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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.

References

1. U.S. Chemical Safety and Hazard Investigation Board (CSB) Reactive Hazard Investigation Report "*Improving Reactive Hazards*" 2002 (Available on CSB website, http://www.csb.gov/reports/)
2. Toxic Catastrophe Prevention Act (TCPA) Program, Proposal number: PRN 2003-76, New Jersey, 2003
3. http://www.thompson.com/hp_newsbriefs/archive/030808e_environment.html
4. http://pffc-online.com/ar/paper_epa_considering_nj/
5. MKOPSC white paper, "Challenges of Regulating or Implementing Reactive Chemicals Hazard Management Program," Prepared for Presentation at the Public Meeting held by the United States Chemical Safety and Hazard Investigation Board September 17, 2002, Houston, Texas