EXECUTIVE SUMMARY

1.0 INTRODUCTION

Ideal chemical and physical properties alongwith their thermodynamic and transport properties rendered CFCs as suitable for a variety of industrial applications. But since 1974 when for the first time it was identified that these chemicals are one of the most important causes of stratospheric ozone depletion and greenhouse warming of the earth, scientists and researchers are trying to find out environmentally acceptable substitutes. Regulatory steps have also been initiated, worldover, to discourage the use of these chemicals in nonessential applications. In view of this status of CFCs, Department of Scientific and Industrial Research (DSIR), Govt. of India, assigned Shriram Institute for Industrial Research (SRI) under the National Register of Foreign Collaboration scheme to prepare a status report on CFCs envisaging production, consumption, technology and available substitutes in the literature, with a special emphasis on refrigerants. The scope of the study covered, carrying out a detailed literature survey on CFCs, its major applications, their effects on ecology and possible substitutes. It was proposed to collect information about golbal production and consumption alongwith the status of Indian Industry. Status of various substitutes was also supposed to be analysed so that future trend could be established. More emphasis has been placed on refrigeration and air-conditioning since 81% of the Indian CFCs production is consumed for this specific application.

In order to achieve these objectives of the study, the methodology adopted was based on realistic and sound practices adopted for such research work. To collect the data in an authentic and expeditious manner a panel of scientists comprising of specialists from various disiplines, was created to chalk out the sequence of exercise. Extensive literature survey was conducted from various books, journals, published catalogues. Chemical abstracts were scanned to identify potential substitutes available for different applications. Meetings between SRI scientists and Indian CFC manufacturers and users have been conducted to collect information about products, R&D activities to upgrade quality and quantity of products and future trend of the industry. Department of Environment and United Nations Offices have been approached to gather information about regulatory steps taken/proposed on international as well as Indian levels to discourage the use of ozone depleting CFCs and measures that should be adopted to identify and envisage acceptable substitutes in the country.

2.0 CFCs AND THEIR APPLICATION

The uses of CFCs have been expanded to include air-conditioning, cleaning of Electronic and mechanical components and expansion of plastics for energy efficient foams. Most of the CFCs have excellent chemical and physical properties, such as stability, nonreactivity, nontoxicity and non-flammability suited for a variety of industrial applications. They usually have high densities and low boiling points, viscosities and surfaces tension.

One of the more critical uses of CFCs is in refrigeration and air-conditioning industry. The reliability of electronic and mechnical components for communication equipment, computers and navigation and control instruments for aircraft depends on CFC cleaning agents. Because of their low vapour phase thermal conductivity, CFCs contribute to the efficiency of plastic insulating foams for refrigeration, freezers, buildings and refrigerated railway cars and trucks, even if the foams could be expanded with air or CO_2, the thermal efficiency would be reduced by about a factor of two. CFCs in aerosols are propellants of choice because they are nonflammable, very low in toxicity, and provide efficient dispersion.

Halons or bromochlorofluorocarbons have come up as potential fire extinguishers only after 1970s. Chlorocarbons like carbon tetrachloride and methyl chloroform are primarily used as solvents and chemical intermediates.

3.0 MANUFACTURE

The most important commercial method for manufacturing CFCs is the successive replacement of chlorine by fluorine using HF. In a continuous vapur phase process that employs gaseous HF in presence of CrO_3 or CrX_6, X=halides, $FeCl_2$ or ThF_4 catalysts, CCl_4, $CHCl_3$ and C_2Cl_6 or $Cl_2C=CCl_2$ are commoly used as starting materials for one and two carbon CFCs.

4.0 OZONE DEPLETION

The very stability of fully halogenated CFCs that make them so useful also renders them dangerous to the stratospheric ozone layer. Chlorine radicals generated by decomposition of CFCs in the stratosphere through a series of catalytic reactions lead to a net decrease in the total ozone concentration in the upper atmosphere, with a net increase in ultraviolet radiation. Increase in ultraviolet radiation could result in adverse effects on plants and animals. To develop a predictive capability, a term Ozone Depletion Potential (ODP) has been defined to measure the impact of various CFCs on ozone layer presuming CFC-11 as a base for comparison and assuming its ODP as unity. In a similar manner relative halocarbon Global Warming Potential (GWP) can be calculated.

The global decrease in stratosperic ozone has been verified by Total Ozone Mapping Spectrometer. In summaty stratospheric ozone is expected towards a declining change in the next few decades which will lead to perturbations in tropospheric chemistry through the supply of ozone and through the increase in the solar ullroviolet light available to generate off radicals. The rate and magnitude of change, however, are subject to human control which serves as the motivation for this report.

