



Pamphlet 164

Reactivity and Compatibility of Chlorine and Sodium Hydroxide with Various Materials

Edition 2



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1. INTRODUCTION

1.1 SCOPE

This pamphlet is intended to provide information to producers, users, and handlers of chlorine and/or 50% sodium hydroxide concerning the compatibility of these two substances with a variety of materials and their reactivity with other chemicals. The information considers only those materials and chemicals typically found in facilities producing, using, or otherwise handling chlorine and/or sodium hydroxide and is not meant to be an exhaustive list.

Users of this pamphlet might include persons responsible for operations and maintenance, hazards analyses, and/or emergency response of facilities producing, using or otherwise handling of chlorine and/or sodium hydroxide.

This pamphlet is not intended to provide detailed technical information needed by process engineers nor is it intended to provide economic evaluations of compatible materials. While the information provided should be of help to emergency responders, this pamphlet is not intended to provide technical guidance to the first persons on the scene in an emergency response. This pamphlet does not address nitrogen trichloride. Pamphlet 152 (Reference 4.1.6) provides a full discussion of this topic.

1.2 CHLORINE INSTITUTE STEWARDSHIP PROGRAM

The Chlorine Institute, Inc. exists to support the chlor-alkali industry and serve the public by fostering continuous improvements to safety and the protection of human health and the environment connected with the production, distribution and use of chlorine, sodium and potassium hydroxides, and sodium hypochlorite; and the distribution and use of hydrogen chloride. This support extends to giving continued attention to the security of chlorine handling operations.

Chlorine Institute members are committed to adopting CI's safety and stewardship initiatives, including pamphlets, checklists, and incident sharing, that will assist members in achieving measurable improvement. For more information on the Institute's stewardship program, visit CI's website at www.chlorineinstitute.org.

1.3 ABBREVIATIONS AND DEFINITIONS

Detonation	A particularly severe form of an explosion and the most
	destructive for the chemicals involved. There is a significant
	difference between the damage potential of a detonation
	compared to other types of explosions. The velocity of a
	detonation reaction always exceeds the velocity of sound.

Dry Chlorine Gas

Chlorine with a water content less than or equal to that which would exist if the gas were in equilibrium with dry liquid chlorine (i.e., by increasing the pressure at the same temperature). See Pamphlet 100 (Reference 4.1.4).

Dry Chlorine Liquid Chlorine with a water content less than or equal to the

solubility of water in chlorine

Exothermic (A reaction that) generates heat

Explosion (reaction) A sudden and violent release of energy, dissipated in a

shock wave.

psi Pounds per square inch

Reaction The combination of chemical substances. It may be fast

(violent) or slow. Heat may be generated or required.

Wet Chlorine Gas Chlorine with a water content greater than that which would

exist if the gas were in equilibrium with dry liquid chlorine (i.e., by increasing the pressure at the same temperature).

See Pamphlet 100 (Reference 4.1.4).

Wet Chlorine Liquid Chlorine with a water content greater than the solubility of

water in chlorine

1.4 CHEMICAL SYNONYMS

Caustic Common name for sodium hydroxide

Caustic soda Another common name for sodium hydroxide

Chlorine Elemental or molecular chlorine

CPVC Chlorinated PVC

EDC Ethylene dichloride (1,2 -dichloroethane)

PCBs Polychlorinated biphenyls

PVC Polyvinyl chloride

Sodium hydroxide As used in this pamphlet, it is meant to be 50 % solution.

VCM Vinyl chloride monomer

1.5 DISCLAIMER

The information in this pamphlet is drawn from sources believed to be reliable. The Chlorine Institute and its members, jointly and severally, make no guarantee and assume no responsibility in connection with any of this information. Moreover, it should not be assumed that every acceptable procedure is included, or that special circumstances may not warrant

modified or additional procedures. The user should be aware that changing technology and/or regulations may require a change in the recommendations herein. Appropriate steps should be taken to ensure that the information is current when used. These suggestions should not be confused with federal, state, provincial, municipal, or insurance requirements, or with national safety codes.

1.6 APPROVAL

The HESS Issue Team approved the second Edition of this pamphlet on March 20, 2007.

1.7 REVISIONS

Suggestions for revisions should be directed to the Secretary of the Institute.

1.8 REPRODUCTION

The contents of this pamphlet are not to be copied for publication, in whole or in part, without prior Institute permission.

2. CHLORINE

This section provides information on the reactivity of chlorine with materials more commonly found in facilities producing, using, or otherwise handling chlorine and on the reactivity of chlorine with chemicals that may typically be found in such facilities.

Chlorine gas or liquid is not explosive or flammable, but it is a strong oxidant and will support combustion. Both chlorine liquid and gas react with many substances. Chlorine is only slightly soluble in water. The gas has a characteristic, penetrating odor, a greenish yellow color and is about two and one-half times as heavy as air. Thus, if chlorine escapes from a container or system, it will tend to concentrate in the lower levels of buildings or outside areas.

Although dry chlorine (gas or liquid) normally does not react with or corrode metals such as copper or carbon steel, it is strongly reactive (strongly corrosive) when moisture is present. Materials may be compatible with both wet and dry chlorine, compatible with neither (i.e., reactive with both), or compatible with wet but not dry chlorine, or vice versa. Dry chlorine is defined as chlorine with its water content dissolved in solution. If water exists beyond that which is dissolved in the chlorine (i.e., separate phase), the chlorine is considered wet). Pamphlet 100 (Reference 4.1.4) gives a fuller discussion of this topic.

2.1 CHLORINE REACTIVITY WITH MATERIALS CHART

See Table 2.1.

