IX. Know Your Chemicals

To safely purchase, handle, store and use chemicals, a science teacher must know what the hazards are associated with the chemicals. Ward's Science cannot put too much emphasis on the importance of "knowing your chemicals". This manual provides the science teacher with the necessary information to gain the proper knowledge for safe use of chemicals. This knowledge should be obtained even before the chemicals are received and put to use. This section should be used in conjunction with information presented on the applicable chemical Safety Data Sheets (SDS's) in defining hazardous chemical properties. Chemical hazardous properties must be understood before many of the safety measures found within this handbook can be initiated. Detailed information on reading and understanding an SDS can be found in *Section IV - Where To Find Information on the Chemicals You Just Purchased.*

Ward's Science has included the following information, taken from the *"Chemical Safety for Teachers and Their Supervisors", American Chemical Society, 2001*, regarding chemical hazards.

Chemical Hazards

"The hazards presented by any chemical depend upon the properties of that chemical. Each chemical is different from all others because it has properties that are different. So, it follows that each chemical presents different hazards. But to use a chemical properly, first we must know the hazards of that chemical; second, we must know and apply the appropriate precautionary measures that will reduce the probability of harm from those hazards; and third, we must know and be prepared to carry out the necessary emergency measures (should our precautions fail) that will minimize the harm, just in case. It would seem that these requirements are formidable. How can I know that much about each of the many chemicals my students and I will use in the lab—to say nothing of teaching all this to the students? Fortunately, there is a practical answer: classification. Chemicals present only four classes of chemical hazards:

Flammability
Corrosivity
Toxicity
Reactivity

The following sections describe each of these hazards separately. Keep in mind that any single chemical may simultaneously present more than one hazard. A few chemicals also possess physical hazards, which are discussed later."

Flammability

The first chemical hazard to be discussed is flammability. Although one chemical may indeed be more flammable, say, than another[5], the precautions and emergency treatment depend principally upon flammability itself, not the degree of flammability.

A flammable chemical (obviously) will burn. Other terms that convey the same hazard potential information include "extremely flammable" and "combustible". Keep in mind that the vapors of flammables, if ignited when

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[5] The degree of flammability of liquids or solids is numerically expressed by "flash point" (also, and more accurately, called "lower flash point"). The smaller the flash point number (expressed in degrees Fahrenheit or Celsius) the greater the degree of flammability. For example, the flash point of unleaded 87 octane gasoline is –40 ºF, compared with the less flammable kerosene, which has a flash point of +63 ºF.

mixed with air in suitable proportions (ranging from 1% to more than 50% [by volume] in some cases) can explode. Flammable solids sublime; hence, their vapors are just as hazardous as the vapors from a flammable liquid. For example, glacial acetic acid (solid or liquid, depending on the temperature) is a flammable chemical as defined here. Keep in mind also that the vapors of most flammables are denser than air and can travel 10, 20, or 30 feet, or even further. The traveling vapors mix with air as they move. Consequently, a source of ignition can be several tens of feet away from the flammable liquid and still cause a fire or explosion by igniting the vapor trail that has traveled from the flammable liquid to the ignition source.

Precautionary measures include the enforced absence of ignition sources, such as lighted burners, hot plates, other hot surfaces (a lighted incandescent light bulb), and sources of sparks (electrical sparks, static charge sparks, and friction sparks). Keep containers closed when not actually in use. Ensure that the air movement in the laboratory is sufficient to keep the concentration of the flammable vapor in the air well below 1%. Minimize the quantities available—usually 100 mL is more than ample for lab use. If more is necessary, provide it in separate containers, 100 mL maximum in each container. Store flammables in an approved flammable liquid storage cabinet, preferably in safety cans. Use fabric, not plastic, tape to tape glass vessels (test tubes, flasks, beakers) beforehand if they are to contain flammable gases or vapors. Otherwise, when handled by students or used by teachers in demonstrations of an exploding gas or vapor, there can be flying glass shards from the ignition of the air–gas mixture. Even with the necessary taping, conduct such demonstrations only behind a sturdy shield that will confine flying fragments.

