ioMosaic

Quickly Develop Chemical Interaction Matrices with SuperChems

An ioMosaic Technical Note

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IOMOSAIC CORPORATION

Technical Notes

Quickly Develop Chemical Interaction Matrices with SuperChems

authored by

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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. SuperChems [1], a component of Process Safety Office [2], 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

[1] SuperChems is a trademark (TM) of ioMosaic Corporation
[2] Process 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 gorups) 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:\IOIC\PSO8.4\SuperChems\BANKS\hzdbanks_v8.5.dat [Active Cell, Press F12 to Update]

Hazard Data | Lookup Table | Incompatibility Codes | Estimate Heat of Reaction

	A	B	C	D
1	Group Name	Group #		
2				
3	Epoxide	38	Last Verified On	03:12:50 PM, Thu Mar 15 2018
4	Combustible and flammable materials	134	Last Verified By	Dona Chakra
5	Explosives	135	Comment A	Version 8.50 Update
6	Polymerizable compounds	136	Comment B	NA
7	...	0	Comment C	NA
8	...	0		
9	...	0	Name	ETHYLENE OXIDE
10	...	0	Formula	C2H4O
11	...	0	CAS #	75218
12	...	0	Molecular Weight	44.053
13				
14	ETHYLENE OXIDE OSHA mass threshold. kg	2267.96		
15	ETHYLENE OXIDE EPA mass threshold. kg	4535.92		
16	ETHYLENE OXIDE NJ TCPA mass threshold. kg	1224.70		
17	ETHYLENE OXIDE Seveso lower mass threshold. kg	5000.00		
18	ETHYLENE OXIDE Seveso upper mass threshold. kg	50000.00		
19				
20	**Toxicity Information	PPM	mg/m3	
21	ERPG-1	0.00	0.00	
22	ERPG-2	50.00	0.00	
23	ERPG-3	500.00	0.00	
24	IDLH	800.00	0.00	
25	TLV	1.00	0.00	
26	PEL	1.00	0.00	
27				
28	☑ Toxicity Probit Data is Available. Y = A + B ln([C^N] t) min, ppm		☑ Probit concentration is in mg/m3 instead of ppm	
29	Probit A	-6.80		
30	Probit B	1.00		
31	Probit N	1.00		
32				
33	☐ ETHYLENE OXIDE is a known carcinogen			
34	☑ ETHYLENE OXIDE is a known skin irritant			
35	☐ ETHYLENE OXIDE is a peroxide former			
36	☐ ETHYLENE OXIDE is water reactive			
37	☐ ETHYLENE OXIDE is pyrophoric			
38	☑ ETHYLENE OXIDE is explosive			
39	☐ ETHYLENE OXIDE is shock sensitive			
40				
41	**NFPA Rating System			
42	Health	3		Corrosive or toxic. Avoid skin contac
43	Flammability	4		Flammable gas or extremely flammable
44	Reactivity	3		May be explosive if shocked, heated u
45	Special Notice	NA		Not assigned
46				
47	☐ Material will decompose when heated, initiated, or shocked			
48	Heat of decomposition. J/kg	0.00		
49	Decomposition onset temperature. C	-273.15		
50	Data Source	NA		
51	Data Reference	NA		
52				
53	☑ Material will polymerize when heated, initiated, or shocked			
54	Heat of polymerization. J/kg	0.00		
55	Polymerization onset temeprature. C	-273.15		
56	Data Source	NA		
57	Data Reference	NA		
58				

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	H2O	7732185	1013	18.015	1.00000	1.00000	0.05551	1.00000
3	ETHYLENE OXIDE	C2H4O	75218	524	44.053	0.00000	0.00000	0.00000	0.00000
4	AMMONIA	H3N	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	H2O4S	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	☑ Use mass basis data to compute fractions						C:\iOiQ\PSO8.4\SuperChems\BANKS\SC6.ID		
14	☑ Perform data quality and consistency checks						C:\iOiQ\PSO8.4\SuperChems\BANKS\SC6.TPP		
15	☐ Sort by normal boiling point		☐ Decreasing						
16	☐ Sort by molecular weight		☐ Decreasing						
17	☐ Mixture is soluble in water at this rate >>>		0.00000 kg/kg-water						
18									
19	BIPS System Pressure Basis. barg	0.00							
20	BIPS System Temperature Basis. C	25.00							
21									
22	Group ID	0	<< Use 0 for default or a non-zero value for grouping and consolidatic						
23									

