DATA ON GENERAL CLASSES OF CHEMICALS

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ACETATES

Most organic acetates are ignitable and soluble or slightly soluble in water.

ACIDS

Inorganic acids are largely noncombustible. The most common are nitric, sulfuric, and hydrochloric. The most hazardous are concentrated acids. These can act as strong oxidizers and start fires or intensify combustion. Acids may also react with metals, generating hydrogen which can accumulate in unvented spaces, creating a fire and explosion hazard.

Organic acids are usually ignitable when undiluted by water. Large organic acid molecules resemble hydrocarbons, and are not very water soluble. They are sometimes referred to as ‘‘fatty acids’’. Small molecule organic acids are water soluble and ignitable, such as acetic acid. Organic acids high in oxygen or nitrogen may be unstable or explosive. Examples are peracetic acid and picric acid.

ALCOHOLS

Alcohols are usually volatile ignitable liquids. Those with few carbon atoms are readily soluble in water. Alcohols should not be mixed with strong oxidizing materials such as hydrogen peroxide. They may form powerful explosives.

See recommended practices for distilled spirits storage in NFPA 491M (Manual of Hazardous Chemical Reactions).

ALDEHYDES

Aldehydes are usually volatile ignitable liquids, soluble in water. When oxidized, aldehydes become acids; when reduced, alcohols.

ALKALIS (CAUSTICS)

Sodium hydroxide (caustic soda) and potassium hydroxide (caustic potash) are the most common caustics. They are noncombustible, but react with water to generate heat. They can react violently with many organic chemicals. See NFPA 491M.

AMINES

Amines are compounds derived from ammonia by substituting various organic radicals for the hydrogens. They are ignitable and more water soluble than comparable alcohols.

ANHYDRIDES

Acid anhydrides are organic acids from which water has been removed. They will react with water to regenerate the acid. They normally have a lower flash point than the corresponding organic acid.

Anhydrides often act as dehydrating agents. If mixed with an acid, they pick up water and effectively increase the concentration of the acid. For example, mixing acetic anhydride with perchloric acid in an electropolishing solution can produce highly unstable and explosive anhydrous perchloric acid. See NFPA 491M.

ARSENATES AND ARSENITES

These are salts of arsenic acid and arsenous acid, respectively. The inorganic salts are low in fire or explosion hazard, but are highly toxic.

AZIDES

Azides are salts of hydrazoic acid, HN_3. Both organic and inorganic azides are highly unstable and explosive materials. Most are so sensitive that they have little commercial use, except lead azide and mercury azide, which are used as components of detonators and percussion caps. As explosive materials they should be handled and stored in accordance with Data Sheet 7-28, *Energetic Materials*

Sodium Azide

Sodium azide (NaN_3) mixed with other components is used as the nitrogen gas generator for automobile air bags. In this configuration, it is classed as a flammable solid by the U.S. Department of Transportation. As an air bag assembly, it does not present the hazards associated with the azide. The assembly has not been found to be sensitive to shock or static sparks, but gas generant mix could decompose and cause the air bag to deploy if exposed to temperatures above 300°F (149°C). The chemical is completely sealed in a waterproof metal container that eliminates its susceptibility to water exposure.

Fire protection should be based on combustibility of the packaging and the assembly components, rather than the azide hazard.

BENZOATES

Benzoates are salts of benzoic acid. They are relatively low in hazard.

BORATES

Borates are salts of boric acid, such as sodium borate (Na_3BO_3), and are generally nonhazardous.

BROMATES

Bromates are salts of bromic acid, such as sodium bromate ($NaBrO_3$). They are oxidizing agents. See NFPA 491 M, *Manual of Hazardous Chemical Reactions.*

BROMIDES

Inorganic bromides are noncombustible salts. Organic bromides may be ignitable or water reactive. They are usually somewhat harder to ignite but more toxic than the corresponding chloride.

