concentration, such as when a solvent is distilled. Although there is no

agreement upon what level of peroxides present a significant hazard, several sources suggest that the "safe" range of peroxide formation is 100 ppm or less. If peroxides are detected at a level above 100 ppm, the material must be decontaminated or discarded as hazardous waste. A list of peroxide forming compounds has been added to the database.⁶ For these compounds, the Reactivity Expert System displays a hazard code of 105 – may form explosive peroxides in the incompatibility matrix.

2.2.2 Water Reactive

The water-reactive compounds react with water or moisture in the air releasing heat or flammable, toxic gas. Bretherick's handbook⁷ lists certain functional groups as water-reactive and these are summarized in Table 2. In addition other known chemicals have been classified as water-reactive.

Table 2. Water-Reactive Functional Groups

Functional Groups

Acid anhydride (RCO.O.COR)
Acyl halide (R-CO-X, R-SO-X, R-SO₂-X)
Alkali metal
Alkylaluminum derivatives
Alkylon-metal halides (R-Metal-H₂)
Complex hydrides
Metal halides (Metal-X_n)
Metal hydrides (Metal-H₂)
Metal oxides

2.2.3 Shock Sensitive

Sometimes, certain chemicals are sensitive to mechanical shock occasionally at elevated temperatures and pressures. A list of shock sensitive compounds has been added to the existing hazard databanks⁸ in the SuperChems Reactivity Expert System.

2.2.4 OSHA's List Of Reactive Chemicals

The Occupational Safety and Health Administration (OSHA) lists highly hazardous chemicals, toxic and reactive chemicals along with their threshold quantities.⁹ The threshold quantity is utilized to decide coverage of a facility. The chemicals in OSHA's list along with their threshold values are included in the SuperChems Reactivity Expert System.

2.2.5 EPA's List Of Reactive Chemicals

Under the accident prevention provisions of section 112(r) of the CAA, EPA developed a list of toxic substances and flammable substances. Threshold quantities (TQs) were established for these substances. The list of substances, TQs and the

requirements for risk management programs for accidental release prevention are found in 40 CFR Part 68. This list of chemicals has been added to the SuperChems Reactivity Expert System's Hazards databanks along with the individual TQs.

2.2.6 TCPA List Of Reactive Chemicals

TCPA provides a list of Reactive Hazard Substances (RHS) along with the recommended thresholds quantities (TQ). RHS are shown in Table 3 and included in the SuperChems Reactivity Expert System.

2.2.7 Pyrophoric

Bretherick's handbook lists certain functional groups prone to catching fire on exposure. These groups are listed in Table 4 and compounds belonging to any of these functional groups display a hazard code of 202 - spontaneously flammable in air.

2.2.8. NFPA Ratings

The diamond ratings for health, flammability, and reactivity available through NFPA 704¹⁰ are included in the Hazard databanks of the SuperChems Reactivity Expert System.

2.3 Experimental Data

The database of reactivity information for the SuperChems Reactivity Expert System has been augmented from three different sources of experimental data, namely Grewer's handbook, Ando, et al.'s paper, and ioMosaic proprietary data.

2.3.1 Grewer

In his book, Grewer has published experimental reactivity data on 177 common chemicals.¹¹ The author reports decomposition energy, onset temperatures, and SADT temperatures and provides references for the data sources.

2.3.2 Ando

The authors report the results of Differential Scanning Calorimeter (DSC) experiments on 849 different chemicals, namely heat of reaction and onset temperature.¹² 829 chemicals exhibited reactive behavior, and this data is retrieved by the SuperChems Reactivity Expert System algorithm during hazard analysis.

Table 3. List of Individual Reactive Hazard Substances (RHS)⁴

| | Substance | CAS # | Threshold Quantity (pounds) | Basis for Listing |
|----|---|------------|-----------------------------|-------------------|
| 1 | Acetyl Peroxide | 110-22-5 | 2500 | e |
| 2 | Butyl Hydroperoxide tertiary | 75-91-2 | 2500 | e |
| 3 | Butyl hypochlorite tertiary | None | 2500 | b |
| 4 | Calcium dithionite or Calcium hydrosulfite | 15512-36-4 | 5000 | b |
| 5 | Chlorodinitrobenzenes | 97-00-7 | 2500 | d, e |
| 6 | Cumene Hydroperoxide | 80-15-9 | 2500 | e |
| 7 | Dibenzoyl peroxide | 94-36-0 | 2500 | f |
| 8 | Diethyl Peroxide | 628-37-5 | 2500 | e |
| 9 | Diisopropyl Peroxydicarbonate | 105-64-6 | 2500 | e |
| 10 | Dinitro phenol, dry or wet, less than 15% water as 2,4 | 51-28-5 | 2500 | a |
| 11 | Dinitro resorcinol (wetted with not less than 15% water) | 35860-81-6 | 2500 | a |
| 12 | Dipicryl sulfide | 2217-06-3 | 2500 | a |
| 13 | Di-tert-butyl Peroxide | 110-05-4 | 2500 | e |
| 14 | Divinyl Acetylene | 821-08-9 | 2500 | e |
| 15 | Ethyl Nitrate | 625-58-1 | 2500 | e |
| 16 | Ethyl Nitrite (solutions) | 109-95-5 | 2500 | d, e |
| 17 | Isosorbide dintrate | 88-33-2 | 2500 | a |
| 18 | Magnesium diamide | 7803-54-4 | 2500 | b |
| 19 | m-Dinitrobenzene | 99-65-0 | 2500 | d |
| 20 | Nitroglycerine (alcohol solution) | 55-63-0 | 2500 | e |
| 21 | Nitromethane | 75-52-5 | 2500 | d, e |
| 22 | o-Dinitrobenzene | 528-29-0 | 2500 | e |
| 23 | p-Dinitrobenzene | 100-25-4 | 2500 | d |
| 24 | Peracetic acid (less than 40%) | 79-21-0 | 2500 | d, e |
| 25 | Picric acid (wet, with not less than 10% water) | 88-89-1 | 2500 | d |
| 26 | Potassium dithionite or Potassium hydrosulfite | 14293-73-3 | 5000 | b |
| 27 | Propargyl bromide (3-Bromopropyne) | 106-96-7 | 2500 | d, e |
| 28 | Silver picrate wetted with not less than 30% water | 146-84-9 | 2500 | a |
| 29 | Sodium dithionite or Sodium hydrosulfite | 7775-14-6 | 5000 | b |
| 30 | Trinitro benzene as 1,3,5 (wetted not less than 30 % water) | 99-35-4 | 2500 | a |

Basis for listing: a = DOT 4.1, b = DOT 4.2, c = DOT 4.3, d = NFPA 49, e = NFPA 325, f = NFPA 432

Table 4. List of Spontaneously Combustible Functional Groups

Pyrophoric Functional Groups
Alkylaluminum derivatives
Alkylborane
Alkylhaloborane
Alkylhalophosphines
Alkylhalosilane
Alkylmetals
Alkylon-metal hydride
Alkylphosphines
Alkylsilanes
Arylmetals
Boranes
Carbonyl metals
Complex Acetylides
Complex hydrides
Haloacetylene Derivatives
Hexamethylnitratodialuminate salts
Metal hydride
Non-metal hydride
Organometallic

2.3.3 ioMosaic Data

Experimental data for over 1,000 chemicals and mixtures collected by ioMosaic personnel are included in the Reactivity Expert System's databank.

