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AEROSOL PROPELLENTS

AN AEROSOL propellant is defined as an essentially non-toxic aeroform fluid capable of exerting pressure when held in a sealed container at room temperatures. A more specific industry definition enlarges the scope to those fluids which boil at or below 105°F (40.6°C) at normal atmospheric conditions. This has the effect of including methylene chloride as a propellant. Another definition considers what is termed the "true propellant": a material capable of expelling the contents of an aerosol container. Such commodities as trichloromonofluoromethane (P-11), isopentane and methylene chloride would then be excluded. According to regulations issued by the Department of Transportation (DOT) in the U.S.A., all true propellents are identified as compressed gasses. Within industry circles, this term is more or less reserved for the high pressure propellents, such as ethane, carbon dioxide, nitrous oxide and nitrogen. Almost all the aerosol propellents exist as liquids at room temperatures. Exceptions are gases like nitrogen and helium. Ethane is borderline, with a critical temperature at 90°F (32.3°C) above which the liquid phase cannot exist.

Propellents can be classified broadly as:

a. Fluorocarbons

- i. True fluorocarbons $C_wH_xF_y$
- ii. Chlorofluorocarbons $C_wH_xCl_yF_z$
- iii. Bromochlorofluorocarbons $C_wBR_xCl_yF_2$

b. Hydrocarbons C_wH_x

c. Ethers

- i. Dimethyl ether and homologues C_wH_xO
- ii. Tetra- and perfluorodimethyl ethers $C_wH_xF_yO$
(Discontinued)

d. Compressed Gases CO_2, N_2O

N_2, A , etc.

e. Methylen Chloride CH_2Cl_2

f. Miscellaneous

i. Methyl bromide (fumigant)	CH_3Br
ii. Ethylene Oxide (sterilant)	$\text{C}_2\text{H}_4\text{O}$

The earliest aerosol propellant was undoubtedly carbon dioxide, recorded as early as the 1860s in U.S. Patent 8,834 and other documents as a means of expelling milk products and other beverages in aerated form. Fifty years later Gebauer and other firms sold cans and glass tubes of ethyl chloride (B.P. = 54°F or 12.3°C) to chill and partly anesthetize the skin prior to minor surgery. The most popular was Kelene, by Gebauer. In Rotheim's early patents, starting about 1931, the Norwegian "father of aerosols" recognized the advantages of using liquefied gases to expel products out of cans. He used various hydrocarbons, methyl chloride and dimethyl ether. Some of his samples survive today, in working order.

During the 1930s Thomas Midgley of E.I. duPont deNemours Co. developed a number of fluorinated refrigerants, of which Freon 12 was the most important. U.S.D.A. scientists Lyle Goodhue and William Sullivan used Freon 12 in 1943 to develop their famous "World War II Bug Bombs", which usually contained about 90% of the propellant. Beginning about 1947 other firms started joining DuPont in the manufacture of chlorofluorocarbons for both aerosols and refrigeration purposes.

The hydrocarbon gases, which became the dominant propellant type worldwide in 1979, did not actually attain any importance until 1954 because of a general lack of low-odor material, plus a strong feeling that they were too flammable to be used safely in aerosols. Three things happened in 1954: the first reliable mechanical break-up valve was developed (at Risdon Manufacturing Co.), Phillips Chemical Co. started to offer bulk quantities of essentially odorless "Pure Grade" propane and butanes, and a famous court battle started that upheld a U.S. Patent on the use of chlorofluorocarbons propellents for shave creams. This had the effect of precipitating the industry into water-based hydrocarbon products, such as window cleaners and shaving creams.

Technically, three ethers qualify as aerosol propellents, using the expanded 105°F (40.6°C) definition: dimethyl ether (B.P. = -12.1°F or -24.5°C), methyl ethyl ether (B.P. = 51.4°F or 10.8°C) and diethyl ether (B.P. = 94.1°F or 34.5°C). Dimethyl ether has unique solvent properties and is fast gaining in importance.

The methyl ethyl ether will probably not ever be used. The pressure is too low and toxicological clearance costs would be very high. In the case of diethyl ether we really have a product, rather than a propellant. It is used uniquely in engine starter aerosols, where a typical formula would contain 90.5%, plus about 0.5% of lubricating oil and 9% carbon dioxide. The carbon dioxide provides a good pressure which survives rather well even at -25°F (-31.7°C), which is a requirement for this particular product.

The fluorinated ether propellents, typified by 1,1,2,2-tetrafluorodimethyl ether ($\text{CHF}_2 \cdot \text{O} \cdot \text{CHF}_2$) and perfluorodimethyl ether ($\text{CF}_3 \cdot \text{O} \cdot \text{CF}_3$) have been offered first by W.R. Grace & Co. and later by Phillips Chemical Co., but are now discontinued, probably due to cost and the expense of completing the toxicological studies. They would have been ideal propellents from a number of important aspects.

Those fluids which are handled as liquid propellents extend from ethane/propane blends (B.P. = -50°F or -45.6°C) to the chlorofluorocarbon known as P-114 (B.P. = 38.4°F or 3.6°C). These pure or blended liquids are contained in sealed pressure tanks and normally gassed into aerosols either through the valve (T-t-V) or around the valve cup (U-t-C). In rare instances, the non-flammable, chlorofluoromethanes may be filled by refrigeration methods, which (incidentally) was once the dominant method for adding propellant to aerosol containers. On the world scene at least two firms are adding hydrocarbon propellents to containers by a cold fill method, but this is considered extremely dangerous from a flammability standpoint.