CARBIDES

Carbides are compounds of carbon and a metal. Most react with water to produce a flammable gas. The carbides of lithium, potassium, calcium, strontium, and barium produce acetylene. Aluminum and boron carbides produce methane. The carbides of magnesium, manganese, and chromium produce hydrogen and methane. Silicone carbide, also known as carborundum, is stable and non-hazardous. See calcium carbide in Data Sheets 7-51, *Acetylene*.

CARBONATES AND BICARBONATES

Carbonates are the salts of carbonic acid, containing the Co_3 group. Bicarbonates contain the HCO_3 group. Carbonates and bicarbonates of metals are generally nonhazardous.

CHLORATES

Chlorates are the salts of chloric acid and contain the ClO_3 group. They are generally strong oxidizing agents. See NFPA 491 M, *Manual of Hazardous Chemical Reactions.*

CHLORIDES

Most chlorides of metals, such as sodium chloride, are non-hazardous. Organic chlorides, compounds containing one chlorine atom, are usually ignitable.

CHLORINATED HYDROCARBONS

The replacement of hydrogen atoms in hydrocarbons by chlorine atoms tends to make the compound less volatile, harder to ignite, but more toxic. Highly chlorinated hydrocarbons such as chloroform and carbon tetrachloride may not be able to support combustion. Compounds such as methylene chloride, trichlorethylene, and perchlorethylene are very weakly ignitable, but may be subject to decomposition by fire or aluminum fines to produce corrosive acid vapors. See Factory Mutual recommended practices for metal cleaning in Data Sheet 7-97, *Metal Cleaning.*

CHLORITES

Chlorites are salts of chlorous acid, containing the ClO_2 group. They are strong oxidizers. See NFPA 491 M, *Manual of Hazardous Chemical Reactions.*

CHROMATES

Chromates are salts of chromic acid, containing the CrO_4 group. Although chromic acid is a strong oxidizer, the chromates generally are much weaker.

CITRATES

Citrates are salts of citric acid, containing the $C_6H_5O_7$ group. They are generally low in hazard.

CYANIDES

Cyanides are salts of hydrocyanic acid, containing the CN group. While hydrocyanic acid is a flammable gas, the cyanide salts of metals are noncombustible, though highly poisonous. Cyanides can react with acids producing the ignitable hydrocyanic acid.

ESTERS

Esters are organic salts formed from an alcohol and an organic acid. Examples are ethyl acetate, methyl benzoate, amyl acetate, and methyl formate. Most are typical ignitable liquids.

ETHERS

Ethers are organic compounds derived from alcohols by replacement of the hydrogen in the OH group by another radical. The structure is two hydrocarbon radicals joined by an oxygen atom. For example, methyl ethyl ether is $CH_3OC_2H_5$ and diethyl ether is $C_2H_5OC_2H_5$. Ethers are generally more volatile and ignitable than corresponding alcohols and have a wider explosive range. In ethers, highly unstable and sensitive peroxides tend to form on long standing, particularly in the presence of oxygen or light and the absence of inhibiters.

FLUORIDES

Fluorides are salts of hydrofluoric acid (HF). Metal fluorides solutions do not support combustion and very stable.

FLUOROCARBONS

Fluorocarbons are hydrocarbons where all or part of the hydrogen atoms are replaced by fluorine. There may also be other halogen atoms present (halons). Highly substituted fluorocarbons solutions do not support combustion and highly stable. They may be used as refrigerants or fire extinguishing agents.

FORMATES

Formates are the salts or esters of formic acid. The metal salts, such as sodium formate, are generally nonhazardous. The organic esters, such as ethyl formate, are ignitable.

FULMINATES

Fulminates are salts of fulminic acid, HNCO. They are highly explosive and are not practically used because they are too sensitive, except for mercury fulminate, which is used in making explosive detonators or initiators. So-called fulminates of gold, silver, or platinum are made accidentally by precipitating solutions of these metals with ammonia. The product formed is probably the nitride, which is equally explosive. Silver nitride has been prepared accidentally and exploded in attempts to dissolve silver oxide from mirror finishing processes with ammonia. See NFPA 491 M.