Figure 3: Ethylene oxide sample mixture chemical interaction matrix

Reactivity Expert >> MY MIXTURE Mixture Summary - C:\IOIQ\PSO8.4\SuperChems\BANKS\hzdbanks_v8.5.dat

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

Chemical Incompatibility Matrix For Mixture MY MIXTURE

		A	B	C	D	E
		WATER	ETHYLENE OXIDE	AMMONIA	SODIUM HYDROXIDE	SULFURIC ACID
		A	B	C	D	E
A	WATER		300, 204	300		300
B	ETHYLENE OXIDE		109, 400	300, 400, 105	300, 400, 105	300, 400, 402, 200, 403, 105
C	AMMONIA			302	300	300, 302
D	SODIUM HYDROXIDE					300
E	SULFURIC ACID					302

105	May form explosive peroxides
109	Explosive
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
403	Innocuous and non-flammable gas generation; causes pressurization
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.

[2] M. Murphy and S. Singh. Chemical interaction matrices, 2016.

[3] S. Saraf and G. A. Melhem. Understanding NJ TCPA for effective reactivity management, 2004.

About the Author

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.

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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-2012[1].

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 ^{o}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 ^{o}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 ^{o}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.	-C≡C-	Acetylenic compounds
2.	-C≡C-M	Metal acetylides
3.	-C≡C-X N=N \ / C	Haloacetylene derivatives Diazirines
4.	-CN2	Diazo compounds
5.	-C-N=O, -N-N=O	Nitroso compounds
6.	-C-NO2 Ar-NO2, Ar(NO2)n C(NO2)n O2NC-CNO2 HC[OCH2C(NO2)3]3, C[OCH2(NO2)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-NO2	Acyl or alkyl nitrates
9.	>C—C< \ / O	1,2-Epoxides
10.	MC=N→O C=N-O-M	Metal fulminates or aci-nitro salts, oximates
40.	-(CH-CH-)n-	Polymerization alkene monomers

Groups Containing Nitrogen		
11.	F-C- (NO2)2	Fluorodinitromethyl compounds
12.	-N-M	N-metal derivatives
13.	-N=Hg+=N-	Poly(dimercuryimmonium salts)
14.	-N-NO2	N-nitro compounds
15.	=N+-N-NO2	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.	-N3	Azides (acyl, halogen, nonmetal, organic)
29.	C-N2±O-	Arenediazonium oxides
30.	-C-N2 +S-	Diazonium sulfides and derivatives, .Xanthates
31.	N+-HZ-, N+EOn-	Hydrazinium salts, Oxosalts of nitrogenous bases
32.	-N+-OH Z-	Hydroxylaminium salts
33.	-C-N2+Z-	Diazonium carboxylates or salts
34.	[N→Metal]+ Z-	Amminemetal oxosalts
35.	Ar-Metal-X X-Ar-Metal	Halo-arylmetals, Haloarenemetal p-complexes
36.	-N-X XN3 -C-N-C- ‖ | ‖ O X O	Halogen azides N-halogen compounds N-haloamides
37.	-N-F2 -C(NF)NF2	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, peroxoacid 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.	-(C-C-O-)n ‖ O	Polymerization ester monomers
41.	-(C-C-N-)n ‖ O	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 document[5] 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 handbook[7] 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
Alkylauminum derivatives
Alkylon-metal halides (R-Metal-H2)
Complex hydrides
Metal halides (Metal-Xn)
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 databanks[8] 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 704[10] 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 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

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
Alkylauminum 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

id	*Functional Groups*	*id*	*Functional Groups*
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(arenediazo) oxides
15	Dithiocarbamates	85	Bis(arenediazo) 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-SO2-X)
38	Epoxide	108	Alkali metal
39	Sulfuric Acid	109	Alkylauminum derivatives
40	Nitric Acid	110	Alkylon-metal halides (R-Metal-H2)
41	Ammonia	111	Complex hydrides

42	Alkanolamine	112	Metal halides (Metal-Xn)
43	Organic Anhydride	113	Metal hydrides (Metal-H2)
44	Vinyl Acetate	114	Metal oxides
45	Acrylate	115	Alkylauminum derivatives
46	Substitutes Allyls	116	Alkylborane
47	Alklene 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, peroxoacid 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).

