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LAWRENCE LIVERMORE LABORATORY

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SAFETY IN HANDLING HAZARDOUS CHEMICALS

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Compiled by:
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SAFETY IN HANDLING HAZARDOUS CHEMICALS

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INTRODUCTION

In every laboratory or shop process using chemicals, we must use certain chemicals which are of a hazardous nature. They can be used and used safely. But occasionally a bottle is dropped, a container upset or wrong materials used. It is the purpose of this paper to diminish errors and accidents by familiarizing you with these chemicals, by discussing their properties, safe means of handling, storage and disposal. Perchloric Acid (HClO_4) will be covered in particular.

- I. Properties Common to All Strong Acids
 - A. React with a large number of metals to form metal solutions and liberate hydrogen gas.
 - B. Usually produce heat when mixed with water.
 - C. React with tissue causing severe burns.
 - D. React with cloth causing decomposition.
 - E. Cold, dilute solutions may penetrate the skin and cause severe damage to tissues.
 - F. Turn blue litmus paper red; indicate a PH of less than seven (7) with PHydrian paper.
 - G. React with bases to form a neutral salt plus water, plus heat.
 - H. Mineral acid concerned with here are water soluble.
 1. Acids are always added to water.
- II. Some Acids are Volatile under Normal Supply and Storage Conditions.
 - A. Hydrochloric (HCl), Hydrofluoric (HF), and Nitric (HNO_3) Acids build up some gas pressure in tightly capped containers at room temperature.
 1. The gas is usually rich in poisonous and corrosive fumes; they should be opened and poured in a hood or well ventilated area. Protective clothing should be worn.

- B. Sulphuric (H_2SO_4), Phosphoric (H_3PO_4) and Perchloric (HClO_4) acids do not build up gas pressure under normal supply and storage conditions. They could be safely opened and poured outside a hood, but should not be.

III. Some Acids are Strong Oxidizing Agents, While Others Are Not.

- A. HNO_3 is a strong oxidizing agent as well as a strong acid. It may react with organic substance to form explosive nitro compounds.
- B. HClO_4 is a strong acid (completely ionized) even when cold, and a strong oxidizing compound when heated. It may react with organic substances to form explosive perchlorate compounds. The dehydrated fumes may form explosive mixtures in air.
- C. H_3PO_4 , HCl and HF do not form explosive compounds.

IV. Each Acid has its own Unique Properties and Uses:

A. Nitric Acid

1. HNO_3 melts at -41°C and boils at 86°C with decomposition ($2\text{HNO}_3 \rightarrow \text{H}_2\text{O} + \text{N}_2\text{O}_5$) becoming more dilute until a temperature of 120.5°C is reached. It forms a constant boiling mixture at this temperature and about 70% by weight. Reagent grade Nitric Acid is supplied as the 70% constant boiling mixture.
 - a. Nitric Acid is also supplied as Red Fuming Nitric Acid. This is prepared by dissolving NO_2 gas in 100% HNO_3 . Do not confuse this reagent with the 70% Nitric Acid.
2. Nitric Acid is a strong oxidizing acid; it oxidizes and dissolves most metals. Al, Cr, Au and Pt metals are the exceptions.
 - a. Oxidation products vary, but NO_2 , NO and N_2 may be formed. Do not breathe these fumes. $\text{Fe} + 3\text{HNO}_3 \rightarrow \text{Fe}^{++} + 2\text{NO}_3 + \text{NO}_2 \text{ (gas)} + \text{H}_2\text{O}$ $\text{Fe}^{++} + \text{HNO}_3 \rightarrow \text{Fe}^{+++} + \text{H}_2\text{O} + \text{NO (gas)}$.
 - b. NO_2 is a dark brown colored gas which reacts with water to form HNO_3 .
 - c. Mixtures of Nitric Acid with Acetone or Ethyl Alcohol should be avoided. Violent explosions can occur.

B. Hydrochloric Acid - is a term usually applied to a water solution of HCl. The pure dry compound is a gas at ordinary temperatures, melting at -111°C and boiling at -85°C .

1. It is a colorless gas with a penetrating and suffocating odor. It is highly toxic and corrosive.
2. Hydrogen chloride gas dissolves in water to about 39% by weight. The reagent grade acid is supplied as 37% - 39% aqueous solution.
 - a. Increasing the temperature reduces the solubility of HCl in water, and when stored in warm areas gas pressure builds up. When tightly capped bottles are opened, HCl gas may escape. It should be opened and poured in a hood or a well ventilated area.
3. HCl forms a constant boiling mixture with water containing 20.4% HCl. If dilute solutions are evaporated, water boils off and the concentration of the acid increases until it reaches 20.4%, so HCl solutions should not be evaporated without ventilation to remove the fumes.
4. Concentrated H_2SO_4 will take water away from HCl solutions and create heat, thereby liberating HCl gas. These acids should be mixed cold and in a hood, pouring the HCl solution slowly down the side of the H_2SO_4 container.
 - a. If H_2SO_4 is first diluted 1:1 with water, no HCl gas will be evolved.
5. Hydrochloric Acid reacts with oxidizing agents to form Chlorine gas and other gaseous products.
 - a. Agents which react with HCl to form chlorine are peroxides of heavy metals, all nitrates, nitrites, chlorates, hypochlorites, chromates and other peroxy-compounds.
 - b. Chlorine gas is extremely dangerous and will react with gold, platinum and just about anything else it comes in contact with.
 - c. Aqua Regia is prepared by mixing HCl and HNO_3

$$3\text{HCl} + \text{HNO}_3 \rightarrow 2\text{H}_2\text{O} - \text{NOCl (gas)} + \text{Cl}_2 \text{ (gas)}.$$