HALOGENS

The halogens are noncombustible but are highly reactive and can support combustion. They are, in decreasing order of reactivity, fluorine, chlorine, bromine, and iodine. See fluorine, chlorine and bromine in NFPA 491M. For hazardous reactions of iodine, see NFPA 491M.

HYDRIDES

Most hydrides are compounds of hydrogen and a metal. They are strong reducing agents and most give off hydrogen when heated and when they react exothermically with water. In general, the fire hazards of metal hydrides are similar to those of sodium, and similar safeguards should be applied.

Alkali-Metal Hydrides

Lithium hydride (LiH), sodium hydride (NaH), potassium hydride (KH), rubidium hydride (RbH), and cesium hydride (CsH) react vigorously with moisture, acids and oxidizing materials, usually igniting immediately and sometimes exploding. They react with carbon dioxide and sulfur dioxide.

Alkaline-Earth Metal Hydrides

Beryllium hydride (BeH_2), magnesium hydride (MgH_2), calcium hydride (CaH_2), strontium hydride (SrH_2), and barium hydride (BaH_2) react vigorously with moisture but normally do not ignite.

Aluminum Hydrides

Aluminum hydrides include aluminum (AlH_3), lithium aluminum ($LiAlH_4$), magnesium aluminum ($Mg(AlH_4)_2$), and sodium aluminum hydrides ($NaAlH_4$). Aluminum hydride is explosive in contact with aluminum chloride or residual ethers. Magnesium aluminum hydride reacts vigorously with water or acetone. Sodium aluminum hydride reacts strongly with ammonia; on contact with water, it ignites and may explode.

Heavy-Metal Hydrides

Cadmium hydride is unstable and decomposes at 32°F(0°C). Copper hydride ignites in chlorine, is unstable, and decomposes suddenly at 140°F (60°C). Columbium hydride burns readily in air. Thorium dihydride (ThH_2) ignites in air at 500°F (260°C), and thorium tetrahydride (ThH_4)is pyrophoric. Titanium hydride ignites in air at 834°F (445°C) and is only moderately reactive with water. Uranium hydride is pyrophoric in air and will burn in carbon dioxide or nitrogen above 435°F (225°C). Zinc hydride reacts slowly with water and decomposes slightly in air at ordinary temperatures. Zirconium hydride ignites in air at 806°F (430°C), and with oxidizers at a higher temperature.

Boron Hydrides

Boron hydrides are extremely reactive and have severe fire and explosion hazards. Three of the boron hydrides have wide industrial use: diborane (B_2H_6), pentaborane-9 (B_5H_9), and decaborane ($B_{10}H_{14}$).

Safeguards for Boron Hydrides.

1. Halogenated extinguishing agents should not be used on boron hydride fires, as they will react with most hydrides. Water should be applied to cool the surroundings until the fuel source is removed.

2. Processes using boron hydrides should be isolated from other plant facilities and protected by automatic sprinkler or water spray systems. Buildings housing such facilities should be of damage limiting construction.

3. Process systems should be closed with no oxygen present. Nitrogen gas may be used for inerting or transfer. Vacuum systems should be avoided to prevent air inspiration.

4. Piping systems, including gaskets, should be suitable for ignitable liquid service and compatible with the chemicals used. Welded and flanged piping is preferable to screwed fittings.

HYDROCARBONS

Hydrocarbons include all compounds of carbon and hydrogen. All are ignitable to varying degrees, depending upon volatility.

Hydrocarbons may be saturated, as in the paraffin or methane series, or unsaturated with double or triple bonds between carbon atoms, such as ethylene, acetylene, and butadiene. Normally, unsaturated hydrocarbons are the most reactive or unstable. Hydrocarbons may also be aromatic, or ring compounds, such as benzene, toluene, or xylene.

HYDROSULFIDES

Hydrosulfides contain the SH group. They correspond to hydroxides or alcohols where the oxygen in the OH group is replaced by sulfur. They include the sulfhydryls, thioalcohols, thiols, and sulfur alcohols or mercaptans. The mercaptans are used for odorizing natural gas because of their strong odor. Calcium, potassium and sodium hydrosulfides are nonignitable. Organic hydrosulfides, such as mercaptans, are ignitable liquids.