2.2 CHLORINE REACTIVITY WITH OTHER CHEMICALS CHART

See Table 2.2.

- 1 Integrity of material is maintained
- ② Integrity of material is variable depending on conditions
- **3** Integrity of material is jeopardized

NOTE:

This table is not intended to provide detailed technical information needed by process engineers, nor is it intended to provide economic evaluations of different materials.

	Wet 0	<u>Chlorine</u>	Dry C	<u>Chlorine</u>	
Material	Gas	Liquid	Gas	Liquid	Comments
Acid brick	1	8	1	6	
Aluminum	•	8	8	8	
Asbestos, compressed	1	1	1	1	See Pamphlet 95 (Reference 4.1.3)
Brass	8	8	8	•	
Carbon steel, non-alloyed	8	8	1	1	For dry chlorine at less than 300°F (149°C) See Section 2.4
Cast iron	6	8	2	2	Materials known to be brittle
Copper	2	2	1	2	
CPVC (chlorinated PVC)	1	2	1	2	Mechanical integrity concerns
Ductile iron	8	8	1	2	For dry chlorine less than 300°F (149°C)
E-brite® (ferritic stainless steel)	8	8	2	2	Stress cracking may occur
EPDM (ethylene propylene diene monomer)	2	2	2	2	
Fiberglass					See specific resins

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NOTE:

This table is not intended to provide detailed technical information needed by process engineers, nor is it intended to provide economic evaluations of different materials.

	Wet Chlorine Dry 0		<u>Chlorine</u>		
Material	Gas	Liquid	Gas	Liquid	Comments
Fluorolube	1	1	1	1	
Glass	1	1	1	1	Mechanical integrity concerns
Graphite	1	2	1	2	Mechanical integrity concerns Resin must be chlorine resistant
Gylon® Style 3504 (blue)	1	1	1	1	
Hypalon® (chlorosulfonated polyethylene)	2	2	2	2	
Hastelloy C	2	2	1	1	For dry chlorine less than 932°F (500°C)
Inconel®	8	8	1	1	For dry chlorine less than 932°F (500°C)
Krytox®	1	1	1	1	
Kynar®	1	1	1	1	Mechanical integrity concerns
Lead	2	2	1	1	
Molybdenum	8	8	2	2	
Monel® 400	8	8	1	1	
Neoprene	2	8	2	8	

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NOTE:

This table is not intended to provide detailed technical information needed by process engineers, nor is it intended to provide economic evaluations of different materials.

	Wet Chlorine		Dry Chlorine		
Material	Gas	Liquid	Gas	Liquid	Comments
Nickel 200	8	8	1	1	
Polyethylene	8	8	8	8	Mechanical integrity concerns
Polypropylene	6	•	6	•	Mechanical integrity concerns
PTFE (polytetrafluoroethylene)	1	1	1	1	Can become impregnated with chlorine (permeability issue)
PVC (polyvinyl chloride)	1	2	1	2	Mechanical integrity concerns
Resin, epoxy	8	8	2	2	
Resin, polyester	2	2	2	2	Mechanical integrity concerns
Silicon, rubbers or lubricants	8	8	8	8	
Resin, vinylester	1	2	1	2	Mechanical integrity concerns for liquid chlorine
Rubber, butyl	2	8	2	8	
Rubber, natural	2	8	2	8	
Stainless Steel, 17-4 PH	8	8	2	2	Stress cracking may occur
Stainless Steel, 304	8	8	2	2	Stress cracking may occur

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NOTE:

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	Wet Chlorine		Dry Chlorine		
Material	Gas	Liquid	Gas	Liquid	Comments
Stainless Steel, 316	8	8	2	2	Stress cracking may occur
Tantalum	1	1	1	1	Less than 300°F (149°C)
Teflon®	1	1	1	1	
Tin	3	8	8	8	
Titanium	1	1	8	8	See Section 2.3
Tygon®	1	2	1	2	Mechanical integrity concerns
Viton® (Fluorocarbon elastomer)	1	1	1	1	
Zinc	8	8	•	8	

Table 2.2: Chlorine Reactivity with Other Chemicals

1 Integrity of material is maintained

② potentially reactive under certain conditions

3 Integrity of material is jeopardized

NOTE:

Chemicals	Reactivity	Comments
Acetaldehyde	8	
Acetic Acid	2	
Acetone	•	
Acetylene	•	Explosive and detonation potential under certain conditions
Alcohols	③	See Ethanol and Methanol
Alkanolamines	•	
Ammonia	•	See Pamphlet 152 (Reference 4.1.6)
Ammonium Acetate	•	
Ammonium Chloride	3	
Ammonium Hydroxide	3	
Benzene	•	
Calcium Carbonate	2	
Carbon Disulfide	3	Can explode when catalyzed by iron
Carbon Tetrachloride	1	
Caustic Soda	•	
Chloroform	2	
Chloroethylene	3	
Copper Sulfate	2	
Dibutylphthalate	•	
Dichloroethane	2	
Dichloroethylene	2	

Table 2.2: Chlorine Reactivity with Other Chemicals

- 1 Integrity of material is maintained
- 2 potentially reactive under certain conditions
- 3 Integrity of material is jeopardized

NOTE:

