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SUMMARY

INTRODUCTION TO REFRIGERANTS

There are about 115 named refrigerants in my ASHRAE Fundamentals Hand Book. At present we are really limited to three types:

Hydrocarbons:

Including, Methane, Ethylene, Propane and Butane

Inorganic:

Including, Ammonia, Water, and Carbon Dioxide

Halocarbons:

The R-12, R-22 and R-502 which have all been outlawed, and all of the new air conditioning and commercial refrigerants, which are really fluorocarbons (carbon and fluorine with a hydrogen molecule thrown in now and then and no chlorine).

This lesson is lumps the fluorocarbons all together, and concentrate on ammonia and fluorocarbons. There will be some mentions of carbon dioxide, sulfur dioxide and a few others.

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This lesson is designed to be read from your computer screen. The lesson is on an Adobe Acrobat 6.0 operating system, and designed to operate as a “full screen”. An Adobe Acrobat Reader is available free from www.adobe.com.

There is an open book quiz at the end of the lesson. Fill it out, email it back to me you will get a completion certificate.

- 1. Open the lesson on your PC.***
- 2. Click on Ctrl F. (This will put you in the full screen mode). You can navigate through the program using the up and down keys or with your mouse, etc. To get out of the Full Screen Mode, click on the Esc key.***
- 3. There is also a Table of Contents that is linked to the various subjects. To return to the Table of Contents, simply click on the -1- number in the right hand corner of the screen. The Toxic has its own Table of Contents.***
- 4. If you would like your PC to read the text to you, click on Shift+Ctrl+V to read aloud one page; Shift+Ctrl+B to read the whole document; Shift+Ctrl+C to stop reading and: Shift+Ctrl+E to stop the read aloud.***

Any questions? My email is indref@sandynet.org. To Table of Contents **THE IDEAL**

REFRIGERANT

The following, on is taken from “Modern Electric and Gas Refrigeration” by authors Althouse and Turnquist, publisher, Goodheart-Wilcox, Chicago, Published in 1933 when the first household refrigerators were just hitting the market.

This may be old, from the time you grandmother or great grandmother had an ice box for household refrigeration. But this is a great analysis of what an ideal refrigerant should be. Actually, the best I have seen anywhere in spite of being over seventy years old.

All refrigerants are **“DANGEROUS!”**. There is a lot of advertising by chemical companies to the effect that their refrigerant is better, safer, and more efficient than anyone else’s. But there is **“NO SAFE REFRIGERANT”**, unless it was the cold water in the old spring house. And even with that the EPA would require a danger label to keep toddlers from falling into the spring or the trough.

This lesson is an effort to level the playing field for you. I will compare current refrigerants with the 1933 Ideal Requirements. Some meet applications or needs better than others. The following are my analysis of the most common refrigerants and some pros and cons. Educate yourself and make up your mind on which to use in a new system, and what you need to know to

work safely with any refrigerants you come across in the older systems.

REFRIGERANTS

To obtain a transfer of heat from the inside of a box to the outside or in order to refrigerate, a heat carrier must be used.

Fluids which can be changed easily from a liquid to a gas and from a gas to a liquid are used as the medium because such a change of state is always accompanied by a change of the heat content. Some fluids are better than others.

REQUIREMENTS FOR REFRIGERANTS:

There are certain desirable characteristics which a fluid used as a refrigerant should possess. They are:

- 1. It should be non-poisonous.*
- 2. It should be non-explosive.*
- 3. It should be non-corrosive.*

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4. *It should be non-flammable.*
5. *Leaks should be easy to detect.*
6. *Leaks should be easy to locate.*
7. *It should operate under low pressure (low boiling point).*
8. *It should be a stable gas.*
9. *It should be easy to lubricate parts moving in its presence.*
10. *It should be non-toxic.*
11. *It should have a well balanced latent heat of evaporation value per unit of weight.*
12. *It must have a small relative displacement to obtain a certain refrigeration effect.*
13. *The difference between the vaporizing pressure and the condensing pressure should be a minimum.*

Common refrigerants in use at present (in 1933)are:

1. *Sulphur dioxide. SO₂ (R-164)*
2. *Methyl chloride, CH₂Cl (R-611)*
3. *Ammonia, NH₃ (R-717)*
4. *Freon -12 CCl₂F₂ (R-12)*
5. *Iso butane (Frezol) (R-600a)*

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6.	<i>Ethyl chloride, C₂H₅Cl</i>	<i>(R-160)</i>
7.	<i>Carbon dioxide, CO₂</i>	<i>(R-744)</i>
8.	<i>Methyl formate, C₂H₄O₂</i>	<i>(R-611)</i>
9.	<i>Methylene chloride, CH₂Cl₂</i>	<i>(R-30)</i>
10.	<i>Dichlorotetrafluoroethane, C₂Cl₂F₄</i>	<i>(R-114)</i>
11.	<i>Dichloromonofluoroethane, CHCl₂F</i>	<i>(R-21)</i>

These eleven refrigerants are an interesting group. The only refrigerant in this 1933 list that is still being used is Ammonia, NH₃, (R-717). Although, Europe is beginning to use some carbon dioxide (R-744) again for freezers.

The following are comments on each of the 1933 Ideal Refrigerant requirements.

1. *It should be non-poisonous.*

Today, the safety bureaucracy (government, environmentalists, and scientists) have essentially done away with the term “Poisonous” and in its place have substituted the word “Toxic”.

“Poisonous” according to the “McGraw-Hill Dictionary of Scientific and Technical Terms”

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“Poison (matter) A substance that in relatively small doses has an action that either destroys life or impairs seriously the function of organs or tissues.”

The same reference defines **“Toxic (med) Relating to the harmful effect by a poisonous substance on the human body by physical contact, ingestion, or inhalation”**. This is what I thought was the definition for toxic until I became involved with the Government. See item **10. Non-Toxic** below for more of an explanation.

I do not believe any of the commonly used refrigerants are “Poisonous”, but all commonly used refrigerants are “Toxic” according to the Governments definitions.

One thing to remember is the importance of the **dosage!** For example what poison do we usually have on our dining tables? The answer is a salt shaker. A small amount of salt (sodium chloride) is commonly used as a flavor enhancer. But, just the amount of salt in many salt shakers is extremely toxic and can be fatal if ingested in a single dosage of about 400 grams (a little less than one pound). This is the reason so many people have died when adrift on the world’s oceans without a fresh water supply. *“Water! Water! Everywhere but Not a Drop to Drink”*.

The dosage (by inhaling) of any of the common refrigerants are not poisons at common

dosages, but in high concentrations are toxic because they displace oxygen.

2. *It should be non-explosive.*

The term “**Explosive**” is frequently misused. There are two types of explosions. Lets go to the “McGraw-Hill” “Dictionary of Scientific and Technical Terms” again.

Detonation

“An exothermic chemical reaction that progresses with such rapidity that the rate of advance of the reaction zone into the un-reacted material exceed the velocity of sound in the material; that is the advancing reaction zone is preceded by a shock wave.”

Most high explosives are based on nitrates, chlorates or per-chlorates which release large quantities almost instantly of oxygen upon detonation.

A high explosive does not require and external source of oxygen. Examples are dynamite, nitro-glycerin, TNT, C-3, C-4, picric acid, ammonium picrate, ammonium iodide, lead azide, fulminate of mercury and of course the grand daddy of them all, a nuclear explosive. Industrial and military

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high explosives are typically detonated with blasting caps, detonators or prima cord. Most high explosives are not detonated in a fire, with a match or lighter. They require an appropriate detonator to initiate the explosion.

Refrigerant Explosions

The type of explosions we might encounter with refrigerants are considerably different than a high explosive. These are a chemical reaction producing heat, and a dramatic increase in pressure and volume, typically contained with an appropriate amount of air or oxygen.” In other words rapidly burning fuel with the expanding gasses building up enough pressure to rupture a vessel, building, or other confined space. These are typically called “Low Explosives” and include gun powder, gasoline or any fuel with enough oxygen to burn in a confined container.