2.4 Toxicity Information

In addition to reactivity information, the toxicity information available through OSHA and ERPG values are displayed by the SuperChems Reactivity Expert System.

2.4.1 OSHA PEL

The Occupational Safety and Hazard Administration (OSHA) has published a list of chemicals and their limits for air contaminants.¹³ The threshold values are called Permissible Exposure Level (PEL) and are normally given as an 8-hour time weighted average (TWA).

2.4.2 ERPG Values

The Emergency Response Planning Guideline (ERPG)¹⁴ values are intended to provide estimates of concentration ranges where one might reasonably anticipate observing adverse effects as described in the definitions for ERPG-1, ERPG-2, and ERPG-3 as a consequence of exposure to the specific substance.

- The ERPG-1 is the maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to one hour with no more than mild, transient adverse health effects or the perception of a clearly defined, objectionable odor.
- The ERPG-2 is the maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to one hour without experiencing or developing irreversible or other serious health effects or symptoms which could impair an individual's ability to take protective action.
- The ERPG-3 is the maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to one hour without experiencing or developing life-threatening health effects.

ERPG values are estimates, by a committee of experts, of the thresholds above which there would be an unacceptable likelihood of observing the defined effects. The estimates are based on the available data that are summarized in the documentation. In some cases where the data are limited, the uncertainty of these estimates is large. Users of the ERPG values are strongly encouraged to carefully review the documentation before applying these values.

3. ORGANIZATION OF DATA

3.1 Hazard Codes

A comprehensive list of hazard codes was created to collate available chemical reactivity data from the different sources discussed earlier. The entire list of hazard codes used in the SuperChems Reactivity Expert System is summarized in Table 5.

3.2 Functional Groups

A comprehensive list of 140 different functional groups was created to encompass different chemicals. The objective of this classification was to enable the use of functional group based rules. For example, metal hydrides are found to be water reactive while constructing the chemical incompatibility matrix.

3.3 Classification Of Substances In Hazard Databank

The compounds in the SuperChems[®] databank were classified into functional groups based on chemical structure or known properties. A chemical can belong to more than one functional group depending on the chemical structure. It should be noted that although interaction between chemical groups is generalized in terms of functional groups there are exceptions to the rule. For example, it is established that ketones are not compatible with aliphatic amines.³ However, acetone is compatible with diethylenetriamine.³ A list of such exceptions has been added to the list of rules for generating compatibility matrix.

Table 5. Hazard Codes for the Interaction Matrix Constructed by the Reactivity Expert System

| ioMosaic Hazard code | Description |
|-------------------------|--|
| 101 | Explosive when dry |
| 102 | Risk of explosion by shock, friction, fire or other sources of ignition |
| 103 | Forms very unstable explosive metallic compound |
| 104 | External heating may cause an explosion |
| 105 | May form explosive peroxides |
| 106 | Explosive due to vigorous reaction or reaction products can detonate |
| 107 | Explosive when mixed with oxidizing substances |
| 108 | Explosive when mixed with combustible material |
| 109 | Explosive |
| 110 | Heat generated from chemical reaction may initiate explosion |
| 200 | May cause fire |
| 201 | Contact with combustible material may cause fire |
| 202 | Spontaneously flammable in air |
| 203 | Fire from exothermic reaction – ignition of products and reactants |
| 204 | Flammable gas generation |
| 205 | Flammable, toxic gas generation; causes pressurization |
| 300 | Heat generation by chemical reaction |
| 301 | Dangerous heat generation due to heat of solution |
| 400 | May cause violent polymerization, possibly with heat/toxic or flammable gas generation or with explosive reaction, causes pressurization |
| 401 | Can become highly flammable in use; causes pressurization |
| 402 | Contact with substances liberates toxic gas; causes pressurization |
| 403 | Innocuous and non-flammable gas generation; causes pressurization |
| 404 | Contact with acids produces combustion enhancer (e.g. O ₂) |
| 500 | Generates water soluble toxic products |
| 600 | May be hazardous but unknown |
| 700 | Reaction may be intense or violent |
| 800 | Possible exposure to radiation |
| 900 | Materials are compatible |
| 902 | Thermodynamically unstable |

Table 6. List of SuperChems Reactivity Expert Functional Groups

| <i>id</i> | <i>Functional Groups</i> | <i>id</i> | <i>Functional Groups</i> |
|-----------|--|-----------|--|
| 1 | Acids, Minerals, Non-oxidizing | 71 | Halogen oxides |
| 2 | Acids, Minerals, oxidizing | 72 | Perchloryl compounds |
| 3 | Acids, Organic | 73 | Chlorite salts |
| 4 | Alcohols, Glycols | 74 | Alkyl perchlorates |
| 5 | Aldehydes | 75 | Aminium perchlorates |
| 6 | Amides | 76 | Dithionites |
| 7 | Amines, Aliphatic | 77 | Fluorodinitromethyl compounds |
| 8 | Amines, Aromatic | 78 | N-metal derivatives |
| 9 | Azo, | 79 | Poly(dimercuryimmonium salts) |
| 10 | Diazo | 80 | N-nitro compounds |
| 11 | Hydrazine | 81 | N-Azolium nitroimidates |
| 12 | Carbamates | 82 | Arenediazoates |
| 13 | Caustics | 83 | Arenediazo aryl sulfides |
| 14 | Cyanides | 84 | Bis(arendiazo) oxides |
| 15 | Dithiocarbamates | 85 | Bis(arendiazo) sulfides |
| 16 | Esters | 86 | Trizenes |
| 17 | Ethers | 87 | High-nitrogen compounds |
| 18 | Fluorides, Inorganic | 88 | Tetrazoles |
| 19 | Hydrocarbons, Aromatics | 89 | Azides (acyl, halogen, nonmetal, organic) |
| 20 | Halogenated Organics | 90 | Arenediazonium oxides |
| 21 | Isocyanates | 91 | Diazonium sulfides and derivatives, Xanthates |
| 22 | Ketones | 92 | Hydrazinium salts, Oxosalts of nitrogenous bases |
| 23 | Mercaptans and Other Organic Sulfides | 93 | Hydroxylaminium salts |
| 24 | Metals, Alkali and Alkaline Earth, Elemental | 94 | Diazonium carboxylates or salts |
| 25 | Metals, Other elemental, and Alloys as Powders, Vapors, or Sponges | 95 | Amminemetal oxosalts |
| 26 | Metals, Other Elemental and Alloy Sheets, Rods, Drops, etc. | 96 | Halo-arylmetals, Haloarenemetal p-complexes |
| 27 | Metals, and Metal Compounds, Toxic | 97 | Halogen azides |
| 28 | Nitrides | 98 | N-halogen compounds |
| 29 | Nitriles | 99 | N-haloamides |
| 30 | Nitro Componds, Organic | 100 | Difluoroamino compounds |
| 31 | Hydrocarbons, Aliphatic, Unsaturated | 101 | N,N,N-trifluoroalkylamidines |
| 32 | Hydrocarbons, Alphatic, Saturated | 102 | N-O compounds |
| 33 | Peroxides Organic | 103 | Polymerization ester monomers |
| 34 | Hydroperoxides,Organic | 104 | Polymerization amide monomers |
| 35 | Phenols and Cresols | 105 | Polymerization alkene monomers |
| 36 | Organophosphates, Phosphothioates, Phosphodithioates | 106 | Acid anhydride (RCO.O.COR) |
| 37 | Sulfides, Inorganic | 107 | Acyl halide (R-CO-X, R-SO-X, R-SO ₂ -X) |
| 38 | Epoxide | 108 | Alkali metal |
| 39 | Sulfuric Acid | 109 | Alkylauminum derivatives |
| 40 | Nitric Acid | 110 | Alkylon-metal halides (R-Metal-H ₂) |
| 41 | Ammonia | 111 | Complex hydrides |