Chemicals	Reactivity	Comments
Diesel Fuel	8	See Section 2.6
Diethyl Ether	•	
EDC (Ethylene Dichloride)	2	
Ethanol	8	
Ethylene	8	Explosive and detonation potential under
Ethane	8	certain conditions Explosive and detonation potential under certain conditions
Ethylene Glycol	8	Certain Conditions
Ferric Chloride	1	
Fluorolube	1	See Section 2.6
Freon®	2	
Gasoline	8	See Section 2.6
Glycerin	8	
Grease (organic)	8	See Section 2.6
Heat Transfer Oils	8	See Section 2.6
Hexachlorobenzene	1	
Hexachlorobutadiene	1	
Hexachloroethane	1	
Hydrocarbons	•	See Section 2.6
Hydrochloric Acid	1	
Hydrogen	•	Explosive and detonation potential under certain conditions
Hydrogen Peroxide	2	oortaan oonataono
Hydrogen Sulfide	2	

Table 2.2: Chlorine Reactivity with Other Chemicals

1 Integrity of material is maintained

② potentially reactive under certain conditions

1 Integrity of material is jeopardized

NOTE:

Chemicals	Reactivity	Comments
Hydroxylamine	8	
Krytox®	1	
Lithium Bromide	2	
Magnesium Chloride	1	
Magnesium Sulfate	2	
Metals (finely divided)	3	e.g., steel wool; See Section 2.4
Methane	•	Explosive and detonation potential under certain conditions
Methanol	③	certain conditions
Methyl Chloroform	3	
Mineral Oil	3	
Naphtha	3	See Section 2.6
Nitric Acid	2	
Nitroparaffins	3	See Section 2.6
Oils (organic)	3	See Section 2.6
PCBs (Polychlorinated Biphenyls)	3	
Potassium Hydroxide	3	
Propylene	③	
Silicone Oil	3	See Section 2.6
Sodium Bisulfite	③	
Sodium Carbonate	3	
Sodium Chlorate	2	
Sodium Chloride	1	

Table 2.2: Chlorine Reactivity with Other Chemicals

- 1 Integrity of material is maintained
- ② potentially reactive under certain conditions
- 3 Integrity of material is jeopardized

NOTE:

Chemicals	Reactivity	Comments
Sodium Chlorite	2	
Sodium Hydroxide	•	
Sodium Hypochlorite	2	
Sodium Sulfide	•	
Sodium Sulfite	•	
Sodium Thiosulfate	8	
Sulfur Dioxide	•	
Sulfur	8	
Sulfuric Acid	2	For wet chlorine. With dry chlorine there is little or no reaction
Trichloroethylene	8	is little of no reaction
VCM (Vinyl Chloride)	8	
Vinyl Acetate	8	
Vinylidene Chloride	•	
Water	2	
Zinc Oxide	2	

2.3 TITANIUM

2.3.1 Hazard Description:

Titanium is frequently used in wet chlorine systems, contributing to the possibility of mistakenly installing this material into a dry application. This potential problem is compounded by the appearance of titanium, which is similar to that of tantalum and stainless steels. Titanium should only be used in chlorine applications where sufficient water is present to passivate the titanium surface so that a chlorine/titanium reaction does not occur.

In the absence of sufficient water, titanium reacts rapidly with chlorine, causing the titanium to burn. This reaction can generate sufficient heat for other materials, such as steel, to ignite. It is most important that each application for titanium be evaluated to insure that sufficient water (see Section 2.3.2) to prevent a chlorine/titanium reaction is always present.

Corrosion of titanium in chlorine can occur under conditions when chlorine is trapped and the water escapes (chlorine becomes dry). This causes a condition called crevice corrosion which is the most common reason for titanium failures. Consequently, any condition that can reduce the available water of the chlorine/titanium interface can be a source of accelerated corrosion. Temperature and pH are among those factors that can affect the corrosion rate of titanium.

2.3.2 Safe Limits of Operation:

Titanium is protected in wet chlorine applications with a titanium oxide layer formed at the water/titanium interface. Chlorine has a specific minimum water concentration that must be maintained to provide a stable titanium oxide layer in the chlorine atmosphere. Chlorine that is wet simply because it does not meet the definition of dry chlorine (see Definitions, Section 1.3) may not contain sufficient amount of water to allow for the use of titanium with chlorine. The paper, How to Use Steel and Titanium Safely, (Reference 4.2.1) provides an excellent discussion of this topic.

A temperature of about 560°F (13°C) is considered the minimum temperature at which the water saturation of chlorine can prevent a chlorine/titanium fire. Water content below about 0.4 wt% at atmospheric pressure is considered unsafe. At temperatures between 56°F (13°C) and 158°F (70°C), the minimum water content to prevent a fire increases only slightly as the temperature rises. At higher temperatures (158°F (70°C) and up), the amount of water needed to maintain a safe condition increases exponentially as the temperature increases.

2.3.3 Examples of Incidents:

(1) A butterfly valve with a titanium disk and a titanium stem was used to control the flow (differential pressure was approximately 5.9 psi) of cold wash water saturated with chlorine. After some months of operation, a fire occurred in the valve burning away the valve disk and part of the stem.

The investigators concluded that the causes were a combination of (1) too low a temperature; (2) drying resulting from the pressure throttling; and (3) continuous movement of the stem, causing the titanium stem to ignite.

By increasing the wash water temperature to above 60°F (16°C) and, in addition, spraying water continuously over the valve, a safe condition was achieved.

Lessons Learned:

Titanium will react violently with dry chlorine.

There is a minimum amount of water that is required to protect the titanium from reacting with the chlorine and igniting.

(2) A chlorine vaporizer system was shut down for annual repair and inspection. The work was completed and upon startup, a gasket "blow out" occurred. The gasket in this flange had been changed during the shutdown. What remained of the failed gasket was examined and it appeared to be appropriate for the service: spiral wound, flexible graphite, the outer ring clearly indicated the metal parts were constructed of nickel. It was puzzling that while gasket filler residue was clearly present on the floor, there was no evidence of any metal gasket winding material.