The hydrocarbon refrigerants such as natural gas, propane, butane, methane and things like gasoline and diesel oil can certainly be the rapid combustion type or “low explosive”.

3. *It should be non-corrosive.*

In 1933 the most common refrigerant for household refrigerators, apartment buildings and

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grocery store refrigeration was R-764 (sulfur dioxide) which when it absorbed any moisture was extremely corrosive. Sulfur dioxide is also currently very undesirable under the EPA's "Clean Air Act" regulations and is not currently available as a refrigerant.

Our current common refrigerants are not corrosive to most common metals, assuming the refrigerant is not wet, the refrigerant has not broken down and the metal containing them has not been abraded (scratched or a sharp rough surface).

The Halogen Refrigerants, (carbon, chlorine, fluorine and hydrogen) when wet, subjected to an electric arc (hermetic and semi-hermetic compressors) can produce hydrochloric acid. Hydrofluoric acid which certainly is corrosive, even to glass and carbonyl halides (phosgene) which had been used as a Military Gas in WWI.

There is a very distinctive odor of the halogen refrigerant breakdown. When you open a burned out hermetic or semi hermetic compressor, or when you are brazing copper in an existing system that contains some of the halogen refrigerant, the acid smell is the typical odor of a halocarbon refrigerant breakdown..

The dosage is normally quite small and I have not met anyone working with halogen

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refrigerants that seems to have suffered health problems from this breakdown. But when you work with any refrigerant, have plenty of ventilation.

However, Firemen recognize the problem and take extreme precautions when fighting a supermarket fire.

The halogen refrigerants can produce a rapid chemical reaction when exposed to some freshly abraded metals such as aluminum. R-40 (methyl chloride) is explosive when exposed to any form of aluminum.

Ammonia, reacts with copper or brass and do not get along together chemically. Copper turns into a greenish - blue powder after some time. It does not take long for ammonia to produce leaks in copper tubing. Use steel pipe or aluminum tubing when piping an ammonia system.

When building an ammonia refrigeration system for a meat processing plant, in the days when most automatic controls were pneumatic, the control contractor insisted on putting his air compressor in the engine room. Upon starting the ammonia compressors we had an ammonia release in the engine room. The air compressor was operating at the time. Six weeks later all of the ¼" copper control tubing was reduced to green stripes on the walls, and had to be totally replaced.

4. *It must be non-flammable*

In the middle 1800's when artificial ice was first being produced by vapor compression, the refrigerant of choice was “**sulfurous ether**”, produced in the engine room by reacting ethyl alcohol (white lightning) with sulfuric acid. This was an extremely flammable and dangerous refrigerant. I assume that is why the flammable issue was included into the 1933 requirements.

Yes, **non-flammable** would be ideal! But we deal with 100 pounds or more of highly flammable gasoline behind and under us in our cars every day with very few problems considering the danger. We move natural or manufactured gas through our homes, streets and buildings for about 150 years for lighting, cooking and comfort heating with few problems. Truck loads of liquid propane and butane under pressure travel our highways and streets daily. Why the “**must be non-flammable**” for a refrigerant be so important?

All of the hydrocarbon refrigerants are flammable, but used in Europe for household refrigerators. Hydrocarbon refrigerants were used exclusively in Australia for the Olympics in the vending stands and distribution points successfully.

Ammonia (R-717) is listed as flammable by OSHA and the EPA. Non-flammable by the

Department of Transportation. Why?

Ammonia vapor can be ignited, but the combustion will die instantly if the ignition source is removed. We do have some incidents of ammonia being accused of being the cause of a fire. But if anyone smells ammonia at a fire the ammonia has not been burned. The products of combustion of ammonia are nitrogen (no nitrous oxide) and water. Neither has any odor or smells like ammonia.

Ammonia either has to be dissociated into hydrogen and nitrogen (about 1,200°F) and the hydrogen is burning, or in an aerosol with a lubricating oil or some other primary fuel such as natural gas to provide a continuous ignition source.

Explosive Limits

We give all kinds of names and numbers to things, specially those we do not like! This term probably should be ***“Ignition Limits”***.

The “Lower Explosive Limit” (LEL) of a flammable vapor is the percentage of that fuel by volume in a mixture with air that will burn if there is an adequate ignition source. Below this percentage level the mixture is too ***“lean”*** to burn.

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The “Upper Explosive Limit” (UEL) of a flammable vapor is the percentage by volume of the flammable vapor in the mixture with air that will not burn, even with an ignition source. The mixture is too “**rich**” to burn. For example your lawn mower. If you do not close the choke or pump some gasoline into the engine the mixture is too “Lean” to burn. When the lawn mower kicks over a couple of times and quits, you forgot to open the choke into the “**run**” position and the mixture was too “rich” to burn.

While we are on this subject. The gasoline and air mixture in your truck, mower etc. typically runs smoothly. The mixture is “**burning**” increasing the pressure in the cylinders. The rapid expansion of the combustion is providing the energy driving the pistons to turn the crankshaft. When you attempt to over load the combustion and the engine “**knocks**”, this is a “**detonation of the fuel**”, and destroying your engine.

There are typically no common refrigerants that can produce a detonation type of explosion.

Ignition Temperature

The ignition temperature is another indication of the danger of a flammable vapor.

Hydrocarbons

The hydrocarbons, R-50 (methane), R-170 (ethane), R-290 (propane), R-600 (n-butane), R-600a (iso-butane), R-1150 (ethylene) and R-1270 (propylene). All of these are refrigerants and all are extremely flammable. The LEL (Lower Explosive Limit) for most of the hydrocarbons is about 2.0% and the UEL (Upper Explosive Limit) is something less than 10%. The auto-ignition temperature for hydrocarbons varies from about 800°F to 1,000°F.

Halogens

The halogens, R-12, R-22, R-502, R-134a, R-404a, and R-507 are not flammable under normal circumstances. But, there has been at least one major fire in an air condition equipment manufacturing plant and many fires in hermetic and semi-hermetic refrigeration compressor motors.

The MSDS sheets warn about the explosive problems if air and the halogens are mixed under pressure. A typical example is isolating a semi-hermetic compressor removing the refrigerant, fixing the problem, sealing it up again, starting the compressor without evacuating the air. There is pressure, there is air with 20% oxygen, and there is an excellent potential ignition source (the

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electrical arcs between the power terminals. There are many, many burned out hermetic and semi-hermetic compressors to prove this.

Ammonia

The official (LEL) lower explosive limit for ammonia vapor is about 16% and the (UEL) upper explosive limit is about 25%. The auto ignition temperature is about 1,274°F. At below 1,200°F ammonia dissociates into hydrogen and nitrogen. The auto ignition temperature of hydrogen is 1,050°F and hydrogen is easily ignited by static electricity while ammonia is difficult to burn without a continuous ignition source.

Ammonia appears to be flammable only when dissociated and then the hydrogen is burning, not the ammonia. There are more fires and explosions with ammonia refrigeration than any other application for ammonia. I believe this is because of the lubricating oil in the compressors is not being well managed. The naphtha based compressor oils are more flammable than the paraffin based lubricating oils. But both are flammable. The ignition temperature is under 500°F. To burn the oil must be vaporized or an aerosol. As a liquid the LEL and UEL are not determined.

If there are quantities of oil in the high pressure side of the refrigeration system. Such as a

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“Super Oil Separator” where the hot gas from the compressor is bubbled up through a tank full of oil, or in a screw compressor that circulates a huge quantity of oil and the oil storage is on the high pressure side of the system, there is some oil vapor present. If there is a leak in the high pressure side of the system, the escaping high pressure vapor, 135 psig to 200 psig range, atomizes the oil and mixes highly flammable oil liquid and vapor with air and ammonia. This is a very flammable mixture! Keep the oil where it belongs, in the compressors. Most of the so called ammonia fire or explosions have been leaks on the high pressure side of the systems and the majority using the “Super Separators”. Only one I know about was the result of mounting the screw compressor on top of the oil separator.

