

## ***CRC HANDBOOK OF LABORATORY SAFETY***

### **4.6.2.4. Perchloric Acid\***

#### 4.6.2.4. 1. Introduction

Considerable interest has been taken in the explosion hazards to be encountered in the use of perchloric acid since a mixture of perchloric acid and acetic anhydride exploded in a Los Angeles factory in 1947, killing 15, injuring 400, and causing \$2 million in damage. On a smaller scale, Robinson reported a detonation of 3 g of a Perchlorate salt of a rhodium-polyamine complex undergoing an evaporation step in a rotary evaporator.<sup>1</sup> A violent explosion destroyed the evaporator, smashed a lab jack, cracked the bench top, and chipped walls over 15 feet away. Fortunately, this happened in an empty laboratory. Literature surveys reveal that descriptions of explosions in laboratories using perchloric acid haven reported over a period of more than a century.

The most detailed available account of the chemistry of perchloric acid and a reference highly recommended to everyone who will be working with perchlorates is given by J.S.Shumacher in the American Chemical Society monograph *Perchlorates, Their Properties, Manufacture, and Uses*.<sup>2</sup> Cummings and Pearson have reviewed the thermal decomposition and the thermochemistry, and in a later report Pearson reviewed the physical properties and inorganic chemistry of perchloric acid.<sup>3,4</sup> Shorter, but very useful, reviews of the chemistry of perchloric acid also have been published<sup>5,6</sup> and several accidents which have occurred in France have been reviewed.<sup>7</sup> A review of the circumstances leading to the Los Angeles explosion and of five laboratory incidents involving perchloric acid has been published<sup>8</sup> and a resumed of five serious accidents has been reported.<sup>9</sup> A summary of a number of accidents reported in the literature is appended to this section.

\* This material is taken from an updated (by Graf) version of an article by K. Everett and F.A.Graf, Jr., which appeared in the second edition of the *Handbook of Laboratory Safety*. The remaining portion of this article forms part of Section 4.5.6.

#### 4.6.2.4.2. General Discussion

Perhaps the most disturbing features of accidents involving perchloric acid are (1) the severity of the accidents and (2) the persons involved are, in the majority of cases, experienced workers. Harris concludes that the basic cause of accidents involving perchloric acid is contact with organic material or the accidental formation of the anhydrous acid.<sup>8</sup> Smith<sup>6</sup> emphasizes the hazard of allowing strong reducing agents to come into contact with concentrated (72%) perchloric acid (Table 4.13).

#### ***Properties of Perchloric Acid Solution***

A review of the latest MSDSs prepared to meet the OSHA hazard communication and laboratory safety standards by each manufacturer is strongly recommended.

The important physical and chemical properties of perchloric acid are that it is a clear liquid like water, it has no odor, the boiling point (of constant boiling mixture at atmospheric pressure) is 203°C (397°F), and while under a high vacuum a 73.6% composition can be produced. Perchloric acid can be dangerously reactive. At ordinary temperatures 72% perchloric acid solution reacts as a strong, nonoxidizing acid. At elevated temperatures (approximately at 160°C, 320°F), it is an exceedingly strong and active oxidizing agent, as well as a strong dehydrating reagent. Contact with combustible material at elevated temperatures may cause fire or explosion.

### ***Relative Oxidizing Power of Perchloric Acid***

Although no data are known to describe the change in the oxidizing power of perchloric acid with temperature and/or concentration, some observations describe the phenomenon sufficiently.

Cold perchloric acid, 70% or weaker, is not considered to have significant oxidizing power. The oxidizing power, however, increases rapidly as the concentration increases above 70%. Acid of 73%+ (which gives off fumes in even relatively dry air) is a fairly good oxidizer at room temperature. The monohydrate of perchloric acid (85% acid strength and a solid) is indeed a very good oxidizer at room temperature, as it will even react with gum rubber, whereas the 73% acid does not.

Temperature increases will also increase the oxidizing power of perchloric acid solutions; therefore, hot, strong perchloric acid solutions are very powerful oxidizing agents.

