



Investigation of CFC Substitutes to Arrest Ozone Depletion

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Abstract: Ozone is a molecule containing three oxygen atoms which is blue in colour and has a strong odour. Ozone is considered as helpful in the stratosphere and harmful substance in the troposphere. Most atmospheric ozone is concentrated within the stratosphere, about 15-30 km above the Earth's surface. Chlorofluorocarbons (CFCs) are a family of chemical compounds developed back in the 1930's as safe, non-toxic, non-flammable alternative to dangerous substances like ammonia for purposes of refrigeration and spray can propellants. Their usage grew enormously over the years. One of the elements that constitute CFCs is chlorine. Very little chlorine exists naturally in the atmosphere. But it turns out that CFCs are an excellent way of introducing chlorine into the ozone layer. The ultraviolet radiation at this altitude breaks down CFCs, freeing the chlorine. Under the suitable conditions, this chlorine has the potential to destroy large amounts of ozone. This has indeed been observed, especially over Antarctica. Since the cognizance of adverse influence of halogenated refrigerants in the stratosphere and in troposphere, as proclaimed at the Montreal protocol with subsequent enactment of NASA Act in 1987, the home appliance manufacturers are seriously considering replacement of Chlorofluorocarbons (CFCs) by alternative fluids in all the factors of their ever increasing market say, on refrigerators, as a blowing agent for foams, as a cleaning agent for printed circuit boards and the like, much ahead of the EPA schedule. The paper presents a scenario of the research efforts in the field, both by individual investigators and entrepreneurs with necessary recommendations.

Keywords: Refrigerant, Chlorofluorocarbons, Threshold Limit Value, Ozone Depletion Potential

1. Introduction

Halogenated refrigerants, termed Freons in informal contexts, are identified by R-numbers that denote the amount of fluorine, chlorine, carbon, and hydrogen present. The wide spread use of Chlorofluorocarbons (CFCs) in the Heating, Ventilating and Air Conditioning (HVAC) equipment, as a foam blowing agent, sterilant gas diluent, and aerosol propellant and as a food processing fluid is because of their better thermodynamic properties, long life and convenience in their use. Earlier the home appliance manufacturers in USA alone were supposed to consume such fluids at the rate of 300 million pounds (136 million kgs) a year. All consumers and most other aerosol products made or sold in USA now use propellants—such as hydrocarbons and compressed gases like nitrous oxide—that do not deplete the ozone layer. The extensive use has been arrested after the revelations of monila and Rowland in 1974 that such fluids being stable at lower atmosphere escape to the stratosphere where these split and release chlorine molecules in presence

of ultra-violet rays and then, to hydroxyl radicals in troposphere that react freely with ozone and deplete their presence as a protective layer against skin cancer and other generic damages to the human race. It has also caused the overall warming of the atmosphere. The Montreal protocol attended by various countries including India in 1987, signed an enactment, as a landmark agreement, which stipulated that the requirements of production of ozone-depleting substances (ODS), R-12 (Dichloro-difluoro-methanes) by the year 1998 be reduced by 50% as compared to 1986 levels. In course of subsequent years it is envisaged that the accords would be more and more stringent. In the year 2000, CFCs were banned from use and guidelines included new phase-outs for HCFCs and HFCs by the year 2020 if possible, and no later than 2040.

The present day manufacturers under such agreement are being faced with an uphill task in finding a substitute because of short time available for design changes, product life tests and for retooling their production lines.

In a bid for searching out the suitable alternative fluids and mixtures, the investigators first enlisted about 940

substances, conducted logical screening and shortlisted to only a few of them that would retain similar properties as low energy consumption, compatible Co-efficient of Performance (C.O.P) and produce minimum impact on ecological balance. Before such an analysis is presented it is advisable to have a kaleidoscopic view of the previous attempts in the history of refrigeration.