5.0 GLOBAL PRODUCTION AND USE OF CFCs

Global production of CFCs increased rather rapidly during 1960s and early 1970s with peak production in 1974 of 812.5 thousand MT. The period was followed by a slight decline and levelling off, thereafter, in the middle of 1980s. In 1985 production of CFCs reached almost 703.2 thousand MT. Current total production of CFCs is almost 1140 thousand MT.

Current spurt in production and use of CFCs has been mainly due to increased demand in most of the developing countries. The production of CFC-11, CFC-12 which account for nearly 80% of the total CFCs is growing by 8-9% yearly. CFC-113 is now the fastest growing member of the family, exceeding the production of 160,000 MT. per annum and mostly consumed by Japan. Growth rate in production of HCFC-22 has been equally drastic at 25% per year. CFC-114 and 115 has remained essentially constant since 1965 at a level of 105,000 MT. and 64,000 MT, per annum, respectively.

Current global production of carbon tetrachloride and methyl chloroform is nearly 1.03 million MT and 545 thousand MT. respectively. Most halon production and consumption occurs in U.S. and other industrialised nations Whereas in the 1970s 70% of CFCs were consumed in aerosols now in 1990 each major application area consumes about 25% of CFC.

The annual per capita consumption is highest in the U.S. with 1.22kg, Europe and Japan having 0.93 kg and 0.91 kg. respectively and on the other hand in India and China it is 0.005 kg.

6.0 PRODUCTION AND USE OF CFCs IN INDIA

In all there are five CFC plants in India and three of them have come up only a year ago. of these five plants one of M/s Aegis Chemical has already gone sick whereas M/s Hindustan Fluorochemical produce only HCFC-22 and consume it as a raw material for PTFE plant.

It can be seen that in addition to producing four banned substances under Montreal Protocol CFC-11, CFC-12 CFC-113, CFC-114 the country also makes HCFC-22. Manufacture of CFC-113 and CFC-114 in the country has just begun. Navin Fluorine Industries has also succeeded in producing Halon-1211.

Most of these companies are producing CFCs using imported technology in collaboration with internationally recognised big companies. CFC manufacturers in India have swing type plant which can be changed over to HCFC-22 from CFC-11/12 whenever the need arises. The basic process for synthesising CFC in all the units is approximately the same by reacting carbon tetrachloride (for CFC-11/12) or chloroform (for HCFC-22) with hydrofluoric acid. Total CFC production in the country was 7113.8 MT. last year of which, 2800 MT were of HCFC-22. Total production capacities have substantially increased recently because of licensing of fresh production capacities. In all, total capacity utilisation in the country is only 30-35% of the installed capacity.

The pattern of CFC use in the country is quite different from rest of the world. Whereas 81% of total CFC use is in refrigeration and airconditioning industry the world uses only 25% of the total consumption in this sector.

The Indian per capita consumption comes out 0.007 kg/year whereas the limit set out by the Montreal Protocol is 0.3 kg/year. Most of the Indian CFC manufacturers expect to increase their production by 10% per annum in view of growing demand, if unrestricted by regulatory measures.

Information on consumer market of CFCs in India is not available. The key areas of CFC use are domestic refrigerators, ice-candy machines and cold stores. Approximate fridge population in India is 6 million units. The approximate population of room-air-conditioners at present is 852,000 and production per annum is 120,000 units. In central air-conditioning sector a population of 23,300 units is assumed for receiprocating units, and 600 for centrifugal units. At present the CFC consumption in foaming agents is 1300 MT/year. The aerosol industry in India is not much developed and current per capita consumption is very low. The Industry consumes about 800 MT of CFCs every year.

7.0 TECHNICAL OPTIONS FOR CFCs

Concern for emissions of fully halogenated hydrocarbons which deplete the stratospheric ozone through chlorine catalysed destruction has prompted the search for safer chemicals. Producers of CFCs are scrembling to develop alternatives to fully halogenated hydrocarbons. Particularly, those envisaged in the Montreal Protocol. In the following discussion we shall mainly consider chemical alternatives for CFCs although some product substitutes as well as enginering controls will also be touched upon, wherever information is available.

7.1 Refrigeration

Thermodynamic properties determine the efficiency and capacity of the vapour compression cycle and thus are the key data needed in designing refrigeration equipment and comparing one refrigerant with another.