| | | | |
|----|--|-----|--|
| 42 | Alkanolamine | 112 | Metal halides (Metal-Xn) |
| 43 | Organic Anhydride | 113 | Metal hydrides (Metal-H ₂) |
| 44 | Vinyl Acetate | 114 | Metal oxides |
| 45 | Acrylate | 115 | Alkylaluminum derivatives |
| 46 | Substitutes Allyls | 116 | Alkylborane |
| 47 | Alkene oxides | 117 | Alkylhaloborane |
| 48 | Epichlorohydrin | 118 | Alkylhalophosphines |
| 49 | Caprolactum Solution | 119 | Alkylhalosilane |
| 50 | Carbon Disulfide | 120 | Alkylmetals |
| 51 | Sulfolane | 121 | Alkylon-metal hydride |
| 52 | Glycol Ethers | 122 | Alkylphosphines |
| 53 | Vinyl Halides | 123 | Alkylsilanes |
| 54 | Acetylenic compounds | 124 | Arylmetals |
| 55 | Metal acetylides | 125 | Boranes |
| 56 | Haloacetylene derivatives | 126 | Carbonyl metals |
| 57 | Diazirines | 127 | Complex Acetylides |
| 58 | Nitroso compounds | 128 | Complex hydrides |
| 59 | Nitroaryl and Polynitroaryl compounds | 129 | Haloacetylene Derivatives |
| 60 | Polynitroalkyl compounds Trinitroethyl orthoesters | 130 | Hexamethylnitratodialuminate salts |
| 61 | Acyl or alkyl nitrites | 131 | Metal hydride |
| 62 | Acyl or alkyl nitrates | 132 | Non-metal hydride |
| 63 | Metal fulminates or | 133 | Organometallics |
| 64 | aci-nitro salts, oximates | 134 | Combustible and flammable materials |
| 65 | Peroxides (cyclic, diacyl, dialkyl) | 135 | Explosives |
| 66 | Peroxyesters | 136 | Polymerizable compounds |
| 67 | Metal peroxides, peroxyacid salts | 137 | Oxidizing agents, strong |
| 68 | Peroxoacids, peroxyesters | 138 | Reducing agent, strong |
| 69 | Amminechromium peroxocomplexes | 139 | Water and mixtures containing water |
| 70 | Hypohalites | 140 | water reactive substances |

4. CONSTRUCTING A BINARY INTERACTION MATRIX USING THE REACTIVITY EXPERT SYSTEM

Once a mixture is specified, the SuperChems Reactivity Expert System analyzes the various databases and rules for potential reactive hazards and displays it as a binary interaction matrix (Fig. 1A and 1B). The SuperChems Reactivity Expert System also generates a hazard report summarizing all properties and hazards for the chemicals under consideration available in SuperChems (Fig. 2).

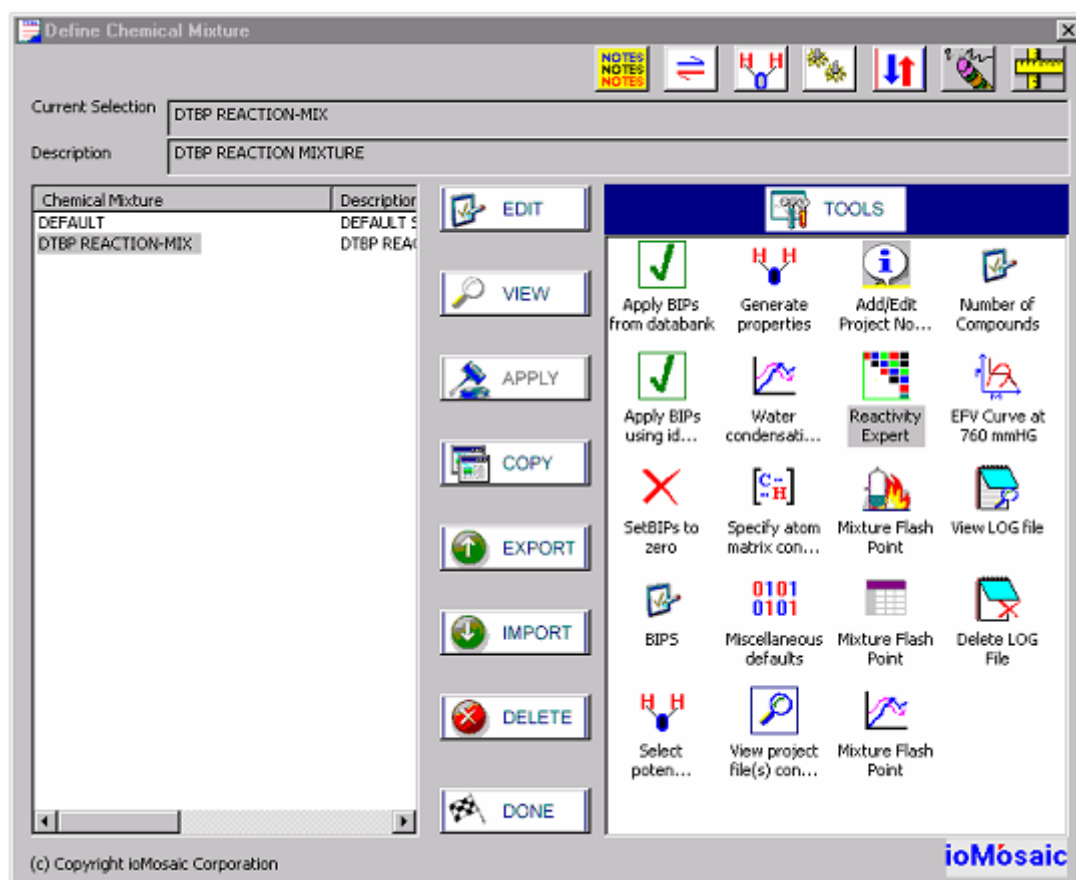
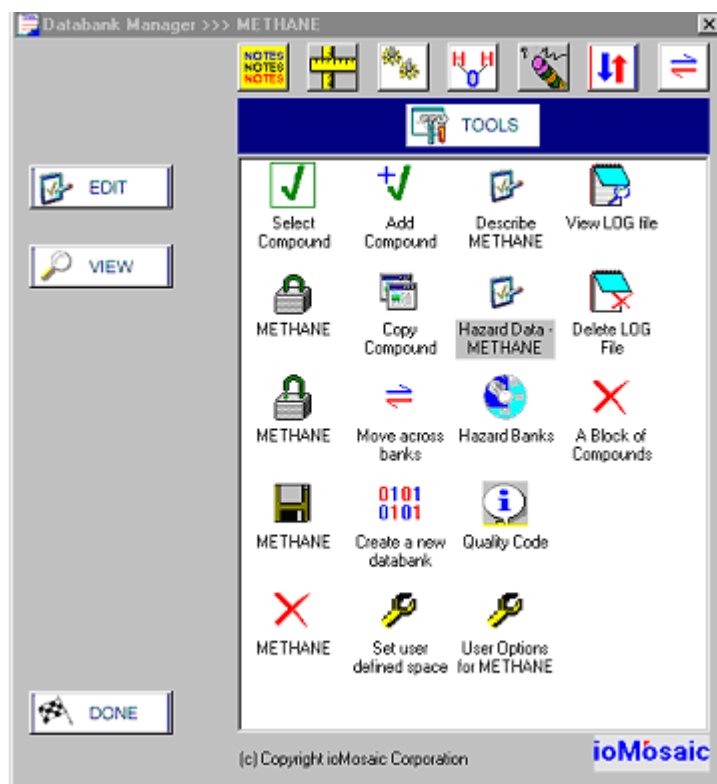