1.1. Back Ground History

A good number of refrigerants have been tried since the days of Jacob Perkins in 1835, who first devised the vapour compression machine with a refrigerant which he called Cadutohnuoine. It was a destructive distillate of India rubber, which was used that time as an industrial solvent for engravings in bank notes [1]. Alexander Turing in 1850 and later, F. Bramwell in 1880 both used ethyl alcohol as refrigerant. Ammonia along with ether and alcohol, called R 717 was recommended and used by James Harrison as a refrigerant mixture, in 1856. In 1863, Charles R. Teller of France devised a methyl ether compression machine, for transporting chilled meat to South America by Sea. It was, however, recognised that ether is flammable and is susceptible to fire hazards. In 1884, W. Raydt used a compression ice making system using carbon dioxide (R 744) as refrigerant; Racul Picket used a sulphur dioxide compressor in 1876, because SO₂ also acted as a self-lubricant. In 1879, C. Vincent of France applied for a British patent using methyl chloride (R 40) as the refrigerant in his vapour compression machine. R 40 was found to have anesthetic and toxic effects and it was mildly flammable. It reacts vigorously with aluminium container. Till the year 1942, R42 was commercially used as refrigerant in household units but its use declined after 1950. Other refrigerants were also tried by several investigators. Ethyl chloride (R160) was used by C. Palmer in 1867 with a trade name, Clothel. In 1860, Charles Teller, and also, Andrew Muhl used a combination of methyl amine (R630) and ethyl amine (R 631) as refrigerant. J. Gamgee in 1870 applied for a British patent for use of methyl acetate or methyl formate (R 611) or, nitrous oxide, asrefrigerating agent. R 611 was used by the General Electric in the year 1930 in their rotary compressors. Carbon tetrachloride (R10) was first introduced by Maurice Le Blanc in 1992. By the year 1920, small compressors were using isobutane (R 60) with a trade name, Freezol. Dr. Willis Carrier of Germany, who is considered to be the father of centrifugal refrigeration, used dichloroethane (1130) in the trade name of Dielene or, Dieline. He also experimented with trichloroethylene (R1120) as a refrigerant but with not much of success. Later, between 1926 and 1933, he introduced the use of methyl chloride or dichloro methane (R32) with the trade name Carrene. By the year 1890, chloro fluoro carbons appeared in the market. Dr. Thomas Midgley Jr. developed dichloro- mono fluoro-methane (R21) in the General Motors Research Laboratory, for use in their Frigidare units. Later, dichloro-difluoro-methane (R12) was introduced by Du Pont for fluorinated products with trade name, Freon. The later was commercially available in the

market by the year 1931. Frigidare Corporation used both F11 and F12 in their refrigeration system. Commercial production of other refrigerants in the series followed in succession namely, R13 in 1943, R14 in 1955 and R502 in the year 1962.

1.2. Study of Chemical Nature

Although Fluorine Chemistry was first published by Swarts in 1890, the detailed study of chemical nature of refrigerants was made by Midgley and Associates. They observed that relatively a few agents in the Periodic Table combine to form compounds that provide refrigerating effects. Attention was first directed to fluorine products like, carbon tetra fluoride (boiling point, B.P. -128⁰C). Because of general toxic character exhibited by such refrigerants, a threshold limit value (T.L.V.) for each refrigerant was established by the American Conference of Government and Hygienists (ACGH) in 1983-84 [2].

Fluorocarbon gases are generally greenhouse gases with global warming potentials 100 to 20, 000 times that of carbon dioxide. These chemicals have atmospheric life time long enough to allow them to be transported by wind to the stratosphere which catalytically destroys ozone.

Exposure to strong UV radiation breaks these molecules to release chlorine or bromine in atomic state. One chlorine atom can destroy over 100,000 ozone molecules. Reduction in ozone levels will lead to higher levels of UVB reaching the Earth's surface. Figure 1 shows the image of the largest Antarctic Ozone hole.

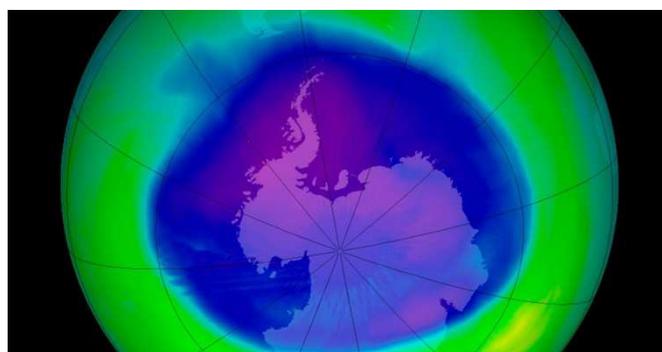
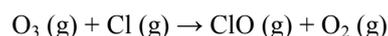
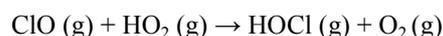
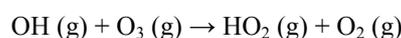
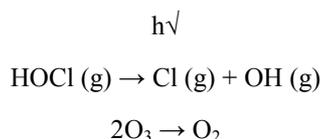


Figure 1. Largest ozone hole (NASA).

$$h\nu$$


Atmospheric models indicate that the chlorine cycle plus the analogous bromine cycle account for more than 70% of the ozone loss in the stratosphere. The remainder of the catalytic cycle for chlorine and ozone depends on OH radicals that exist throughout the atmosphere. OH reacts with ozone to form the intermediate HO₂.