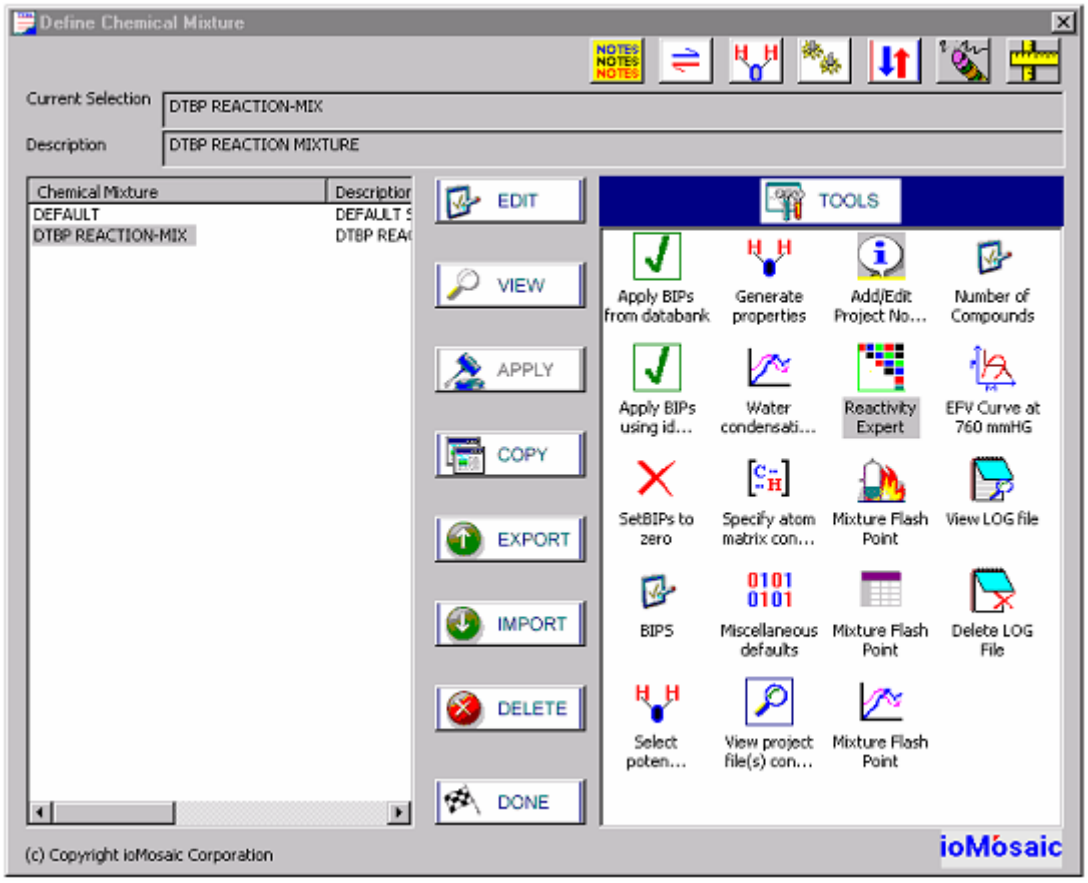
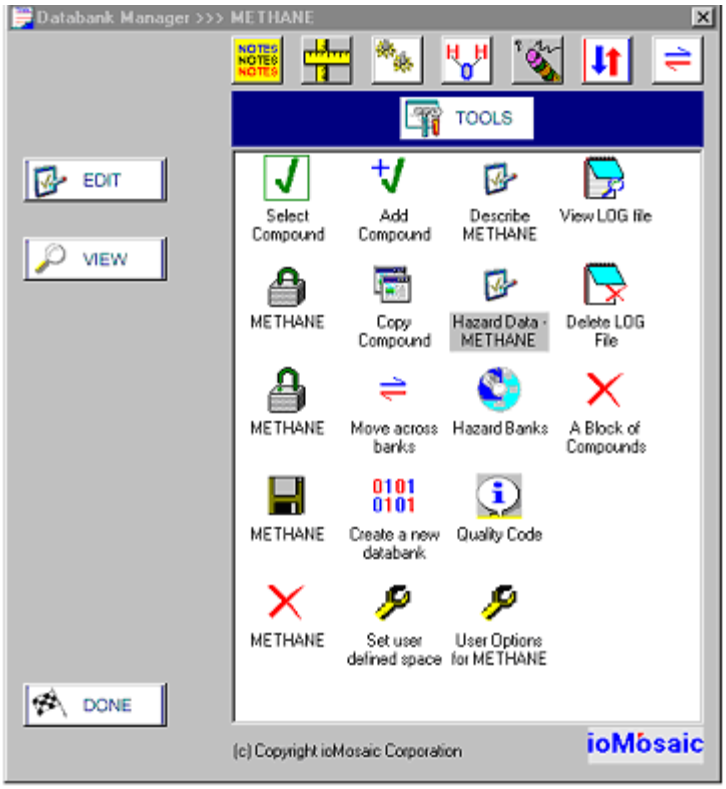