The higher pressure aeroform liquids, such as carbon dioxide, are stored in "receptacles," where the internal pressure is maintained at about 300 psig (2.07 MPa) by a combination refrigeration and heating system. A gas stream is withdrawn from the outage space and piped to the gassers or gasser-shakers, as the case may be, for injection into aerosol units. Even though the liquid temperature in the heavily insulated "receptacle" tank approximates 0°F (-17.8°C) at equilibrium, significant withdrawals from the gaseous phase results in cooling of the liquid, so that a heating unit must be used to restore the original temperature.

Of the non-liquefiable propellents only nitrogen gas is of commercial importance. The gas is purchased normally in the form of unitized banks of five-foot (1.52 m) cylinders, all piped to a common outlet. The cylinder pressures, which start about 3000 psi (20.7 MPa), are

reduced to about 250 psig (1.72 MPa) using a pressure regulator and the medium-pressure gas stream is then piped to the U-t-C gasser or gasser-shaker machine used to inject the propellant into aerosol cans. Larger installations are very rare, but in such cases cylinders of liquid nitrogen are used. The gas may be employed also in aerosol plants for dry blanketing of tanks containing moisture sensitive materials, and for the purging of moist air from aerosol containers to be filled with these same materials.

The non-liquefiable propellents could also include argon, air and methane, all of which have been looked at, although probably none have been used to any significant commercial extent. They are sometimes called "fixed" or "permanent" gases. Nitrogen and the related gases probably are not used to pressurize more than about 0.1% of all aerosol cans.

Many aerosol formulations are pressurized using a single propellant, and this has certain advantages in terms of pressure uniformity during use of the product, but limits the formulator in terms of pressure selection, delivery rate and other parameters. As a result, many aerosols use blends of two and sometimes three propellents. In addition to improvements in the product, these blends sometimes provide economic advantages. Perhaps the most common of all propellant mixtures are those of propane and isobutane. They offer the formulator a pressure range of from 31 to 109 psig at 70°F (214 to 751 kPa at 21.1°C).

Although very few blends are technically contraindicated, there are many that provide no particular formulation or economic advantage. Examples of useful blends include the addition of modest amounts of propane to isobutane to get Propellant A46, which is the standard blend for shaving creams. With isobutane alone, a puff of shave cream foam would undergo some residual expansion, but with Propellant A46 this does not occur. Going higher in pressure than Propellant A46 serves no purpose and could even require an extra-strength container. Another example is the addition of P-11 to isobutane to reduce the production of irritating, air-borne dust in the case of hydrocarbon-propelled antiperspirants. The P-11 helps to carry the aluminum chlorhydrate particles to the underarm area, after which it evaporates quickly. This particular application of P-11 is now prohibited by regulation in the U.S.A. but a very similar effect can be achieved by replacing the isobutane with a mixture of about equal parts of propane and isopentane. In this case, the isopentane

acts as the carrier fluid. As a last example, a rather old patent covers the addition of 15% carbon dioxide to nitrous oxide, to give a blend that has neither the tart taste of CO₂ or the sweetish taste of N₂O. The blend, sometimes called "White's Propellant", has been used in pressurizing whipped creams.

Production considerations are important whenever propellant blends are specified. For the filler without propellant blending equipment, the stipulation of a new blend may require the allocation or purchase of a bulk storage tank and associated foundation, pump, filter, piping system and so forth. In 1979, such a storage system cost \$45,000 installed; by 1981 this had risen to \$56,500. Many of the larger aerosol fillers have either manual or digital (automatic) blending equipment. In 1979 a typical Foxboro Corp. two-stream manual system cost about \$11,500 exclusive of tankage requirements. The cost rose to \$14,000 during 1981. Automatic installations are more convenient, but breakdowns require repairs by the supplier's service personnel as a rule, with more lengthy downtime of the equipment. For a two-stream automatic system the 1981 price was \$46,500 and for a three-stream system \$57,500, again excluding tankage needs. One thing to keep in mind with such systems is that the quantity of blended propellant should not exceed the production requirement. If it does, the heel quantity in the line tank will have to be adjusted specially to revise it to the subsequent blend.

A final approach to the production of aerosols with two propellents is to fill the propellents separately. The chlorofluorocarbon antiperspirants provide a classic example of this technique. The concentrate, consisting mainly of aluminum chlorhydrate and isopropyl myristate, is slurried with cooled P-11 in a sealed vessel. The mixture is then transferred to a filler by means of a recirculating piping system. After filling into cans the P-12 is added. In a more complex fashion, blends of carbon dioxide and hydrocarbon are added separately to aerosol cans, first by injecting the CO₂ via the Kartridg-Pak "Under-the-Cap" (U-t-C) gasser by an impact gassing technique, after which the sealed units move downstream to a "Through-the-Valve" (T-t-V) gasser where the hydrocarbon is added. Careful attention must be paid to the relationship of pressure and container strength in this type of gassing operation.

The Chlorofluorocarbon Propellents

During 1971 the U.S.A. aerosol industry used about 420,000,000 pounds of chlorofluorocarbon (CFC) pro-

pellents, about 57,000,000 pounds of hydrocarbon gases, and only a few million pounds of the other propellents. The hydrocarbons were almost always used as propellents for water-based aerosols, but rarely for anything else. In fact, their only significant application in anhydrous formulas was in hair sprays. They were added in amounts up to about 11% to make the product more economical yet not too flammable.

