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SOME SAFETY STUDIES OF A TERNARY REFRIGERANT

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ABSTRACT

A ternary blend of refrigerants composed of HCFC-22, HCFC-142b (chlorodifluoroethane), and a small amount of isobutane, has been used as a drop in substitute for CFC-12 and R-500 refrigerants. It's use as a refrigerant was presented at the Purdue 1992 International Refrigeration Conference--Energy Efficiency and New Refrigerants[1].

This paper will cover safety related issues and testing performed to date. Results of fractionation and flammability testing will be presented. Comparisons of flammability, energy of combustion, and rate of combustion with ammonia, and hydrocarbons will also be shown.

INTRODUCTION

There are several problems to developing a "*drop-in*" substitute for CFC-12 for use in existing equipment. The substitute must have suitable thermodynamic properties, be nonexplosive and nonflammable or very weakly flammable at best, must be miscible with mineral oil, must be compatible with system materiels, must be low toxicity or be an "old" substance which has established toxicity, and finally it must be affordable.

While acceptable for new equipment manufacture, HFC-134a is not a simple drop-in for CFC-12 in existing applications. HCFC-134a is not miscible in mineral oils used in CFC-12 systems. Nonmisicibility may cause oil to become entrapped "logged" in the evaporator, causing low performance and compressor failure due to oil starvation. Newly developed lubricants, such as polyalkylene glycol (PAG) based (for automotive use) and polyol ester based (for most everything else) lubricants, are useable in newly manufactured equipment, which is usually built in clean, uncontaminated environments.

However, for equipment which has to be serviced in the field, such as CFC-12 equipment which has been retrofitted to HFC-134a and one of the above oils, there are still be problems to be overcome. PAG oils are very sensitive to moisture contamination, and will break down in the presence of chlorides (from CFC-12 previously being run in the system). It is usually impossible to "flush" the chlorides since they are tightly embedded on the inside surface of parts. Aluminum, in particular, will have the inside surfaces partly converted to aluminum chloride. Ester based oils are more tolerant of residual chlorides, but *are very sensitive to moisture contamination.* Ester oils may break down into fatty acids and alcohols from contamination. Also, both PAG and Ester oils may sometimes have problems maintaining enough lubricity in CFC-12 equipment. Much research is underway worldwide to solve or reduce these problems. In addition, materiels used in components of some older compressors are incompatible with many synthetic oils. Both PAG and ester oils may also have thermal stability problems[2], although it is possible that the use of various additives may mitigate this problem.

There currently exist suitable blends which may be "*near*" drop-in substituted for CFC-12 in some applications, provided the oil and desiccants are changed. R-401a/b/c may be used if the oil is changed to an alkylbenzene based lubricant, and driers may possibly need to be replaced with XH-9 molecular sieve. However, it may sometimes be a hassle to change out the oil, especially if the compressor does not need replacing. The HFC-152a in these blends might have some problems of breakdown above internal temperatures (valves and bearings) over 150°C (302°F) [3]. It also may be possible for some R-400 series blends which contain flammable component(s) to remain nonflammable during *a single fractionation vapor leakdown* in the currently tested temperature range (-20°C to +80°C) and receive an A1/A1 safety classification. However, if partial leakage occurs in the field, and systems are repeatedly topped off, it might be possible to become flammable (ignoring the oil for the moment). Even some R-500 series azeotropes may fractionate under certain temperatures[4]. In most cases, the flammability will be of a "*weak*" nature and not be a problem. It has been the experience of these authors that service personnel will top off leaking systems with R-400 series (zeotropic blends which change composition upon vapor leaking) blends, even when told not to. The time and/or expense of removing the existing fractionated charge, and charging with virgin refrigerant seem to override the topping off prohibition. Any weak flammability incurred from repeated topping off a leaking system, for the most part will be inconsequential compared to other flammability risks, such as the compressor oil dissolved in the refrigerant.