C. Sulphuric Acid

1. H_2SO_4 is usually supplied as 93-96% solution and is a heavy, colorless, oily liquid having a density of about 1.8.
2. When heated to 168°C dense white fumes of sulphur trioxide (SO_3) are given off. If heating is continued, H_2SO_4 fumes are given off at about 338°C .
3. Fuming sulphuric acid has SO_3 gas dissolved in 100% H_2SO_4 . When container is opened, clouds of SO_3 fumes are given off. DO NOT CONFUSE fuming sulphuric acid with reagent grade H_2SO_4 .
4. When H_2SO_4 is heated with volatile acids such as HCl , HNO_3 , and HF , the volatile acids will boil off leaving concentrated H_2SO_4 .
5. If concentrated H_2SO_4 is mixed with water or water solutions of other acids, a great amount of heat is produced which may cause boiling or spattering. It will liberate HCl , HF or NO_2 gases if mixed too rapidly with HCl , HF or HNO_3 .
 - a. Diluting H_2SO_4 1:1 with water before mixing with volatile acids reduces heat formation, and the possibility of liberating poisonous gases.
 - b. If it is necessary to add water or other acids to a container which has evaporated down to concentrated H_2SO_4 , cool the H_2SO_4 vessel down and pour the liquid additive very slowly with mixing down the side in a hood. If it gets warm, stop and cool down before adding more.

D. Hydrofluoric Acid (H_2F_2)

1. Reagent grade HF is supplied as 48-51% HF in water solution. It will build up moderate vapor pressure in closed containers.
2. It is a fairly weak acid, but the fluoride ion is highly reactive. It will etch glass and penetrate the skin even in cold, dilute solutions.
3. It does not cause a burning sensation immediately, and may be mistaken for water in dilute solutions. Protective clothing should be always worn when working with HF solutions. Damaged tissue heals very slowly because of the penetration of the fluorine with the tissue.

4. Some metals, such as Al and Be react vigorously with HF solutions.

E. Phosphoric Acid - H_3PO_4

1. It is supplied as a 85% water solution.
2. It is non-volatile, non-oxidizing, non-explosive and can be safely mixed with other acids in the cold state.
3. The concentrated acid will cause severe burns if not washed off immediately.

F. Perchloric Acid - HClO_4 . This acid and its peculiarities will be covered quite thoroughly because of the general lack of knowledge about it and the dangers that can arise during its use.

1. HClO_4 is a liquid at ordinary temperatures, melting at -112°C and boiling at 203°C .
2. The anhydrous acid, meaning an acid destitute of water gradually turns straw color, then brown, and finally explodes at room temperature. Decomposition is accelerated by sunlight.
3. It is usually supplied as a stable 70% water solution which boils at about 200°C .
4. The cold 70% solution is not volatile, is a strong acid and non-oxidizing.
5. The hot solution is a strong acid and a strong oxidizing agent and when dehydrated, may explode. Adding water to hot 70% HClO_4 may cause violent splattering.
6. DO NOT LET HOT HClO_4 COME IN CONTACT WITH OIL, GREASE OR OTHER ORGANIC MATERIAL.
 - a. Organic materials are materials containing compounds of carbon.
 - b. In addition to oils and greases, other organic materials are all wood materials, paper, rags, cotton swabs, brushes, etc.
7. Chemicals, compounds and elements commonly found around the laboratory with which HClO_4 should not be mixed or allowed to come into contact, unless under strict, direct supervision of a knowledgeable person.

a. Acetic Acid and/or Acetic Anhydride. (Organic substances)

- (1) While it is true that either one or both of the Acetics in carefully measured solution with HClO_4 make excellent electropolish solutions for a goodly number of metals, the mixing temperatures, the quantities and the rate of addition of one acid to the other must be extremely well controlled. A small miscalculation in the percentage of HClO_4 can lead to spontaneous combustion.
- (2) If these acids must be mixed it is recommended practice to slowly add the HClO_4 to the Acetics.
- (3) Mixtures of Acetic Acid and HClO_4 used for electropolishing have exploded, sometimes with the violence of a true high explosive. Avoid heating Acetic Anhydride with HClO_4 as the Anhydride will dehydrate the water from the 70% azeotrop thus producing anhydrous HClO_4 .
- (4) Mixtures of the three acids have a sensitivity to shock and the vapors above the heated mixture are flammable.
- (5) An electropolish mixture of Acetic Anhydride and HClO_4 exploded in Los Angeles in 1947 wiping out a square block of the city. The quantity of this mixture was 240 gallons.

b. Alcohols, Glycols, Glycol ethers and Ketones undergo violent decomposition in contact with HClO_4 due to the formation of unstable perchlorate esters.