5. *Leaks should be easy to detect.*

Halogen Refrigerants

Leaks of halogen refrigerants are very difficult to detect. Halogens have essentially no odor, have no color, there is a slight sound from fairly large leaks but the back ground noise typically dampens out this sound to the human ear.

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Audio

Electronic high frequency sound detectors work well to survey piping and to locate the general position of a leak in piping a condenser or evaporator coil with halogen refrigerants.

The telephone companies use this type of leak detector to locate leaks in multi-wire overhead cables. The cable is pressurized, usually with nitrogen (you may see the red pressure vessels leaning against a pole) then driving down the street or road with the microphone out the window pointing at the cable. These work well with refrigerant leaks as well.

Flame and Catalyst

The old standby is very good at locating a leak, once you know you have one. The leak detector for halogens is a portable propane torch with the combustion chamber on the end of a hose. The air intake consists of a small sampling hose. In the combustion chamber there is a piece of hot copper in the flame. When there is no halogen in the intake air, the flame is a normal color. If there is halogen vapor in the air intake, the flame turns green. It is very obvious where the leak is, depending on where the air the sampling hose is taking in air. Too much halogen will put out the fire.

UV and Fluorescent Dyes

This is a not bad at knowing whether or not you have a leak. But it is better in locating the leak than learning whether or not you have a leak.

Some of the manufactures of the halogen refrigerants offer a fluorescent dye, factory added. Or the fluorescent dye is available for injection into the system. This system can identify the location of a leak as low as $\frac{1}{8}$ ounce per year.

A “Black Light” kit is used to make the leaks glow in the dark. The fluorescent dye is carried around the system in the compressor lubricating oil and does not vaporize at the leak but forms a semi-permanent luminous marker under black light at the point of the leak.

Once a leak is repaired, be sure to clean the oil and fluorescent dye off the spot, leaving the area clean for the next guy not to detect a leak that has been fixed.

Electronic Leak Detectors

Electronic leak detectors for halogens are a heated P-N junction. The halogens change the

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conductivity of the junction. They come with a varying frequency and dB sound output and a pointer type of indicator. Simply put the tip of the wand, where you think the leak might be and it will whistle or beep and swing the pointer if there are halogens present. These frequently will also indicate the exhaust gases of a propane powered fork lift or pallet jack trucks.

If there is a large. leak the electronic detector will indicate there is a leak, but it gets overloaded and it is nearly impossible to pin point the leak.

Soap Bubbles

This is a fairly common method of find leaks halogen type of leaks. But not very helpful in determining if you have a leak. You put a bubbling dish washing soap in a spray bottle. Squirt to thoroughly soak the suspected leak and usually a whole lot of bubbles form. I suggest wiping up the soap, but it really is not necessary. Low cost and very effective.

Hydrocarbons

Hydrocarbon refrigerants do not normally have any odor, color or other identification or alarm. But it is difficult to obtain any hydrocarbon refrigerants without the odorizer.

Odor

However, because of the flammability and the usage in buildings and fear of natural gas leaks by the general public the halocarbons have an odor alarm added. The “GAS” odor you smell with hydrocarbons (except gasoline and diesel oil) is a unique odorizer. It is detectable to humans at about 0.001 ppm (ammonia is detectable at about 4 ppm). The chemical is ethyl mercaptan. It also is highly flammable and the products of combustion do not have any noticeable odor. So you detect the odor only if the hydrocarbon has not burned.

An excellent method to determine if there is a leak and very effective safety alarm. But it may be confusing whether the leak is a compressed gas fuel, natural gas, or a refrigerant.

Soap Bubbles

Soap bubbles are not effective in knowing if you have a leak, but effective in pin pointing the source of the leak once you decide there is a leak and you can smell the general validity.

Ammonia (R-717)

Anhydrous ammonia has been used safely and successfully for refrigeration since 1723 when Michael Faraday discovered that ammonia was not a “Noble Gas”. Ammonia did not hit full stride until about 1870 when Carl Von Linde introduced ammonia and the compressors to manufacture ice.

Odor

Ammonia has a very pungent and distinctive odor. Everyone can identify ammonia in the air at about 4 ppm. You know you have a leak, but where is it exactly?

Liquid Ammonia Leaks

Liquid ammonia leaks are easy to see and smell. When liquid ammonia leaks it is usually under a substantial pressure. When the pressure is reduced to atmospheric pressure, the remaining liquid ammonia is at -28°F. Being very cold, the liquid droplets attract moisture out of the air. A liquid ammonia leak typically results in little droplets streaking around the space. It looks something like shooting stars or a comet with a white ball and a white following tail. When it hits something warm, it frequently bounces or scatters.

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Do not get hit by any of the flying white droplets on bare skin or your face or eyes.

It is not difficult to pin point the leak if you can stand the odor.

Ammonia Vapor Leaks

Ammonia vapor leaks are more difficult to find. You know there is a leak, because you can smell it. But ammonia vapor is lighter than air (about 60% the density of air), clear in color and rises and disperses quite quickly. I have never had any problems determining if there is a leak and the general location using my nose and eyes.

Sulfur Sticks

Sulfur sticks are useless when identifying whether or not you have a leak. Sulfur sticks are great when attempting to pin point a leak.

The truck driver delivering ammonia will have a pocket full of sulfur sticks. Ask him for some. To find a leak, light one end of the stick. Put out any flame and leave it smoldering. Like the punk that is used to light firecrackers. Wave the smoldering stick in the vicinity of where you think the leak is. The sulfur dioxide fumes and the ammonia vapor will react, forming a very white smoke that will

identify where the leak is. Sulfur sticks work great for the smallest of leaks.

The current Safety Bureaucracy is convinced that ammonia is highly flammable and this procedure will start a fire or explosion. Sulfur sticks were reported invented in China about 600 AD and I do not believe there has ever been a catastrophic fire or explosion caused by sulfur sticks.

Hydrochloric Acid

ASHRAE (American Society of Heating Refrigeration and Air Conditioning Society) the majority of have never smelled ammonia, recommends using hydrochloric acid to find ammonia leaks. No fire involved. The fumes from the hydrochloric acid and ammonia vapor will produce a white smoke like the sulfur stick. Do not spill any hydrochloric acid on you or anything else while you are climbing ladders or working your way around the piping and over the compressors.

I have yet to find anyone that has successfully used the ASHRAE recommendations for hydrochloric acid to find ammonia leaks. I do not believe that it will either identify whether or not you have a leak or that it will easily pin point one.

Litmus Paper

Some genius recommended using litmus paper to find ammonia leaks. Litmus paper comes in lots of sizes, but mostly about ¼” wide and 2½” long. To use the litmus paper wet it with pure water and put in the vicinity of where you expect the leak. If the litmus paper turns red the leak is acidic below a 4.5 pH and it is definitely not ammonia. If the leak being tested is basic it turns blue above a 8.3 pH the leak is probably ammonia.

Litmus paper is cheap. But it takes a lot of strips of litmus paper and a lot of time before you will ever find a leak. I have tried it. The litmus paper does not change color at a 35 ppm. I had to bring the ammonia level to over 100 ppm before it would change to light blue. So you probably should wear SCBA gear and a bunny suit to test for a leak.

Mass Spectrometer

A leak of air into the refrigeration system operating in a vacuum is more critical to the operation of the system than a pressure leak. Purgers are installed to extract and reject the non-condensable gases. A purger will indicate there are vacuum leaks but will not tell you where.