In the subsequent investigation, a trace analysis of the graphite filler revealed small amounts of titanium were present. Examination of other gaskets in the plant found two gaskets which were stamped consistent with nickel construction, but were actually made of titanium.

Lessons Learned:

The gasket markings CLEARLY indicated it was identical to the one it was replacing. But, when the replacement gasket was installed, a change had occurred - one which seriously compromised safe operation of the facility. Materials of construction markings can be inaccurate. If proper material of construction is critical for safe operations, testing may be needed to verify appropriate materials were used.

2.4 CARBON STEEL

2.4.1 Hazard Description:

A chlorine/steel fire is one of the most serious plant disruptions. Chlorine/steel fires will occur spontaneously when the iron or steel temperature is at or above 483°F (250°C). Depending on other factors (e.g., impurities, surface area), this reaction can occur at much lower temperatures.

To prevent chlorine/steel fires from occurring, the Institute recommends that the maximum temperature that chlorine/steel systems encounter be less than 300°F (149°C). This limit should be monitored and alarmed. Special attention should be given to systems subject to localized high temperatures (e.g. individual discharge valves on reciprocating chlorine compressors).

Since chlorine is a very strong oxidant, chlorine fires are very difficult to extinguish. One method for fighting a chlorine/steel fire when the fire is inside equipment is:

- 1. stop the chlorine feed
- 2. purge the equipment with an inert gas such as nitrogen to remove the chlorine
- 3. use water to reduce the outside surface temperature of the steel to prevent structural collapse.

2.4.2 Safe Limits of Operation

Normally steel can be used in dry chlorine at temperatures below 300°F (149°C). However, incidents of ignition of steel have been reported at temperatures as low as 212°F (100°C) when impurities (e.g., rust, carbon) were present. Dry steel wool will ignite with chlorine at about 122°F (50°C). The reason for the substantial range of temperatures is the important roles that surface area and ferric chloride films play in affecting chlorine/steel reactions. Pamphlet 6 (Reference 4.1.1) provides detailed recommendations for steel components in chlorine service.

2.4.3 Examples of Incidents:

(1) A tower packed with steel pall rings ruptured 9 hours after the tower was shut down and an air purge was put on the tower to evaporate the liquid chlorine. The temperature downstream from the tower rose slowly to 74°F (23°C) over 2.5 hrs and then increased to 200°F (93°C) over about 15 minutes. The temperature held at 200°F (93°C) for 6 hours and then rose rapidly for 12 minutes before the explosion. The steel pall rings were found to be heavily corroded when they were removed from the tower.

Lessons Learned:

Investigators concluded that a substantial amount of chlorine hydrate was present in the tower packing. The air melted the chlorine hydrate accelerating the corrosion of the carbon steel pall rings resulting in the ignition of the pall rings.

Chlorine corrosion of steel can be vigorous enough to achieve the combustion temperature of the carbon steel.

(2) Welders had just completed welding a short section of two inch carbon steel pipe attached to a long insulated carbon steel chlorine line. The weld that joined the new section of piping was about six inches from the adjacent thermal insulation that covered the long chlorine line.

After completion, an operator/loader pressurized the line with dry air and determined it was leak- free. He then opened the valve connecting the new two inch line to 160 psig chlorine gas.

Within seconds the pipe caught fire and the escaping gases roared like a jet with a brownish-orange plume of ferric chloride. The operator extinguished the fire by closing the valve which stopped the chlorine feed.

The subsequent accident investigation determined that the fire started, not at the weld, but under the adjacent insulated pipe which trapped the heat and had not sufficiently cooled

Lessons learned:

Chlorine/carbon steel fires can occur any time process temperatures exceed safe limits.

Practices such as welding on chlorine lines need to be approached with chlorine fires in mind. Carbon steel must be cool before returning the equipment to chlorine service.

(3) An astonished operations crew witnessed a body of a carbon steel filter used to filter chlorine spontaneously ignite and burn after maintenance personnel installed a replacement filter cartridge. The cartridge was selected from the warehouse inventory that had been originally specified for other chemical services. The cartridges consisted of fiberglass filter media on a tin-coated steel core. Investigators theorized that the tin reacted with the chlorine generating sufficient heat to ignite the carbon steel filter.

Lessons learned:

Only equipment approved for chlorine service should be used in chlorine service.

Chlorine reactions can generate high enough temperatures to start carbon steel burning.

2.5 HYDROGEN AND AIR

2.5.1 Hazard Description

Hydrogen is a co-product of the chlorine manufacturing process and can react explosively with either chlorine or air. The explosive force of chlorine and hydrogen is not as great as that of air (oxygen) and hydrogen. However, chlorine/hydrogen explosions can generate pressures up to fifty times the initial pressure. Chlorine, hydrogen, and air coexist in some processes (e.g., chlorine production processing and liquefaction areas). Care should be taken to prevent these materials from coexisting within the explosive range. Chlorine/hydrogen and air/hydrogen) reactions are dependent on concentration, temperature, and pressure. As the hydrogen concentration increases relative to chlorine or air, the ignition temperature required to produce an explosion will decrease.

2.5.2 Safe Limits of Operation

The concentration/ignition relationship between chlorine, hydrogen, and air is shown by the table entitled "Effect of Initial Temperature on Ignition Limits" in Section 7 of Pamphlet 121 (Reference 4.1.5). Information provided in the table is based on hydrogen content, percent by volume. See Pamphlet 121 for a fuller discussion of this topic.