As in previous years, the main CFC propellant was P-12, followed closely by P-11 and then by P-114. The remaining CFCs aggregated only to about 1 or 2% of the total usage. The CFCs were used in about 55% of all U.S.A. aerosol products. In Europe, which in 1971 had an aerosol production about half the size of that in North America, the CFCs accounted for at least 85% of the units sold.

During the following five years (1971 thru 1976) modest additional inroads were made by the hydrocarbon propellents, so that in the peak CFC production year of 1976 in the U.S.A. only about 51% of all aerosols still used CFCs, either as the total propellant or as a significant portion of a blended CFC/hydrocarbon propellant. This was the lowest percentage figure of any country. In the U.K. during 1976 about 64% of all aerosols contained CFC propellents. In the less advanced countries domestic productions carried from about 80% to 100% CFC type propellents.

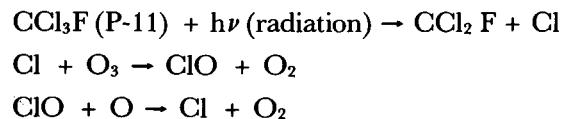
In 1972 the CFC producers became concerned about the ultimate fate of these very stable gases after they were released into the atmosphere, so they formed what is now the Fluorocarbon Program Panel under the aegis of the Chemical Manufacturers Association (CMA) in Washington, D.C. to study the situation. Among other activities, the panel retained Dr. J.E. Lovelock of Reading University (England) as a consultant. Using extremely sensitive gas chromatographic detection equipment he was able to detect traces of P-11 and P-12 in the troposphere. Concentrations were in the order of 100 ppt (parts per trillion) and the measuring threshhold of the instrument was about 10 ppt. Lovelock's figures were a key factor in advancing the research of two atmospheric scientists in California, Professor F.S. Rowland and Dr. M.J. Molina, who published their hypothesis of ozone depletion by CFCs in 1974. This highly controversial theory, which is still unproven eight years later, brought untold agony to the aerosol industry worldwide, but nowhere more acutely than in the U.S.A., where regulators in the E.P.A. and F.D.A. invoked a virtual ban on non-essential aerosol uses of the CFCs.

Rowland and Molina Theory

The theory specifically dealt with P-11 and P-12, which are by far the most common two CFCs and probably make up about 85 to 90% of all CFC emissions to the atmosphere. However, Roland and Molina considered other fully halogenated CFCs, such as P-114 and P-113, to be just as dangerous, and suggested that there were significant risks in the case of hydrogen-containing chlorofluorocarbons (as P-22) and some chlorinated hydrocarbons. The degree of risk was related directly to the stability of the vapors in the atmosphere and the chlorine content.

The main elements of the theory can be summarized as follows:

- a. For CFCs P-11 and P-12 the quantities measured in the atmosphere are approximately equivalent to the total amount produced since the 1930s, thus there appear to be no destructive processes of any significance in the troposphere.
- b. The CFCs are diffusing slowly into the stratosphere.
- c. At sufficiently high altitudes they are decomposed by the sun's ultraviolet radiation to liberate chlorine atoms which are then available to initiate a cycle that has the destruction of ozone as the net result:



- d. The Cl is removed from its active ozone-destroying status by certain reactions, for instance with methane gas to produce HCl, which is inactive so far as ozone is concerned. Eventually the HCl diffuses downward and is removed by rain. Not all the HCl suffers this fate however; some reacts with OH radicals, forming water and regenerating the original Cl.
- e. All the relevant stratospheric chemistry had been taken into account in building their model.

Based upon the new hypothesis, Rowland and Molina then did a calculation utilizing the limited information then available about reactions, reaction rates and other phenomena in the lower stratosphere, about 20 miles (32 km) high, where ozone has its greatest density. There are over a hundred reactions now recog-

nized as important within the ozone layer. The significance of many was not recognized in 1974. Where rates were not available, they were estimated, sometimes arbitrarily. Thus, having reduced the complexity of atmospheric physics into mathematical equations, the scientists cranked them into a computer capable of doing a time-dependent one-dimensional analysis (the single spatial dimension was vertical) and came up with results that indicated that the continued release of CFCs at the 1972 rate would result in an eventual reduction of stratospheric ozone of about 7 to 13% — and that this would take about 100 years to develop, owing to the slow transport of CFCs to the ozone layer and the mechanisms involved.

Even though most CFC vapors are four or five times as dense as air, when they are released at the earth's surface, wind currents disperse them throughout the troposphere within just a few months. The troposphere is the turbulent atmospheric layer nearest the earth, extending up between 6 to 12 miles (10 to 20 km), where winds blow, rain falls and temperatures decrease with altitude. At the top of the troposphere is the tropopause, the transition layer separating the troposphere and stratosphere. The temperature at the tropopause averages -67°F (-55°C). Above the tropopause lies the huge stratospheric layer, extending up another 20 miles (32 km) or so to the stratopause and, above the stratopause, the mesosphere. The stratosphere is characterized by lateral wind currents (the lowest of these are the familiar "jet streams"), relatively little vertical air motion, an absence of particulate moisture except for very tall thunderheads, and a gradual warming with increasing altitude, up to about 28°F (-2°C).