The only method I know of to find vacuum leaks is a “Mass Spectrometer”. This device is set

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up to detect helium, both the quantity of the leak and the location. Finding the leak is still a slow and tedious project. The low pressure (vacuum) side of the refrigeration system is shut down and isolated. The mass spectrometer is connected so that it can pull a vacuum on the low pressure side of the system. With a hose connected to a cylinder of helium, the vessels, compressors and piping are bathed slowly with helium. When the horn on the mass spectrometer goes off, mark the spot of a vacuum leak. Then move on until all of the low pressure side of the system has been checked for leaks. Break the vacuum, repair all of the leaks. Then run the vacuum leak test again, until all of the leaks are identified and repaired and the refrigeration system is vacuum tight.

A good ultra sound leak detector can be used to locate vacuum leaks.

Pressurizing a Low Pressure Side of a Refrigeration System to Find Vacuum Leaks

Perhaps a more reasonable method of finding vacuum leaks guess where the leak is. Then isolate that vessels, pipe or compressor. Remove all of the ammonia. Pressurize the isolated section with nitrogen or air. Build the pressure to say 100 psig. Then start looking for a leak with soap bubbles. Once the leak is found and fixed (vacuum leaks are much harder to fix than pressure leaks) evacuate the air or nitrogen to at least a 22 " Hg vacuum. Retest. Then put that portion of the system back into operation.

6. *Leaks should be easy to locate*

No refrigerant leaks are really easy to locate. The big problems are to know you have a leak, then getting it down to a reasonable area to look. Practice locating leaks helps a whole lot once you have some successful experience.

7. *It should operate under low pressures (low boiling point).*

Ideally the boiling (evaporating) pressure of the liquid refrigerant in the evaporator should be a bit higher than the atmospheric pressure. Vacuum's are difficult to deal with, specially when looking for leaks.

8. *It should be a stable gas.*

The common refrigerants in use today are all very stable when operating within the normal conditions in a refrigeration system.

Halogens

The halogen refrigerants are very stable chemically except when seriously over heated, subjected to electric arcs, or high energy radiation.

The new halogen refrigerants will break down into hydrofluoric acid and carbonyl halides when over heated. The older halogens will break down into hydrofluoric acid, hydrochloric acid and carbonyl halides when overheated.

The carbonyl halides are extremely toxic and a close relative of carbon monoxide. Phosgene is an example of a carbonyl halide that was used in WWI as a military poison gas (Chemical Asphyxiant).

If you are brazing copper tubing in a supermarket refrigeration system using any of the halogens as the refrigerant, remember the acidic odors you smelled? These are the break down products of the halogen refrigerants. Unpleasant but seldom in a dosage that has any critical or chronic affect on the health of the individual doing the brazing. However, use your head. Use lots of ventilation. Do not breath any more than you absolutely have to. Why take chances?

Hydrocarbons

You are not likely to run into hydrocarbon refrigerants in the US. Europe, however, is beginning to use hydrocarbons in all kinds of refrigeration systems.

Hydrocarbons, overheated without oxygen will break down into carbon soot, and hydrogen. And if burned produce carbon dioxide, possibly carbon monoxide if oxygen is restricted.

Ammonia

Ammonia is extremely hygroscopic and will react with water to form ammonium hydroxide. Ammonia is also biodegradable and acts as a 81-0-0 nitrogen fertilizer. Ammonia is frequently used to side dress corn as a liquid plowed between rows at a rate of about 100 pounds per acre. The ammonia reacts with the moisture and minerals in the soil and does not get into the atmosphere.

Anhydrous ammonia is stable below 800°F to 1200°F depending on what catalysts are present. Above that temperature, ammonia disassociates (breaks down) into nitrogen and hydrogen (no odor). The nitrogen does not get hot enough to form any nitrous oxides.

The powdered metallurgy industry dissociates ammonia as a source of nitrogen for nitriding

metal parts and the hydrogen for heat in the sintering ovens.

If we are going to be running our transportation on hydrogen, ammonia is a good source of hydrogen, easy to manufacture, transport, and to store. Liquid ammonia would be a whole lot safer to carry in a fuel tank than liquid hydrogen. Then disassociating the ammonia as needed with heat from the exhaust system.

There is a huge production capability to manufacture ammonia all ready in existence all around the world.

9. It should be easy to lubricate parts moving in its presence.

Today's common refrigerants present some strange lubrication problems. For example, mineral oil separates from most halogens and floats on the liquid surface, with the exception of R-12 in which mineral oil dissolves. The typical small air conditioning and commercial refrigeration systems circulate the mineral oil with the refrigerant. With R-22 and R-502, a small amount of R-12 was frequently added to dissolve the mineral oil in the liquid refrigerant.

The industrial refrigeration systems (ammonia) do not circulate the mineral oil. Oil is separated and kept in the compressors and oil separators. Oil sinks to the bottom of ammonia liquid where it is

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easily drained off. The major problems are keeping the oil in the compressors and not out in the system.

The fluorocarbon refrigerants require a synthetic polyester lubricant (POE). The POE lubricant and the fluorocarbon refrigerants are very soluble. But any system with flooded evaporators, such as chillers tend to concentrate the POE oil in low temperature evaporators.

If you are using POE lubricants please note they are hygroscopic (will absorb moisture). POE cannot be packaged in the plastic bottles as it will absorb moisture through the bottles from the air. POE is packaged in specially dried metal containers. The manufactures recommend that for the life of the POE lubricants they not be exposed to the atmosphere for more than one hour. Moisture will break down POE lubricants into corrosive acids and may become electrically conductive in hermetic compressors.

In industrial refrigeration systems we do not use hermetic compressors and therefore there is not a problem of medium voltage (100 to 500 volts) arcing through the refrigerant.

For ammonia compressors we used a paraffin based lubricant until shortly after WWII when air conditioning took off. The paraffin based lubricant and R-22 had problems of extracting the paraffin from the refrigerant so a naphtha based lubricant was introduced to the market, and most ammonia

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systems gradually switched. The naphtha based lubricants, in my opinion, are not as good as the paraffin based for ammonia compressors. And a paraffin based lubricant is once again available for ammonia refrigeration.

Many industrial refrigeration systems circulate some oil which accumulates in the bottom of the receivers and flooded evaporators and is removed with oil pots. As a suggestion, keep records of the oil added to the system and of the oil removed. The two should balance out quite closely. If they do not, discover why? Find out where the oil is in the system and fix the problem. Switching from naphtha to paraffin will probably bring a lot of the naphtha lubricant back into the oil separators, receivers and flooded evaporators. This is not a problem but do remove the surplus and dispose of it.

In a new freeze drying operation, we removed about 1,500 gallons of naphtha lubricating oil from flooded scraped surface evaporators after three months of operation. The new operators thought the oil level in the screw compressor sight glasses should show clear oil, not an oil level, or the yellow oil foam.

The lubricant in our compressors perform more functions than just lubricating rubbing parts. The lubricants also separate and seal refrigerant vapors at different pressures and seal refrigerant liquid or vapor from ambient air. The lubricants also cool the machinery in all compressors, and in the case of both single screw and twin screw compressors desuperheat the compressing refrigerant

vapor making the compressors pretty useless as heat recovery systems.

10. *It should be non-toxic.*

Until the EPA came along, non-toxic meant not a poison. Now a toxic means any one or more of eleven effects on humans and other plants and animals.

All currently available refrigerants are “toxic” according to the Government definitions of Toxicity.

The table below and the explanation of the various columns is extracted from the “Handbook of Chemical Hazard Analysis Procedures” published by Federal Emergency Management, U.S. Department of Transportation, and U.S. Environmental Protection Agency, and the various manufactures Material Safety Data Sheets.

