PROGRESS IN THE DEVELOPMENT OF CHLOROFLUORCARBON (CFC) ALTERNATIVES

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ABSTRACT. Chlorofluorocarbons (CFCs) are now believed to be major contributors to the seasonal ozone depletion over the Antarctic continent. They are so important for society that substitutes must be rapidly found and commercialized. Several substitutes have been selected by the industry and significant research and development programs are underway to commercialize them. Unlike the simple, fully-halogenated CFCs which can be made in a single step, there are many potentially viable routes to the alternatives, requiring significant improvements in catalysis. Many other important issues such as materials compatibility, energy efficiency, developing country needs and product life cycle of the alternatives need to be resolved before a timely transition to substitutes can be accomplished.

1. Introduction

Early refrigeration systems were developed with cooling fluids such as CH₃Cl, SO₂, NH₃, C₂H₂Cl₂, CH₂Cl₂ and hydrocarbons. From a thermodynamic standpoint, they gave good refrigerating performance but were flammable and toxic. In 1928, two scientists, Thomas Midgley and Albert Henne, at the Frigidaire Division of General Motors were asked to develop non-flammable, non-toxic replacements for these hazardous cooling fluids in home refrigerators. Albert Henne used the chemistry pioneered by Swarts [Swarts, F., (1892); Swarts, F., (1893)] at the University of Gent, Belgium during the late 1890s for the synthesis of chlorofluorocarbons. Within two days, Midgley and Henne had selected CFC-12 (CF₂Cl₂) as an ideal refrigerant. The initial stoichiometric reaction between SbCl₅ and CCl₄ was developed into a continuous process in a joint venture between Du Pont and General Motors during the 1930s. The carbon tetrachloride and HF were continuously fed to a reactor containing pentavalent antimony, and by adjusting process conditions the degree of fluorination on the carbon could be controlled. This synthetic route was further developed and formed the basis for modern-day commercial chlorofluorocarbon processes to make the important refrigerants, cleaning agents, and blowing agents: CFCs-11 (CFCl₃), CFC-12 (CF₂Cl₂), HCFC-22 (CHF₂Cl), CFC-113 (CF₂ClFCl₂), CFC-114 (CF₂Cl₂F₂Cl) and CFC-115 (CF₃CF₂Cl).

By 1988, total CFC world consumption had grown to over 10⁶ tons. In the U.S. some 5000 businesses at nearly 375,000 locations produced CFC-related goods and services worth more than $28 billion a year [Glas, J.P., (1989)]. CFC-related jobs totalled more than 700,000. Within the United States, the three major uses are as refrigerants (30%), as foam-blowing agents for polystyrene and polyurethane (28%), and as industrial solvents and cleaning agents (19%).
Outside North America, a significant amount (>1.5x10^8 kg) of CFCs have continued to be used as aerosol propellants, even though that application was essentially banned in the U.S. in 1978. Information contained in the International Ozone Trends Panel Report [WMO, (1988)] and supported by more recent information including the ozone trend results from analysis of the Total Ozone Mapping Spectrometer (TOMS) data [Stolarski, (1991)] provides compelling evidence that production and use of CFCs should be phased out to reduce risk of ozone depletion. In 1990 the Montreal Protocol, an international agreement regarding CFC production and use, was strengthened to require a phaseout of production in developed countries by 2000 and by 2010 in developing countries.

2. Selection of Suitable Alternatives

A recent market projection by Du Pont [Du Pont, (August 1989), Du Pont, (January 1989)] has attempted to determine how the current markets that use CFCs will be satisfied in the year 2000. Increased awareness to environmental issues and costs will result in about a 30% reduction in the market through improved conservation measures. These include better maintenance systems and product recovery, recycle, and reclaimation. Another 30% of the market will switch to less expensive, not-in-kind replacements. For example, organic/H2O-based systems may be used for certain cleaning applications and mixtures of CO2, hydrocarbons and water could be used as foam blowing agents. Du Pont, however, predicts that the remaining 40% of the projected market will still require fluorocarbon-based products because of the unique properties associated with these molecules, particularly in the refrigeration industry. The unique vapour phase thermal conductivity of CFCs contributes to the efficiency of plastic insulating foams for refrigerators, freezers, buildings, refrigerated railway cars and trucks. Even if the foams could be expanded with air or carbon dioxide, the thermal efficiency would be reduced by about a factor of two. The energy penalty associated with the elimination of hydrochlorofluorocarbons from insulating foams could be equivalent to several billion gallons of additional fuel consumed in the United States annually. Hydrofluorocarbons and hydrochlorofluorocarbons have emerged as alternative fluorocarbon products for the remaining market segment and will form the basis for the remainder of this discussion.

Selecting appropriate substitutes for an industry that has developed over 50 years is no trivial task. Many factors must be considered and thoroughly evaluated. Foremost is environmental acceptability for the ozone and other environmental concerns such as global warming and acid rain, but economic factors are important as well. There is an estimated $135 billion worth of equipment in the U.S. which depends on CFCs, with an expected lifetime of 20-40 years. Therefore, it is very important that the physical properties of the alternatives closely match those of the CFCs they are replacing.

The ozone depletion potential (ODP) of a compound can be calculated by dividing the cumulative calculated ozone depletion caused by the release of a compound by the calculated ozone depletion of an equal emission (by weight) of CFC-11. In a similar manner, relative halocarbon global warming potential (GWP) can be calculated. Thus, ODP is an estimate of relative effects and should, therefore, be used to determine the relative long-term environmental benefits of alternative compounds. Since the HFCs do not contain chlorine and therefore have an ozone depletion potential (ODP) of zero, they are very attractive alternatives. The absence of chlorine in HFCs, however, often results in a higher vapour pressure and lower solubility than CFCs. These two characteristics limit their use for some applications. Significantly-reduced ODPs can be obtained by introducing H atoms into the molecule, even if it contains chlorine.