Figure 1A. Incompatibility Matrix Generated Using the SuperChems Reactivity Expert System



Chemical Incompatibility Matrix for Mixture TEST MIXTURE

| | DI-t-BUTYL PEROXIDE | ACETONE | METHANE |
|---------------------|---------------------|---------|---------|
| DI-t-BUTYL PEROXIDE | A | B | C |
| ACETONE | A | B | C |
| METHANE | C | | |

| | |
|-----|--------------------------------------|
| 105 | May form explosive peroxides |
| 109 | Explosive |
| 200 | May cause fire |
| 300 | Heat generation by chemical reaction |
| 900 | Materials are compatible |

Figure 1B. Incompatibility Matrix Generated Using the SuperChems Reactivity Expert System

Chemical Hazard Report

Reactivity Expert >> TEST MIXTURE

Mixture Summary

| | | | |
|---|---------------------|--------------------|--------------------|
| Chemical Name >> | DI-t-BUTYL PEROXIDE | ACETONE | METHANE |
| Chemical Formula >> | C8H18O2 | C3H6O | CH4 |
| CAS No. >> | 110054 | 67641 | 74828 |
| Molecular Weight. kg/kmol | 146.230 | 58.080 | 16.043 |
| Melting point. K | 233.150 | 178.450 | 90.670 |
| Normal boiling point. K | 384.150 | 329.440 | 111.660 |
| Critical temperature. K | 547.000 | 508.200 | 190.580 |
| Critical pressure. bar | 24.800 | 47.015 | 46.043 |
| Liquid density. kg/m3 | 789.91 | 785.602 @ 298 K | 424.056 @ 112 K |
| Latent heat of vaporization. J/kg | 229613.619 @ 384 K | 512940.691 @ 329 K | 508879.141 @ 112 K |
| Lower flammability limits. Vol % | 0.900 | 2.600 | 5.000 |
| Upper flammability limits. Vol % | 8.200 | 12.800 | 15.000 |
| Flash point temperature. K | 291.000 | 255.372 | |
| Autoignition temperature. K | | 810.927 | 873.000 |
| Minimum ignition energy. J | | | |
| Heat of combustion. J/kg | -3.3782E+07 | -2.8567E+07 | -5.0010E+07 |
| NFPA Rating: Health, Flammability, Reactivity | 3, 2, 4 | 1, 3, 0 | 2, 4, 0 |
| Ideal gas Heat of formation. J/kg | -2.3319E+06 | -3.7388E+06 | -4.6656E+06 |
| Thermodynamic Stability | | | |
| Peroxide Former | | | |
| Water Reactive | | | |
| Pyrophoric | | | |
| Explosive | EXPLOSIVE | | |
| Shock sensitive | | | |
| Polymerizable | | | |
| Heat of decomposition. J/kg | -1.6000E+06 | | |
| Decomposition onset temperature. K | 373.15 | | |
| Heat of polymerization. J/kg | | | |
| Polymerization onset temperature. K | | | |
| EPA Threshold Quantity. kg | | | 4,536 |
| OSHA Threshold Quantity. kg | 2,268 | | |
| NJ TCPA Threshold Quantity. kg | 1,134 | | |
| SEVESO Threshold Quantity. kg | | | |
| Carcinogen | | | |
| Skin Irritant | | | |
| ERPG-1 | | | |
| ERPG-2 | | | |
| ERPG-3 | | | |
| IDLH | | | |
| TLV | | | |
| PEL | | 1000 PPM | |

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ioMosaic Corporation

Figure 2. Hazard Report Generated by the Reactivity Expert System

5. APPLICATION OF REACTIVITY EXPERT SYSTEM TO 167 CSB INCIDENTS

The Chemical Safety Board has published a report summarizing reactive chemical incidents between 1981 – 2001.¹⁵ To test the applicability of the interaction matrix for recognizing chemical hazards, we generated chemical interaction matrices for chemicals involved in each of these incidents. Of the 167 incidents insufficient chemical information has been provided for 40 cases; therefore, 127 incidents are available for analysis. We generated 127 binary interaction matrices and a reactive hazard was indicated for 126 incidents. The one incident where no reactive hazard was indicated involved Freon TF – a Chlorofluorocarbon. Interaction matrices generated by the SuperChems Reactivity Expert system for the CSB systems are available on request.

6. CONCLUSIONS

The SuperChems Reactivity Expert System is a highly sophisticated program to develop chemical compatibility matrix. It relies on different qualified sources of information to recognize potential reactive hazards between chemicals. Moreover, users can record data on newer compounds in the Hazard Banks thereby enhancing the “knowledge-base” of the program. The SuperChems Reactivity Expert System thus provides a framework for storing reactivity data available in various forms and is a valuable tool for generating chemical hazard information.

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B ioKinetic Chemical Interaction Matrices Publication



Chemical Interaction Matrices

An ioKinetic White Paper

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Abstract

Despite the promulgation of the “PSM Standard” by OSHA in 1992, chemical accidents continue to occur at an alarming rate. As part of the process safety information element of the standard, OSHA requires reactivity data on the chemicals in the process. Part of this reactivity data is a chemical interaction matrix. Several software programs provide simple approaches to generating these interaction charts for common materials using assigned reactive groups. If your process involves materials not included, you are left to determine the reactivity and incompatibilities on your own. This presentation will explain a process for assigning reactive groups using chemical classification and structural analysis. This process can be used for less commonly understood materials such as additives, lubricants, etc. that may come into contact with process chemicals.