Corrosivity

A corrosive chemical either destroys living tissue or causes permanent change in such tissue through chemical action. (A chemical that corrodes iron, for example, wet salt [sodium chloride], is not corrosive under this definition—which pertains to chemical safety. Sulfuric acid will corrode iron but is also a corrosive in this safety context.) Corrosives can destroy both skin and tissues underneath the skin; corrosives destroy eyes, the respiratory system, and any other living tissue. Corrosive effects include impaired sight or permanent blindness, severe disfigurement, permanent severe breathing difficulties, even death.

Promptly flush splashes of corrosives off the skin with copious flowing water for at least 15 minutes. If splashed on clothing, the clothing must be removed while under a safety shower. Do not remove the clothing and then get under the shower. While under the shower, remove all clothing, including shoes, socks, wristwatch and strap, and other jewelry if they are splashed with corrosives (this is no time for modesty). Stay under the shower for at least 15 minutes while someone else calls a doctor. (It helps if the water is tepid, not cold.) Make certain in advance that the safety shower is working and that students know how to use it.

A splash of a corrosive chemical in the eye is a very serious matter. Get the victim to an eyewash fountain within 10 seconds. The eyewash fountain must be capable of delivering a gentle but copious flow of fresh water (preferably tepid) for at least 15 minutes to both eyes. (Most portable eyewash devices cannot meet this requirement.) Ensure in advance that safety showers and eyewash fountains are working and that students know how to use them.

While the victim is flushing the eyes for at least 15 minutes, someone else should call the doctor for further instructions. (The doctor’s phone number should already be posted by the telephone.) The victim should hold both eyelids open with thumb and forefinger and roll the eyeballs up, down, left and right, continuously, so as to work the flushing water around to the back of the eyeball and wash any chemical away from the optic nerve. If the chemical destroys a portion of the optic nerve, permanent blindness ensues. If instead the chemical destroys a portion of the front of the eye, the prognosis may be less dire.

In all cases of contact with corrosives, take the victim to a physician for further evaluation and treatment.

Irritants are chemicals similar to corrosives except that they do not destroy tissue by chemical action. Irritants cause inflammation, itching, and so on. The effects are usually reversible but may or may not be severe or long lasting; victims should be referred to a physician.

Finally, some chemicals are sensitizers. The first exposure does not usually cause any notable symptoms. The second, or perhaps the third or fourth or more, exposure does cause symptoms because the victim has been sensitized by prior exposure(s). Poison ivy is an example of this kind of effect; some victims can be exposed several dozens of times before that next, and then often quite serious, exposure incident.

From the above discussion, it would seem that the use of corrosive chemicals in grades 7–12 should be severely limited or perhaps not used at all. Corrosive chemicals are potentially seriously harmful. There is no need for their use in pre-high school laboratory work. At that level, purchase and use diluted solutions of the strong acids and bases. Other corrosives such as elemental bromine are not needed at all.

On the other hand, high school students can use corrosives if the precautions described above are followed. After all, as adults in training, older students can profit from supervised instruction in matters that would be inappropriate for less mature students.

Toxicity

Broadly speaking, there are two different toxic effects, chronic and acute. A chronic toxic effect is noted only after repeated exposures or after a single, long exposure. Commonly known chronic toxic effects include cancer and reproductive malfunctions. Acute toxic effects occur promptly upon exposure, or within a short time—a few hours at most. Ingestion of methyl and ethyl alcohol are examples. Both exhibit the same acute toxic effect: inebriation. Ethyl alcohol exhibits a chronic effect: cirrhosis of the liver.

Methyl alcohol exhibits two additional acute toxic effects: blindness and death. To understand this, consider the “dose–response” phenomenon, a characteristic of all toxins, both acute and chronic: the greater the dose, the more severe the response to the toxin. Thus, *a very small* amount of methyl alcohol inebriates, a bit more causes blindness, yet a bit more is fatal. All toxic substances share this characteristic; exposure to a larger amount of the toxin is worse than exposure to a smaller amount; an exposure of longer duration has a greater toxic effect than exposure of a shorter duration.

One precautionary measure for toxins is now obvious: Minimize the exposure. Use the smallest amount of a toxin that is suitable for the purposes of an experiment. Minimize the time an experimenter will work with a toxin. Work with toxins only in a fume hood that is known to be operating properly.

In addition to minimizing the exposure by using the least amount necessary for the shortest possible period of time, precautionary measures for toxins include **barriers**, **cleanliness**, and **avoidance**. Thus, one avoidance precaution is, simply, good ventilation throughout the laboratory as well as the use of fume hoods. Wearing impervious gloves is an example of a barrier precaution.