Small equipment such as beverage coolers, ice machines, walk-in coolers, etc, contain appropriate service fittings for charging or removing refrigerant, but they often lack access methods to for conveniently changing the oil. Retrofit procedures from CFC-12 to HFC based refrigerants often call for multiple oil changes, with each change reducing the amount of mineral oil down to some standard, usually a few percent[5]. Often, the compressor must be removed by unsweating (unbrazing) the refrigerant lines to effect an oil change. In the field, proper service techniques are often skipped, such as using dry nitrogen in refrigerant lines during brazing operations. Refrigerant gas in the lines quickly decomposes info hydrofluoric (also hydrochloric if CFC/HCFC gas) acids and other byproducts under temperatures of 1200°F (648°C) or more. The same process occurs during a hermetic compressor motor "*burnout*" which fills a system with acids and other contaminates and necessitates a proper cleanup such as flushing, acid removal driers and filters, and oil changes. Most service technicians realize the consequences of a motor burnout, however, a much smaller number realize the contamination added to a system by the numerous brazing operations (without an "inert" filler gas) needed to carry out multiple oil changes. A retrofit procedure calling for changing oil five times, may need the compressor removed five times, 5 unbrazings, 5 rebrazings, on 2 lines or 20 total brazing operations on a system, compared to two operations for a compressor change. This greatly increases the chances of contamination and subsequent burnouts on a system. Often, the HFC refrigerant or the lubricant will take the "blame" instead of the excessive brazings or other poor service techniques.

A refrigerant blend has been developed as a *drop-in* replacement for CFC-12. It uses the existing compressor mineral oil and does not require an oil change (unless the oil is already contaminated from a burnout). This blend is composed of 4/41/55 weight percent of R-600a/HCFC-142b/HCFC-22. For the noncommercial purposes of this paper, it will be known as BLEND-A. The ASHRAE SPC-34 committee has recommended a number assignment of R-406A and a safety classification of A1/A2[4]. This implies the blend is the lowest toxicity group and nonflammable as formulated. The /A2 classification applies to conditions where the blend may have leaked (fractionated) and changed composition, and may have possibly become weakly flammable[6]. A2 refrigerants have much less flammability, higher lower and upper ignition limits, and have lower heats of combustions than do the "*highly*" flammable and explosive classification of A3 (e.g. pure propane or isobutane).

SERVICE EXPERIENCE

BLEND-A has been used in several thousand pieces of equipment, including automobiles, semi trucks (both for passenger A/C and cargo refrigeration), vending machines, ice machines, tractors, beverage coolers, ice cream machines beginning in late 1990. There have been no reports of any problems related to flammability during either service, use or accidents. There have been several cases of hoses bursting in mobile A/C service, due to mechanical defects in the hose, or from related problems such as condenser fan failures. In all cases, the usual refrigerant/oil fog cloud was observed and no ignition occurred.

BLEND-A has been removed from equipment with CFC-12 recovery systems in the vapor state. This induces worst case fractionation in the system being emptied of refrigerant. Unbrazing the lines to the compressor (slight positive pressure) showed no abnormal signs of fire. Only the usual small flames from the oil coating inside the lines were observed. The same conditions were observed for unbrazing lines when the system contained CFC-12. Compressors were also unbrazed after removing BLEND-A to 20 inches (50.8 cm) vacuum. Flame from the torch was sucked into the compressor shell along with air as the connection came apart. No fire or explosion resulted. During a deliberate test, a compressor suction line was unbrazed with 27 PSIG (186 kPa) vapor-only charge of BLEND-A. As expected, burning oil was blown onto the front of the service technician (in full fire fighting gear). Other than burning oil, no other fire or explosions were noted. Unbrazing a pressurized CFC-12 system produced similar results (no liquid refrigerant).

FRACTIONATION AND FLAMMABILITY TESTING

BLEND-A was tested by a commercial safety testing laboratory for flammability and fractionation[7,8]. Gas compositions were measured using a gas chromatograph. Helium was the carrier gas. The worst case fractionation composition was tested for flammability using the ANSI/ASHRAE Standard 34-1992 and pressure output using a 7.8-liter chamber. A wooden kitchen match, fired by a electric heating coil was used for the ignition source.