HYDROSULFITES

Hydrosulfites are salts containing the S_2O_4 group. They may be ignitable.

HYDROXIDES

Hydroxides are inorganic compounds containing the OH group. The most reactive of these compounds are sodium and potassium hydroxides. (See alkalis [caustics].) Ammonium hydroxide is ammonia gas in water solution.

HYPOCHLORITES

Hypochlorites are compounds containing the group ClO. As a liquid do not support combustion but are strong oxidizing agents. See calcium hypochlorite in NFPA 491 M, *Manual of Hazardous Chemical Reactions.*

HYPOPHOSPHITES

Hypophosphites are salts of hypophosphorous acid, containing the PO_2 group. They are moderately combustible, giving off phosphine, a flammable gas, when heated. They may react violently with strong oxidizing agents. See NFPA 491M.

HYPOSULFITES (THIOSULFITES)

Hyposulfites, also known as thiosulfites, contain the S_2O_3 group. Sodium hyposulfite is used in photographic processing. Hyposulfites are relatively nonhazardous.

IODATES

Iodates are salts of iodic acid, containing the IO_3 group. The iodates are oxidizing agents. They should be classified the same as corresponding bromates.

IODIDES

Iodides are salts of hydriodic acid, or hydrocarbons with one hydrogen atom replaced with an iodine atom. See bromides and chlorides.

LACTATES

Lactates are salts or esters of lactic acid ($CH_3CHOHCOOH$). They may be combustible but are relatively nonhazardous.

NITRATES

Nitrates are salts of nitric acid. The nitrates of metals are strong oxidizing agents. Ammonium nitrate can be explosive. See Data Sheet 7-89, *Ammonium Nitrate and Mixed Fertilizers Containing Ammonium Nitrate.* Organic nitrates such as ethyl and methyl nitrate can be subject to decomposition and are used as rocket propellants.

NITRIDES

Nitrides are compounds of nitrogen and a metal. Most nitrides are noncombustible. Some are decomposed by water, yielding ammonia. Nitrides of noble metals such as silver and gold can be sensitive explosives.

NITRITES

Nitrites are salts of nitrous acid. Although they are less active than nitrates, they are also oxidizing materials and should be treated similarly.

NITRO COMPOUNDS

Nitro compounds are organic compounds with one or more NO_2 groups substituted for hydrogen atoms. Their explosion hazard is proportional to the degree to which they have been nitrated. For example, trinitrotoluene (TNT) is more hazardous than dinitrotoluene. Other examples of potentially explosive nitro compounds are cellulose nitrate, nitromethane, and nitroglycerine. Organic nitrates and nitrites may be considered nitro compounds. See the particular chemical involved in Data Sheet 7-28.

OLEATES

Oleates are salts of oleic acid. They may be combustible but are relatively nonhazardous.

ORGANOMETALLIC COMPOUNDS

Organometallic compounds are organic compounds in which metal atoms have replaced one or more hydrogen atoms, excluding the metallic salts of common organic acids. Examples of organometallic compounds are Gringard reagents; metallic alkyls such as butyllithium, tetraethyl lead or triethyl aluminum, tetrabutyl titanate, sodium methylate and nickel carbonyl. The hazards vary, but most of the materials are ignitable liquids or solids. Most are very reactive and some will react with air or moisture at room temperature. See alkylaluminums, butyllithium, diethylaluminum chloride, diethylzinc, nickel carbonyl, and motor fuel antiknock compounds in NFPA 491M.

OXALATES

Oxalates are salts of oxalic acid. Most are nonhazardous, except silver oxalate, which is explosive.