Cleanliness includes good housekeeping practices, such as minimizing dust from solid toxins, mist from liquid toxins, prompt spill cleanup, and probably most important of all, **thorough washing** of hands and arms and scrubbing under fingernails as a habitual practice before leaving the laboratory.

Further precautions involve your awareness of the most likely symptoms of toxic overexposure: headache, nausea, and dizziness. Whenever you experience any of these three while you or someone else nearby is working with a toxic chemical, get to fresh air immediately and do not return until the symptom has disappeared. If on your return the symptom recurs, leave immediately and call a physician; it is likely that you have been overexposed.

However, the absence of these or other symptoms does not necessarily indicate no exposure. In advance, read the SDS's for the chemicals you and your students will be handling. Consult with a local physician in advance, advising him or her of the toxic chemicals used in the lab, and ensure that the physician will be prepared in advance to treat victims of toxic exposures.

For each toxic chemical, after reading the SDS:

1. Evaluate the toxic risk posed to your students in their use, with precautions, of the chemical;
2. Evaluate the educational benefit to be gained if the chemical is used, with precautions, by your students; and
3. Based on the balance between risks and benefit, decide whether or not to use the chemical.

If you decide to use a particular chemical, be sure that you know:

- whether or not, in case of ingestion, vomiting should or should not be induced,
- the symptoms of exposure to that chemical, and
- if applicable, the recommended procedure in case of unconsciousness.

Reactivity

Container labels do not always describe the fact that a chemical is self-reactive, for example, that it will spontaneously explode, or that if mechanically disturbed it could explode. Nor do labels always state that a chemical, if mixed with certain other chemicals, will react rapidly and release a large amount of energy. For reactivity information, refer to the SDS for a chemical; if applicable, that information should be described in the SDS.

Precautionary measures for self-reactive chemicals include, of course, not providing students with any such chemicals. These include picric acid, wet or dry (when dry—as it may become in students' use—picric acid can detonate when mechanically disturbed). Peroxide formers are similarly hazardous. They include metallic potassium, diethyl ether, and other ethers such as dioxane and tetrahy-drofuran; their peroxides are explosively unstable when mechanically disturbed.

The other reactive hazard is reactive incompatibility. Even dilute acid is reactively incompatible with dilute base. Other combinations include oxidizing agents and reducing agents—chlorates and powdered metal, to cite one example. There are other kinds of incompatible pairs. For this, the SDS is the usual information source.

Precautionary measures include providing reactively incompatible pairs to students only when that provision is deliberately determined by the teacher—and even then providing very small quantities, and only under direct supervision.

Physical Hazards

We come now to our last hazard category, physical hazards. Some physical hazards are associated with chemicals, some with objects, and some with people. A physical hazard that once was quite common among teachers of chemistry was their tendency to accept donations of chemicals from well-meaning donors. An example of a physical hazard that is associated with some chemicals is slipperiness. Concentrated sulfuric acid is very slippery. It is reported to be impossible to remain standing in the middle of a spill of this acid.

Radiation from radioactive species is a physical hazard. Dry ice can cause freeze burns and is another example of a chemical with a physical hazard. Various nonchemical physical hazards include loose clothing (sleeves, blouses, neck ties), loose long hair, bulky jewelry, horseplay, hot surfaces, and unattended but still-lit Bunsen burners. For all of these, the precautionary measures are obvious.

Incompatible Chemicals

Various chemicals will react dangerously when mixed with certain other materials. Some of the chemicals regularly used by science teachers, along with the chemicals that they are incompatible with, are listed below. This list should not be considered all-inclusive. The absence of a chemical from this list should not be taken to indicate that it is safe to mix with any other chemical! Understand and double-check your data before starting your demonstrations.