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REFRIGERANT HAZARDS																
Hazards	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P
Halogens	†	†	N	†	†	N	Y	Y	Y	?	Y	Y	?	Y	N	Y
Hydrocarbon	†	†	?	†	?	N	Y	Y	Y	?	Y	Y	Y	?	N	Y
Ammonia	†	N	Y	N	N	Y	Y	Y	Y	?	N	N	?	N	Y	N
CO ₂	†	N	N	N	N	N	Y	Y	N	?	N	N	N	N	N	N
SO ₂	†	N	Y	N	Y	N	Y	Y	Y	?	N	N	N	N	N	N

Hazard, Toxic or a Problem **Not a Hazard or a Problem** **Maybe a Hazard or a Problem**

- A Asphyxiation
- B Chemical Asphyxiant
- C Alarm
- D Anesthetics and Narcotics
- E Sensitizers
- F Fish Toxicity
- G Skin
- H Eyes
- I Inhalation
- J Ingestion
- K CNS (Central Nervous System)
- L Epinephrine
- M Fire or Explosion
- N Carcinogen
- O Ozone, Global Warming
- P Toxic Break Down Products

A Asphyxiation

All refrigerant vapors are asphyxiants.

Some refrigerant vapors, such as the halogens, carbon dioxide and the hydrocarbons are considerably heavier than air and will gather in storm sewers, depressed truck docks, basements, ships engine rooms, and other confined spaces in lethal concentrations.

Others, such as ammonia vapor are lighter than air, and will rise and dissipate quite rapidly, unless physically contained.

A fishing factory vessel, using a halogen refrigerant (R-502) with the compressors and condensers in the engine room, had a refrigerant release. It killed three men manning the engine room. Then with no odor or any other indication, fellow workers went to the rescue of their buddies. The total death toll was eleven before anyone figured out that the atmosphere was not fit to breath.

B Chemical Asphyxiants

Chemical asphyxiants are substances that in one way or another prevent the body from using oxygen. Carbon monoxide for example blocks the oxygen receptors preventing oxygen from getting

into the blood stream.

Examples of chemical asphyxiants are carbon monoxide, and various carbon - nitrogen compounds (cyanides) and carbonyl halides.

None of the refrigerants in common usage in their normal operating chemistry are chemical asphyxiants.

The burning hydrocarbons such as propane and butane possibly could produce carbon monoxide in a situation where the fire is starved of oxygen and the hydrocarbons are only partially oxidized.

It is possible that some of the products of overheating of the halogen refrigerants, in the event of a fire may form carbonyl halides, a very close relative of carbon monoxide. The carbonyl halides are known commonly as phosgenes. Phosgene was used as a military poison gas in WWI.

Both phosgene and carbon monoxide are definitely a chemical asphyxiants.

C Alarms

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Some refrigerants are self alarming. Ammonia and sulfur dioxide are very self alarming because of their distinctive, noxious odor that are detected by humans long before the vapor is either an acute, or chronic hazard to health or life.

The hydrocarbons in their native state do not really have a distinctive odor. But an odorizer substance, such as ethyl mercaptan is added during the processing, which give the hydrocarbons a distinctive “rotten egg” odor that everyone recognizes as a “gas” leak.

The halogens and carbon dioxide do not have any unusual odor or anything else to identify when you may be in serious trouble. To keep you out of trouble where you may encounter either halogens or carbon dioxide gas detectors for the specific substance should be installed with loud and distinctive alarms.

D Anesthetics and Narcotics.

Numerous hydrocarbon and organic compounds are classified as hazardous materials with anesthetic or narcotic effects. These depress the central nervous system (CNS). Alcohols and ethers are examples. The MSDS data for the halogen and hydrocarbon refrigerants indicate that all have a depressing effect on your central nervous system.

E Sensitizers.

There are a few toxic materials that act as sensitizers. A sensitizer is a material that a person may not react to on the first exposure, but may react the second, tenth or what ever exposure. After the first reaction, continued exposures result in reactions that get worse and worse.

Many people, including me, are sensitized by bee stings or spider bites (formic acid). The solution is to carry “Bee Sting” kits with them.

Nothing is mentioned about sensitizing in the MSDS data on any refrigerant. So I would guess it is not a major problem among refrigeration service personnel or operators.

However, there is a refrigeration service man in Chicago that worked mostly on supermarket refrigeration. He evidently got a lot of sensitizing from halogen refrigerants. The typical, pounding pulse, feeling like he was on the verge of getting drunk, joints hurting etc.

He was in great physical condition. A body builder, non-drinker, non-smoker.

Then one day he was changing out a semi-hermetic, fairly large R-502 compressor in an enclosure on the roof of a supermarket. The service valves were not holding well but he had the

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replacement compressor right there. He proceeded to change out the compressor successfully. Cleaned up and went home.

About four hours later he was in his kitchen and suffered a seizure. Bit his tongue, blood all over the place. Scared his wife and kids. The paramedics were called and off to the hospital.

It was discovered later that he had broken his back in several places. His muscles were stronger than his bones. He was more than eighteen months out of work on a disability. Since then, he has worked on nothing but ammonia systems.

I do not know of any other incidents like this. But I also suspect that records are not gathered for other similar incidents. If the reader knows of any, please let me know.

From all the data I have seen and my personal experience, I cannot justify any designation that would require the halogen or hydro-carbon refrigerants to be classified as a sensitizer hazardous material. But I would suggest that those of you using these refrigerants observe your reactions, and if there is any increase in your reactions to any of them, take adequate pre-cautions.

F Fish Toxicity.

Most of these refrigerants are not soluble in water and therefore should not affect fish. However, Ammonia, R-717) is the exception and is deadly to fish.

Ammonia (R-717) is an excellent detergent and as such removes the slime film from the gills and skin of fish. The slime helps the fish extract oxygen from the water. Removing the slime causes asphyxiation of the fish.

Never dump ammonia or water with ammonia dissolved in it, down a storm sewer, a sanitary sewer or into any sort of waterway.

Dumping ammonia into a sanitary sewer can get you in big trouble with the sewage treatment plant. When the ammonia hits the sewage treatment plant digesters it provide excess nitrogen (81-0-0) fertilizer. The digester bacteria has a sudden growth surge and will probably overflow making a big, stinky mess in the treatment plant.

One method of getting rid of ammonia or an ammonia-water solution, spread it on or in the soil (81-0-0) fertilizer. Typical soils will absorb as much as 500 pounds of ammonia per acre as nitrogen fertilizer. You may turn grass and other vegetation brown, but it will recover and grow more rapidly

than usual.

If the ammonia that you want to dispose of is not dissolved in water, it can easily be burned off with the products of combustion being nitrogen and water. You will need some form of external heat such as a propane weed burner and a stack with some broken cast iron in it to effectively burn the ammonia. Be sure and tell the local Fire Department what you are doing. Your neighbors will not smell a thing.

G Skin.

The vapors from most refrigerants do not appreciably affect the skin. Some people will get an itch or a rash, and drying of the tissue. The itch is usually sweat attracting the ammonia and producing a diaper rash.

The liquid forms of the halogen and hydrocarbon refrigerants dissolve and extract fats for the skin. This is considerably more dangerous than diaper rash.

All refrigerant liquids that evaporate at atmospheric pressure and at temperatures below 32°F are shown in the MSDS data as causing frostbite. I have had some injuries from frostbite, while working in the Antarctic, Greenland and Baffin Island.

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I also have some scars from freeze burns caused by liquid from R-12, R-22, R-502, propane, carbon dioxide and ammonia (R-717). I do not consider the skin damage from liquid refrigerants to be the same as frost bite.

A “freeze burn” from liquid refrigerants probably causes as much damage to the skin as a “First Degree Burn” from a fire. **DO NOT** put yourself in a position where liquid refrigerants of any kind can splash directly on your skin.

Ammonia (R-717) liquid, in addition to causing **Freeze Burns** can also cause additional damage to the skin.