For the thermodynamic properties the level of data that is required includes normal boiling points, critical point temperature, molecular structure, saturated liquid density, vapour pressure and ideal gas heat-capacity, over a range of temperature and the critical temperature, pressure and density. In the transport properties measurements of thermal conductivity and/or viscosity at some reference conditions are of importance The transport properties are somewhat lower in priority than the thermodyanmic properties and initial screening studies of many fluids often do not consider the transport properties, implicitly assuming that fluids with similar thermodynamic properties will have comparable transport properties. An exception would be in the selection of blowing agents for insulating foams where thermal conductivity of the vapour which is trapped in the foam is important for the insulating value of the final product.

Mixture data is needed to allow an assessment of the near azeotropic mixtures as CFC replacements and to aid in the identification of possible azeotropic mixtures.

Besides all these properties, long term toxicity and flammability characteristics are of main concern. In addition the identification of a suitable lubricating oil may require lengthy, trial and error experimentation. Included in this process would be the tests of chemical stability of oil/ refrigerant mixtures in contact with common materials of construction and possible contaminants, such as water.

7.2 Domestic Refrigeration

For low temperature CFC-12 refrigeration equipment a switch to HCFC-22 would be possible if loss in efficiency of 5-8% is accpetable which can be overcome by redesigning the system like increasing the condenser capacity. HFC-134a, also, has been widely hailed as the most likely substitute for CFC-12. A large number of researchers have reported lower volumetric capacity and lower thermodynamic efficiencies and incompatibility with lubricants. The thermal conductivity of HFC134a vs. CFC-12 is higher, leading to improved heat transfer. Given the adequate optimisation of all components the energy penalty in the use of HFC-134a would be negligible. However, the selection of components need further investigations because it may influence the outcome for this application. There are indications that in the case of application of flammable refrigerants e.g. HFC-152a or DME an increas in efficiency is possible without redesigning the equipment. this also applies to mixtures of these refrigerants with HCFC-22. The use of flammable refrigerants requires a critical consideeration of existing standards and also logistics, manufacturing and consumer safety concerns, additional capital investments required.

Drop-in mixtures, with medium ODP as substitute for CFC-12 are known. In small equipment, reductions can be made by using azeotropic mixtures CFC-500 (73% CFC-12, 27% HCF-152a) or CFC-12/DME (87% CFC-12, 13% DME). Combinations of commercially available and acceptable liquids in nonazeotropic refrigerant mixtures may also be used as CFC substitutes. Different investigators have, so far, been evaluating the HCFC-22/HCFC-142b mixtures and found small advantages compared to the application of CFC-12 without redesign of the system. It must be understood that these comments apply to two compartment refrigerator/freezer combinations where both compartments use separate evaporators. Recently, a technological breakthrough was announced in the form of a ternary (three part) mixture of HCFC-22, HFC-152a and HCFC-124. The mixture has thermodynamic properties which match CFC-12 more closely than HFC-134a and has an ODP of 0.03.

7.3 Retail Refrigeration

Common refrigerants used in retail refrigeration are CFC-12, HCFC-22, CFC-502 and ammonia. The use of HCFC-22 in place of CFC-12 and CFC-502 can be further encouraged in medium temperature systems. Oils in which HCFC-22 is soluble are available and not much expensive. To avoid high discharge temperature (if CFC-502 is replaced with HCFC-22) the use of two stage intercooled compressors systems or oil cooled screw compressors is possible; but more complicated and expensive.

HFC-23 is the only refrigerant with an ODP zero, which is not flammable and which is already in the market. As a component in a nonazeotropic refrigerant mixture, or together with a sorption fluid in a compressor driven substitute for CFC-12. A large number of researchers have reported lower volumetric capacity and lower thermodynamic efficiencies and incompatibility with lubricants. The thermal conductivity of HFC134a vs. CFC-12 is higher, leading to improved heat transfer. Given the adequate optimisation of all components the energy penalty in the use of HFC-134a would be negligible. However, the selection of components need further investigations because it may influence the outcome for this application. There are indications that in the case of application of flammable refrigerants e.g. HFC-152a or DME an increas in efficiency is possible without redesigning the equipment. this also applies to mixtures of these refrigerants with HCFC-22. The use of flammable refrigerants requires a critical consideeration of existing standards and also logistics, manufacturing and consumer safety concerns, additional capital investments required.

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7.4 Transport Refrigeration

For ships, cargo refrigeration is substantially limited to HCFC-22 and as it is proposed to become a controlled substance, early restrictions on its use may not be necessary. Moreover, the amount used in this application as a proportion is very small. Alternatively all new ships would have to have alternative systems which would require a complete redesign of not only the refrigeration components overall refrigeration layout relative to cargo and screw spaces.