1. Introduction

Often called chemical incompatibility charts or matrices, means of classifying incompatibilities of materials using chemical interaction matrices have been around for decades. An EPA publication by Hatayama, Chen, de Vera, Stephens, and Storm in 1980 [1] documents this approach for classifying incompatibilities in hazardous waste. Since that time, many government and military departments have utilized the approach. Saraf and Melhem [2] provide a detailed summary of various approaches and applications.

More recently, many software programs have been developed to simplify the process of constructing the matrix, including the SuperChems™ component of ioMosaic’s Process Safety Office™ [3], the NOAA’s and EPA’s CAMEO Chemicals [4], and CCPS’ Reactivity Management Tool [5]. For simple or well-known chemicals, creation of the matrix is a trivial matter using any one of these programs. For non-standard materials, including mixtures, new formulations, or proprietary materials, another approach must be used.

The basis for determining chemical incompatibility lies in the assignment of reactive groups. The process involves the following steps:

1. Chemicals are chosen from a database which has pre-assigned reactive groups
2. Software predicts the type of chemical reactions likely to occur based on the groups
3. List of potential outcomes of those interactions is produced

The challenge lies when the chemicals of interest are not included in the provided databases. The process described here provides a system for adapting the method to allow incorporation of unique materials using basic chemistry.

The approach can be used for both intentional and unintentional interactions. For intentional interactions, it can be a first step in understanding if high temperatures and pressures may be expected from a given reaction system. For unintentional interactions, it can provide the basis for implementation of engineering and administrative controls to avoid hazardous interactions.

It is important to note that chemical interaction matrices are one input into a comprehensive evaluation of chemical reactivity hazards. As a binary tool, they are limited in that they only identify reactivity between two species and do not incorporate process and storage conditions. Mixtures of three (3) or more materials or analysis of process conditions requires additional evaluation. A short description of additional evaluation methods, including hazard assessments and reactivity testing, is provided below.

2. Methodology

For commonly known chemicals, putting a matrix together is a trivial matter, using any one of the available software programs discussed above. Figure 1 shows a chemical interaction matrix for several well-known chemicals made with SuperChems. Figure 2 shows the same chemical interaction matrix made with CAMEO [4]. The CAMEO program provides a color-coded assessment as Incompatible (red), Caution, (yellow) or Compatible (green). The cells also contain short phrases that summarize the reactive hazard predictions, such as "Corrosive" or "Generates heat". Figure 3 zooms in on one of the interaction pairs from CAMEO.

Table 1 compares the numbers of reactive groups and interaction types in the two most commonly applied software programs. (Note that the CCPS Reactivity Management Tool applies the CAMEO reactive groups and interaction types to analyze reactive hazards.)

Table 1. Numbers of Reactive Groups by Software

| Column Title | Basis | # in Basis | # Interaction Types |
|--------------|-------------------|------------|---------------------|
| SuperChems | Functional Groups | 142 | 31 |
| CAMEO | Reactive Groups | 64 | > 9 |

It is important to keep the matrix to a workable size for ease of use. A 50 page matrix will be of little value for implementation. Some ways to limit the size include:

- Determine a minimum quantity for inclusion (e.g., > 1 gal)
- Set a minimum concentration for inclusion (e.g., > 1%)
- Assess if two materials really can come into contact
- Assign reactive groups to a mixture rather than every chemical in the mixture [6]

For less commonly used chemicals, the reactive group must be determined and assigned accordingly. For specialty chemical and pharmaceutical companies, handling of unknown materials is an everyday occurrence. Even in refining and petrochemicals, many materials that come into contact with process chemicals are not well understood from a reactivity perspective.

A four step approach is presented to allow development of chemical interaction matrices that incorporate all materials of interest.

1. Identify all chemicals within the process
2. Assess the hazards and assign reactive groups
3. Develop matrices
4. Evaluate results

This approach is outlined in the sections that follow.

2.1 Identify Chemicals

When determining which materials to include in the matrix, a review of all materials that may come in contact needs to be undertaken. In addition to process chemicals this should consider [7]:

- Environmental (e.g., air, water/humidity)
- Utilities (e.g., steam, nitrogen)
- Materials of construction and gasket materials
- Contaminants (e.g., rust, scale lubricating oil)
- Other materials handled nearby

Some steps to develop this inventory include:

1. Review of heat and material balances and process flow diagrams
2. Facility walk-throughs to understand where chemicals are stored/used, including raw materials, products, lubricants, additives, etc.
3. Interviews with facility personnel to help identify/understand chemical handling and storage
4. Evaluation of inclusion of each material depending on quantity and usage

| | Chlorine | Ethylene | Air | Nitrogen | Sodium Hydroxide | 1, 2-Dichloroethane | Hydrogen Chloride | Water |
|---------------------|------------|-------------------|---------------|----------|------------------|---------------------|-------------------|----------|
| | A | B | C | D | E | F | G | H |
| Chlorine | A 302 | 200, 300, 402 300 | | | 300 | 300, 402 | 300 | 300 |
| Ethylene | B 400, 902 | 200, 300, 402 300 | | | 300, 400 | 300 | 200, 300, 400 300 | 300 |
| Air | | | 200, 300, 402 | | | 300, 402 | | |
| Nitrogen | | | | | | | | |
| Sodium Hydroxide | | | | | | 204, 300 | 300 | |
| 1, 2-Dichloroethane | | | | | | | 200, 300, 402 | |
| Hydrogen Chloride | | | | | | | | 300, 204 |
| Water | | | | | | | | |

| | |
|-----|--|
| 200 | May cause fire |
| 204 | Flammable gas generation |
| 300 | Heat generation by chemical reaction |
| 302 | Water reactive |
| 400 | May cause violent polymerization, possibly with heat/toxic or flammable gas generation or with explosive reaction, causes pressurization |
| 402 | Contact with substances liberate toxic gas; causes pressurization |
| 900 | Materials are compatible |
| 902 | Thermodynamically unstable |