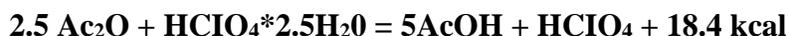
### ***Explosive Reactions***

A chemical explosion is the result of a very rapid increase in volume due to the evolution of gas or vapor, the reaction normally being exothermic. The force of the shock wave is governed by the rate at which the reaction takes place. The point is made by Burton and Prall' that, apart from the thermochemical aspects of explosions, it is the velocity of the decomposition which determines whether or not a reaction is explosive, and that the power of the explosive is governed largely by the pressure of the gases produced in the decomposition. Where the temperature of the explosion is several thousand degrees celsius, the power of the explosion is increased further by the thermal expansion of the gases.

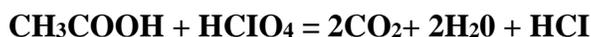
When considering the hazards involved in the use of perchloric acid this point should be clearly recognized: many of the reported serious laboratory accidents involved only small quantities (<1 g) of reactant (see Appendix included within this section).

### ***The System: Perchloric Acid and-Acetic Anhydride-Acetic Acid***

Both Shumacher<sup>2</sup> and Burton and Praill<sup>5</sup> examined the perchloric acid-acetic anhydride system in some detail, the former reproducing a triangular diagram for the system. Burton and Praill quote the equation:



showing that there is a considerable evolution of heat when mixing the reagents, and that if excess acetic anhydride is present the solution may be considered to be a solution of anhydrous perchloric acid in acetic acid. The most explosive mixture is given as the one in which complete combustion occurs.



These authors give the explosion temperature as 2400°C and calculate that 1 gram of the mixture instantaneously produces about 7 liters of gas at the explosion temperature. Finally, they state that for this system, all the investigated explosions have been due to the use of potentially dangerous mixtures, together with faulty equipment or technique.

In 1961 in a university laboratory, a young metallurgy student lost the sight of both eyes when an explosion took place while he was preparing an acetic anhydride-perchloric acid-water electropolishing mixture. Bartlett and Turner<sup>12</sup> investigated the process and discovered that the reagents should be mixed in the following order:

1. Add the perchloric acid to the acetic anhydride.
2. Add water to the mixture, slowly, and in small portions.

### *The Use of Magnesium Perchlorate as a Drying Agent*

Several cases are on record in which magnesium Perchlorate (anhydrous) has exploded while being used as a desiccant (Appendix 1). Smith<sup>6</sup> regards the use of magnesium Perchlorate for the drying of alcohol vapors as permissible, but Burton and Praill<sup>5</sup> warn that if magnesium Perchlorate is to be used for drying organic liquids, the purity of the drying agent should be determined since the preparation may have left traces of free perchloric acid in the salt. Explosions involving magnesium Perchlorate may have been caused by the formation of perchloric esters in the system. It should be noted that methyl and ethyl perchlorate are violently explosive compounds.

### *Miscellaneous Reactions*

Burton and Praill<sup>5</sup> state that it is impossible to overemphasize that the simple alkyl esters are extremely dangerous. They note that many documented explosions resulted from the standard method of determining perchlorates or potassium as potassium Perchlorate during which an ethyl alcohol extraction is used. The same authors state that most organic Perchlorate salts, with the exception of the diazonium salts, are safe unless

they are overheated or detonated, but mention that pyridine Perchlorate can be detonated by percussion.

### ***Reducing Agents***

In general, mixtures of strong reducing agents and concentrated 72% perchloric acid should be regarded as very hazardous<sup>6</sup> (see Appendix I).

### ***Safe Handling of Perchlorates***

Shumacher<sup>2</sup> states that:

Perchlorates appear to fall into two broad categories: those (1) more or (2) less sensitive to heat and shock. Included in the group of those qualitatively less sensitive are pure ammonium perchlorate, the alkali metal perchlorates, the alkaline earth perchlorates, and perchloryl fluoride. Among the more sensitive compounds are the pure inorganic nitrogenous perchlorates, the heavy metal perchlorates, fluorine Perchlorate, the organic perchlorate salts, the perchlorate esters, and mixtures of any perchlorates with organic substances, finely divided metals, or sulfur. Any attempt to establish a more precise order of the degree of hazard to be expected from any given Perchlorate seems unwarranted on the basis of available data. Each Perchlorate system must be separately (and cautiously) evaluated.