For containers, dependence on CFC-12 is total until such time as permanent alternatives are available. Alternatives include HFC-134a which is approved for toxicity but incompatible with normal compressor lubricants and is not energy efficient. HCFC-22 and CFC-502 are also not suitable candidates because of practical considerations. Ternary mixtures of HCFC-22/152a/124 have recently been proposed by manufacturer may be an option, but testing is needed. Ammonia is a conceivable alternative but is unlikely to be favored for a multiple small units on safety grounds, but considerable development would be necessary. At present there is no suitably qualified alternative refrigerant to CFC-12 for this application and any future alternatives are unlikely to be compatible with existing equipment.

For lorries, most equipments have a lifetime of 7-12 years, so there is scope for replacement with systems using interim refrigerant such as CFC-500 and CFC-502, whilst, improved refrigerants (e.g. HFC-134a) are developed and tested. Mixtures such as blends of CFC-12 with DME or of HCFC-22 with HFC-142b have been suggested.

7.5 Cold Storage/Food Processing

Most large scale industrial chilling, freezing and cold storage plants utilise ammonia. There are, however, certain areas and countries that use CFC-12, HCFC-22 and CFC-502. These include countries where dense population areas and/or earthquake areas are a common feature.

There can be three kinds of possible and existing alternatives.

(a) Ammonia.

(b) HCFC-22 other CFCs where required for operation, safety or climatic reasons.

(c) Greater use of indirect refirgeration for all refrigeratns.

Codes, regulations and laws have been developed to deal with toxic and flammable characteristics of ammonia, which if followed provide a high degree of safety. Ammonia is recommended for freezing operations; close coupled, confined compressor-evaporator system and frozen food storages where the systems are well managed and not far flung geographically. Unitised designs can reduce ammonia charge and risk in may applications.

HCFCs and CFCs have to be used in densely populated areas and severe earthquake zones. HCFC-22 should be utilised as it has least effect on ozone layer. CFC-502 in future may be replaced by HFC-32. At present, new installations may be designed with minimum refrigerant charges and low recharge rates.

Greater use may be made of systems which use either ammonia or HCFC/CFC refrigerants in a close coupled arrangements to cool/chill water or a brine solution in a heat exchanger. The water or brine solution is piped and circulated to the area requiring refrigeration. Indirect systems will provide for a reduced refrigerant charge, in most applications as well as a close coupled refrigerant circuit that can be a reduced risk for refrigerant losses. Indirect systems are theoretically less efficient than direct systems due to the extra heat transfer step to cool the water or brine solution. Practical experience, however, shows that because of simultaneity many indirect systems have better performance characteristics than direct systems.

7.6 Industrial Refrigeration

The areas of application covered by this section include the chemical, pharmaceutical and petrochemical industries, the oil and gas industry, the metallurgical industry, civil engineering, sports and leisure facilities, industrial ice making and other miscellaneous uses. Blends are the only drop-in refrigerants available today and will probably remain so, also in future. Most blends are nonazeotropic. One exception is CFC-12/DME (87/13% by weight) which is introduced as an intermediate drop-in refrigerant for CFC-12. Changeover for one component refrigerant in existing systems necessitates system modification in most cases CFC-12 per unit volume. Possible alternative refrigerants are CFC-500, CFC-502, HCFC-22, ammonia and hydrocarbons. None of these alternatives can be used in low pressure systems designed for CFC-11 but may replace CFC-12.

CFC-500 is an azeotrope containing CFC-12 and HFC-152a (74% CFC-12 by weight) CFC-502 is also an azeotropic mixture composed of HCFC-22 (49%) and CFC-115 (51%) (ODP 0.3). CFC-502 in particular may be regarded as part of the short term solution. In the long-term, however, both chemicals become part of the problem. For this reason other options are preferred for existing systems.

The substitute refrigerants HFC-134a (for CFC-12) and HCFC-123 (for CFC-11) are not considered as 'drop-in' refrigerants. Compatibility problems have been reported and a suitable lubricant for HFC-134a has not yet been found. From technical point of view HCFC-22 may replace CFC-12 in new plants today for most industrial refrigeration sector. The main exception is plants operating with high condensing temperatures (heat recovery), where HCFC-22 will cause too high a pressure. For low temperature purposes, 2-stage compression may have to be used as the most important short-and mid-term solution.

Ammonia can cover most applications in the industrial sector, with the equipment available today. In practice, the growth of ammonia usage is limited by safety regulations and at least in the short-term by lack of experience with this refrigerant by many companies. Apart from being the most efficient refrigerant ammonia has no ozone depletion potential at all. For these reasons together with uncertainties connected with the future of HCFC-22, the companies familiar with ammonia refrigeration forsee a substaintial growth in their use of this chemical. Whereas the expected cost effect on an average is +15% the approximate energy effect should be -5%.