Once the CFC molecules pass through the tropopause and into the stratosphere they take an average of ten years to travel upward another 15 miles (24 km) or so into the upper reaches of the broad ozone layer, where they can be bombarded effectively by the shorter wavelengths of the sun's ultraviolet light, as yet not filtered out by resident oxygen and ozone molecules. The bombardment slowly generates Cl which, it is theorized, then attacks the ozone. This extended time-scale, or lag effect, prompted Rowland and Molina to state that we could not afford to wait for empirical proof that the ozone layer was being depleted, thus proving the hypothesis, before deciding whether or not to take action. In addition, they said that the accumulating burden of CFCs in the troposphere provided the system

with so much inertia that even with a total immediate ban on further production the depletion of ozone would increase for about 15 years. Another 50 years would be needed for the depletion to fall to half the maximum value.

In 1974, the year the hypothesis was first publicized, worldwide CFM (the saturated chlorofluoromethanes; e.g. predominantly P-11 and P-12) was 2,028 million pounds or 920 metric tons. This figure includes an estimated 10.8% contribution from the communist countries, in addition to the reported data. About 93.9% of the annual production figure, or some 1,904 million pounds (865 metric tons) in 1974 was emitted to the atmosphere in either that year or shortly thereafter. CFCs packed into aerosols, or used for sterilant gas mixtures, flexible foams or solvents were 100% emitted. Those used in refrigerators, air conditioners and rigid foams were emitted slowly. Aerosols accounted for 75.6% of the total emissions, and just two categories, antiperspirant/deodorants and hair sprays, made up over 77% of the aerosol total. Rowland and Molina recognized these relationships, at least to some extent, and they responded by calling for an immediate total ban on the use of CFCs in aerosols, which they deemed "non-essential" in any event. The news media were quick to single out aerosols as destroyers of the earth's protective ozone layer, and concentrated their attack on underarm and hair care products, calling them the worst offenders of all.

The scientific community reacted quickly to the Rowland and Molina Theory, and to their strident warning that the situation was critical. Despite the fact that the supporting evidence was very limited, and that experimental verification of the theory was largely lacking, many atmospheric scientists regarded the hypothesis as sufficiently plausible to be taken seriously. The prestigious National Academy of Science studied the theory and its portents in 1975 and concurred that there might indeed be a looming problem of major proportions. One committee chairman suggested strong federal action to limit CFC emissions, at least until more scientific investigations could be conducted to prove or disprove the theory.

Investigations were started rather quickly, and produced isolated results of limited merit, especially when the authors concluded that they either proved or disproved the hypothesis. A very large number of more detailed and difficult experiments are now in progress and sound results have begun to emerge.

Preliminary Atmospheric Chemistry

Without any doubt the presence of stratospheric ozone is beneficial to life on earth by absorbing harmful ultraviolet radiation. Non-melanoma skin cancers have been ascribed to many years of human exposure to sunlight high in ultraviolet content. While non-melanoma skin cancers are the most common skin cancer for Caucasians, they are also the most treatable form of skin cancer. Malignant melanoma, a much less common but life-threatening skin cancer, on the other hand, does not appear to be linked directly to exposure to sunlight. Some scientists feel that Caucasians may suffer about a 2% increase in the incidence of non-melanoma skin cancer for every 1% reduction in the amount of stratospheric ozone. During the mid-1970s a German team even went so far as to develop a tenuous hypothesis that the precipitate demise of the dinosaurs was coincident with a supernova some 90 million years ago, which depleted the ozone layer by at least 50%. Not having the protection of a furry, hairy or scaly coat, they succumbed to skin malignancies. Fanciful stories such as these were very much in the news during 1975 and 1976.

A second concern was the effect that increased ultraviolet radiation might have on the food chain. Animals should be relatively immune, but marine life forms might be affected, since ultraviolet light can penetrate several meters into clear water. Bacteria, algae and plant life also might be affected. The major question of all this is the matter of degree. Life forms can adapt to environmental changes up to certain limits. Thus, a 5% depletion of the ozone layer might pose no significant problems, while a 50% reduction could be disastrous. Although much of the science has yet to be developed, there are many known examples of beneficial effects in insect, plant, marine and crop life, but they have received scant mention outside of trade and technical journals.

The third and last concern is that of the so-called greenhouse or temperature elevating effect that might result from an attenuated stratospheric ozone layer. In 1980 the EPA claimed that climatological effects of a projected eventual 16.5% ozone depletion would include an increase in the mean, global temperature of perhaps 0.6°F (0.3°C) and that this would be significant, causing an expansion of desert areas, reductions in crops and melting of polar icecaps. Yet, in other reports prepared for the agency in that same year, it was concluded that modest warmings of up to about 1.5°F

(0.9°C) might be beneficial, whereas larger ones like that projected for CO₂ effects — 5.5°F (3.0°C) from 1982 to 2035 — would be adverse. Actually, the warming trend predicted from many sources indicates that CO₂ will be ten times as important as CFCs as the causative agent. CO₂ levels have risen from an assumed pre-industrial level of about 250 ppm (more scientifically expressed as 250×10^{-6} VMR, or Volume Mixing Ratio) to 340 ppm in 1983 and might increase to 680 ppm by the year 2035. Aside from the noted average global increase, such warmings are calculated to reach as high as 13 to 18°F (7 to 10°C) during the winter over the North Pole area and could lead to a 20 foot (6 m) higher ocean level by the end of the next century. All of these effects are based on projections with large uncertainties.

