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The International Ban on Ozone-depleting Chloro-fluorocarbons

Chlorofluorocarbons, CFC's, are organic molecules consisting of carbon, chlorine and fluorine atoms. CFC's appear in products such as refrigerants, propellants, solvents and aerosols. While applications are numerous, CFC's injure our environment. These carbon compounds are the main perpetrators of ozone depletion. They readily react with Ozone (O_3) that is needed to prevent ultraviolet (UV) radiation from damaging trees and plants and from injuring animals and humans. Excessive use of CFC's has created an ozone-poor hole in the atmosphere. Thus, there has been political pressure to limit the use of CFC's by means of an international treaty, known as the Montreal Protocol.

History of CFC's

Chlorofluorocarbons first appeared in commercial usage in 1928. The molecular structure of CFC-12 consists of a single carbon with two chlorines and two fluorines (Sparling). CFC's were developed in response to calls for a safer alternative to sulfur dioxide and ammonia refrigerants (Ciesen).Compared to sulfur dioxide and ammonia, CFC's are nontoxic, nonflammable and noncorrosive. Within a few years, numerous other CFCs were developed to serve a variety of purposes for refrigeration, air conditioning, cleaning solvents for electronic components, blowing agents for foam production, propellants for hairspray, insecticides, whipped cream, etc (Ciesen). By 1988, chlorofluorocarbons became mainstream industrial products produced and consumed worldwide, estimated at over one billion kilograms per year.

Despite the enhanced usefulness of CFCs, there was a major environmental cost. In 1974, M.J. Molina and F.S. Rowland published a study showing that CFC's have the ability catalytically to breakdown Ozone in the presence of high frequency UV light (Sparling). Further studies estimated that atmospheric ozone would be 7% depleted within 60 years. In 1985, the British Antarctic Survey reported that the ozone over Antarctica had been reduced to about half its natural level with a yearly 2.5% decrease (Harris). The "Ozone Hole" was caused by CFCs. While there were indications of Ozone breakdown in other regions, the decline of Ozone over Antarctica was the worst. During the late summer months, the ozone hole expands to a size larger than the area of the U.S.

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Reaction of CFC's and Ozone (O_3)

Ozone is a molecule with 3 oxygen atoms that resides mostly in the stratosphere. The stratosphere is the second layer in the earth's atmosphere and contains 90% of the world's Ozone. Ozone in this layer prevents UV radiation from reaching the biosphere, the zone below the troposphere where all ecosystems reside (Figure 1).

The production of O_3 results from the breakup of oxygen molecules by high-energy UV radiation. O_2 molecules absorb radiation and are broken into radical O atoms. One O joins with an O_2 to create O_3 .

$$O_2 + hv_{(wavelength < 240nm)} \rightarrow O + O$$

 $O_2 + O \rightarrow O_3$

Ozone molecules absorb radiation from the sun and convert it to heat, dissipating UV radiation. Because ozone is created by sunlight, it tends to be concentrated over tropical latitudes and less concentrated over polar latitudes. Therefore, polar regions tend to be more susceptible to ozone depletion.

CFC's are long-living compounds capable of reacting with Ozone. They diffuse into the stratosphere, and catalyze ozone decomposition (Harris). When CFC's are present, high-energy UV



rays from the sun break the chlorine-carbon bond. The primary reaction occurs when the chlorine atom reacts with Ozone and "steals" away its third oxygen, leaving molecular oxygen (O_2) molecules that are ineffective for blocking UV radiation. The chlorine oxide formed reacts with free lone oxygen atoms, resulting in O_2 and a chloride compound. The chlorine atom is a catalyst capable of decomposing more O_3 .

$$Cl + O_3 \rightarrow ClO + O_2$$

 $O + ClO \rightarrow Cl + O_2$

The breaking down of ozone by chlorine atoms cripples the ability of the atmosphere to block radiation. A single chlorine atom can destroy $>10^5$ molecules of O₃. (Harris)