Chemical	Incompatible with
Acetic acid	Chromic acid, nitric acid, hydroxyl compounds, ethylene glycol, perchloric acid, peroxides, permanganates
Acetic anhydride	Hydroxyl-containing compounds such as ethylene glycol, perchloric acid
Acetone	Concentrated nitric and sulfuric acid mixtures, hydrogen peroxide
Acetylene	Chlorine, bromine, copper, fluorine, silver, mercury
Alkali and alkaline earth metals, such as sodium, potassium, lithium, magnesium, calcium, powdered aluminum	Carbon dioxide, carbon tetrachloride, other chlorinated hydrocarbons (also prohibit the use of water, foam, and dry chemical extinguishers on fires)
Ammonia (anhydrous)	Mercury (in manometers, for example), chlorine, calcium hypochlorite, iodine, bromine, hydrogen fluoride
Ammonium nitrate	Acids, metal powders, flammable liquids, chlorates, nitrites, sulfur, finely divided organics, combustible
Aniline	Nitric acid, hydrogen peroxide
Arsenates and arsenites	Any reducing agents
Azides	Acids, heavy metals and their salts, oxidizing agents
Bromine	Ammonia, acetylene, butadiene, butane, other petroleum gases, sodium carbide, turpentine, benzene, finely divided metals
Calcium oxide	Water
Carbon (activated)	Calcium hypochlorite, other oxidants
Carbon tetrachloride	Sodium
Chlorates	Ammonium salts, acids, metal powders, sulfur, finely divided organics, combustibles
Chlorine	Ammonia, acetylene, butadiene, butane, methane, propane (or other petroleum gases), hydrogen, sodium carbide, benzene, finely divided metals, turpentine
Chlorine dioxide	Ammonia, methane, phosphine, hydrogen sulfide
Chromic acid and chromium trioxide	Acetic acid, naphthalene, camphor, glycerol, turpentine, alcohol, other flammable liquids
Copper	Acetylene, hydrogen peroxide
Cumene hydroperoxide	Acids (organic or inorganic)
Cyanides	Acids
Flammable liquids	Ammonium nitrate, chromic acid, hydrogen peroxide, nitric acid, sodium peroxide, halogens
Fluorine	Isolate from everything
Hydrides	Water
Hydrocarbons (benzene, butane, propane, gasoline, turpentine, etc.)	Fluorine, chlorine, bromine, chromic acid, peroxides
Hydrocyanic acid	Nitric acid, alkalis

Chemical	Incompatible with
Hydrofluoric acid (anhydrous); Hydrogen fluoride	Ammonia (aqueous or anhydrous)
Hydrogen peroxide	Copper, chromium, iron, most metals or their salts, any flammable liquid, combustible materials, aniline, nitromethane
Hydrogen sulfide	Fuming nitric acid, oxidizing gases
Hypochlorites	Acids, activated carbon
Iodine	Acetylene, ammonia (aqueous or anhydrous)
Nitrates	Acids, reducing agents
Nitric acid (concentrated)	Acetic acid, acetone, alcohol, aniline, chromic acid, hydrocyanic acid, hydrogen sulfide, flammable liquids, flammable gases, nitratable substances
Nitrites	Acids, oxidizing agents
Nitroparaffins	Inorganic bases, amines
Oxalic acid	Silver, mercury, and their salts
Oxygen	Oils, grease, hydrogen, flammable materials (liquids, solids, or gases)
Perchloric acid	Acetic anhydride, bismuth and its alloys, alcohol, paper, wood, grease, oils (all organics)
Peroxides, organic	Acids (organic or mineral); avoid friction, store cold
Phosphorus (white)	Air, oxygen, alkalis, reducing agents
Phosphorus pentoxide	Alcohol, strong bases, water
Potassium	Carbon tetrachloride, carbon dioxide, water
Potassium chlorate (see also chlorates)	Acids
Potassium perchlorate (see also perchloric acid)	Acids
Potassium permanganate	Glycerol, ethylene glycol, benzaldehyde, sulfuric acid
Selenides	Reducing agents
Silver and silver salts	Acetylene, oxalic acid, tartaric acid, ammonium compounds, fulminic acid (produced in nitric acid-ethanol mixtures)
Sodium (see also alkali metals)	Carbon tetrachloride, carbon dioxide, water
Sodium nitrite	Ammonium nitrate and other ammonium salts
Sodium peroxide	Any oxidizable substance, such as ethanol, methanol, glacial acetic acid, acetic anhydride, benzaldehyde, carbon disulfide, glycerol, ethylene glycol, ethyl acetate, methyl acetate, furfural
Sulfides	Acids
Sulfuric acid	Chlorates, perchlorates, permanganates
Tellurides	Reducing agents