There do not appear to be any uniform recommendations for the safe handling of perchlorates which are generally applicable. A number of heavy metal and organic perchlorates, as well as hydrazine Perchlorate (hydrazinium diperchlorate) and fluorine Perchlorate, are extremely sensitive and must be handled with great caution as initiating explosives. Mixtures of any perchlorates with oxidizable substances are also highly explosive and must be treated accordingly. For all of these, it is essential to avoid friction, heating, sparks, or shock from any source (as well as heavy metal contamination), and to provide suitable isolation, barricades, and protective clothing for personnel.

However, the more common ammonium, alkali metal, and alkaline earth perchlorates are considerably less hazardous.

Synthesis of new inorganic or organic perchlorates should only be undertaken by an experienced, cautious investigator who is familiar with the literature.

A simple test to evaluate impact sensitivity can be conducted by placing a crystal or

two of the perchlorates on a steel block and striking with a hammer. The degree of noise and relative impact to produce an explosion can be roughly correlated with the impact sensitivity.

A simple thermal stability test can be conducted by placing a crystal or two on a hotplate and observing the time to create a violent decomposition reaction. A gram of the material can be heated slowly in a loosely closed vial for a more exact determination of thermal stability.

***Recommendations for the Safe Handling of Perchloric Acid***

Several organizations have drawn up recommendations for the safe handling of perchloric acid, among them the Association of Official Agricultural Chemists, the Factory Mutual Engineering Division, and the Association of Casualty and Surety Companies. Graf updated these recommendations in a paper.<sup>13</sup> The recommendations from these and other sources are combined and summarized below.\*

**Floors**--Perchloric acid should be handled in a masonry building with concrete or tile floors. Handling acid on wooden floors is dangerous, especially after the acid has dried. The wooden floor will then become sensitive to ignition by friction. Note that since the original preparation of this article, commercial equipment specifically designed to be used with perchloric acid has become generally available--specifically hoods and ejector ducts to exhaust perchloric fumes well above roof level.

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**Table 4.13. Materials Compatible With and Resistant to 72% Perchloric Acid Compatible**

<b>Materials</b>	<b>Compatibility</b>
Elastomers	
Gum rubber	Each batch must be tested to
determine compatibility	
Vitons <sup>a</sup>	Slight swelling only
Metals and alloys	
Tantalum	Excellent
Titanium (chemically pure grade)	Excellent
Zirconium	
Niobium	Excellent
Hastelloy C*	Excellent

Plastics Slight corrosion rate  
Polyvinyl chloride  
Teflon<sup>a</sup>  
Polyethylene  
Polypropylene  
Kel-F<sup>b</sup>  
Vinylidene fluoride  
Saran<sup>c</sup>  
Epoxy

Others  
Glass  
Glass-lined steel  
Alumina  
Fluorolube

### **Incompatible**

Plastics  
Polyamide (nylon)  
Modacrylic ester, Dynel (35-85%) acrylonitrile  
Polyester (dacron)  
Bakelite  
Lucite  
Mica  
Cellulose-based lacquers

Metals  
Copper  
Copper alloys (brass, bronze, etc.) for very shock-sensitive perchlorate salts  
Aluminum (dissolves at room temperature)  
High nickel alloys (dissolves)

Others  
Cotton  
Wool  
Wood  
Glycerin-lead oxide (lethargic)

<sup>a</sup> du Pont trademark ; <sup>b</sup>3M Company trademark; <sup>c</sup> Dow Chemical Corporation trademark.

For conventional wooden wall construction, which is [not] desirable, it is highly recommended that a 6-inch concrete curb be provided for the walls to rest on. In this way, acid seepage under the wall is minimized.

Concrete of course, is not resistant to acids, and thus should be covered. Epoxy paints in general are resistant to room temperature perchloric acid spills; however, epoxy paint will peel off concrete if pools of water stand for several days. Therefore, the floor should have a gentle slope to a drain and contain no low spots.

No equipment of any kind should ever be bolted to a floor by using bolts that screw into the floor. Perchlorates can enter and form hazardous metallic perchlorates that can be initiate a detonation when the bolt is removed. Studs, firmly and permanently set into the floor to which the equipment can be bolted, are far safer. The nuts can then be flushed with water and sawed off with a hacksaw under a constant water spray or remove that equipment.