The carbon dioxide greenhouse effect is based on the concept that increased carbon dioxide would alter the way the earth loses heat. Incoming radiation warms the earth's surface, which loses heat by radiating infrared radiation into space. Observed temperatures thus result from the dynamic balance between incoming solar radiation and outgoing infrared radiation. Certain gases, including carbon dioxide, ozone and CFCs, absorb and emit infrared radiation. Increased concentrations of carbon dioxide, for instance, would absorb more of the outgoing infrared radiation, but the net process causes a "high-CO₂ planet" to emit radiation less efficiently than a "low-CO₂ planet." Since incoming and outgoing energy must balance, the high-CO₂ planet warms up slightly to reestablish the dynamic balance.

The process, which incidentally has virtually nothing to do with greenhouses, is extremely complex because many other factors, including ice and snow cover, clouds, etc. would also be affected by temperature changes and can themselves affect radiation equilibria. These other factors can potentially enhance (positive feedback processes) or counteract (negative feedback processes) the highly simplified concept described. These feedback processes are, therefore, major sources of the large uncertainties associated with these calculations of long-term temperature changes.

Solar radiation that includes wavelengths throughout the entire ultraviolet range strikes the upper atmosphere, but wavelengths shorter than about 180 nm do not penetrate as far as the stratosphere. Those in the range of 180 to 260 nm reach into the upper stratosphere and are absorbed by molecular oxygen, which ruptures into oxygen atoms. The energetic oxygen

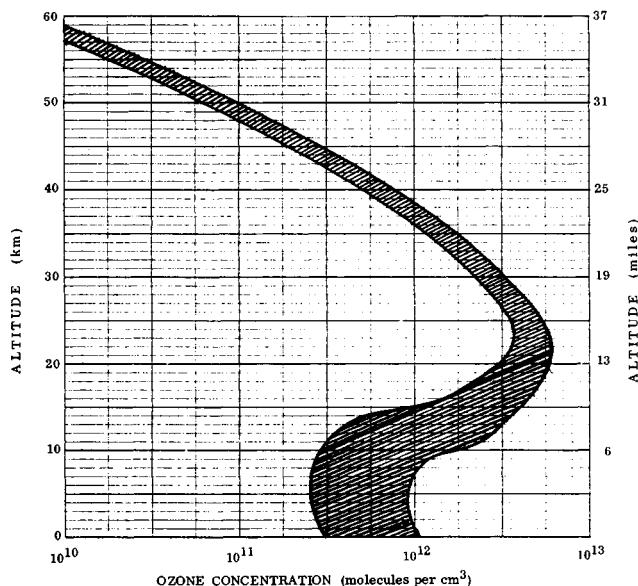


Figure 1. Concentration Profile of Atmospheric Ozone

atoms combine with oxygen molecules to produce ozone. All the ozone in the stratosphere is formed in this fashion.

The ozone inventory of the atmosphere stretches continuously from the earth's surface to at least 50 miles (80 km) in the mesosphere, by which time it has thinned out to an estimated 5×10^6 molecules per cm^3 , too attenuated to be measured. Figure 1 shows the concentration profile of ozone with altitude.

The concentration is expressed in absolute terms: as molecules per cm^3 . If it had been given in relative terms, such as ppm or ppb, a very different shape would have resulted, since the air thins so profoundly at upper altitudes. For example, at 12.5 miles (20 km) the air pressure is only about 13 mm (0.25 psi or 1.7 kPa), which is 1.7% of normal pressure at sea level. Considering the maximum of the measured ozone range, an easy calculation suggests a relative ozone concentration of 2.4 ppb at sea level and one of 1.8 ppm at 12.5 miles (20 km), about 750 times higher. The ozone layer provides its greatest absorption of ultraviolet radiation at an altitude of about 13 miles (21 km). It is not truly a "layer" at all, although if one were to be fantasized it would lie conveniently in the range of 8 to 20 miles (13 to 31 km), since this band should generally contain at least 3×10^{12} molecules per cm^3 .

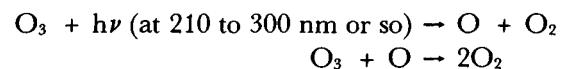
The concentration of ozone is quite variable at different points on the earth. It ranges from a low of about

225 milliatmosphere-cm (Dobson Units) at the equator to almost 400 D.U. at the northern tip of Quebec. The NYC area has about 320 D.U. of coverage while southern Florida has only 275 D.U. and this 14% difference in ozone overlay accounts, in part, for the faster tanning or burning of skin in southern Florida. The comparison invites the suggestion that a 14% reduction of ozone in the stratosphere, ignoring other factors such as latitude, would cause the equivalent of Florida sunshine in NYC, and one notes that the flora and fauna of Florida are doing well.

The amount of ozone at any one location also undergoes a substantial change. Ozone decreases slightly during the night and increases slightly by day. In the spring, ozone may be 30% more plentiful than in the autumn. Strong weather fronts may change the concentration by as much as 34%, although equilibrium is restored quickly. And finally there are the so-called eleven year sun spot cycles which change ozone by about 5%.

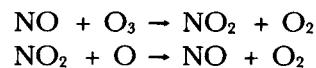
Once formed, ozone itself can absorb the sun's ultraviolet radiation, breaking down into an oxygen atom and oxygen gas in the process. It absorbs most strongly at about 250 nm, and absorption is also important between about 200 to 310 nm. (A modest absorption range also exists from about 460 to 750 nm in the visible spectrum, which is why concentrated ozone looks blue.) In addition, atomic oxygen is capable of attacking ozone to form oxygen gas. Much of the early work on these reactions was done by Chapman, and they have become known as the Chapman reactions. More recently they have been described as "odd-oxygen processes" since an atomic oxygen unit or ozone itself has been involved in each. The term also has a relationship to other processes that deplete ozone.