Excessive Risk Chemicals – Risk Exceeds Educational Utility

Chemical	Hazards
Acetic anhydride	Explosive potential, corrosive
Acetyl chloride	Corrosive, dangerous fire risk, reacts violently with water and alcohol
Acrylamide	Toxic by absorption, suspected carcinogen
Acrylonitrile	Flammable, poison
Adipoyl chloride	Corrosive; absorbs through skin, lachrymator
Aluminum chloride, anhydrous	Water reactive, corrosive
Ammonia, gas	Corrosive lachrymator
Ammonium bifluoride	Reacts with water, forms hydrofluoric acid
Ammonium bichromate	May explode on contact with organics, suspected carcinogen
Ammonium chromate	Oxidizer, poison; may explode when heated
Ammonium dichromate	Reactive, may cause fire and explosion
Ammonium perchlorate	Explosive; highly reactive
Ammonium sulfide	Poison, corrosive, reacts with water and acids
Aniline	Carcinogen, toxic, absorbs through skin
Aniline hydrochloride	Poison
Antimony oxide	Heath and contact hazard
Antimony powder	Flammable as dust, heath hazard
Antimony trichloride	Corrosive; emits hydrogen chloride gas if moistened
Arsenic compounds	Poison, carcinogen
Asbestos, friable	Inhalation health hazard, carcinogen
Azide compounds	Explosive in contact with metals, extremely reactive, highly toxic
Barium chromate	Poison
Benzene	Flammable, carcinogen
Benzoyl peroxide	Organic peroxide, flammable, oxidizer
Beryllium and its compounds	Poison, Dust is P-Listed & highly toxic, carcinogen
Bromine	Corrosive, oxidizer, volatile liquid
Cadmium compounds	Toxic heavy metal, carcinogen
Calcium fluoride (fluorspar)	Teratogen, emits toxic fumes when heated
Carbon disulfide	Flammable, toxic, P-listed, extremely hazardous
Carbon tetrachloride	Toxic, carcinogen
Chloral hydrate	Hypnotic drug, controlled substance
Chlorine	Poison gas, corrosive
Chlorobenzene	Explosive limits 1.8% to 9.6%, toxic inhalation and contact hazard
Chloroform	Carcinogen; if old, forms deadly phosgene gas
Chlorosulfonic acid	Toxic, aka sulfuric chlorohydrins
Chromic acid	Strong oxidizer, poison
Collodion	Flammable, explosive when dry; nitrocellulose compound
Cuprous cyanide	Toxic
Cyanogen bromide	Poison, strong irritant to skin and eyes
Cyclohexene	Flammable, peroxide former
Dichlorobenzene	Toxic
Dichloroethane	Flammable, toxic
Dinitro phenol	Explosive, "Bomb Squad"
Ethyleneimine	Flammable; toxic; P-listed
Ferrous sulfide	Spontaneously ignites with air if wet
Formaldehyde (formalin)	Toxic, carcinogen, sensitizer
Gunpowder	Explosive
Hydrazine	Flammable; absorbs through skin; carcinogen, corrosive