7.7 Comfort Air Conditioning

In comfort air-conditioning centrifugal compressor chillers which use CFC-11, CFC-12 and to some extent CFC-114, CFC-500 and HCFC-22 are the main focus of ozone depletion reduction. Because centrifugal water chillers are designed for specific refrigerant direct refrigerant substitution can only be made in cases where the properties of the substitute refrigerant are nearly the same as-those of the refrigerant being replaced.

A probable replacement for CFC-11 is an azeotrope of HCFC-123/CFC-11 containing 78% HCFC-123. The azeotrope is said to have a boiling point close to that of pure CFC-11 making it more attractive than HCFC-123 especially for substitution in existing system. The nature of azeotrope appears to be such that HCFC-123 may be added to CFC-11 chillers as needed to replace CFC-11 removed by servicing through leaks. However, no thermodynamic data exists on HCFC-123/CFC-11 so that performance calculation can not be made at this time. Furthermore, HCFC-123a is a more aggressive solvent offering a lot of material incompatibility problems.

Replacement of CFC-12 with HFC-132a would require impeller and/or gearbox replacement. CFC-12 oil and desiccants are not suitable for HFC-134a, thus requiring a thorough flushing of the system before replacement HFC-134a cycle efficiency is slightly lower than CFC-12 and existing heat transfer surfaces wil not work as well, if the small nucleate cavities retain residual oils. Some desiccants (e.g. activated alumina) commonly used in CFC-12 system are not compatible with HFC-134a.

HCFC-124 has been suggested as an alternative to CFC-114 in centrifugal chillers such as in naval applications. But the thermal properties of HCFC-124 are not well documented, so accurate analysis is not possible at this time.

7.8 Mobile Air Conditioning (MAC)

Presently, the most viable candidate to replace CFC-12 in mobile air-conditioning is HFC-134a because it does not contain chlorine and therefore, would not contribute to ozone depletion. The system changes required for the use of HFC-134a are relatively modest, the pressure/temperature characteristics of HFC-134a are similar to those of CFC-12 although enhanced condensing will be required to restore CFC-12 performance and durability levels. Besides a suitable lubricant has to be developed and toxicity tests have to be carried out. Complete mobile air-conditioning, industry conversion to HFC-134a is estimated to require

3-5 years due to anticipated component changes, critical supply pipelines, service traning needs, equipment supply bottlenecks etc. Although HCFC-22 can be used in mobile air-conditioning but would only, be an *interim substitute and requires major investments. The chemical can be* used only in refrigernat blends. *Blends such as HCFC-142b/HCFC-22; CFC-12/DME and CFC-500 have been proposed as interim substitute until* an environmentally acceptable refrigerant with little or no ODP can be implemented. In HCFC-142b/HCFC-22 blend HCFC-22 selectively escapes out of seals and hoses eventually creating a flammable system mixture. CFC-12/DME blend is also not a 'drop-in substitute for CFC-12. A new desiccant compatible with DME would be required. Copper plating tendencies need to be evaluated relative to compressor wear. DME material compatibility needs to be evaluated to determine its impact on various systems, that presently exist in the field.

DuPont recently announced two ternary refrigernat blends for consideration as interim refrigerants pending the development of HFC-134a. The first blend of HCFC-22, HFC-152a and CFC-114 with a reported ODP of 0.38 and the second is a blend of HCFC-22, HFC-152a and HCFC-124 with a reported ODP of 0.02. Intial evaluation has revealed that they can not be considered as drop-in replacements of CFC-12 because majority of the current mobile air conditioning hoses are not capable of containing the HCFC-22 in the blends and existing desiccants will be chemically attacked and completely destroyed by the HFC-152a present.

7.9 Refrigerant Recycling

The purpose of recycling refrigerant is to remove moisture and other contaminants that lead to equipment failures. The contaminants include dirt, metallic particles, noncondensible gases, and products from motor burn-out. Noncondensible gases can result from incomplete evacuation of the refrigeration system, and are produced either from component release gases, low side leaks or chemical reactions. Additional contaminants in hermetic refrigeration systems would be products from decomposing organic minerals like oil, insulation, motor varnish, gaskets, and adhesives which produce sludge, wax and tars.

As existing sources of new CFCs dwindle recycling will become, both more attractive and necessary. Recycled and reclaimed refrigerant can be an important source of resticted CFCs and will be especially useful for equipments for which there are no alternatives as yet. The most immediate application will probably be mobile air conditioning and centrifugal chillers. There is a growing market for recycling equipment. Standards for recycled refrigerants are being established, that will dictate the maximum level of contaminants, allowed. It is also possible to use recycled refrigerants in applications other than the original use.