Figure 1: Example Interaction Matrix made with Process Safety Office™ SuperChems™

| | ETHYLENE P | | | |
|------------------------------|--|--|--|---|
| AIR, COMPRESSED | Incompatible ■ Explosive Generates gas Generates heat Intense or explosive reaction Polymerization hazard | AIR, COMPRESSED | | |
| NITROGEN | Compatible ■ | Compatible ■ | NITROGEN | |
| SODIUM HYDROXIDE SOLUTION | Incompatible ■ Generates heat Intense or explosive reaction Polymerization hazard | Incompatible ■ Corrosive Generates gas Generates heat Intense or explosive reaction Toxic | Compatible ■ | SODIUM HYDROXIDE SOLUTION |
| ETHYLENE DICHLORIDE | Caution ■ Potentially hazardous | Incompatible ■ Explosive Generates gas Intense or explosive reaction Toxic | Compatible ■ | Incompatible ■ Corrosive Flammable Generates gas Intense or explosive reaction Toxic |
| | | | | ETHYLENE DICHLORIDE |
| HYDROGEN CHLORIDE, ANHYDROUS | Incompatible ■ Generates heat Intense or explosive reaction Polymerization hazard | Incompatible ■ Corrosive Explosive Flammable Generates gas Generates heat Intense or explosive reaction Toxic | Compatible ■ | Incompatible ■ Corrosive Generates gas Generates heat Intense or explosive reaction |
| | | | | HYDROGEN CHLORIDE, ANHYDROUS |
| WATER | Caution ■ Polymerization hazard | Incompatible ■ Corrosive Generates gas Generates heat Toxic | Compatible ■ | Incompatible ■ Corrosive Generates gas Generates heat Toxic |
| | | | | Caution ■ Corrosive Generates gas Generates heat |

P = Potentially self polymerizable

Figure 2: Example Interaction Matrix made with CAMEO

| | CHLORINE |
|--|---|
| ETHYLENE  | Incompatible  Corrosive Explosive Flammable Generates gas Generates heat Intense or explosive reaction Polymerization hazard Toxic |

Source: CAMEO Chemicals

Figure 3. Example Interaction Pair made with CAMEO

2.2 Assess Hazards and Assign Reactive Groups

The most critical and time-consuming step in the process involves assessing the hazards. The matrix will only be as good as the information input. For chemicals not well understood, a detailed analysis by a chemical reactivity expert is necessary. This assessment includes a literature search and a structural analysis.

- Some potential sources of reactivity information:
- Safety data sheets (SDSs)
- NIST Chemistry Webbook and other online references
- Books (e.g., Sax's, Bretherick's, Kirk-Othmer)
- Chemical reactivity worksheets/spreadsheets (e.g., CAMEO from EPA/NOAA, Reactivity Management Tool from CCPS)

Once those have been exhausted, a structural analysis is completed by a chemist. The list of applicable hazard groups will be a function of the software chosen to use in the matrix development as indicated in Section 2.1. Before starting the process, a program must be chosen such that the hazard groups are defined. To complete this analysis, the chemist develops the chemical structure of the given material. Evaluating the functional groups of the molecule allows assignment of applicable hazard groups.

An example application is provided in Section 3.

2.3 Develop Matrices

Once the reactive groups have been assigned, the software program will use these groups to determine interactions.

In addition to the interaction matrix and hazard statements shown above, the software programs provide a chemical interaction listing that details the hazards identified for each chemical pairing. Figure 4 shows an example summary of interactions for chlorine and other chemicals in the matrix.

| | |
|-----------------|---|
| CHLORINE | CHLORINE <ul style="list-style-type: none"> • Water reactive |
| CHLORINE | ETHYLENE <ul style="list-style-type: none"> • May cause fire • Heat generation by chemical reaction • Contact with substances liberate toxic gas; causes pressurization |
| CHLORINE | AIR <ul style="list-style-type: none"> • Heat generation by chemical reaction |
| CHLORINE | SODIUM HYDROXIDE <ul style="list-style-type: none"> • Heat generation by chemical reaction |
| CHLORINE | 1, 2-DICHLOROETHANE <ul style="list-style-type: none"> • Heat generation by chemical reaction • Contact with substances liberate toxic gas; causes pressurization |
| CHLORINE | HYDROGEN CHLORIDE <ul style="list-style-type: none"> • Heat generation by chemical reaction |
| CHLORINE | WATER <ul style="list-style-type: none"> • Heat generation by chemical reaction |

Figure 4. Chlorine Interactions



As shown in Table 1, the number of interactions varies with the software program chosen. CAMEO relies on defined hazardous interactions, such as:

Red:

- Large heat producing reaction (≥ 100 cal/gram); examples include acid/base or polymerization
- Formation of hazardous products; examples include unstable, flammable, or toxic materials

Yellow

- Intrinsic instability
- Potential impurities
- Slow reaction

This same method is applied within the CCPS Reactivity Management Tool.

The SuperChems software uses a slightly different approach. As explained earlier, it incorporates reactive groups and interactions from multiple sources to predict behavior. Examples of SuperChems interactions include:

- Water reactive
- May cause fire
- Heat generation
- Liberation of toxic gas
- Pressure generation
- Thermodynamic instability

2.4 Evaluate Results

It is important to be aware that the methodology applied will result in worst-case reactivity predictions as noted by Davis, Silva, and Murphy [5]. A critical part of using these matrices is to evaluate the magnitude of the potential hazard in light of the process operations being evaluated. A process hazard analysis can be used to understand the magnitude of consequences and the likelihood of the interactions. See the CCPS Book, Guidelines for Hazard Evaluation Procedures [7].

Several additional references address the topic of hazard assessment of identified chemical interactions, including the ASTM E2012 Standard Guide for the Preparation of a Binary Chemical Compatibility Chart [8] and Davis et al. [5]. Johnson, Rudy, and Unwin, [9] describe these as extrinsic factors which include quantity, form, process conditions, and location of materials.

Once highly reactive pairs have been identified, the next step would be chemical reactivity testing. This testing can define the extent of the reactive hazard. Basic experiments (such as differential scanning calorimetry and thermogravimetric analysis) measure temperature vs. time for reactive systems. Advanced calorimeters (e.g., Adiabatic Reaction Calorimeter®, Automatic Pressure Tracking Adiabatic Calorimeter™) also measure pressure vs. time. With these instruments, the following parameters can be defined:

- Onset temperature, T_o
- Maximum pressure generated, P_{max}
- Maximum temperature generated, T_{max}
- Adiabatic temperature rise, ΔT_{ad}
- Heat release rates, dT/dt
- Mechanical energy release rates, dP/dt
- Adiabatic heats of reaction, ΔH_r

3. Example Hazard Group Assignment

Loctite® is a common material used in chemical process plants. It is used as a gasket sealant. It may come into contact with any process chemical in its normal application. Due to its

proprietary nature it won't be listed in a typical chemical hazard database. An SDS provides the following composition for Loctite:

- 60-100% Polyurethane methacrylate resin (proprietary)
- 5-10% Silica
- 10-30% Polyglycol dimethacrylate
- 1-5% Acrylic acid
- 1-5% Cumene hydroperoxide
- 0.1-1% Ethylene glycol
- 0.1-1% 1-Acetyl-2-phenylhydrazine
- 1-5% Saccharin

Using a concentration limitation of > 1%, the Ethylene glycol and 1-Acetyl-2-phenylhydrazine can be ignored. For the remaining materials, a review of available literature provides some insight into potential hazard groups. For most of the materials, a structural analysis is the best approach.