- (1) The above statement is very true. However, an electropolish bath consisting of Methanol and HClO_4 , mixed at -76°C and kept at that temperature was developed at Ames Laboratory and called a "Universal Electropolish Method" because it can be used to polish 51 of the elements on the periodic table.

c. Antimony Compounds (Trivalent)

- (1) These compounds form explosive mixtures with HClO_4 when hot.

d. Bismuth

(1) Bismuth with HClO_4 can explode violently.

e. Charcoal

(1) A drop of Anhydrous HClO_4 on charcoal explodes violently.

f. Ethyl Alcohol

(1) A drop of Anhydrous HClO_4 on ethyl alcohol explodes violently.

g. Glycerine and Lead Oxide (Letharge)

(1) Over a period of time, HClO_4 fumes from a hood condensed on the cover plate of the exhaust fan which was sealed with a cement of Glycerine and lead oxide. When a workman tapped the plate with a chisel a violent explosion occurred, killing one man, injuring two and wrecking the laboratory.

h. Other facts and data about HClO_4 .

(1) HClO_4 , like all acids, should be cleaned up immediately if a spillage occurs. HClO_4 , however, requires certain precautions. It should be flushed with large amounts of water and all rags, mops or brooms used to clean up the spill should be rinsed thoroughly, allowed to dry and then disposed of, preferably by burning. If the acid is allowed to dry on the floor or other surfaces the perchlorate residue can ignite or explode at a later time.

(2) The HClO_4 container should be rinsed off around the capping area before opening and recapping. There have been cases where a container that has been used and tightly capped without rinsing and allowed to stand long enough for the acid to dry and form perchlorates has exploded when attempting to open due to the friction of the tight cap.

(3) HClO_4 explosions can and have occurred when being used by the most experienced, professional chemists. A very recent one occurred at LLL.

Six rare earth organic fluoride samples were being processed in duplicate. All were wet ashed with

perchloric, nitric and sulphuric acid mixture and then titrated with DTA. Three gave low results and it was felt that possibly all of the fluoride had not been removed. The three low result solutions were reworked by wet ashing back to rare earth sulfate salts.

At the beginning of reworking the samples contained 5 to 10 ml of 0.02 M EDTA and approximately 5 to 10 ml of pyridine. Five mls each of H_2SO_4 , HClO_4 , and 50 ml of HNO_3 were added. The beakers were on the hot plate all afternoon and had two more additions of about 50 mls of HNO_3 after fuming had commenced. Two were then taken almost to dryness. The third one became yellow; an indication that the HClO_4 was in a dehydrated condition. It also had a half an inch of foam over the surface which suddenly increased to approximately an inch; a condition not observed in this operation before. This indicated to the operator that the material was either very dangerous or going to boil over.

The operator decided to leave rather than take a chance on saving the sample. He glanced back when approximately eight feet away from the sample and the beaker was filled with yellow foam. The explosion occurred at that moment. He received three minor cuts on the left arm through his lab coat.

Many pieces of glass were scattered around the room from the exploding beaker and the two other beakers that were on the same hot plate. Other beakers that were also in the hood that were to be later dumped in the waste jug under the hood were broken and the contents spilled in the hood. The surface of the hot plate was bent down and the imprint of the bottom of the beaker was evident on the hot plate.

The fume hood was badly damaged. The side near the hot plate was cracked with two holes. One pie shaped with a radius of approximately eight inches, the other

was a small square hole. The back panel of the hood had many of the Kel F screws broken off. The cover for the roof light was shattered and the safety glass in the window cracked.

V. Safety Precautions

The following general rules should always be observed when using HClO_4 solutions.

- A. Rubber protective equipment should be used in handling the mixtures and should be cleaned promptly when it has been contaminated with the acids. HClO_4 is very corrosive to the skin.
- B. HClO_4 should be stored away from all inflammable materials.
- C. Bakelite, lucite, micarda and cellulose based lacquers and materials should not be used around HClO_4 .
- D. Polyethylene, Polystyrene, PVC and Teflon materials can be safely used.
- E. HClO_4 and other acids should be mixed in a hood.
- F. All spills should be cleaned up immediately.
- G. Safety glasses or face shields, rubber gloves, rubber apron or lab coat should be worn when working with hazardous chemicals of all kinds.

VI. Conclusion

It is said "Familiarity Breeds Contempt." It is hoped that "Familiarity breeds respect" in the field of acids. No one can fault anyone for being alert enough to recognize their limitations, for seeking advice or asking questions. In seeking to bring together information concerning Perchloric Acid it becomes apparent that the search must cover many, many sources because most of the information is the result of experiences of persons who have had things happen and sought the reasons why; this leads to negative impressions. It is good that we can take advantage of these experiences to learn the cautions we need to take in our approach to solving problems.

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