As stated earlier, the exhaustive list of 940 substances as alternatives to R12 and the CFC Family, was pruned in succession by first excluding those which fell under “hard criteria” like, toxicity, instability, Ozone Depletion Potential (ODP) and chemical hazard, that could not be compromised under existing regulations and then, flammability and commercial availability. The later can be relaxed to some extent in selection.

All toxic substances with Threshold Limit Value (T.L.V.) above 200 ppm, carcinogenic and teratogenic substances were eliminated from the list, because of stringent regulations of Environment protection Agency (EPA). Instability, being expressed as possibility of reacting with

itself or, reacting with materials used heat pumps like, aluminium, copper, iron etc., with lubricating oil (polymerization) was taken as the next criterion for elimination. Of course, any halogenated refrigerant that would cause depletion of ozone layer in the stratosphere were not considered at all.

The rest of the substances were scrutinized according to the compatibility of physical properties with CFCs like boiling point, critical temperature and pressure. A general performance measure was evolved by relative weighing technique of characteristics like, Coefficient of Performance (C.O.P), volumetric heat storage, pressure ratio, voltage consumption of home compressors and others. A logical priority was made for the remaining substances as potential candidates for replacement of CFCs. Table 1 provides a collection of seventeen prospective substitutes, along with R11 and R12 refrigerants for comparison.

Table 1. Thermodynamic Properties of Screened Refrigerants.

Refrigerants		Formula	Physical Properties			Performance Characteristics		
No	Name		Boiling point	Critical Temp. °C	Critical Pressure	Volume 1000 M ³ / Kg	C.O.P.	Capacity Kw
R11	Trichlorofluoro ethane	CCl ₃ F	23.8	198	4409	1.8	4.96 ⁺	–
R12	Dichlorodifluoro Methane	CCl ₂ F ₂	29.8	112	4146	1.8	4.39 ⁺	–
R22	Chlorofluoro Methane	CH ₂ ClF	40.8	96	4978	1.9	3.0(4.3 ⁺)	9.65
R32	Methylene Fluoride	CH ₂ F ₂	51.6	78			3.1	5.5
R123	Dichlorotrifluoro Ethane	HCCl ₂ -CF ₃	27.6					
R124	2-Chloro-1,1,2,2-tetra fluoro Ethane	F ₃ C-CClF	12	146	3544	1.85	2.8	2.8
R124a	1-Chloro 1,1,2,2- tetra Fluoro ethane	ClCF ₂ -CHF ₂	10.2	127	3720	1.8		
R125	Penta Fluoro Ethane	F ₃ C-CHF ₂	48.5	68	3834	2.3	2.6	9.23
R134	1,1,2,2-Tetra Fluoro Ethane	F ₂ CH-CHF ₂	19.8	114	3430	2.1	2.4	
R134a	1,1,2,2- Tetra Fluoro Ethane	F ₂ CH-CHF ₂	26.5	101	4067	1.95	2.9	5.9
R142b	Chloro Difluoro Ethane	ClCH ₂ -CHF ₂	9.8	137	412.3	2.3	3.0	3.2
R143a	Trifluoro Ethane	F ₃ C-CH ₃	47.6	73	3760	2.3	2.8	10.6
R152a	1,1-Difluoro Ethane	F ₂ CH-CH ₃	25	114	4496	2.7	3.0	5.7
R218	Octafluoro propane	F ₃ C-CF ₂ -CF ₃	39	72	2689	1.6		
C318	Octafluoro Cyclo Butane	C ₄ F ₈	5.8	115	278	1.6	2.6	2.5
717	Ammonia	NH ₃	33.3	133				
160	Ethyl chloride	C ₂ H ₅ Cl	12.4	187.2	5271	3.0	4.39 ⁺	
	Ethyl Bromide	C ₂ H ₅ Br		230	6230		4.63 ⁺	
	Propyl Chloride	C ₃ H ₇ Cl		230	4580		4.6 ⁺	

Several mixtures of refrigerants were also included in the list. There has been a consensus opinion about six top ranking alternatives which are categorised as follows:

1. Pure category: R152a; R134 and R134a
2. Binary mixture: R134a/ R152a, in proportions of 75/ 25
3. Sandwich type ternary mixture: R22/ R152a / 124 in proportion of 35 / 25 / 40 and R134a / R152a / 124 in proportions of 60 / 25 / 15.