**Laboratory benches**-Laboratory benches should be constructed of resistant materials

and not wood to prevent acid absorption, especially at the bottom surface which rests on the floor and would be subject to the greatest exposure from acid spills. Bench tops of resistant and nonabsorbent materials such as chemical stoneware, tile, epoxy composites, and polyethylene are recommended.

**Shelves and cabinets**-Shelves and cabinets of epoxy-painted steel are highly recommended over wood.

**Heating source**-Hot plates (electric), electrically or steam-heated sand baths, or a steam bath are recommended for heating perchloric acid. Direct flame heating or oil baths should not be used.

**Vacuum source**-Smith describes a simple apparatus, using a water aspirator or pump, for drawing fumes from a reaction vessel. The use of this apparatus is to be commended in that the contamination of the fume cupboard duct with a dust/perchloric acid layer is avoided and the vapors are drawn into water and discharged safely to the drain.\* A similar apparatus is marketed for carrying out Kjeldahl digestions. Vacuum pumps from which all traces of petroleum lubricants have been flushed and refilled with halocarbon, Kel-F, or fluorolube are recommended.

Silverman and First have described a self-contained unit which has been developed and field tested for collecting and disposing of chemical fumes, mists, and gases.<sup>15</sup> It is portable and compact and, when assembled, only requires connection to an electrical receptacle and water tap to be completely operational. Although originally designed for use in filter-type radiochemical laboratory hoods for safe disposal of perchloric acid fumes arising from acid digestions, it may be used as a substitute for a permanent hood in a variety of [low risk] locations. Collection and disposal of the acid at the source of emission is the guiding design principle.

The conventional vacuum pump has been used both in the laboratory and in a pilot plant handling large quantities of 72% perchloric acid. The pumps were protected by the use of well-designed cold traps and desiccant columns as well as maintaining the practice of changing petroleum-based oil daily. The desiccant was also routinely changed, along with the frequent thawing and removal of the cold trap contents.

**Glassware.** The hazards that may ensue if an apparatus cracks or breaks due to

thermal or mechanical shock are sufficient to make it desirable that quartz apparatus be considered, especially as it is necessary in many experiments to chill rapidly from the boiling point.

Glass-to-glass unions, lubricated with 72% perchloric acid, seal well and prevent joint freezing arising from the use of silicon lubricants. Rubber stoppers, tubes, or stopcocks should not be used with perchloric acid due to incompatibility.

**Stirrers.** Pneumatically driven stirrers are recommended rather than the electric motor type. Repeated exposure of the motor windings to perchloric acid vapor could result in a fire, unless the motor is an explosion-proof type, which would be unlikely.

**Sundry items-**The choice of tongs for handling hot flasks and beakers containing perchloric acid mixtures should be given due thought. Since the use of radioactive materials has become commonplace, much thought has been put into the design of indirect handling equipment. The cheap, commonly used crucible tongs are most unsuitable for picking up laboratory glassware. If possible, tongs with a modified jaw design should be used to ensure that a safe grip is obtained.

\* For an individual laboratory, such a practice should pose no problem. However, if the facility is big enough, eventually such practices may become regulated, especially if the water treatment works is marginal. The same concern may eventually become involved in maintaining air quality near facilities with a large number of hood exhausts.

### ***Handling 73 % or Less Perchloric Acid in the Laboratory***

1. Use chemical splash and impact-rated goggles for eye protection whenever the acid is handled.
2. Always transfer acid over a sink in order to catch any spills and afford a ready means of disposal.
3. In wet combustions with perchloric acid, treat the sample first with nitric acid to destroy easily oxidizable matter.
4. Any procedure involving heating of perchloric acid must be conducted in a perchloric acid fume hood, with the sash down.
5. No organic materials should be stored in the perchloric acid hood.
6. Do not allow perchloric acid to come into contact with strong dehydrating agents (concentrated sulfuric acid, anhydrous phosphorous pentoxide, etc.).
7. Perchloric acid should be used only in standard analytical procedures from well-recognized analytical texts.  
(This does not apply to analytical research workers.)
8. Keep the quantities of perchloric acid handled at the bare minimum for safety