Figure 1A. Incompatibility Matrix Generated Using the SuperChems Reactivity Expert System



Chemical Incompatibility Matrix for Mixture TEST MIXTURE

		DI-t-BUTYL PEROXIDE	ACETONE	METHANE
		A	B	C
DI-t-BUTYL PEROXIDE	A	109	105, 300, 200	300, 200
ACETONE	B			
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 temperatue. K	291.000	255.372	
Autoignition temeprature. 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 temeprature. K	373.15		
Heat of polymerization. J/kg			
Polymerization onset temeprature. 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	

SuperChems Expert Version 5.90 (08-21-05) **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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An ioMosaic Corporation White Paper

Understanding NJ TCPA for Effective Reactivity Management

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Abstract

The New Jersey Toxic Catastrophe Prevention Act (TCPA) has recently been amended to cover *reactive chemicals* and is the only regulation that requires as 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.

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.

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)

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

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.

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
-CN2	Diazo compounds
-C-N=O, -N-N=O	Nitroso compounds
-C-O-N=O	Acyl or alkyl nitrites
-C-O-NO2	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, peroxoacid salts
-O-O-E	Peroxoacids, peroxyesters
S_2O_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
-N3	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.
$100 \le -\Delta H \le 200$	13100
$200 \le -\Delta H \le 300$	8700
$300 \le -\Delta H \le 400$	6500
$400 \le -\Delta H \le 500$	5200
$500 \le -\Delta H \le 600$	4400
$600 \le -\Delta H \le 700$	3700
$700 \le -\Delta H \le 800$	3300
$800 \le -\Delta H \le 900$	2900
$900 \le -\Delta H \le 1000$	2600
$-\Delta H \ge 1000$	2400

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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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 (■), Caution, (■) or Compatible (■). 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, 400	300	200, 300, 400	300
Air	C						300, 402		
Nitrogen	D								
Sodium Hydroxide	E						204, 300	300	
1, 2-Dichloroethane	F							200, 300, 402	
Hydrogen Chloride	G								300, 204
Water	H								