2.5.3 Example of Incidents

(1) In the diaphragm cell chlorine manufacturing process, chlorine and hydrogen are separated by an asbestos fiber diaphragm. The diaphragm integrity is sensitive to pressure fluctuations. An explosion resulted in the separation of the end of a 60 inch pipeline and propelled it against a building 50 feet away. The pipeline moved two feet and was knocked off of its support beams.

The subsequent investigation concluded that a hole in a diaphragm occurred. The hole allowed chlorine and hydrogen to mix which created an explosive condition. An ignition source, possibly electrical arcing within the cell, created an explosion.

Lessons Learned:

This incident demonstrates the destructive force that a chlorine/hydrogen explosion can generate.

2.6 OIL, GREASES, LUBRICANTS, AND OTHER HYDROCARBONS

2.6.1 Hazard Description

Chlorine is a very strong oxidizing material and can react violently with a number of organic materials. Caution should be exercised before organic materials are used in chlorine service. A study should be completed before using new materials in chlorine systems. New valves and piping should be degreased before placing in service the first time. Pamphlet 6 (Reference 4.1.1) provides further information.

Organic materials present hazards because they react with chlorine. The reactions between chlorine and some hydrocarbons are potentially very violent and explosive. Under certain conditions, detonations can occur. The reactivity is dependent on the concentrations of the chlorine and the hydrocarbon.

The reaction between chlorine and oil/grease or some other hydrocarbons is highly exothermic. The heat liberated can be sufficient to initiate a chlorine/iron fire. Reactions of oils with chlorine can cause the oils to lose their lubricating properties. Other organic materials can cause fires or form other chemicals and polymers that can accumulate in chlorine systems.

2.6.2 Safe Limits of Operation:

Safe limits of operation between chlorine and specific hydrocarbons vary for each hydrocarbon. Procedures should be in place to specify compatibility and safe limits of operation.

2.6.3 Examples of Incidents:

(1) An employee unknowingly applied a generic hydrocarbon grease, instead of fluorolube, to hold a gasket on a chlorine exchanger. The grease was in an unlabeled one gallon bucket that looked identical to the fluorolube bucket. Fortunately, the incident resulted only in a near miss as an experienced employee observed the slight color difference between the grease and fluorolube and corrected the situation before contact between the incompatible lubricant and chlorine occurred.

Lessons Learned:

All chlorine approved materials should be marked for chlorine service and only those materials so marked should be used with chlorine.

(2) While attempting to free up a two inch plug valve in chlorine service, a chemical plant operator located a lubricant gun that was marked "for chlorine service". The operator checked the cartridge and it was properly labeled as the specified chlorine compatible grease. The operator connected the grease gun to the valve fitting and injected a small amount of grease. Before the operator could disconnect the grease gun, the grease and chlorine reacted and destroyed the valve. The subsequent incident investigation determined that, prior to the incident; someone had contaminated the gun with grease that is incompatible with chlorine.

Lessons Learned:

Procedures and training should be in place to prevent contamination of chlorine approved material.

(3) A one-quarter inch stainless steel ball valve in liquid chlorine service ruptured violently. Silicone oil leaked into the chlorine feed line due to corrosion of the stainless steel diaphragm in a flow transmitter causing the subsequent violent reaction with liquid chlorine.

Lessons Learned:

Equipment specifications should be written to exclude materials that will react with chlorine (such as silicone oil) from being used in applications where direct contact with chlorine is possible.

(4) An article published in 1925 describes an accident at a natural gasoline plant in which gasoline backed into a cylinder of liquid chlorine and detonated. In a subsequent demonstration test, 14 pounds of gasoline was introduced into an inverted cylinder containing 100 pounds of liquid chlorine.

The pressure rose slowly for about 40 minutes then a detonation fragmented the cylinder and tore down a 14 inch diameter oak tree standing 20 feet away.

Lesson learned:

Liquid chlorine reacts violently with most hydrocarbons.

(5) A filter in liquid chlorine service violently exploded and propelled steel shrapnel as far away as 50 feet. Liquid chlorine was being fed from a one ton container through a polypropylene cartridge type filter. Prior to the explosion, new polypropylene filter elements recommended by the vendor for chlorine service had been installed. The filter exploded releasing a white cloud of fumes (probably hydrogen chloride) followed by a large amount of chlorine gas. The reaction between chlorine and polypropylene was probably initiated by zinc chloride. Analysis of the filter core indicated a high concentration of zinc oxide present as a filler in the polypropylene.

Lesson Learned:

Chlorinated organics, including partially chlorinated hydrocarbons and most polymers, should not be used for chlorine service despite manufacturer's recommendations. Traces of metal elements could contribute to catalyzing explosive reactions.

2.7 <u>SELECTED SAFE PRACTICES FOR CHLORINE</u>

Figure 2.1 is a brief summary highlighting some of the key concerns one should consider when addressing reactivity and compatibility issues associated with chlorine. The figure is not meant to be a comprehensive listing of such concerns, but is meant to highlight selected issues.