Dehydration Burns caused by liquid ammonia. Liquid ammonia is extremely hygroscopic. The ammonia liquid will absorb moisture from your tissues. And until the liquid ammonia has absorbed a lot of water diluting it, the liquid ammonia will move under your skin, increasing the damage. The ammonia liquid has to be neutralized by moisture from your tissues before it quits doing damage.

Caustic Burns caused by liquid ammonia. Liquid anhydrous ammonia has a Ph of 12 plus. The anhydrous liquid ammonia can actually dissolve tissue at first contact.

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The combination of Freeze Burns, Dehydration Burns and Caustic Burns is nasty and takes a long time to heal. The prevention is simple, do not get any liquid ammonia on your skin or in your eyes. If you do, immediately get a **LOT** of water on it to dilute the ammonia. If the water is slightly acidic, such as a soda pop, boric acid solution, or vinegar helps, But just plain old water works wonders, even mud.

The important thing is to act quickly.

H Eyes

Everything said above about the skin applies to the eyes, except you probably do not want to get mud in your eyes. I have seen far too many eyes damaged or completely blinded by splashing refrigerant liquids.

I suggest always wearing eye protection when working with any possibilities of liquid refrigerants spraying or splashing.

I have a lot of problems and discomfort with glasses with side shields, and with chemical goggles fogging up. A much better eye protection is an SCBA (Self Contained Breathing Apparatus) if the ammonia vapor concentrations require an oxygen supply. But my favorite protection is a full face

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shield mounted on a hard hat. Something like you should wear when doing grinding. I get good circulation of air between my face and the shield. No splashing or spraying liquid refrigerant has ever touched my face when wearing the full face shield.

Do not do anything stupid that would allow any type of liquid refrigerant get splashed or sprayed into your eyes.

All refrigerant vapors, specially R-717, will irritate they eyes, make them water and run. But it is doubtful that you will receive any permanent damage to the eyes from just the vapors. Splashing liquid is the bad guy.

In the South East a soft drink bottling plant had a flooded ammonia ice bank sitting outside in the sun shine. The surge drum had a 140 psig relief valve (per code), and was shut down. The low side liquid float valve leaked through and filled the coil and surge drum completely full of liquid ammonia. The dual 150 psig relief valves were brand new. The contractor that had installed them was called because the plant smelled ammonia. Upon inspection by the contractor, the valves were what he called “sputtering”. So to solve the problem, he pounded the relief valves with a hammer. One valve opened, while he was looking directly into the outlet with no face or eye protection. And he attempted to sue the bottling company for his own stupidity.

I Inhalation.

Inhalation of any refrigerant is not desirable. Above we see asphyxiants, anesthetics, narcotics, depression of the central nervous system, possible carcinogens, and toxic products from burning or over heated refrigerants.

The refrigerants, such as the halogens provide no warning, too much and you will simply pass out and die from asphyxiation.

Ammonia will warn you, long before you have any serious threat to health or death. Anyone can identify ammonia at about 4 ppm. OSHA will allow the owner of a business to chronically expose employees to 35 ppm forty hours per week for their working life. This is very stinky! At 50 ppm I get a respirator or SCBA just for comfort working. The EPA tells us that we can safely escape from a 200 ppm ammonia atmosphere in thirty minutes. Who ever wrote this has never tried it out. The problem is the **PANIC** created. Your body will not let you inhale much more than 200 ppm. Your brain says **ENOUGH** and temporarily shuts down your lungs. Talk about panic the first time this happens do you, you know what panic really is. Get **low** and get **out** fast. Ammonia vapor is lighter than air, so stay down, but move.

A good idea is each time you enter a confined space (cooler, freezer, engine room, dock, roof,

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basement where there is ammonia, just think to your self: ***“If ammonia is released while I am in here, what are two safe routes out?”*** You probably will not be able to see very well and if you panic you may run into something very hard. A couple of seconds planning ahead is well worth the effort. You will probably never have to use the planning. But in any event you are a whole lot better off that if you were in the same space and the refrigerant was a halogen or carbon dioxide.

In my opinion, **THERE IS NO EXCUSE** to chronically (long term) be exposed to the vapors of any refrigerant.

However, the State of California has been tracking halogen refrigerants used in supermarkets, and has published a document that indicates that the average annual losses of halogen refrigerants in supermarkets is about 50% of the total charge. This is probably about 1,000 pounds of halogens per year or more that the customers and employees are exposed to and do not know it. There is absolutely no excuse for this. The losses are just plain lazy, sloppy management, construction and maintenance or possibly thievery by employees or service personnel. The newer halogen refrigerants are very expensive, and there is a profitable black market for the older ones.

J Ingestion.

The specifications for writing MSDS data requires statements of the results of ingestion. This is

what I get:

“Ingestion is unlikely because of the physical properties and is not expected to be hazardous. Do not induce vomiting unless instructed to do so by a physician”

Ingestion of any refrigerant is extremely unlikely. Most common refrigerants are a vapor at atmospheric pressure and temperature. But you can contain a liquid refrigerant in an insulated open cup for some period of time and it is possible that someone might pick up a cup, not knowing what he is doing and drink it. I suspect the result would be fatal. The stomach, if the liquid refrigerant got that far would probably explode.

R-134a for example, the liquid in a cup would be at about -15°F. One ounce, ingested would instantly freeze the lips, mouth and tongue. The one ounce would almost immediately expand to about 16 cubic feet of vapor at body temperature. Talk about gas on your stomach!

K CNS (Central Nervous System).

The MSDS data for the halogen and hydrocarbon refrigerants mention depression of the CNS. Dizziness, disorientation, narcosis or narcotic effects. Personally, with a big whiff of any of these, my blood pressure goes up, my heart pounds, my joints ache for several days. This cannot be healthy or

safe for anyone and you do not know it is happening until it is too late to put on SCBA gear.

L Epinephrine (adrenaline).

The MSDS data for halogen and hydrocarbon refrigerants all state for the doctors information, not to use ***epinephrine*** for a patient that has inhaled a lot halogen or hydrocarbon types of refrigerants. Epinephrine, in this situation, can cause heart failure.

The problem is no one knows this. I have quizzed supermarket managers, where most of the incidents occur. They have no idea. I have asked emergency room doctors and paramedics about this and no one knows it is a problem. I have asked the HAZMAT teams. They do know they do not want to breath the smoke from a supermarket fire, but no one has heard of this problem. At least the forty to fifty people I have talked to had never heard that Epinephrine is a problem!

M Fire or Explosion

The halogens are flammable and explosive only when mixed with air or oxygen and under pressure, such as in a hermetic or semi-hermetic compressor that has been serviced and then not adequately evacuated and started. Or in a case where the compressor suction is in a vacuum and there is an air leak on the low pressure side. The sources of the ignition are arc tracks between the

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motor electrical connections and a little water in the refrigerant.

The hydrocarbon refrigerants are flammable in open air at relative small concentrations. Propane for example has a lower explosive limit of 2.2% and an upper explosive limit of 9.5% with an auto-ignition temperature of 896°F. Butane has a lower explosive limit of 1.9% and an upper explosive limit of 8.5% with an auto-ignition temperature of 788°F. Either will ignite with a match, over an open cup of liquid.

This should not create a problem using the hydrocarbons as refrigerants. We pipe hydrocarbons through our buildings for heating and cooking without any panics, and with very few fires or explosions. Europe is using propane for household refrigerators.

Ammonia is listed by the Department of Transportation as “Non-Flammable”. The safety bureaucracy lists ammonia as 16.0% for a lower explosive limit and 27% for the upper explosive limit and an auto-ignition temperature of 1,204°F.

This is interesting. Pure liquid anhydrous ammonia at atmospheric pressure cannot be ignited and will not sustain combustion, with a burning match over an open cup.