200 **May cause fire**

204 **Flammable gas generation**

300 **Heat generation by chemical reaction**

302 **Water reactive**

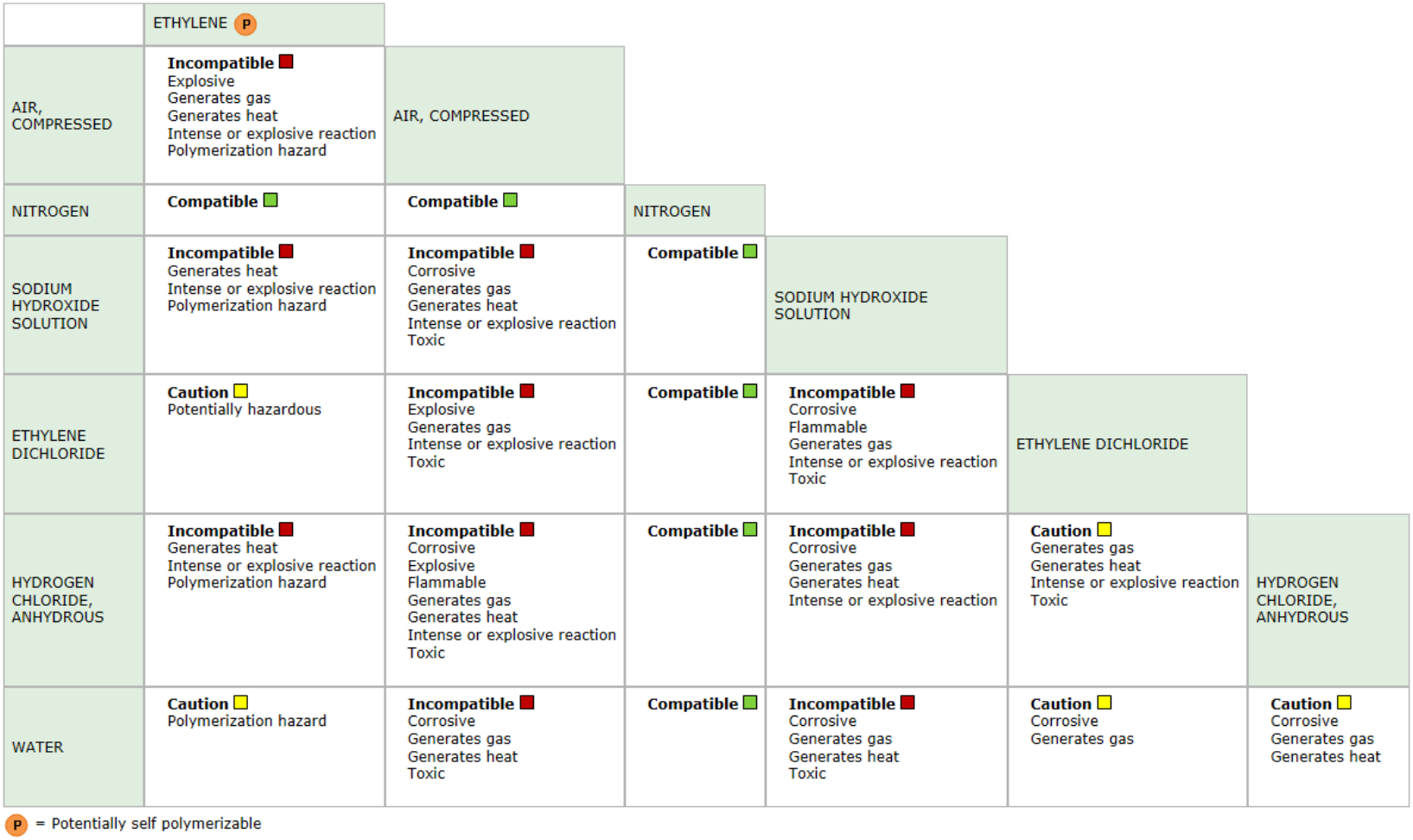
400 **May cause violent polymerization, possibly with heat/toxic or flammable gas generation or with explosive reaction, causes pressurization**

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	**Caution** ■ Generates gas Generates heat Intense or explosive reaction Toxic	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	**Caution** ■ Corrosive Generates gas Generates heat

(P) = Potentially self polymerizable

Figure 2: Example Interaction Matrix made with CAMEO

	CHLORINE
ETHYLENE P	**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** • Water reactive
CHLORINE	**ETHYLENE** • May cause fire • Heat generation by chemical reaction • Contact with substances liberate toxic gas; causes pressurization
CHLORINE	**AIR** • Heat generation by chemical reaction
CHLORINE	**SODIUM HYDROXIDE** • Heat generation by chemical reaction
CHLORINE	**1, 2-DICHLOROETHANE** • Heat generation by chemical reaction • Contact with substances liberate toxic gas; causes pressurization
CHLORINE	**HYDROGEN CHLORIDE** • Heat generation by chemical reaction
CHLORINE	**WATER** • 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, To
- Maximum pressure generated, Pmax
- Maximum temperature generated, Tmax
- Adiabatic temperature rise, ΔTad
- Heat release rates, dT/dt
- Mechanical energy release rates, dP/dt
- Adiabatic heats of reaction, ΔHr

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

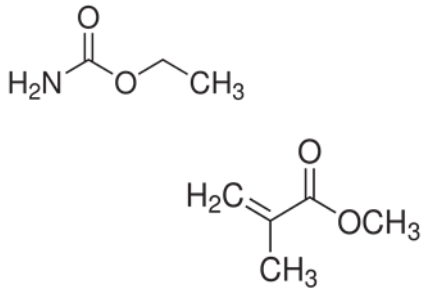


Figure 5: Structures of urethane and methylmethacrylate

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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