FIGURE 2.1

Selected Safe Practices for Chlorine

- 1. Do Not Allow Nitrogen Trichloride to Accumulate.
 - a. Nitrogen trichloride is very unstable. Maintain low concentrations.
 - b. Minimize the flashing of liquid chlorine containing nitrogen trichloride. Remove chlorine as a liquid or mix with inert solvent before flashing.
- 2. Do Not Allow Systems Containing Hydrogen to Reach Explosive Limits.
 - a. Chlorine/hydrogen mixtures can be explosive.
 - b. Hydrogen concentrations above 4-6% in chlorine systems are explosive.
- 3. Do Not Allow Moisture/Water to Enter Dry Chlorine Systems.
 - a. Water can cause corrosion, pluggage and can result in fires.
 - b. Dew points should be maintained below -40°F (-40°C) before putting in chlorine service.
 - c. Air addition systems in chlorine service should be maintained below -40°F
- 4. Do Not Allow Chlorine to Come into Contact with Organic Oils and Greases.
 - a. Chlorine reacts violently with most organic oils and greases.
 - b. All equipment and packing must be free of organic oils and greases before entering chlorine service.
 - c. Fluorolube is a fluorinated hydrocarbon (organic) lubricant and can be used.
 - d. Oil-free air compressors must be used.
- 5. Avoid High Temperatures in Chlorine Systems.
 - a. Carbon steel will burn in the presence of chlorine at 483°F (250°C).
 - b. The maximum recommended temperature for carbon steel equipment is 300°F (149°C).
- 6 Select Correct Materials of Construction.
 - a. Titanium will burn in dry chlorine service.
 - Carbon steel is not suitable in wet chlorine service.

3. SODIUM HYDROXIDE (50%)

This section provides information on the reactivity of sodium hydroxide with materials more commonly found in facilities producing, using, or otherwise handling sodium hydroxide and on the reactivity of sodium hydroxide with chemicals that may typically be found in such facilities.

Sodium hydroxide is not combustible, has no flash point, no auto-ignition temperature and no explosion limits. Generally sodium hydroxide is regarded as stable, but the chemical reactivity of sodium hydroxide with many inorganic and organic substances makes it an important raw material in a wide variety of industrial applications. Solutions of sodium hydroxide are strongly alkaline and have a high pH.

Improper mixing of water with sodium hydroxide can be hazardous and should be approached with the basic understanding that heat will be generated. Always mix strong sodium hydroxide with the coolest water available and stir the solution. The user must be mindful that strong solutions of sodium hydroxide release large amounts of heat when diluted. The high heat of dilution can result in violent boiling and generate steam explosively causing this corrosive solution to spray and spatter. When mixing sodium hydroxide solutions or sodium hydroxide with water, it is better to slowly add the stronger sodium hydroxide to the weaker (or water). Continuous stirring is strongly advised to help dissipate the heat generated. If there are no provisions for stirring, a layer of concentrated solution may form, accumulate and later suddenly mix with a layer of less concentrated solution resulting in some combination of spray, splatter or boiling.

Sodium hydroxide will react violently with acidic materials such as sulfuric acid and hydrochloric acid. Sodium hydroxide will react vigorously with some metals such as aluminum, tin, and zinc and with organic compounds. Sodium hydroxide destroys material such as hair, leather and wool, and less aggressively attacks matter such as wood, cotton and linen.

3.1 SODIUM HYDROXIDE (50%) REACTIVITY WITH MATERIALS CHART

See Table 3.1.

3.2 SODIUM HYDROXIDE (50%) REACTIVITY WITH OTHER CHEMICALS CHART

See Table 3.2.

Table 3.1: Sodium Hydroxide (50%) Reactivity with Materials

- 1 Integrity of material is maintained
- ② Integrity of material is variable depending on conditions
- 3 Integrity of material is jeopardized

NOTE:

Material	Reactivity	Comments
Acid brick	2	
Aluminum	8	See Section 3.3
Asbestos, compressed	1	
Brass	8	See Section 3.4
Carbon steel, non-alloyed	2	See Section 3.4
Cast iron	2	
Copper	3	See Section 3.4
CPVC (chlorinated PVC)	1	Mechanical integrity concerns with elevated temperature
Ductile iron	2	See Pamphlet 94 (Reference 4.1.2)
E-brite® (ferritic stainless steel)	1	
EPDM (ethylene propylene diene monomer)	1	
Fiberglass		See specific resins
Glass	2	Susceptible to etching
Graphite	1	
Gylon® Style 3504 (blue)	1	
Hastelloy C	2	
Hypalon® (chlorosulfonated polyethylene)	1	
Inconel®	1	
Kynar®	2	
Lead	8	

Table 3.1: Sodium Hydroxide (50%) Reactivity with Materials

1 Integrity of material is maintained

- ② Integrity of material is variable depending on conditions
- 3 Integrity of material is jeopardized

NOTE:

Material	Reactivity	Comments
Molybdenum	2	
Monel® 400	1	
Neoprene	2	
Nickel 200	1	
Polyethylene	1	Mechanical integrity concerns with elevated temperature
Polypropylene	1	Mechanical integrity concerns with elevated temperature
PTFE (polytetrafluoroethylene)	1	
PVC (polyvinyl chloride)	1	Mechanical integrity concerns with elevated temperature
Resin, epoxy	1	
Resin, polyester	1	
Resin, silicon	2	
Resin, vinylester	1	
Rubber, butyl	1	
Rubber, natural	1	
Stainless Steel, 17-4 PH	1	
Stainless Steel, 304	1	
Stainless Steel, 316	1	
Tantalum	2	Tantalum is susceptible to damage by hot sodium hydroxide
Teflon®	1	
Tin	8	
Titanium	1	Mechanical integrity concerns with elevated

Table 3.1: Sodium Hydroxide (50%) Reactivity with Materials

- 1 Integrity of material is maintained
- ② Integrity of material is variable depending on conditions
- 3 Integrity of material is jeopardized

NOTE:

Material	Reactivity	Comments
		temperature
Tygon®	1	
Viton® (Fluorocarbon elastomer)	2	
Zinc	8	Suitable for use in galvanized coating external to process