At present, there are three general categories of CFC recycling equipment plant based distillation units, vapor phase solvent recovery units, and portable recycling units. Vapor phase solvent recovery units apply to CFCs which are used as solvents in the manufacture of electrical components. Plant based distillation units are in use both at chemical plants which manufacture CFCs and at facilities operated by independent CFC reclaimers. These units are used to purify refrigerants to acceptable standards and for large scale reclaimation. Portable recycling units are designed for small scale operations. Typical applications are for equipments which are being serviced and which requires the temporary recovery and storage of the CFC charge. Cleaning and purification of refrigerant is also performed during this application.

The dominant method of purification is distillation because CFCs are highly volatile. The recovered CFC contaminant mixture is first processed to remove dirt and particulates. Next, the mixture is passed into a distillation column. Components of the mixture are separated by boiling off and vaporising of CFCs which have a lower boiling point than the contaminants. The contaminants which mainly consist of lubricating oils and water are drained off at the bottom of the column. Both, on-site and off-site recycling holds great potential for recovery of CFCs and prevention of emissions.

A number of policy related issues still need to be resolved with regard to recycling and reuse of used CFCs. For instance standards, must be adopted for the quality of used refrigerants. Procedures have to be developed to recommend practices that will reduce inadvertant release of fully halogenated CFC refrigerants during manufacture, installation, testing, operation, maintainance and disposal of refrigeration and air-conditioning equipment and systems. Unless requlations are imposed, recycling may not become widespread until driven by economies some time in future. Though, it is possible to reclaim refrigerants to high levels of purity, until recycled refrigerants are proven safe to use, there may be substantial market resistance from equipment manufacturers and service personnel.

7.10 Aerosols

Considerable pressure has been exerted to discourage the use of non essential aerosols containing CFCs, especially in developed countries, since 1974. It has been rather easy to substitute CFCs in aerosol applications.

The compressed gas propellants are not liquids in conventional aerosol containers. They are nontoxic, non-flammable, low in cost and very inert. However, the vapor pressure in the container drops as the contents are depleted, possibly causing changes in the rate and the characteristics of the spray. This situation can be considerably improved when the contents are materials in which the compressed propellants is at least somewhat soluble, therefore CO_2 and N_2O are preferred. Because of concern with the use of halocarbons, considerable development efforts are being devoted to the formulations as well as hardware for the use of CO_2 and N_2O. These efforts are directed at offsetting, as much as possible, the pressure decay encountered when CO_2, N_2O, N_2 or air are used. When contents are used which dissolve some of the compressed gas, partialreplenishment of the head space results as the gas is expelled, hence the greater the solubility, the more gas available to maintain the initial conditions. This establishes CO_2 and N_2O as the ethanol appears to have the potential for intense use. Other applications like insecticide products and spray paints which use acetone, petroleum distillates or acetate esters can be formulated. In case of liquified propellants, the head space plays no part in the system design since pressure is constant throughout. Nitrous oxide is presently used in food items and is likely to find wide applications in cosmetics and othe rproducts as well.

Most of developed countries have successfully adopted propane, butane, dimethyl ether and HCFC-22 as alternative propellants. However, there are some specialist propellant applications where alternatives still need to be found, in medical and electronic aerosols. It is hoped that HCFC-22 will prove a suitable alternative to CFC-11 and CFC-12 used as aerosol propellants. Moreover, use of DME as aerosol propellants looks set to grow in some areas as consumption of CFC-11 and CFC-12 declines. Battelle Research Instiitute (Frankfurt) claims to have developed a way of using hydrogen as a friendly and safe propellant in aerosol sprays. The key to the new design is storage of hydrogen in free space of metal lattice and release at quasi constant pressure until complete discharge. The sprayer is environmentally friendly, safe to handle and inexpensive, and would prove an adequate substitute for the conventional sprayer using CFCs.

7.11 Blowing Agents

Regardless of type, a blowing agent should possess the following desirable qualities :

- Long term storage stability under fairly ordinary conditions.
- Gas release over a controlled time and temperature range.

- Low toxicity, odor and color of both the blowing agent and its decomposition products.
- No deleterious effects on the stability and processing characteristics of the polymer.
- The ability to produce cells of uniform size.
- The ability to produce a stable foam, i.e., the gas must not be lost from the cell and cause it to collapse.
- Good cost performance relation and availability.