Montreal Protocol

Because massive ozone breakdown by CFC's degrades the ozone layer and exposes humans to the sun's harmful UV radiation, an international effort was made to reduce the amount of CFC's produced in the industrial world. In the fall of 1987, a document was written to lay out a timeline for the gradual phase-out of CFC's. This is the Montreal Protocol, originally intended to limit production of ozone-depleting substances (ODC's). The primary clauses call upon those at the convention to be mindful, to take appropriate measures to protect human health, to be conscious of the effect of CFC emissions which degrades the ozone layer and to be determined to protect the ozone layer by taking precautionary measures (Montreal). If the ozone layer is depleted, plant and human life will be exposed to UV radiation, which penetrates, degrades and destroys deep cell tissues in living organisms. The original document was negotiated in 1987 by 100 countries including the US. Since then, it has been revised numerous times in London, Copenhagen, Vienna, Montreal and Beijing. Addition of amendments has greatly increased its impact. Most crucial was the revision in Copenhagen where a most stringent CFC phase-out schedule was presented and signed by over 100 nations, accounting for up to 95% of the world's CFC consumption (Sparling). In addition, the U.S. Congress passed legislation to limit CFC's. The 1989 Budget Reconciliation Act levied a tax on eight different ODCs. The Clean Air Act established a ceiling on production and a complete phase-out of class 1 compounds by the year 2000. Class 1 compounds are those with a high ozone-depleting potential, usually derivatives of CFC's. Regulation has continued to tighten usage and recycling of class 2 CFC compounds. Class 2 compounds are those that have less ozone-depleting potential but are still harmful in the long run. Continued efforts have been made to restrict the use of CFC's and to ensure the survival of Ozone. Today, the Montreal Protocol, a monumental piece of legislation, has been fully ratified by 196 countries with the Philippines the latest addition. With sufficient care and strict adherence to of the Montreal Protocol, scientists predict that depletion of the ozone layer will cease within the next 10-20 years and recover to 1980 levels by about 2050 (Lerner).

Looking to the Future: Alternatives for CFC's

Since the banning of CFC's, alternatives were sought to replace these useful industrial compounds. Industries now turn to HCFC's as potential alternatives; they are compounds containing hydrogen, carbon, chlorine and fluorine. They tend to have a shorter life and contain

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less reactive chlorine. The chlorine atoms released from an HCFC typically react with water vapor in the troposphere, the layer below the stratosphere, to form compounds that dissolve in water and are removed by precipitation, rain. When HCFC compounds are destroyed, the chlorine atom of the compound does not reach the ozone-rich stratosphere. By making HCFC compounds more unstable, chlorine atoms do not destroy Ozone.

Another alternative is provided by HFCs, fluorocarbon compounds without chlorine atoms. These compounds are highly favored because they possess properties similar to those of CFCs such as high volatility, low thermal conductivity, low surface tension and lowflammability (Wen-Tsai). HFC's have near zero ozone-depletion potential and have been widely accepted as commercial replacements of CFC's. They are currently used as refrigerants, cleaning solvents and blowing agents. They also have a shorter lifetime because their C-H bonds are more vulnerable to attack by hydroxyls in the atmosphere. However, large amounts of industrial emissions (primarily CO₂) contribute to global warming, the trapping of heat inside the atmosphere.

Although there are alternatives such as HCFCs and HFCs, they are not as effective as CFC for some industrial purposes; these new compounds are expensive, difficult to work with and have undesirable short lifetimes. Scientists are continually looking for new alternatives to CFC's. There has been no stable and efficient substitute to date. However, various companies are investigating and developing substitutes that are more efficient, less expensive and less destructive for the atmosphere (Baker).

Despite the lack of ideal alternatives, the push for political reform worldwide has been encouraging. The Montreal Treaty represents a striking example of international cooperation. Initiated by pioneering scientists who identified the cause of a major potential danger, essentially all nations agreed to take joint preventive action. Regrettably, such cooperation is rare. Nevertheless, the Montreal Treaty has shown that effective international cooperation can be achieved. Baker, Scott; Price, Kirstin. Student's Guide to Ozone and UV. http://www.biospherical.com/nsf/student/ (accessed Feb 23, 2010); BSI.

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