This ternary type is included in the list with two fold objectives of overcoming immiscibility problems and of minimising heat transfer degradation through minimum temperature glide.

2. Results of Experimental Investigations

The Latest Experimental work in the field has been directed in identifying suitable alternatives by the screening process and in validating their performance characteristics with the CFCs presently in use. Some of the pertinent observations reported in the process are summarised below:

One of the earliest set of investigators [3] have identified three distinct cases of industrial use of compressor heat pumps:

Case I: for boosting temperature from 20°C – 70°C using low grade waste heat.

Case II: for boosting temperatures from 60°C - 120°C, using low grade industrial waste heat.

Case III: for boosting temperatures from 90°C -150°C with high grade industrial waste heat.

For case I, ethyl chloride showed the highest C.O.P. and comparable volumetric heat storage.

For case II, ethyl bromide and propyl chloride were found to be superior to R₁₁₄ (1, 2 dichloro tetrafluoro ethane, CClF₂-CClF₂) and R₁₁₄ B₂ (1, 2 dibromo tetrafluoro ethane, CBrF₂-CBrF₂).

For Case III, no refrigerant was found suitable, pure water may be taken as a candidate but it leads to high compressor outlet temperature and low volumetric heat storage and is thus found unsuitable.

Another investigator used standard experimental procedure to measure the isochoric PVT data of R_{134a} and compared with R 12 refrigerant [4]. He observed that both have similar properties and both are non-flammable. R 12 has a slightly higher value of critical temperature, pressure and density, whereas it has a lower boiling point than R_{134a} (B.P. -26.5°C). The vapour pressure curves overlap within the range of -60°C and 30°C. Considering idealised cycles under identical flow conditions within the fixed evaporator and condenser temperatures and a high heat of vapourisation over R 12 refrigerant by about 50KJ / Kg.

Considering the fact that R_{134a} and R₁₂₃ refrigerants are the leading candidates to replace R₁₁ and R₁₂, the thermo dynamic properties like, critical point, vapour pressure, saturated liquid and vapour volumes, superheated PVT surfaces, etc., for these two new substitutes were recorded in detail by Mc Linden et al [5], in the form of diagrams and tables, using Modified Benedict Webb Rubin (MBWR) equation of state and a FORTRAN sub-routine. Although these are quite valuable for reference, the leading manufacturers in U.S.A. are having their own data base, taking into account the commercial impurity inherent in such refrigerants.

The feasibility of ammonia as a substitute to R 12 under the prevalent stringent conditions was reconsidered [6]. Ammonia has a valuable property that it is benign to environment although it has drawbacks like possessing detectable toxicity, requiring periodic filling (charging) and attacking copper base alloys. It has better heat transfer properties as regards reduction of high pressure at the heat exchanger by a maximum of 30% when compared to R₁₂. The limitations are in the use of desuper heater to take away large amount of heat generated in the system and because of the problem of breakdown of lubricant at high discharge temperature. However, the said author recommends the process of recycling liquid ammonia back to compressor so as to keep the vapour cool and thereby avoid the above mentioned ill effects.

Separate attempts were made by independent authors in using Non-Azeotropic Refrigerant Mixtures (NARMs) as substitutes [7]. They concluded that in order to improve the C.O.P. of NARMs for their application in air conditioning, the temperature glide of the mixture in the condenser and evaporator should range from 10 to 44 for better trade off. The efficiency gain up to a temperature glide of 16.7°C is

optimal, beyond which it decreases.

While selecting the ingredients in this mixture it is the normal practice to pick one of them as flammable and combine it with another that is non-flammable. Further for better compatibility, the polyglycol base lubricants are replaced by ester base oils that yield higher efficiency and long term life. The said author recommended the use of R32/ R124 and R143 / R124 mixtures in his final analysis.

HCFC compounds react differently from CFCs because HCFCs contain a hydrogen atom, which causes these chemicals to decompose photochemically before they reach the stratosphere. HFCs do not contain chlorine and thus do not attack the ozone layer. HCFCs and HFCs survive in the atmosphere for 2 to 40 years, compared with about 150 years for CFCs. Important HCFCs include R-22, chloro difluoro methane, and R-141b. The main HFC is R-134a with a new type of molecule HFO-1234yf, a Hydro fluoro olefin (HFO) coming to prominence owing to its global warming potential of less than 1% that of HFC-134a.