OXIDES

Acid oxides are compounds of non-metals and oxygen, such as sulfur dioxide (SO_2), carbon dioxide (CO_2), and phosphorus pentoxide (P_2O_2). They react with water to form acids. Basic oxides are compounds of metals and oxygen, such as sodium oxide (Na_2O), calcium oxide (CaO), and aluminum oxide Al_2O_3. They may react with water to form hydroxides or bases. Sodium and calcium oxides can react quite violently with water, releasing sufficient heat to ignite combustible material. Organic oxides such as ethylene oxide are only partially oxidized and can be ignitable and reactive.

PALMITATES

A palmitate is a salt of palmitic acid, a vegetable fatty acid. Palmitates may be combustible, but are relatively nonhazardous.

PERBORATES

Perborates are salts of perboric acid, containing the BO_3 or B_4O_8 groups. They are strong oxidizing agents.

PERCHLORATES

Perchlorates are salts of perchloric acid, containing the ClO_4 group. They are strong oxidizing agents.

PERMANGANATES

Permanganates are salts of permanganic acid, containing the MnO_4 group. They are strong oxidizing agents.

PEROXIDES

Inorganic peroxides include hydrogen peroxide and metal peroxides. They are strong oxidizing agents and may be subject to exothermic decomposition. See Data Sheet 7-80, *Organic Peroxides and Oxidizing Materials.* Organic peroxides have the peroxy (—O—O—) group in their chemical structure, making them

highly reactive and unstable. In addition to peroxides they may be known by such names as hydroperoxide, peracetate, perbenzoate, percarbonate, etc. See Data Sheet 7-80, *Organic Peroxides and Oxidizing Materials.*

PERSULFATES

Persulfates are salts of persulfuric acid, containing the S_2O_8 group. They are strong oxidizing agents.

PHOSPHATES

Phosphates are salts of phosphoric acid, containing the PO_4 group. Phosphates of metals are noncombustible and nonhazardous. Organic phosphates such as tributyl or tricresyl phosphate may be combustible but are relatively low in hazard.

PHOSPHIDES

Phosphides are compounds of phosphorus with a metal. Phosphides react with moisture to produce phosphine, a highly toxic and spontaneously flammable gas.

PHOSPHORUS COMPOUNDS

In addition to phosphates and phosphides, phosphorus forms compounds with halogens, oxygen, and sulfur. Many of these compounds react with moisture to give off corrosive or toxic gases.

PHTHALATES

Phthalates are salts of phthalic acid, $C_6H_4(COOH)_2$. They may be combustible, but most are low in hazard.

SALICYLATES

Salicylates are salts or esters of salicylic acid, HOC_6H_4COOH. The metal salicylates may be combustible but are relatively low in hazard. The organic esters, such as methyl salicylate, may be ignitable liquids.

STEARATES

Stearates are salts or esters of stearic acid, $C_{17}H_{35}COOH$. Some stearates (lead or zinc) are combustible. Others are high flash point ignitable liquids. Calcium, potassium and sodium stearates are noncombustible.

SULFATES

Sulfates are salts of sulfuric acid. Inorganic sulfates are noncombustible. Organic sulfates are normally ignitable.

SULFIDES

Sulfides are salts of hydrogen sulfide. Inorganic sulfides are moderately combustible. Organic sulfides are toxic ignitable liquids.

TARTARATES

Tartarates are salts of tartaric acid, $HOOC(CHOH)_2COOH$. Tartarates are low in hazard, except mercury and silver tartarates, which are unstable and explosive. References

REFERENCES

FM

Data Sheet 7-28, *Energetic Materials*
Data Sheet 7-51, *Acetylene*
Data Sheet 7-97, *Metal Cleaning*
Data Sheet 7-89, *Ammonium Nitrate and Mixed Fertilizers Containing Ammonium Nitrate*
Data Sheet 7-80, *Organic Peroxides and Oxidizing Materials*

Other

NFPA 491M, *Manual of Hazardous Chemical Reactions*

GLOSSARY OF TERMS

Ignitable Liquid: Any liquid or liquid mixture that is capable of fueling a fire, including flammable liquids, combustible liquids, inflammable liquids, or any other reference to a liquid that will burn. An ignitable liquid must have a fire point.

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