Table 3.2: Sodium Hydroxide (50%) Reactivity with Other Chemicals

NOTE:

- **1** little or no reaction
- 2 potentially reactive under conditions
- 3 rapid reaction

Chemical	Reactivity	Comments
Acetaldehyde	3	See Section 3.5
Acetic Acid	8	
Acetone	8	
Acetylene	2	
Acrolein	8	
Acrylonitrile	3	See Section 3.5
Alcohols		See Ethanol and Methanol
Aldehydes	3	See Section 3.5
Alkanolamines	1	
Ammonia	1	
Ammonium Acetate	1	
Ammonium Chloride	2	Releases ammonia when in contact with sodium hydroxide
Ammonium Hydroxide	1	
Benzene	1	
Calcium Carbonate	1	
Carbon Disulfide	2	
Carbon Tetrachloride	1	
Chlorine	3	
Chloroform	8	See Section 3.5
Chloroethylene	3	
Chlorophenol	•	See Section 3.5

Table 3.2: Sodium Hydroxide (50%) Reactivity with Other Chemicals

NOTE:

1 little or no reaction2 potentially reactive under conditions

3 rapid reaction

Chemical	Reactivity	Comments
Chlorothene	8	
Copper Sulfate	1	
Dichloroethane	2	
Dichloroethylene	2	
Diesel Fuel	1	
Diethyl Ether	1	
EDC (Ethylene Dichloride)	2	
Ethane	1	
Ethanol	8	Large heat of dilution
Ethylene	2	
Ethylene Dichloride	2	
Ethylene Glycol	2	
Ferric Chloride	8	
Fluorolube	8	
Gasoline	1	
Glycerin	2	
Grease (organic)	1	
Hexachlorobenzene	8	
Hexachlorobutadiene	8	
Hexachloroethane	8	
Hydrocarbons	2	See Section 3.5
Hydrochloric Acid	3	

Table 3.2: Sodium Hydroxide (50%) Reactivity with Other Chemicals

1 little or no reaction

- 2 potentially reactive under conditions
- 3 rapid reaction

NOTE:

Chemical	Reactivity	Comments
Hydrogen	1	
Hydrogen Peroxide	2	
Hydrogen Sulfide	8	
Hydroxylamine	1	
Krytox®	2	
Lithium Bromide	2	
Magnesium Chloride	2	
Magnesium Sulfate	2	
Metals (powders)	3	
Methane	1	
Methanol	3	Large heat of dilution
Mineral Oil	1	Applies to distilled petroleum products
Naphtha	1	
Nitric Acid	3	
Nitromethane	8	See Section 3.5
Nitroparaffins	3	See Section 3.5
Nitrophenol	8	See Section 3.5
Oils (organic)	1	
PCBs (Polychlorinated Biphenyls)	2	
Phosphorous Pentoxide	③	
Potassium Hydroxide	1	
Propylene	2	

Table 3.2: Sodium Hydroxide (50%) Reactivity with Other Chemicals

1 little or no reaction

2 potentially reactive under conditions

3 rapid reaction

NOTE:

Chemical	Reactivity	Comments
Propylene Oxide	8	See Section 3.5
Silicone Oil	1	
Sodium Bisulfite	1	
Sodium Carbonate	1	
Sodium Chlorate	2	
Sodium Chloride	1	
Sodium Chlorite	2	
Sodium Hypochlorite	1	
Sodium Sulfide	1	
Sodium Sulfite	2	
Sodium Thiosulfate	1	
Sulfur Dioxide	3	
Sulfuric Acid	8	
Trichloroethane	8	See Section 3.5
Trichloroethanol	8	See Section 3.5
Trichloroethylene	8	See Section 3.5
VCM (Vinyl Chloride)	8	
Vinyl Acetate	8	
Vinylidene Chloride	8	
Water	•	See Section 3. Large heat of dilution.
Zinc Oxide	1	

3.3 <u>ALUMINUM</u>

3.3.1 Hazard Description

Sodium hydroxide and aluminum readily react and cause catastrophic failure of the metal. The reaction of sodium hydroxide and aluminum produces hydrogen gas as a byproduct. Accumulation of hydrogen can cause a combustible atmosphere.

3.3.2 Safe Limits of Operation

Aluminum should not be used in applications involving sodium hydroxide.

3.3.3 Examples of Incidents

(1) An experiment was conducted to demonstrate the reaction of sodium hydroxide solution with aluminum. A test tube containing coarse aluminum powder was placed in a glass beaker. The beaker was used to provide secondary containment of the material within the test tube. A small amount of 40% sodium hydroxide solution was poured over the aluminum powder in the test tube. Within minutes, the material in the test tube began to foam and overflow into the beaker.

Lessons Learned:

The foaming was caused by the hydrogen produced from the reaction of the two substances. The experiment shows the violent effects of mixing the two materials and why exposure of the two materials to each other should be avoided.

(2) During a major sodium hydroxide plant expansion, industrial refrigeration units were purchased and installed that were equipped with safety relief valves made of aluminum bodies. The safety relief valves protected the refrigerant side. The engineers assigned to the project were inexperienced and failed to consider the materials aspects. Several years later the aluminum safety relief valves were removed for testing and found to be corroded shut. Incidental contact with sodium hydroxide over a period of time was believed to be the cause.

Lessons Learned

Sometimes equipment which is obtained as a packaged unit allows "out-of-spec" components to enter a chemical plant. The correct materials of construction are important for both the chemical containing components and those components that may be exposed to an occasional chemical drip or mist. Air compressor systems, refrigeration units and packaged boiler systems are prime examples of units which, if improperly specified, may allow out-of-spec elements into a chemical plant.