3. Consequences of Green House Effect

The report of weather satellite NIMBUS -7 has convincingly proved the presence of an ozone hole in the Arctic, and a decline in ozone layer in the southern sky by 2.5% within the period 1975 and 1985. Another effect of global warming has been revealed by the melting of polar ice. The later has been caused by free release of industrial gases like carbon dioxide in the atmosphere (49% contribution), methane (18%), and nitrous oxide (6%), apart from CFCs contribution to 14%. It is really quite late to realise the extent of damage done to the environment, threatening the very existence of mankind. As per statement of E.P.A.,

“It will take 100 years to reach the present level and another 75 to 100 years to reach the concentration level, before CFCs”.

Some of the global changes recorded as a result of greenhouse effect are listed below:

Increase in the number of hot days in a year.

Rise in the level of sea water due to melting of polar ice.

Topographical changes including increase in the moisture content of the soil.

Surface erosion.

Reduction in the yield of crops like wheat, rice and sugar maple.

As per 2009 figures, many countries have been found to be responsible to add to the Greenhouse effect [8]. Figure 2 shows the details in a pie chart. Further, as per reports of IPCC (UN) in September, 1990, we are certain of the following: Emissions resulting from human activities are substantially increasing the atmospheric concentrations of Greenhouse gases (GHG).

Global Energy Related Emissions by Region - 2009

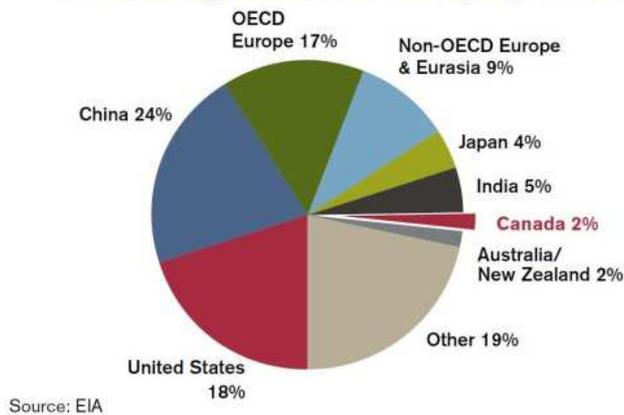


Figure 2. Global GHG Emissions.

These increases will enhance the Greenhouse effect, resulting on additional warming of earth's surface.

The changes predicted to occur by about middle of the next century due to increase in the Greenhouse gas concentrations from the business as usual emissions, will make the global mean temperatures higher than they have been in the last 150,000 years.

The long live gases would require immediate reduction in emissions from human activities of over 60% to stabilise their concentrations at today's levels.

It is further estimated that in case, the 18 cft. (0.51m³) home refrigerators are allowed to use CFC 11 and CFC 12 refrigerants at the present rate, it will raise the environmental temperature, in general, by about 0.0269°C, by year 2075 A.D [9]. With substitutes like R 134a, R152a and NARMs, the general rise within the same period is estimated to be of the order of 0.0246, 0.0222 and 0.0207°C respectively. If the NARMs are used with superinsulation, the rise would be insignificant of the order of 0.0126°C only. Because of such alarming future estimates, most of the countries have not their own targets either for stabilization or reduction in the use of CFCs.

Leading manufacturers are also searching for alternatives independently. Their engineers and scientists are rather redesigning components for increasing the overall efficiency of their system. Use of some bio- substances like orange peels or mixture of pulp wood and citrus fruit rinds with limonene and other agents (Bioact-KC-7) have been tried as replacement for CFC 113, with a grand success[10].

AT & T has eliminated the use of CFCs in cleaning printed circuit boards and is using 'low solidus flux' instead. A modified vertex tube has been designed by Texas instruments to provide a stream of cold air at minimum 40°C as alternatives to CFC sprays.

4. Conclusion

Although there appears to be an all-out effort to curb the use of environmentally active agents, it is a fact that no development can progress without disturbing the environment. The engineering fraternity and environmentalists can definitely take it as a challenge to make good of the ill effects like ecological degradation, environmental pollution as well as in resource depletion through other means rather than simply finding a substitute [11]. As an international response in 1987 an international meeting in Montreal, Canada, produced the Montreal Protocol on phasing out most use of CFCs by 2000. CFC production in most developed countries has fallen sharply since 1989. CFCs are being substituted by HCFCs (hydro chloro fluoro carbons) which release much less chlorine per molecule. In 50 years or so, stratospheric ozone levels are expected to be back to normal. However the final recovery is expected to require several lifetimes in a natural way.

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