### ***Handling 73 to 85% Perchloric Acid in the Laboratory***

Use the same precautions as above

### ***Handling Anhydrous Perchloric Acid (Greater than 85%)***

1. Only experienced research workers should handle anhydrous perchloric acid. These workers must be thoroughly familiar with the literature on the acid.
2. A safety shield must be used to protect against a possible explosion, and the acid must be used in an appropriate hood with a minimum of equipment present. No extraneous chemicals should be present in the hood.
3. A second person should be informed of the intended use of anhydrous acid and be in the same room with the research worker using this extremely strong oxidizer.
4. Safety goggles, face shield, thick gauntlets, and a rubber apron must be worn.
5. Only freshly prepared acid should be used
6. Do not make any more anhydrous perchloric acid than is required for a single day's work.
7. Dispose of any unused anhydrous acid at the end of each day by dilution and neutralization.
8. Contact of the anhydrous acid with organic materials will usually result in an explosion.
9. Any discoloration of the anhydrous acid requires its immediate disposal

### ***Acid Disposal***

**Spills**-Perchloric acid spilled on the floor or bench top represents a hazard. It should not be mopped up, nor should dry combustibles be used to soak up the acid. The spilled acid should first be neutralized and then soaked up with rags or paper towel. The contaminated rags and paper towel must be kept wet to prevent combustion upon drying. They should be placed in a plastic bag and sealed and then placed in a flammable waste disposal can. If the spill can be rinsed down a chemical drain, neutralization of the wetted area is recommended followed by additional rinsing. Other recommendations in the literature include wearing a face shield and gloves while working on the spill. Cover the spill with a weak solution of sodium thiosulfate, and then transfer the slurry into a large container of water, where it should be neutralized with soda ash. After neutralization, it can be drained into the sewer, accompanied by abundant water.

**Disposal**-Stir the acid into cold water until the concentration is less than 5%; follow by neutralization with aqueous sodium hydroxide; then dispose of the resulting mixture in the sanitary system, accompanied by abundant water. Larger quantities in the original unopened containers may be acceptable to a commercial hazardous waste vendor. If it is potentially explosive, the best option available is to hire a firm specializing in disposal of exceptionally hazardous materials. This will be expensive.

### ***Dismantling an Exhaust Ventilation System Suspected of Contamination with Perchlorates***

Dismantling a laboratory exhaust system contaminated with shock-sensitive perchlorates is a hazardous operation, as evidenced by published and unpublished case histories. The procedures used by one university to reduce the hazards were described by Peter A. Breysse in the *Occupational Health Newsletter* (15 [2, 3] 1, 1966) published by the Environmental Health Division, Department of Preventive Medicine, University of Washington. The problem, procedures, and confirmation of Perchlorate contamination were reported as follows.

A short time ago, the manager of maintenance and operations was requested to dismantle and relocate six laboratory exhaust systems. The possibility of perchloric acid contamination of these systems was considered. An investigation indicated that several laboratories serviced by the exhaust systems were utilizing or had in the past used perchloric acid for wet ashing of tissues. Furthermore, the exhaust hoods were constructed with sharp corners and cracks, permitting the accumulation of contaminants not readily noticed or easily removed. The ducts were made of ceramic material and contained numerous joints as well as a number of elbows, areas conducive to Perchlorate buildup. Organic compounds were also used to pack the duct joints, as an adhesive for the flexible connectors, and as a sealing compound for the fan.

Recognizing the potential dangers of dismantling these systems, the following procedures were established and successfully carried out:

1. It was deemed desirable to dismantle the systems on the weekend when occupancy would be at a minimum.
2. The entire system was washed for 12 hours, just prior to dismantling, by introducing a fine water spray within the hoods, with the fans operating.
3. The fans were then tied down.
4. Fan mounting bolts and connectors were carefully removed. Nonsparking tools were and should be used throughout.
5. The fans were immediately removed to the outdoors. As an added precaution during removal the fans were covered with a wet blanket.
6. After all the fans were taken outdoors, one fan at a time was placed behind a steel shield for protection during dismantling. This fan was again washed down.
7. Plate bolts were evenly loosened to remove the plate without binding. If a fan puller is necessary, it should be nonsparking.
8. All disassembled parts were washed and cleaned. The gasket material contained on the flanges was scraped off with a wooden scrapee.
9. Ordinarily the ceramic ducts would be removed by breaking them apart with a sledge hammer. In this instance, the ducts were washed down again just prior to and during dismantling. A high-speed saw was used to remove the ductwork.