Chemical	Hazards
Hydriodic acid	Corrosive, toxic
Hydrobromic acid	Corrosive, poison
Hydrofluoric acid	Corrosive, poisonous
Hydrogen	Flammable
Hydrogen sulfide, gas	Poison; stench
Immersion oil (old)	May contain 10-30% PCBs such as arochlor 1260
Isopropyl ether	Flammable, highest risk peroxide former
Lithium aluminum hydride	Flammable; reacts with air, water and organics
Lithium metal	Reacts with water, nitrogen in air
Mercaptoethanol	Flammable; corrosive; intense stench
Mercury compounds	Poisonous heavy metal
Mercury, liquid	Toxic heavy metal; carcinogen
Methylene chloride	Toxic, carcinogen, narcotic
Methyl ethyl ketone	Flammable, dangerous fire risk, toxic
Methyl iodide (Iodomethane)	May be a narcotic; carcinogen; lachrymator
Methyl isocyanate	Flammable, dangerous fire risk, toxic
Methyl isopropyl ketone	Toxic
Methyl methacrylate	Flammable; vapor causes explosive mix with air
Naphthylamine, a-	Combustible, toxic; carcinogen
Nickel oxide	Flammable as dust; toxic, carcinogen
Nicotine	Poison, P-listed; extremely hazardous
Nitrilotriacetic acid	Corrosive
Nitrobenzene	Highly toxic
Nitrocellulose	Flammable, explosive; call ETSI
Nitrogen triiodide	Explosive; “Bomb Squad”
Nitroglycerin	Explosive; “Bomb Squad”
Osmium tetraoxide (osmic acid)	Highly toxic; P-listed; Extremely hazardous
Pentachlorophenol	Extremely toxic
Perchloric acid	Powerful oxidizer, reactive
Phosphorus pentasulfide	Water reactive; toxic; incompatible with air and moisture
Phosphorus pentoxide	Oxidizer, toxic
Phosphorus, red	Flammable solid
Phosphorus, yellow or white	Air reactive, poison
Picric Acid, trinitrophenol	Explosive when dry
Potassium cyanide	Poison, P-listed; extremely hazardous
Potassium perchlorate	Powerful oxidizer; reactively hazard
Potassium sulfide	Flammable; May ignite spontaneously
Potassium, metal	Water reactive; peroxide former (orange fog/crystals)
Pyridine	Flammable, toxic; Vapor forms explosive mix with air
Selenium	Toxic
Silver oxide	Poison
Silver cyanide	Extremely toxic
Sodium metal lump	Water reactive; ignites spontaneously in dry hot air, corrosive
Sodium arsenate	Toxic; carcinogen
Sodium arsenite	Toxic; carcinogen
Sodium azide	Poison; explosive reaction with metals. P-Listed; extremely hazardous
Sodium borohydide	Flammable solid; water reactive
Sodium cyanide	Poison; P-Listed; Extremely hazardous
Sodium fluoride (bifluoride)	Highly toxic by ingestion or inhalation; strong skin irritation
Sodium fluoroacetate	Tox-X Deadly poison

Chemical	Hazards
Sodium peroxide	Water reactive; may cause fire and explosion
Strontium	Flammable. Store under naphtha; reacts with water
Testosterone HCl	Controlled substance
Tetrahydrofuran	Flammable, peroxide former
Thioacetamide	Toxic; carcinogen; combustible
Thionyl chloride	Corrosive
Thiourea	Carcinogen
Titanium trichloride	Flammable; fire risk
Triethylamine	Flammable; toxic; irritant
Trinitrobenzene	Explosive; “Bomb Squad”
Trinitrophenol	Explosive; “Bomb Squad”
Trinitrotoluene	Explosive; “Bomb Squad”
Uranium/Uranyl compounds	Radioactive

High Risk Chemicals – Only Allow Very Limited Amounts in Storage

Only Appropriate for Advanced-Level High-School Science Classes

Chemical	Hazards
Acetamide	Carcinogen; P-Listed, Extremely Hazardous
Ammonium nitrate	Powerful oxidizer, reactive
Barium peroxide	Fire and explosion risk with organic materials, oxidizer, toxic
Butyric acid	Corrosive; intensive stench
Cadmium sulfide	Highly toxic; carcinogen
Calcium carbide	Flammable; reactive with water
Chromium trioxide	Oxidizer, poison
Ethidium bromide	Potent mutagen
Hexamethylenediamine	Corrosive; absorbs through skin, lachrymator
Hexanediamine, 1-6	Corrosive; absorbs through skin, lachrymator
Hydrogen peroxide, >29%	Powerful oxidizer, corrosive to skin
Lead compounds	Highly toxic
Lead nitrate	Toxic heavy metal; oxidizer
Magnesium, power	Flammable
Mercury thermometers	Toxic heavy metal; corrosive
Phenol	Poison
Potassium chlroate	Powerful oxidizer, reactive
Potassium chromate	Oxidizer; toxic
Potassium dichromate	Powerful oxidizer, carcinogen
Radioactive materials	Radioactive
Sebacoyl chloride	Corrosive fumes; lachrymator
Silver compounds	Toxic
Sodium chlorate	Powerful oxidizer
Sodium chromate	Oxidizer
Sodium dichromate	Reactive; may cause fire or explosion
Sodium, metal, small chips	Water reactive; corrosive
Strontium nitrate	Oxidizer; may explode when heated or shocked
Thermite	Flammable solid
Toluene	Flammable, dangerous fire risk, toxic
Wood’s Metal	Poison
Xylene	Flammable, toxic