Although innumerable substances have been proposed as blowing agents, few posses sufficient desirable properties to achieve commercial importance. Producers of extruded foam have been prompted to seek environmentally safe and economically acceptable alternative blowing agents. Some of the approaches proposed for significantly reducing CFC emissions in extruded polystyrene and polyethylene foam production include using:

- Carbon dioxide (CO_2) as a second blowing agent.
- CFC/hydrocarbon blends.
- Hybrid blowing agents, such as HCFC/CFC blends or HCFC/hydrocarbon/CO_2 blends.

Three of the alternates are nonflammable and two HCFC-142b and HFC-152a are flmmable than hydrocarbons. The alternates also have low order of toxicity. The toxicity of HCFC-124 and HFC-134a are currently under study. Moreover, HCFC-22 has been widely hailed and less amount of it is required than CFC-12 to achieve comparable extruded foam densities of PS foam sheet extrusion. Several successful plant trials at Allied Signal using HCFC-22 alone or in blends with hydrocarbons (92 HCFC-22 and 8% n-pentane) and CO_2 for the commercial production of extruded polystyrene sheet goods have been conducted. Although HCFC-22 is costlier than CFC-11 the difference can be offset by better blowing efficiency of HCFC-22. It is possible to obtain HCFC-22 based PU foams with free rise densities equal to those foams, made from CFC-11 and with thermal conductivities similar to those of foams containing 50% CFCs using Easy-Forth process which allows a high degree of HCFC-22 to be dissolved in polyol.

Although, partial success has been reported in reducing the consumption of CFC blowing agents and several alternatives are being forwarded like HCFC-124, HCFC-141b, HFC134a, HFC152a, CO_2, N_2, H_2O and/or hydro-carbons but none has proved to be a potential long term alternative. Progress in research for using HCFC-123 has been most remarkable in rigid polyurethane foams where CFC-11 blowing agents contribute to thermal insulation. While direct substitution of CFC-11 in existing systems gave foams with inferior thermal conductivity, novel polyols and isocyanates have been found to correct that effect and competitive systems based on HCFC-123 and CO_2 have been produced. Use of carbon black as an inert filler could minimise or even eliminate expected increase in thermal conductivity, besides it will significantly imporve tensile strength and dimensional stability if the material is properly dispersed in one of the liquid components prior to foaming. Unlike rigid foams trial of HCFC-123 in flexible foams have been restricted to lab-scale experimentation. For flexible foams with low density new water based processes have been reported. Water added to the polyol component reacts with some toluene di-isocynate to form CO_2 which fluffs the resin into a foam expanding it to a large bun in the mould. One limitation of any water blown technology is inability to rach densities lower than about 1.4 lb per ft.. This is because the evaporation of CFCs not only moderates the heat of polymerisation within buns but also foams the resin. Thus for the moment water blown foams can't capture the market for 0.9 lb/ft. now used in backs and arms rests and in cushions of low cost furnitures. For especially soft grades, provided their density is above a certain minimum level, all major raw material producers can now offer a practicable solution through the use of additives. In moldable foams, the number of different requirements from end users is much lower than in slabstock, so polyol modification is considered more feasible. Most requirements can be satisfied with alternative polyols or additives.

7.12 Cleaning Agents and Solvents

At present CFC-11, methyl chloroform and carbon tetrachloride are the major chemicals being used for cleaning/degreasing electronic components like removal of solder fluxes from printed circuit boards and cleaning of electronic equipments like TV sets, computers, telecommunication units etc. In general three kinds of replacements have been observed for this application in literature, hydrocarbons, HCFCs and terpenes. In the first category a new process called 'ice-cleaning' which uses fine particles of ice and frozen alcohol at temperature below -50° C. The process helps blow dust off semi-conductor without harming them and the results are comparable to CFCs. The use of particles as small as 0.1 micron helps remove dust of submicron levels of grease and oil from semi conductors and PCBs.

In HCFCs category HCFC-123, HCFC-141b, HCFC-225ca, HCFC-225cb have been mostly gaining ground to replace CFC-113. In a Du Pont patent a blend of HCFC-123 and HCFC-141b having almost 94% less ODP than CFC-113. It has been shown that the azeotropic blend matches not only in physical properties but also have comparable cleaning ability. CFC-113 can also be replaced by a ternary blend of HCFC-123 HCFC-141b and methanol without much damage to ozone layer. Two more substances HCFC-225ca and HCFC-225cb with surface tension values equal to CFC-113 have been identified. Having finished the basic tests for their toxicity the test concerned with cancer producing effects and acute toxicity on them show that the two have no toxicity problem.