For polyurethane methacrylate resin, no true compound could be identified. A detailed analysis by a chemical reactivity expert is necessary. To begin, the base components of the polymer are evaluated, urethane and methylmethacrylate. Figure 5 shows the structure of these two materials. Structural analysis shows the following potential hazard groups:

- Carbamate
- Acrylate

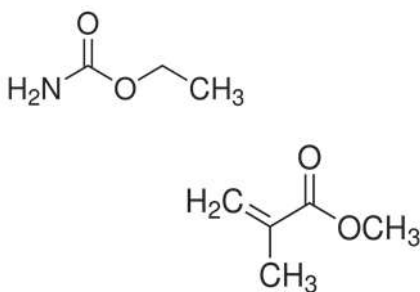


Figure 5: Structures of urethane and methylmethacrylate

Continued analysis of the remaining materials results in identification of nine reactive groups. To minimize the size of the matrix, these can be added together and inserted as one chemical in the matrix. Figure 6 shows the applicable reactive groups for Loctite.

| Group Name | Group # |
|--|---------|
| Acrylate | 45 |
| Carbamates | 12 |
| Glycols | 109 |
| Acids, Organic | 3 |
| Hydrocarbons, Aliphatic, Unsaturated (Also check if polymerizable) | 31 |
| Polymerizable compounds | 136 |
| Hydroperoxides, organic | 34 |
| Sulfolane | 51 |
| Amides (also check if polymerizable – 106) | 6 |

Figure 6: Reactive groups for Loctite

When evaluated against the reactive groups in chlorine, four possible interactions were identified.

- May cause fire
- Heat generation by chemical reaction
[Source: Process Safety Office™](#)
- Contact with substances liberates toxic gas; causes pressurization
- Innocuous and non-flammable gas generation; causes pressurization

This is confirmed by the LocTite® Fluid Compatibility Chart. It states that the material is not recommended for use with liquid or dry chlorine.

4. Conclusion

A method of determining potential hazardous interactions for non-standard materials has been presented. The method strives to make use of available technologies while presenting a means for incorporating and extending their application to non-standard materials. Utilizing a basic chemistry evaluation of chemical functional groups, a set of reactive groups can be developed and applied. These groups can then be used in standard chemical interaction matrix programs to develop interaction matrices.

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C Understanding NJ TCPA for Effective Reactivity Management Publication



Understanding NJ TCPA for Effective Reactivity Management

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Understanding NJ TCPA for Effective Reactivity Management

An ioMosaic Corporation White Paper

Abstract

The New Jersey Toxic Catastrophe Prevention Act (TCPA) has recently been amended to cover *reactive chemicals* and is the only regulation that requires an assessment of reactivity hazards and mitigation of associated risks. The *Reactive Chemicals* section of this regulation lists specific chemicals and functional groups along with corresponding threshold values that serve as trigger points for conducting reactive hazard assessments. This paper provides a brief overview of TCPA.

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Introduction

Based on previous incident investigations, the U.S. Chemical Safety and Hazard Investigation Board (CSB) has concluded that reactive hazards pose a serious challenge to the Chemical Process Industry (CPI). Of the 167 uncontrolled chemical reactivity incidents reported between January 1980 and June 2001, CSB findings indicate that over 50% of chemicals involved in the incidents were not covered by existing OSHA Process Safety Management (PSM) or EPA Risk Management Program (RMP) requirements. Based on their analysis, the CSB has recommended regulating reactive chemicals, which continues to be a focus of debate in the manufacturing industry.

The New Jersey Department of Environmental Protection (DEP) has taken the first step towards regulating reactive chemicals by extending its Toxic Catastrophe Prevention Act (TCPA) to include reactive chemicals. Approximately forty companies would likely be required to comply with the amended TCPA regulations, which will cover thirty reactive hazardous substances and forty-three chemical groups. Another amendment to the TCPA standard requires covered facilities to assess technologies every five years that can help alleviate potential risks and if feasible, implement such technologies.

Industry officials have warned that regulations pertaining to reactive chemicals, such as the new TCPA requirements, will be highly taxing on the industry, specifically for smaller manufacturers. This paper provides a simplified description of the *Reactive Chemicals* section of TCPA and associated compliance issues.

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TCPA and Reactive Chemicals

The TCPA came into effect in January 1986 with clearly defined objective of protecting the public from catastrophic accidental release of extraordinarily hazardous substances (EHS). The act required owners or operators of facilities processing EHS at certain threshold quantities to understand circumstances that could lead to accidental EHS release and to take appropriate measures to mitigate such releases.

Over the years, a reduction in the use of EHS has been confirmed and the number of facilities registered under TCPA has decreased from 600 in 1988 to 100 in 2002.² Currently, over 100 toxic chemicals are listed as EHS by the TCPA.

In addition to EHS, the amended TCPA includes two other categories for coverage of reactive chemicals :

- ⇒ *Reactive Hazard Substances* (RHS), a list of chemicals, and
- ⇒ *Reactive Hazard Substance Mixture* (RHSM), a list of functional groups. Details of each are provided below

Reactive Hazard Substances (RHS)

Certain chemicals such as peroxides and hydro-peroxides that are known to be unstable and have the potential to cause runaway reactions are classified as RHS. A list of such chemicals and their corresponding threshold quantities (TQ) as defined by TCPA is provided in Table 1.

The TNT equivalency equation was used to calculate TQs:

$$TQ = (D/24)^3 (1024/E)$$

TQ – Threshold quantity of RHS (lbs)

D – Distance to property line (100 m)

24 – Scaled distance for the mass of TNT that results in a blast pressure of 2.3 psi

E – Energy of explosion of RHS (cal/g)

1024 – Energy of explosion of TNT (cal/g)

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Table 1: TCPA Part D, Group I, List of Individual Reactive Hazard Substances (RHS)²