One of the flexible connectors and a piece of duct-joint seating compound were collected and taken to the laboratory for examination. Qualitative analysis by X-ray fluorescence and chemical tests indicated the presence of perchlorates in both samples. While these procedures for dismantling and decontamination seem unduly severe, the uncertainty requires that they be followed.

One of the problems in conducting such an operation is providing appropriate liability insurance. This question should be considered before doing such work in-house, and contracts for work done by outside vendors should have provision of liability insurance as a specific requirement.

Some additional words of caution include: (1) do not unscrew any nuts or bolts--cut them off after water flushing, (2) do not produce any impact upon the hood parts, and (3) do not cause any friction between parts of the hood during dismantling

### ***Summary and Conclusions***

The use of perchloric acid is becoming increasingly widespread and the properties of both the acid and its derivatives make it likely that the trend will continue. Safety hazards associated with the use of perchloric acid may be reduced, provided that its hazardous properties are clearly recognized, the purpose of the acid in a process is fully understood, and measures are taken to avoid known possibilities.

It is clear, however, that no one should attempt to use perchloric acid who is not fully conversant with the chemistry of the material, who has not made a careful appraisal of operating conditions and techniques, and who exhibits an unsafe attitude about his work.

### ***Appendix 1: Some Accidents Involving Perchloric Acid***

1. Explosions may occur when 72% perchloric acid is used to determine chromium in steel, apparently due to the formation of mixtures of perchloric acid vapor and hydrogen. These vapor mixtures can be exploded by the catalytic action of steel particles.<sup>2</sup>
2. Two workers are reported to have dried 11,000 samples of alkali-washed hydrocarbon gas with magnesium Perchlorate over a period of 7 years without accident. However, one sample containing butyl fluoride caused a purplish discoloration of the magnesium Perchlorate, with the subsequent explosion of the latter.<sup>2</sup>
3. A worker using magnesium Perchlorate to dry argon reported an explosion and warned that warming and contact with oxidizable substances should be avoided.<sup>2</sup>
4. An explosion was reported when anhydrous magnesium Perchlorate used in drying unsaturated hydrocarbons was heated to 220°C.<sup>2</sup>
5. An explosive reaction takes place between perchloric acid and bismuth or certain of its alloys, especially during

electrolytic polishing.<sup>2,5</sup>

6. Several explosions reported as having occurred during the determination of potassium as the perchlorate are probably attributable to heating in the presence of concentrated perchloric acid and traces of alcohol. An incident in a French laboratory is typical: an experienced worker in the course of a separation of sodium and potassium removed a platinum crucible containing a few decigrams of material and continued the heating on a small gas flame. An explosion pulverized the crucible, a piece of platinum entering the eye of the chemist.<sup>7</sup>
7. A violent explosion took place in an exhaust duct from a laboratory hood in which perchloric acid solution was being fumed over a gas plate. It blew out windows, bulged the exterior walls, lifted the roof, and extensively damaged equipment and supplies. Some time prior to the explosion, the hood had been used for the analysis of miscellaneous materials. The explosion apparently originated in deposits of perchloric acid and organic material in the hood and duct.<sup>8</sup>
8. A chemist was drying alcohol off a small anode over a Bunsen burner in a hood reserved for tests involving perchloric acid. An explosion tore the exhaust duct from the hood, bent a portion of the ductwork near the fan, and blew out many panes of window glass.<sup>8</sup>
9. An employee dropped a 7-pound (3.2 kg) bottle of perchloric acid solution on a concrete floor. The liquid was taken up with sawdust and placed in a covered, metal waste can. Four hours later, a light explosion blew open the hinged cover of the can. A flash fire opened three sprinklers which promptly extinguished the fire.<sup>8</sup>
10. A 7-pound bottle of perchloric acid solution broke while an employee was unpacking a case containing three bottles. The spilled acid instantly set the wood floor on fire, but it was put out quickly with a soda-acid extinguisher.<sup>8</sup>
11. At a malleable iron foundry, perchloric acid had been used for about 4 years in the laboratory for the determination of the silicon contents of iron samples. A cast iron, wash-sink drain at the bench used for this purpose had corroded and the leaking acid had soaked into the wood flooring, which was later ignited while a lead joint was being poured. This fire was extinguished and part of the wood flooring was removed. Later in the day, at a point slightly removed from the location of the first fire, a similar fire occurred when hot lead was again spilled. This time the fire flashed with explosive violence into the exhaust hood and stack above

the workbench. Laboratory

equipment and records were wetted down extensively and damaged.