3.4 OTHER METALS

3.4.1 Hazard Description

In addition to aluminum, sodium hydroxide reacts vigorously with some other construction metals such as magnesium, tin and zinc. The reaction with these metals is violent and creates hydrogen. In certain equipment configurations, this hydrogen can accumulate above the reaction to form a flammable or explosive pocket. Sodium hydroxide should not be used with these metals. Other metals that are not satisfactory for long term sodium hydroxide service because of a high corrosion rate include brass, bronze, copper, lead, tantalum, and alloys of these metals.

3.4.2 Safe Limits of Operation

Carbon steel can be safely used with sodium hydroxide below about $120^{\circ}F$ ($49^{\circ}C$). Corrosion rates increase rapidly with increasing temperatures. Sodium hydroxide can be stored as a 50% solution in bare steel tanks, but is usually not recommended above $120^{\circ}F$ ($49^{\circ}C$), due to potential stress corrosion cracking. Pamphlet 94 (Reference 4.1.2) provides more information on this topic.

Nickel and nickel alloys have outstanding resistance to sodium hydroxide solutions over a wide range of concentrations and temperatures. Many stainless steels (e.g., 304, 316) and Monel are also commonly used in sodium hydroxide services.

3.5 HYDROCARBONS

3.5.1 Hazard Description

Sodium hydroxide will react vigorously with many organic chemicals and caution is required. Sodium hydroxide in prolonged contact with trichloroethylene or tetrachloroethanes can produce toxic, explosive products. Many organic compounds such as propylene oxide, acetaldehyde, and acrylonitrile can react violently on contact with sodium hydroxide. Reactions with nitromethane and nitrophenols produce shock-sensitive explosive salts.

3.5.2 Safe Limits of Operation

Before using sodium hydroxide with any hydrocarbons, the user should become knowledgeable about the possible reactions between the substances. The user should insure that any possible reactions between the substances are appropriately controlled, and possible consequences of such reactions are fully considered in the design of the system.

3.5.3 Examples of Incidents

- (1) A large quantity of chlorophenol left in contact with concentrated sodium hydroxide solution for 3 days decomposed, producing heat and liberating fumes which ignited explosively.
- (2) Rags soaked in sodium hydroxide and in aldehyde overheated and ignited when they came into contact in a waste bin.

- (3) Accidental contact of 50% sodium hydroxide solution with residual trichloroethanol in a pump caused an explosion.
- (4) A chloroform-methanol mixture was put into a drum contaminated with sodium hydroxide. The substances reacted vigorously, and the drum exploded. The presence of methanol (or other solubilizer) increases the rate of reaction between chloroform and sodium hydroxide

Lessons Learned (for all four examples):

Sodium hydroxide reacts vigorously with many hydrocarbons.

(5) A tank of an organic solvent product was found to be high in acidity and was out of specification due to color. The solvent contained an inhibiting stabilizer (nitromethane). It was the practice to neutralize slight acidity in such solvents in a pressure vessel (called a neutralizer) that was filled with solid sodium hydroxide flakes or beads. Such treatment was a common method to upgrade off-spec inventories of solvent intermediates and products. However, this particular product was solvent treated with about two percent of nitromethane stabilizer and was not like other intermediates or products previously processed.

Subsequently, an explosion occurred creating a hole about 7 feet in diameter and 3 feet deep in the soil. The explosive forces were generated within a vessel that was 15 inches in diameter and 6 feet high. The explosive force ripped apart the bolts on the vessel and propelled a two feet diameter thick steel plate over 450 feet away.

The accident investigators concluded that when the nitromethane contacted the caustic soda, a highly unstable sodium fulminate was probably created resulting in the explosion.

Lessons Learned:

This accident serves as a good example of the need to study any modifications involving reactive chemicals. Sometimes reactions between chemicals are taken for granted.

3.6 SELECTED SAFE PRACTICES FOR SODIUM HYDROXIDE (50%)

Figure 3.1 is a brief summary highlighting some of the key concerns one should consider when addressing reactivity and compatibility issues associated with 50 % sodium hydroxide. The figure is not meant to be a comprehensive listing of such concerns, but is meant to highlight selected issues.

FIGURE 3.1

Selected Safe Practices for Sodium Hydroxide (50%)

- 1. Sodium Hydroxide Reacts Violently/Explosively with Acids.
- 2. Always Add Sodium Hydroxide to Water.
 - a. Diluting sodium hydroxide with water is highly exothermic and proper precautions must be taken to minimize the effects.
 - b. Cooling systems should be considered when sodium hydroxide and water are mixed.
- 3. Sodium Hydroxide Reacts with Aluminum, Tin, Copper, Zinc.
 - a. Use of these materials should be avoided.
 - b. Reaction between sodium hydroxide and any of these materials will produce hydrogen gas which is highly flammable.
- 4. Sodium Hydroxide Corrodes Carbon Steel at Temperatures in Excess of 120 °F.
 - a. Sodium hydroxide causes excessive corrosion of carbon steel at temperatures above 120 °F.
 - b. Do not store sodium hydroxide in carbon steel vessels above 120 °F.
- 5. Sodium Hydroxide Reacts with Many Organic Chemicals.
- 6. Welding on Piping/Equipment Can Cause Embrittlement, Stress Cracking, and the Evolution of Flammable Hydrogen Gas.
 - a. Clean piping and equipment before welding.
 - b. Metal surfaces must be cleaned/acidized prior to welding, cutting, or performing other forms of heat treatment.

4. REFERENCES

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