| Sr. No. | Substance | CAS # | Threshold Quantity (lbs) | Basis for listing |
|---------|---|------------|--------------------------|-------------------|
| 1 | Acetyl Peroxide | 110-22-5 | 2500 | e |
| 2 | Butyl Hydroperoxide tertiary | 75-91-2 | 2500 | e |
| 3 | Butyl hypochlorite tertiary | None | 2500 | b |
| 4 | Calcium dithionite or Calcium hydrosulfite | 15512-36-4 | 5000 | b |
| 5 | Chlorodinitrobenzenes | 97-00-7 | 2500 | d, e |
| 6 | Cumene Hydroperoxide | 80-15-9 | 2500 | e |
| 7 | Dibenzoyl peroxide | 94-36-0 | 2500 | f |
| 8 | Diethyl Peroxide | 628-37-5 | 2500 | e |
| 9 | Diisopropyl Peroxydicarbonate | 105-64-6 | 2500 | e |
| 10 | Dinitro phenol, dry or wet, less than 15% water as 2,4 | 51-28-5 | 2500 | a |
| 11 | Dinitro resourcinol (wetted with not less than 15% water) | 35860-81-6 | 2500 | a |
| 12 | Dipicryl sulfide | 2217-06-3 | 2500 | a |
| 13 | Di-tert-butyl Peroxide | 110-05-4 | 2500 | e |
| 14 | Divinyl Acetylene | 821-08-9 | 2500 | e |
| 15 | Ethyl Nitrate | 625-58-1 | 2500 | e |
| 16 | Ethyl Nitrite (solutions) | 109-95-5 | 2500 | d, e |
| 17 | Isosorbide dintrate | 88-33-2 | 2500 | a |
| 18 | Magnesium diamide | 7803-54-4 | 2500 | b |
| 19 | m-Dinitrobenzene | 99-65-0 | 2500 | d |
| 20 | Nitroglycerine (alcohol solution) | 55-63-0 | 2500 | e |
| 21 | Nitromethane | 75-52-5 | 2500 | d, e |
| 22 | o-Dinitrobenzene | 528-29-0 | 2500 | e |
| 23 | p-Dinitrobenzene | 100-25-4 | 2500 | d |
| 24 | Peracetic acid (less than 40%) | 79-21-0 | 2500 | d, e |
| 25 | Picric acid (wet, with not less than 10% water) | 88-89-1 | 2500 | d |
| 26 | Potassium dithionite or Potassium hydrosulfite | 14293-73-3 | 5000 | b |
| 27 | Propargyl bromide (3-Bromopropyne) | 106-96-7 | 2500 | d, e |
| 28 | Silver picrate wetted with not less than 30% water | 146-84-9 | 2500 | a |
| 29 | Sodium dithionite or Sodium hydrosulfite | 7775-14-6 | 5000 | b |
| 30 | Trinitro benzene as 1,3,5 (wetted not less than 30 % water) | 99-35-4 | 2500 | a |

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Basis for listing:

a = DOT 4.1

b = DOT 4.2,

c = DOT 4.3

d = NFPA 49

e = NFPA 325

f = NFPA 432

The threshold quantities are based on the amount of RHS required to cause an impact beyond an assumed property boundary of 100 meters using an overpressure value 2.3 psi. The 100 meter factor represents an average distance from covered processes to the property line for facilities. An overpressure of 2.3 psi was selected as damage to nearby buildings and other structures, severe enough to cause serious personal injuries, has been documented at that value. Since the energy of explosion is not readily available, TCPA uses 28% of heat of combustion or decomposition for E.

Reactive Hazard Substance Mixtures (RHSM)

The RHSM section of TCPA covers intentional mixing of two or more chemicals that can result in a potential catastrophe. To understand and define such chemicals, TCPA has provided a list of functional groups (Table 2) believed to be inherently unstable. If any of the intentional mixtures that are products, byproducts, or reactants contain functional groups listed in Table 2, the operating facility is required to obtain a heat of reaction (ΔH). Threshold quantities for a known ΔH , based on the TNT equivalency method discussed earlier, are provided by TCPA (Table 3).

Compliance Requirements

If the quantities of RHS or RHSM exceed the TQ, it qualifies for coverage under the TCPA program. The hazard assessment includes gathering flammability and reactivity data, analyzing fire and explosion hazards, collecting data on unstable products / intermediates, and performing consequence analyses and risk assessments. Additionally, TCPA requires covered facilities to assess technologies to alleviate potential risks and perform a review of inherently safer technologies for the covered processes.

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Table 2: TCPA Part D, Group II, Reactive Hazard Substance Mixtures Functional Groups

Abbreviations: Ar = aromatic (benzene); M = metal; R = organic chain; X = halogen; E = nonmetal; Z = anion; n = integer variable; all other abbreviations are for the element symbols from the periodic table of elements Note: (1) Not all chemical bond symbols are shown. (2) This is a partial list of the functional groups, the complete list is available in reference 2, or can be obtained from the author.

| Groups containing Carbon | |
|--|--|
| -C≡C- | Acetylenic compounds |
| -C≡C-M | Metal acetylides |
| -CN ₂ | Diazo compounds |
| -C-N=O, -N-N=O | Nitroso compounds |
| -C-O-N=O | Acyl or alkyl nitrites |
| -C-O-NO ₂ | Acyl or alkyl nitrates |
| MC=N→O C=N-O-M | Metal fulminates or aci-nitro salts, oximates |
| Groups containing Oxygen | |
| -O-O-M, EOO ⁻ , MOO ⁻ | Metal peroxides, peroxyacid salts |
| -O-O-E | Peroxoacids, peroxyesters |
| S ₂ O ₄ | Dithionites |

| Groups Containing Nitrogen | |
|--------------------------------------|--|
| F-C- (NO ₂) ₂ | Fluorodinitromethyl compounds |
| -N-M | N-metal derivatives |
| -N-NO ₂ | N-nitro compounds |
| =N ⁺ -N-NO ₂ | N-Azolium nitroimidates |
| Ar-N=N-O-R | Arenediazoates |
| ArN=N-S-Ar | Arenediazo aryl sulfides |
| Ar-N=N-O-N=N-Ar | Bis(arenediazo) oxides |
| -N ₃ | Azides (acyl, halogen, non-metal, organic) |
| -N ⁺ -OH Z ⁻ | Hydroxylaminium salts |
| Ar-N=N-S-N=N-Ar | Bis(arenediazo) sulfides |
| N-O- | Compounds containing N-O bond |

Table 3: Reactive Hazard Substance Mixture Threshold Quantities

| Heat of reaction | Threshold quantity |
|------------------|--------------------|
| cal/g | lbs. |
| 100 ≤ -ΔH ≤ 200 | 13100 |
| 200 ≤ -ΔH ≤ 300 | 8700 |
| 300 ≤ -ΔH ≤ 400 | 6500 |
| 400 ≤ -ΔH ≤ 500 | 5200 |
| 500 ≤ -ΔH ≤ 600 | 4400 |
| 600 ≤ -ΔH ≤ 700 | 3700 |
| 700 ≤ -ΔH ≤ 800 | 3300 |
| 800 ≤ -ΔH ≤ 900 | 2900 |
| 900 ≤ -ΔH ≤ 1000 | 2600 |
| -ΔH ≥ 1000 | 2400 |

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Conclusions

Regulating reactive chemicals is a complicated and controversial subject that has attracted wide-spread industry attention. Compliance with the amended TCPA regulation that now covers reactive chemicals does increase documentation requirements for operating companies and in certain cases extensive hazard assessment may not be necessary. However, effective utilization of the TCPA lists of chemicals and functional groups can deliver an excellent methodology for screening and mitigating reactive hazards.

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About ioMosaic Corporation

Our mission is to help you protect your people, plant, stakeholder value, and our planet.

Through innovation and dedication to continual improvement, ioMosaic has become a leading provider of integrated process safety and risk management solutions. ioMosaic has expertise in a wide variety of disciplines, including pressure relief systems design, process safety management, expert litigation support, laboratory services, training, and software development.

As a certified ISO 9001:2015 Quality Management System (QMS) company, ioMosaic offers integrated process safety and risk management services to help you manage and reduce episodic risk. Because when safety, efficiency, and compliance are improved, you can sleep better at night. Our extensive expertise allows us the flexibility, resources, and capabilities to determine what you need to reduce and manage episodic risk, maintain compliance, and prevent injuries and catastrophic incidents.

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