Odd-oxygen processes (Chapman Reactions):

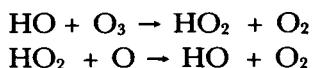


Three additional processes act to deplete ozone. Each of these is a cyclic type; that is, the original initiating compound is regenerated in a catalytic fashion and continues to react until it is removed from the site by diffusion or by reacting with other compounds to form temporary or permanent sinks. The odd-nitrogen process is the most important:

Odd-nitrogen process:



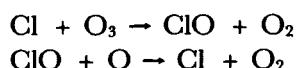
The odd-hydrogen process is very similar:



By summing up either of these cyclic reactions the overall process is seen as one where a molecule of ozone and an oxygen atom (itself a precursor of ozone) is transformed to two molecules of oxygen gas, thus depleting ozone.

The last significant reaction cycle for the possible depletion of ozone was that discovered in 1973 or so and termed the chlorine oxide cycle. Chlorinated organic compounds injected into the stratosphere from such diverse sources as volcanoes, biospheric reactions, the space shuttle, industrial emissions and aerosols could be stripped of their chlorine content by ultraviolet radiation, and the chlorine atoms might then attack ozone.

Chlorine oxide cycle:



As before, ozone and oxygen atoms are transformed to oxygen molecules as the net result.

Finally, there are a host of minor reactions that can, at least theoretically, act to deplete ozone. For example, bromine can be stripped by radiation from bromine compounds, and can then react in a bromine oxide cycle, perhaps even synergizing the chlorine oxide cycle in the process, making it about 10% more potent, according to some researchers. Also, some ozone is undoubtedly lost from the stratosphere as a result of downward travel to the troposphere, even though this is partially offset by ozone in the troposphere formed as a result of electrical storms, combustions and other reactions, which diffuses to the stratosphere.

An extremely important aspect of the three cyclic reactions is how long they can be sustained. On a statistical basis, does an NO, HO or Cl particle react with ozone a hundred times or a hundred thousand times before something happens to break the chain? The NO₂ and OH entities are required for the perpetuation of their respective cycles, yet they can also react with each other to form nitric acid in the presence of a third body. Nitric acid is reasonably stable, but can be attacked either chemically or photolytically to some extent so that the initial oxides are reintroduced. In this sense it functions as a temporary sink, eliminating reactants only for a limited time. However, if it diffuses down and is removed by rain, then it can be regarded as a permanent sink.

During 1976 an important new sink was discovered, involving the reaction between ClO and NO₂ to form ClNO₃, chlorine nitrate. As a sink, ClNO₃ has both temporary and permanent properties. It can be degraded more readily than nitric acid, but it is also able to rapidly hydrolyse to HCl, HClO and HNO₃ with moisture and be rained out. The introduction of ClNO₃ in the calculations caused many theoreticians to reduce their ozone depletion figures downward to about half the earlier values.

The relative importance of the known major sinks involve many factors, including the concentration of the reactants and the reaction rates. Both of these vary with altitude and temperature. In a crude sense, the ozone inventory can be likened to the amount of water in a bathtub, with the faucet adding more and the drain partially open to take some away. The rate of "addition" is as constant as the quantity of the sun's ultraviolet radiation. The rate of "drainage" can be affected by the level of both natural and anthropogenic injections of ozone-depleting chemicals into the stratosphere and by the amount of ozone present. Using the data available in 1978, estimates are made of the relative importance of the major depletion reactions. This is illustrated in Table I.

An indication of the sensitivity of the data to concentration and reaction rate factors can be obtained from the Cress Report No. 131, prepared by SRI International for the EPA in mid-1980. In contrast to the Sanders* data the report claims that nitrogen oxides (NO_x) are less effective in reducing ozone than CFCs. Also, other halogenated species are less important depleters than CFCs. During the 1970s several potential ozone threats, including the SST and nitrogen based fertilizer episodes, have waxed and waned as new information has caused changes in the results from the computer calculations.

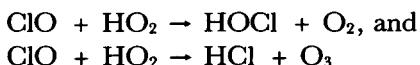
*Dr. Paul Sanders of E.I. du Pont de Nemours & Co.

TABLE I
Stratospheric Removal of Ozone (Estimated)

1. Odd-oxygen processes (Chapman)	15 to 20%
2. Odd-nitrogen cycle	50 to 70%
3. Odd-hydrogen cycle	10 to 15%
4. Chlorine oxide cycle	20 to 0%
5. Other processes	1 to 2%
Bromine oxide cycle	
Transport to troposphere	
Others - known and unknown	

Another factor of extreme importance is the continuing search for sinks: mechanisms that remove effectively potential ozone-depleting compounds and thus act to decrease ozone depletion rates. One type of sink would act to prevent or delay potential ozone depleters from forming in the first place. For instance, very dry sand particles, in the presence of strong sunlight, absorb P-11 and perhaps P-12 from the troposphere and possibly change them to P-21 (CHCl_2F) and perhaps P-22 (CHClF_2), respectively. The presence of unexplained higher levels of P-21 downwind from the Sahara Desert has been suggested as empirical evidence of such a sink. However, researchers have not yet been able to quantify this effect. Another possible sink involves the entrapment of P-11 in the upper layers of the Antarctic ice mantle. Some CFC emissions find tropospheric sinks in the seas, but the concentrations are quite low and fall off rapidly with increasing depth. Again, the significance of this effect is not known. The intriguing point of all this is that the model calculations are very sensitive to such CFC sinks. Even slow tropospheric removal processes could reduce substantially ozone depletion calculations.