Fractionation tests were conducted at -20C, 20C, and 80C. Both liquid and vapor were leaked, while measuring both remaining liquid and vapor compositions. At 80C, vapor leak, almost no fractionation occurred. At 20C, and -20C fractionation did occur for vapor leaking, but not for liquid leaking. Colder temperatures produced more severe fractionation. In the remaining liquid and vapor, the mass percent of HCFC-22 decreased with vapor leaked, the mass percent of HCFC-142b increased, and the mass percent of R-600a remained constant or decreased slightly. Figure 1 gives room temperature fractionation. Figure 2 shows the flammability limits of various concentrations of HCFC-142b and HCFC-22 while holding the R-600a constant at 5 percent (by volume).

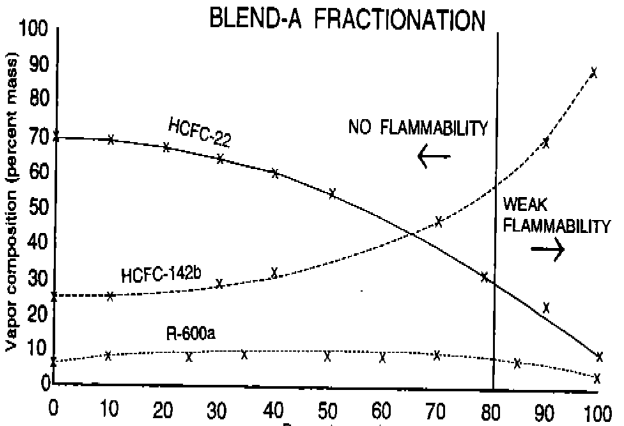

Figure 1. Vapor composition (by mass) verses mass loss during vapor leak at 68° F (20° C)

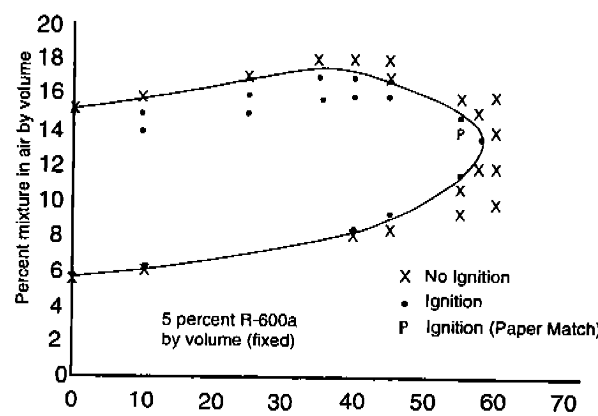

Figure 2. Flammable zone curve for 5 percent R-600a, HCFC-22 and HCFC-142b

As one can see, BLEND-A can fractionate to a weakly flammable state. The extremely flammable R-600a (isobutane), more or less remains constant and then slowly decreases. The worst case fractionation closely approximates the weak flammability of HCFC-142b. Pure HCFC-142b has no flash point, and has a LFL-UFL (lower/upper flame limits vol. % in air) 7.1-18.6 using a match for ignition (ASTM E-681 in 5L vessel)[9,10]. On the other hand, pure hydrocarbons, such as R-600a have much lower LFL-UFLs (1.8-8), much higher heats of combustion, and much higher rates of combustion pressure rise than HCFC-142b. HCFC-142b LFL-UFLs show quite a bit of variation depending on conditions, and ignition sources which implies this fluid is difficult to ignite and keep burning. Other reported LFLs for HCFC-142b range from 6.7-9.0[9,11] and UFLs range from 14.3-18.6. Highly explosive/flammable hydrocarbons, have easily determined/reproducible LFL-UFLs which are almost independent of source/method of ignition[10]. One can pour worst case fractionated BLEND-A or pure HCFC-142b on the ground, ignite it, and stomp out the flame with one's foot. Often the flame self extinguishes from combustion byproducts. The same fluids poured into a coffee cup will self extinguish in about one second. Using a propane torch to ignite vapor or liquid venting from a cylinder only results in combustion only while the ignition source is present. One the torch is removed, neither liquid nor vapor remain ignited. One cannot do these things with isobutane or propane. Test shots in a flammability test chamber, contain measured amounts of the substance under test and air, which are stirred into a uniform mixture before ignition.