Ammonia is made up of hydrogen and nitrogen. Ammonia disassociates at about 1,000°F in

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the presence of a catalyst into its basic compounds (N_2 and H_2). And no odor. I do not know what the testing amounts to. But I very much suspect that the safety bureaucracy is burning hydrogen not ammonia in their testing.

If any one smells ammonia at a fire, the ammonia is blamed for the fire. The products of combustion from burning ammonia are water and nitrogen. The temperature of combustion is not high enough to produce any nitrous oxides, and **there is no odor**.

However, if there is a high pressure ammonia leak and there is a lot of compressor oil in the resulting aerosol (oil, ammonia, and air), the aerosol is very flammable. The oil will burn hot enough to sustain combustion and the dissociated hydrogen will add energy to the fire.

Carbon dioxide and sulfur dioxide are both fully oxidized and there is nothing left to burn. Nor are there any breakdown products from over heating.

N Carcinogens

At present no refrigerants are listed as carcinogens.

However, Harvard University Dental School has been looking into an increase of bone cancers

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in boys from about 6 to 10 years old and the possibility that the fluorine used in drinking water and in tooth paste to protect teeth, may be the culprit. This is the same fluorine that makes up most of the new halogen refrigerants.

There is some serious concern that the fluorine used in drinking water and tooth paste to protect teeth may be a problem. Research indicates that fluorides may be a part of the cause of the substantial increase of osteoporosis problems with elderly women.

The EPA is running investigations along the Ohio River in South Eastern Ohio and Northern West Virginia. It appears that the rate of some specific types of cancers in that area is about four times the national norms. The suspected culprit is a carbon-fluorine product (C_8F_{18} I believe is the formula), in any event it is called C-8 and has been used in that area for fifty years as a raw material for producing Teflon. In the winter of 2006 the press announced that Dupont was fined \$16.5 million for lying about the safety of C-8 and DuPont did not dispute the fine.

All of the current halogen refrigerants are carbon and fluorine, some have a hydrogen molecule compounds or mixes.

For example R-14 (CF_4), R-134a (CF_3CH_2F), R-C318 (C_4F_8), R-410A (50% CHF_3 plus 50% CHF_2CHF_3), R-507A (50% CHF_2CF_3 plus 50% CF_3CH_3), and R-407C (CH_2F_2 , CF_3CHF_2 , CH_2FCF_3).

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There have been rumors in the industry that the fluorocarbon refrigerants are about to go the way of the chlorine based refrigerants.

I seriously doubt that the halogen refrigerants are a chronic health problem to refrigeration service personnel, with the possible exception of the very leaky supermarket refrigeration systems in California where the State reports they are losing 50% of the refrigerant charge annually. This is ridiculous in my opinion.

O Ozone, Global Warming

The idea that Ozone Layer in the stratosphere is being depleted by mankind is still very much a theory. The major blame by the pseudo scientific world is being placed on the chlorine in halogen refrigerants such as R-12, (CCl_2F_2) getting into the stratosphere. The stratosphere exists between 50,000 feet to 115,000 feet above the sea level. Once the chlorine containing halogen refrigerant is exposed to the sun's ultra violet radiation in the stratosphere, the very stable halogen refrigerant is broken down to elemental chlorine, carbon and fluorine.

I have a number of questions.

- a. How does a vapor, such as R-12 at 70°F and atmospheric pressure that has a specific

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volume of 3.12 ft³ per pound, rise to say 75,000 feet elevation, through air at the same temperature and pressure with a specific volume or 13.5 ft³ per pound? More than four times the molecular weight of air. I always thought lighter things went up and heavy things came tumbling down.

- b. A whole lot more chlorine used to bleach clothes, treat water supplies, disinfect bathrooms, swimming pools and cooking surfaces, and bleach paper. Why supposedly would this chlorine not affect the ozone layer?

The answer I get is all these other uses of chlorine washed out of the air by rain. And the halogen refrigerants are chemically very stable and do not break down in the troposphere (where we live). What if it does not rain? Why then do we smell chlorine around a swimming pool, after a clean-up in a food processing plant or in a glass of water out of the tap? If we had elemental chlorine out of the tap it would have a specific volume of 5.38 cubic feet per pound, only 2.6 times the weight of air. Lighter than R-12 but still heavier than air. Does this make sense to you?

- c. Assuming the very heavy R-12 does magically get to 100,000 feet intact and then is broken down into elemental carbon, fluorine and chlorine by unfiltered ultra violet radiation from the sun. How much ultra violet energy does it take to break down the

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CCl_2F_2 molecule? And break down into what? Every one talks about the UV-B producing elemental chlorine. What happens to the carbon molecule and the two fluorine molecules in the break down process? Do we get an unstable CF_2 molecule? Or perhaps two elemental fluorine molecules and one elemental carbon molecule all looking for something like an elemental oxygen molecule to fill the empty twelve places to bind up an elemental oxygen molecules to balance out the chemistry?

- d. The NASA data states that the Ozone Hole over the Antarctic was noticed in 1970's at the British Antarctic Survey Halley Station. In 1985 the "TOMS" satellite was measuring ozone and discovered the "hole", over the antarctic in the winter and late spring. Ozone in the stratosphere is produced by ultra violet radiation from the sun breaking up oxygen molecules which re-associate at O_3 (ozone). During the Antarctic winter, roughly April through September, the earth is between the sun (the source of the UV) and the antarctic. Would it be reasonable for less ozone to be produced in the shade of the earth and during the summer more ozone be produced when the antarctic is in the sunshine?
- e. The white women living in Johannesburg. South Africa, Hobart, Tasmania, Invercargill, New Zealand, Punta Arenas, Chile all knew about the UV or sun burn problems one hundred or more years ago. Women, men and children all wear hats that protect the eyes, face, ears and the back of the neck from the sun. The little kids wear hats that

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resemble the French Foreign hats with a towel in the back, hanging down protecting the ears and back of the neck.

And we just discover the hole in the ozone layer in 1985?

- f. I was privileged to spend considerable time in the Antarctic in 1955 and 1956. I frequently ate with Admiral Byrd, Dr. Paul Siple, Captain Richard Black, Jack Tuck and other Antarctic Explorers. The main topic of discussion was the sun-burn problem (ultra violet radiation). The general agreement was that the 1928 - 1929 was the worst sunburn problem that they had ever experienced. **Almost before the halogen refrigerants had been invented.**

Global Warming, if it is really a problem, will probably eliminate the possibilities of using the hydrocarbons and carbon dioxide as refrigerants in the future. There are a lot of very good Geophysics PHD's, Climatologists PHD's, Geologists PHD's, that believe the seas are warming because of increased volcanic activity. More rain, more snow, and another ice age in the next 100 years. Again theory, but I kind of like the second theory.

P Break Down Products.

Ammonia R-717

The only currently available refrigerant that is biodegradable is ammonia (R-717). Ammonia is a low cost, very smelly and very efficient refrigerant, which is difficult to break down inside a refrigeration system, but readily breaks down when released into the soil or atmosphere..

No one would ever allow 50% of an ammonia refrigerant charge to leak out a supermarket refrigeration system per year. They would fix any ammonia leak as quickly as possible.

Mankind has been using ammonia as a refrigerant for nearly 180 years. Ammonia has been an economical, safe and effective refrigerant much longer than any other refrigerant. The big problem with ammonia is it is cheap and no one could make money selling it to refrigeration or air conditioning.

Ammonia is also a very good nitrogen fertilizer. 81-0-0. It is used directly side dressing crops such as corn. When plowing liquid ammonia into the soil about 8" deep at a rate of 100 pounds per acre, you can walk behind the tractor and not smell any ammonia odor. The ammonia reacts with the moisture and the soil very rapidly forming plant usable nitrates and nitrites almost instantly. Ammonia for agriculture usage is not regulated by OSHA or the EPA. A whole lot more ammonia is used as a

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fertilizer, cleaning solutions, munitions, plastics, metallurgy than is used for refrigeration.