Other processes with the potential to alter present calculations are possibly to be found in the stratosphere. The products from the reaction between hypochlorite (ClO) radical and hydroperoxyl (HO_2) radical are of current interest because they might help explain the high 2 and 8 ppb ClO levels found by James G. Anderson in mid-1977 and later. The theory calculates about 1.0 to 1.5 ppb. If confirmed, they could alter the ozone depletion calculations. One research team has considered the two most probable reactions:



commenting that, if the second reaction accounts for as much as 10% of the total mechanism, current predictions for eventual ozone depletion would drop by a factor of about three.

In measuring reaction rates, frequently only the disappearance of reactants is measured, not the rate of reaction product formation, and sometimes the nature of the products is only assumed. Yet they are quite important. If there is a significant reaction between the ClO and HO_2 radicals, any HCl formed would provide the Cl moiety with an enhanced downward path to the troposphere where it could be rained out. In the same fashion, any HOCl formed would be decomposed by ultraviolet radiation. If $\text{Cl} + \text{O}$ were formed, the ozone

should increase; if $\text{OH} + \text{Cl}$ were formed, it should have almost no effect, and if $\text{H} + \text{ClO}$ were to be formed, there should be a decrease in ozone.

The values given for the degree of ozone depletion have generally been based upon the model suggesting a continuous emission of CFCs at the 1976 levels, until a steady state is reached, sometime after about 2100. Steady state is approached asymptotically, so that the selection of an actual date becomes somewhat arbitrary after about 2060. The values start with a 1974 range of 13 to 18% ozone depletion, as proposed by Rowland and Molina. As the science progressed they fluctuated, both up and down, and the present values are mostly between 5 to 7%. The theoretical variations are shown in Figure 2.

In addition, it is appropriate to recognize that uncertainties remain with the latest and much lower calculations, and that further revisions are likely.

A limitation in the theories set forth by Stolarski and Cicerone, Rowland and Molina and other atmospheric scientists during the mid-1970s is that they were

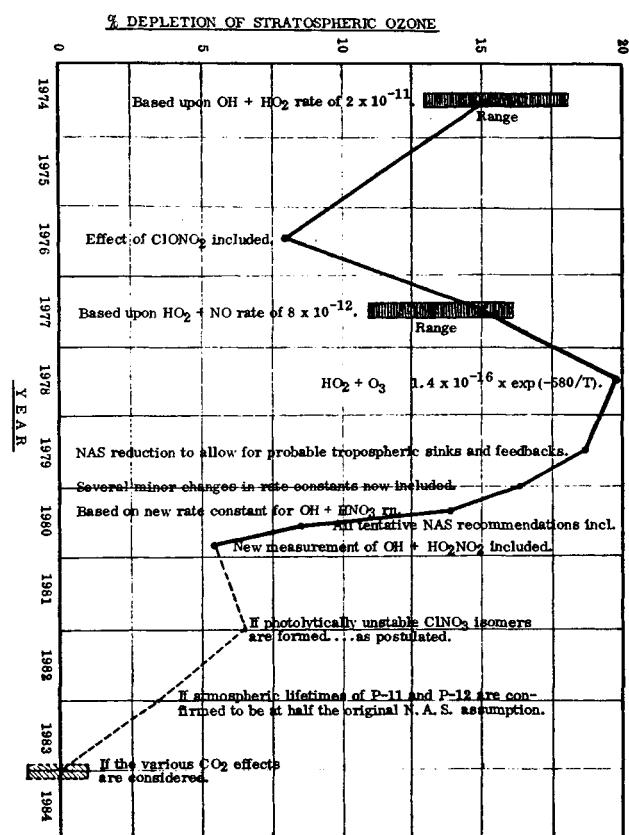


Figure 2. Per Cent Distribution of Stratospheric Ozone

necessarily based upon one-dimensional computer models. The atmosphere obviously has three dimensions, and to analyse such complex components as the ozone system by the use of a one-dimensional scenario requires major simplifications. Crudely put, it is a bit like trying to define and describe a person by looking at the individual through an extremely thin slit. In addition to assumptions that had to be made concerning reactions and rate constants, further assumptions were required to accommodate limitations of the computers. Although the investigators admitted that they could not handle many known complexities, because of the fixed parameterization of atmospheric dynamics which is an adjunct of one-dimensional modeling, and were therefore resorting to consensus assumptions, this important fact was apparently lost on the press and the regulators. These groups only recognized that a number of supposedly independent groups were coming up with very similar results and conclusions, not that they were using essentially the same science, the same assumptions and the same computer hardware, so that the development of an equivalent end product was reasonably well assured.

Limited two-dimensional computer models, used since about mid-1978, show that ozone concentrations, and any depletion, is somewhat dependent upon latitude. As mentioned earlier, ozone levels are much higher near the poles, and particularly in the north Hudson's Bay area of Canada. Somewhat greater ozone depletions are now predicted to take place during the polar winters where the intensity of ultraviolet radiation is small to begin with, and where the attendant increase in radiation would also be low. The population above 60°N latitude is quite small and that

below 60°S latitude is nil. Sunbathing or other activities involving high exposure of the skin to sunlight would be impossible in climates where the sun is generally below the horizon and the temperatures range from -30 to -75°F (-34.5 to -59.5°C).