'Pine Alpa-ST 900 Series' the terpene based cleaning agents for PCBs have been developed by 'Aracawa Chemical Industryies' when the treatment temperature rises the new products have two to three times more cleaning capability than CFC-113. They are classified into two types of hydrocarbon based products for room temperature cleaning and four types of higher alcohol based ones for heated cleaning. The new products are capable of completely cleaning the surface of phenol/epoxy boards with damaging them. A dipping, flushing or mechanical brushing method can be applied when cleaning PCBs using the new products.

8.0 CONCLUSIONS

Ideal chemical and physical properties of CFCs render them suitable for many versatile applications, however, after their use they remain in the atmosphere until transported to the stratosphere where they are photolysed releasing chlorine atoms which catalyse conversion of stratospheric ozone into oxygen depleting its concentration. This ozone depletion makes greater amount of ultraviolet radiation falling on earth adversely influencing human life as well as vegetation. Over the years the producion of CFCs has increased substantially. In India total production of CFCs is almost 7,000 Tonne/year and global production is approximately 1.14m MT/year. Regulatory initiatives have been taken to discourage the use of ozone depleting chemicals in industry. Adoption of Vienna Covnention for the protection of the Ozone Layer in March 1985 and Montreal Protocol on substances that deplete the Ozone Layer in September 1987 under the guidance of UNEP have been some very significant steps by international community in this direction. Importance is being increasingly realised to replace CFCs with environmentally acceptable substitutes. For most of the applications suitable alternatives are now available. Some time consuming toxicity tests and evaluation of their environmental impacts are still in progress. HFC-134a, HCFC-22, HFC-152a, HCFC-123, HCFC-141b alone or in blends have been shown as some potential mid to long term substitutes. Some non CFC chemicals like ammonia, DME, propane, butane, carbon dioxide and even water have been shown to prove useful depending on their judicious utilisation. Creation of a recycling industry has been suggested. Such an industry would serve not only to reduce consumption of CFCs towards the terminal phase out dates but would also serve to generate extra employment and possibly provide additional environmental benefits. In parallel, other conservation measures in various other CFC applications like foams, aerosols, solvents etc. can help in reducing CFC demand. This is especially important in the near term while processes and equipments are redesigned or other production changes are made to eliminate CFC use altogether. Non CFC containing products compete in some subsectors of the foam market, with the possible exception of appliance insulation.

These technologies can effectively help in reducing CFC demand if adopted but only after a thorough evaluation by an expert panel. Moreover good housekeeping techniques and creating awareness among the masses about the subject can help in reducing demand of the chemicals.

Keeping in view the information collected on the subject during the project tenure and also inlight of the proceedings of the National Interaction Meet on CFCs/Refrigerants and their substitutes, following explicit conclusions can be drawn.

- Service conditions vary from region to region and need to be redefined explicitly.
- Product alternatives will play a deciding role to reduce CFC phasing down schedule.
- Improved leackage controls reduce CFC release.
- Incentives for reducing leakage and for recyling practices can reduce CFC release.
- Aerosols use can be minimized in applications such as perfume sprays etc. and alternative product are also available.
- Alternative products for CFC blown products specifically for insulation purpose are now common.
- Alternate blowing agents including endotherms and inert gases such as water, N_2, CO_2, N_2O, etc. can replace CFCs in certain applications.
- Use of indirect refrigeration practice in cold storage and food processing sector save CFCs use & release.
- Non CFC solvents for cleaning are also available.

More stringent standards and specifications particularly for halons are required.
There is no substitute for good house keeping resulting, reduction in CFC demand.

9.0 RECOMMENDATIONS

The science community may witness a reversal of international trends when there are murmurs from many corners that ozone hole is a hoax. Under such uncertainities, self supporting R&D efforts and flexibility in policies and strategies may be adopted. Further in time to come substitutes and/or alternatives will play a definite role in CFC trade. Multiple switch-overs can never be advised.

One of the surest methods to eliminate the use of CFCs and other ozone depleting substances until suitable substitutes are available, is product substitution. It is recommended that research and development efforts should begin in this direction before it is too late. International scientific community be joined in identifying and evaluating potential substitutes. Uptodate environmental impacts besides their thermodynamic and transport properties at one place can result in their effective utilization.

Some general recommendations for a safer future are as follows :

Redefining explicitly service/performance conditions and thereby reduce CFC charge.
Development of substitutes and/or alternatives.
Steps for minimum leakages.
Ozone depletion be considered along with energy consumption, flammability characteristics.
Redesign considerations for new equipments.
Improvement in equipment design for blowing processes.
More stringent standards and specifications.
Move in direction of minimum or CFC free systems.
Restricted use of aerosols.
Adoption of CFC free cleaning agents.
Recycling and reuse of CFCs.
Preferable single switch-over particularly for developing and under-developed countries.