Another major use for ammonia is to produce your automobile engines. Parts are manufactured using powder metallurgy technology. A relatively small plant manufacturing such things as camshafts, valve rockers and other small parts may use 10,000 to 20,000 pounds of anhydrous ammonia per week.

A new use for ammonia is to clean the air to reduce the NO_x (nitrous oxide) emissions for both coal fired and natural gas fired electric power plants. Huge quantities of ammonia are dissociated into hydrogen and oxygen in the stacks. This process removes about 95% of the NO_x by turning the NO_x into N₂ and H₂O, completely natural emissions.

In the event of a FIRE, the break down products for ammonia are water and nitrogen. No odor, no toxicity and no danger to you or the firemen.

Carbon Dioxide and Sulfur Dioxide

In the event of a fire, there are no break-down products from carbon dioxide and sulphur dioxide refrigerants. Both are fully oxidized and will not break down.

Hydrocarbon Refrigerants

The hydrocarbon refrigerants are common fuels. The break-down products from the hydrocarbons burning with adequate oxygen are water and carbon dioxide. However, if the burning hydrocarbons are starved for oxygen, some carbon monoxide, (a chemical asphyxiant) can be produced.

Halogen Refrigerants

The real problem in the event of a fire are the halogen or fluorocarbon refrigerants!

The break down products of the older refrigerants are hydrochloric acid and hydrofluoric acid, carbon dioxide and carbonyl halides.

The break down products of the **New, Safe, Refrigerants** are hydrofluoric acid, carbon compounds such as carbon dioxide, carbon monoxide and carbonyl halides.

The carbonyl radical is CO (one atom of carbon, and one atom of oxygen). In the case of carbonyl halides, they are carbonyl fluoride (COF₂), carbonyl chloride (COCl₂) and carbonyl bromide (COBr₂).

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Carbonyl fluoride is extremely toxic and extremely dangerous. Carbonyl chloride (phosgene) is also a highly toxic chemical asphyxiant, used as a war gas in WWI, and as feed stock to produce organic compounds. Carbonyl bromide was also used as a war gas in WWI. But we are not likely to run into any bromine in a refrigeration system unless you are using R-13B1 as a refrigerant.

I have had no luck in finding any real MSDS data from the manufactures of the halogen refrigerants for Carbonyl Fluoride or Carbonyl Chloride, although in the MSDS data for all halogen refrigerants do mention the carbonyl halides as break down products.

The carbonyl halides listed are also manufactured and shipped as very dangerous pressurized gases. In our case, the problems may be break down toxic problems with carbonyl halides in the event of a fire, with a lack of oxygen and high temperatures.

Back to the 1933 requirements for the ideal refrigerant.

11. It should have a well balanced latent heat of evaporation value per unit of weight.

I believe to be reasonable I should also calculate the cubic feet of compressor displacement to evaporate one pound of the refrigerant for comparison.

For example:

Water (R-718) used as a refrigerant. At 40°F the one pound of water evaporated to one pound of steam at 40°F will grow to 2,444 cubic feet of steam to be removed by a compressor while absorbing 1079 Btu's.

1070 Btu's Latent Heat per Pound of Water

2.27 Cubic Feet of Displacement per Btu of Refrigeration Effect

Or:

Ammonia (R-717) as the refrigerant. At 40°F the one pound of liquid ammonia will expand to 3.97 cubic feet while absorbing 536.2 Btu's.

In bulk quantities ammonia (R-717) sells for about \$760 per ton (\$0.38 per pound) delivered and installed in your system.

536.2 Btu's Latent Heat per Pound of Ammonia

0.0074 Cubic Feet of Displacement per Btu of Refrigeration Effect

Or:

R-134a as the refrigerant. At 40°F the one pound of liquid R-134a will expand to 0.95 cubic feet while absorbing 84.01 Btu's.

The Whole-Sale Price for R-134a to a service company is about \$12.00 per pound at your local dealer. The service man will probably charge about \$25.00 per pound installed.

84.01 Btu's Latent Heat per Pound of R-134a

0.0113 Cubic Feet of Displacement per Btu of Refrigeration Effect

12. *It must have a small relative displacement to obtain a certain refrigeration effect.*

Using **11.** as an example:

Water:

To produce a ton (12,000 Btu's per hour) of refrigeration effect, you would have to remove 27,181 cubic feet of the steam.

Ammonia:

To produce a ton (12,000 Btu's per hour) of refrigeration effect, you would have to remove 88.9 cubic feet of ammonia vapor.

R-134a:

To produce a ton (12,000 Btu's per hour) of refrigeration effect, you would have to remove 135.7 cubic feet of R-134a vapor.

It should be fairly obvious why we do not use water as a refrigerant. Besides turning to ice at most of your required refrigeration temperatures, it would take an absolutely huge compressor to handle and compress the vapor.

13. *The difference between evaporating pressure and the condensing pressure should be a minimum.*

Using **11.** as an example and a condensing temperature of 90°F:

Water:

At 40°F the saturated evaporating temperature of water the evaporating pressure is 0.12172 psia and at 90°F the saturated condensing temperature of steam is 0.69880

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psia. Or a compression ratio of 5.74:1. Or a difference of 0.5771 psi. That is a pretty small difference in pressure, but it is all in a vacuum.

Ammonia:

At 40°F the saturated evaporating temperature of ammonia the evaporating pressure is 73.32 psia and at 90°F the saturated condensing temperature of ammonia vapor is 180.6 psia. Or a compression ratio of 2.46:1 and a difference in pressure of 107.3 psi.

R-134a:

At 40°F the saturated evaporating temperature of R-134a the evaporating pressure is 49.724 psia and at 90°F the saturated condensing temperature of R-134a is 119.0 psia. Or a compression ratio of 2.39:1 and the difference is 69.3 psi. A bit better than ammonia in compression ratio, and a lot better in the pressure difference.

I am going to add an item that was not of importance to refrigerants in 1933. And that is disposal of surplus or used refrigerants.

14. *Disposal of Surplus or Used Refrigerants*

In general, government regulations will not allow any release of any refrigerant to the

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atmosphere. All lubricants and refrigerants, by regulations are to be handled as a hazardous material and by licensed disposal companies, and by personnel trained in the proper disposal methods.

Halogens are to be recovered, reworked and reused.

Hydrocarbons are not regulated at present.

Ammonia is not really regulated, but do not release it and cause a panic. If you have some ammonia to get rid of, it can be sold to the electric power plants and they will use it to control their NOx emissions. It can be sold to the sintered powdered metallurgy plant and they will dissociate it for their production uses. It can be sold to a farmer that uses ammonia for a fertilizer. He will drain off any oil before application. Or you can flare it off yourself. No panic, no air or water pollution and little expense. By regulations you are not allowed to release more than one hundred pounds in any 24 hour period without immediately notifying the U. S. Coast Guard. The government does not tell us whether “immediately” means at the beginning of the 24 hours or at the end.

Summary

I probably have less emotional prejudice than anyone in the refrigeration or air conditioning business for or against any refrigerant. I realize that there are huge emotional ties (frequently not very

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logical) to refrigerants, types of systems and equipment in this business. I have attempted to be fair, but provide real technical information.

My real prejudice is for the life, health and safety of the operators, maintenance and contract service personnel involved in operating and maintaining any type of refrigeration system.

All refrigerants are dangerous. Specially if the person involved, including middle management, normal plant labor, and outside contractors that have not been trained, and does not know what they are doing or directing someone else to do.

The more you know about the equipment and the refrigerants you are dealing with, the safer you and those around you will be. Use your head, do not take chances, and learn everything you possibly can. And do not be afraid to say NO if you get an unsafe or stupid order to do something. It is your responsibility to work safely and not someone else's.