12. A stone table of a fume hood was patched with a glycerin cement and several years later, when the hood was being removed, the table exploded when a worker struck the stone with a chisel. The hood had been used for digestions with perchloric acid and, presumably, acid spills had not been properly cleaned up.<sup>9</sup>

13. A conventional chemical hood normally used for other chemical reactions, including distillation and ashing of organic materials, was also used during the same time for perchloric acid digestion. During a routine ashing procedure, the hot gases went up the 12-inch tubular transit exhaust duct and one of a series of explosions occurred that tore the duct apart at several angles and on the horizontal runs.<sup>9</sup>

14. During routine maintenance involving partial dismantling of the exhaust blower on a perchloric acid ventilating system, a detonation followed a light blow with a hammer on a chisel held against the fan at or near the seal between the rear cover plate and the fan casing. The intensity of the explosion was such that it was heard 4 miles away. Of the three employees in the vicinity, one sustained face lacerations and slight eye injury; the second suffered loss of four fingers on one hand and possible loss of sight in one eye; the third was fatally injured with the 6-inch chisel entering below his left nostril and embedded in the brain.<sup>9</sup>

15. A 6-pound (2.7 kilograms) bottle of perchloric acid broke and ran over a fairly large area of a wooden laboratory floor. It was cleaned up, but some ran down over wooden joists. Several years later a bottle of sulfuric acid was spilled in this same location and fire broke out immediately in the floor and the joists.<sup>9</sup>

16. A chemist reached for a body of perchloric acid stored on a window sill above a steam radiator. The bottle struck the radiator, broke, and the acid flowed over the hot coils. Within a few minutes the wooden floor beneath the radiator burst into flame.<sup>9</sup>

17. An explosion occurred when an attempt was made to destroy benzyl celluloses by boiling with perchloric acid.<sup>11</sup>

18. An explosion occurred as anhydrous perchloric acid was being prepared via sulfuric acid dehydration and extraction with methylene chloride when a stopper was removed from the separatory flask.<sup>14</sup>

19. A rat carcass was dissolved in nitric acid, the fat skimmed off, and perchloric acid added. The mixture was heated to dryness and touched, setting off an explosion that cracked the fume

hood and nearly blew out the sash.<sup>16</sup>

20. A perchlorate-doped polyacetylene film was prepared and stored under argon in a sealed vessel. Two weeks later, the film detonated when the vessel top was being removed. Earlier safety testing failed to show any reaction to flame or impact.<sup>17</sup>

21. Perchlorate-doped polyacetylene samples combusted violently in the oxygen atmosphere of a Schoniger flask.<sup>18</sup>

22. An explosion occurred in a fume hood upon ether drying of a second crop of crystals of hexaminechromium (111) perchlorate that were washed with absolute ethanol and anhydrous diethylether. Following aspiration of the ether wash, the ether damp filter cake was agitated with a glass stirring rod and the mass detonated.<sup>19</sup>

23. Perchlorate-doped, highly conducting polythiophene Pt-CIO, exhibits excellent ambient stability, but the film should not be heated above 100°C. Touching an extremely dry Pt-CIO, film (kept in a desiccator over P20,) with tweezers might cause an explosion of the film.<sup>20</sup>

24. Some samples of rare earth organic fluoride were re-ashed with perchloric, sulfuric, and nitric acid in 1-liter beakers. One of the beakers started foaming, turned yellow, and then exploded. The surface of the hot plate was bent downward, and the imprint of the beaker was left in the metal surface of the hot plate by the force of the explosion.<sup>1</sup>

25. Drying an acetonitrile adduct of neodymium Perchlorate at 50°C in vacuum apparently produces a compound that can detonate on mechanical contact.<sup>21</sup>

## ACKNOWLEDGMENT

This section was based on and developed from a safety assessment prepared for use at the University of Leeds, England, and is reprinted with permission, as well as the work of Graf and associates at Thiokol Chemical Corporation, Brigham City, Utah.

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