Refrigerant leaks, often result in the refrigerant hugging the ground in a highly concentrated region and may produce different results than a test chamber. In a real leak of weakly flammable refrigerant, the flame tends to exist only at the air/refrigerant boundary. Many building codes, fire codes and flammability standards, make the false assumption, that for flammability calculations, the leaking mixture will disperse and evenly mix with the entire volume of the area under question. Unless leaked into a moving air stream, most refrigerant gasses (except for hydrogen, helium, methane, and ammonia) are heavier than air and will creep along the floor seeking out ignition sources. Thickness of the leaking gas cloud is often in the range of 6 inches (15 cm). This can be safely demonstrated by pouring liquid nitrogen on the floor and observing the "cloud" (cold nitrogen is more dense than room temperature air and behaves like a refrigerant gas cloud).

Heat of combustion comparisons

Table 1 presents the heat of combustions of fractionated BLEND-A and some various other materials for comparison. The calculations[7,8] were made using the REFVAP1 computer program. DIPPR[12] data is also presented. Note that BLEND-A, fractionated worst case (80% mass leaked, 68° F (20° C)) shows a heat of combustion very close to that of pure HCFC-142b which is around 4,100 KJ/Kg. Note that this heat of combustion for the weak flammability of fractionated BLEND-A or HCFC-142b is an order of magnitude less than that of R-600a. Also note, that HCFC-22 does show a small heat of combustion, although it is nonflammable at 1 ATM pressure. However, HCFC-22 does burn with large quantities of air under pressure of around 50 psig (345 kPa) or greater.

Combustion pressure output

Table 1 compares combustion pressure rise results, using a 7.8 L metal chamber with wooden match ignition, of BLEND-A with R-600a and R-717 (Ammonia). Although R-717 is classified as "*nonflammable*" by the US Department of Transportation, it does indeed burn and results in similar pressure rise to fractionated BLEND-A. The rate of pressure rise for R-717 is around 2.7 times greater than that of BLEND-A. The rate of rise for BLEND-A is 6.5 times less than that of R-600a.

Table 1. HEATS OF COMBUSTION CALCULATIONS

MATERIAL	ΔH COMBUSTION KJ/Kg (DIPPR DATA])	ΔH COMBUSTION KJ/Kg SCE CALCULATIONS
R-600a (Isobutane)	45,576	45,583
HCFC-142b	2,620	4,098
HCFC-22	760	1,658
BLEND-A fractionated worst case 34 % wt R-22 63 % wt R-142b 3 % wt R-600a	-	4,129

Table 2. COMBUSTION PRESSURE OUTPUT RESULTS

Material Tested	Concentration (percent Vol)	Pressure Rise (psig)	Pressure Rise Rate (psi/sec)
BLEND-A (fractionated) 35% R-22 60% R-142b 5% R-600a by volume and air	10	No pressure output	-
	12	56	262
	13	52	166
	14	51	120
	15	52	466
	16	10	-
R-717 (Ammonia) and air (reference)	16	No Pressure output	-
	20	25	832
	22.5	25	832
	25	57	1,248
	27	57	832
	28	25	872
R-600a (Isobutane) (reference)	2	45	832
	3	118	3,052
	4	122	2,790
	5	102	1,308
	6	24	174
	7	15	436

CONCLUSIONS

BLEND-A is nonflammable for the first 50-80 percent of mass loss due to vapor leaking, and only becomes "*weakly flammable*" after that. Given the difficulty of igniting and maintaining combustion of BLEND-A (worst case fractionated) or HCFC-142b, both with low heats/rates of combustion, we feel that the added risk is minimal for the use of BLEND-A or other weakly flammable refrigerants in many small to medium sized systems as a replacement for CFC-12. It may also be practical in larger systems, when "*composition management*" is employed (Adding HCFC-22 to a leaking system every now and then to restore static pressures after "topping off" with BLEND-A) to keep the refrigerant nonflammable and functioning within limits.

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