Further work elaborating on the earth's ozone system is continuing, with a significant portion funded by industry. Studies are concentrated in a number of key areas. For example, the reaction rate constants of the interactions between OH radicals and various species are leading to a lessening of the discrepancies between theoretical and actual ClO concentrations. A better knowledge of vertical transport rates in the stratosphere is needed, since modelers have cautiously assumed very low rates, and such assumptions have acted to increase the calculated figures for eventual ozone depletion. Still further confirmations are needed to prove that HCl concentration decreases with increasing altitudes over about 19 miles (30 km), since the observed decreases fly in the face of the theory. More work is also in progress to better define the significance of some unpredictably high ClO variations to date. Studies are needed to extend our knowledge of coupling (reciprocal interference) between the various catalytic cycles. They are interrelated so closely that they cannot be assessed on a separate basis. The continuing question of tropospheric sinks urgently needs further study. The investigators of the mid-1970s felt there was no reduction; that P-11 and P-12 had lifetimes in excess of 100 years. For example, if it could be shown that these CFCs are sunked (removed more or less permanently) at 5% per year, the ultimate ozone decrease predicted by the theory would have to drop by 60% or so. And finally, there is the question about the effects of increasing carbon dioxide injections into the stratosphere.

TABLE II
Increase in Carbon Dioxide Volume Mixing Ratio (1800 - 2060)

Year	CO ₂ Level (VMR × 10 ⁶)
Historic level)	250
1800	275
1925	290
1972	325
1983	340
2020*	425
2030*	600
2060*	1100

*Assuming the burning of fossil fuels and deforestation trends are sustained.

The data of Manabe, et al (*J. Atmos. Sci.*, 1975) and other teams have suggested a growing CO₂ presence in the atmosphere, as shown in Table II.

Using this data, Luther, et al (*J. Geophys. Res.* 1977), Groves, et al (*Nature* 1978 and 1979) and other investigators have considered the effect of increasing concentrations of CO₂ on the ozone inventory. The computations all point to a lowering of upper stratospheric temperatures which would result in significant increases in total ozone column density. The photonic Chapman reactions that generate ozone are expected to proceed with increased efficiency, while the rate of any CFC depletion reactions is expected to slow. Since OH and HO₂ radicals have key roles in controlling ozone

above 25 miles (40 km), any increase in tropospheric temperature resulting from CO₂ increases would affect ozone by increasing the supply of water vapor to the stratosphere through the equatorial "cold trap". Although computers available to date have not been able to handle such attendant complexities as the sensitivity of atmospheric circulation to changes in radiative field in the lower stratosphere, the dynamics of transferring ozone downward, where it is better conserved, and the effect of concentrations of CO₂ in excess of two times the current atmospheric levels, still the overall effect from these parameters can be analysed to show that increased CO₂ significantly increases ozone.

The latest paper by Groves, et al (1979) considers the effect of raising the CO₂ concentration from 275 to 600 ppm (volume) in an atmosphere also containing 0.75 ppb methyl chloride (CH₃Cl), 0.13 ppb carbon tetrachloride (CCl₄), 0.8 ppb P-11 and 2.3 ppb P-12, with the latter two molecules relating to steady state 1975 rates. This so-called chlorine chemistry model showed that the effect of increasing the CO₂ level would result in an overall increase in ozone of 2.3%.

A recent development of substantial interest is the ability to perform model calculations in which several emissions calculated to affect stratospheric ozone are considered simultaneously. Previously, calculations varied one emission, for instance CFCs, while the other atmospheric inputs were kept constant. This was clearly an unrealistic scenario. When CFCs, carbon dioxide and nitrogen oxides from aircraft operations and denitrification of synthetic nitrogenous fertilizers are considered simultaneously, important offsets and interactions are found to occur. To date, only calculations for the period 1960-1965 have been published (National Aeronautical & Space Agency and World Meteorological Organization [NASA/WMO]: The Stratosphere 1981 - Theory and Measurement), but these show that the overall effect upon ozone is negligible — less than a 0.2% increase or decrease for the period. It is important to emphasize that this does not eliminate the concern, since major uncertainties in the calculations remain and further scientific research is essential. However, what it does mean is that, as far as the urgency for further regulation is concerned, (1) we are clearly not faced with a crisis, (2) there is ample time to obtain a clearer scientific picture without significant risk to human health and the environment, and (3) to date there is no proof that CFCs or any of these other activities are having any real impact on ozone.

Empirical Ozone Measurements

The high variability of the earth's ozone inventory according to diurnal, seasonal and sunspot cycles has been mentioned. It also changes with latitude in a complex fashion. Even vulcanism is a factor. During the 1976 eruptions of Mount St. Augustine in Alaska some 400 million pounds (180 million kg) of chlorine (as various vaporized compounds) were injected straight into the stratosphere. This amounted to about 36% of the chlorine going into CFCs in that year. These disturbances have made actual measurements difficult and the construction of hemispheric or total world inventory figures even more difficult.

The classical instrument for measuring atmospheric ozone is the Dobson spectrophotometer. Measurements are made in Dobson Units (D.U.), layer thickness expressed in milliatmosphere-cm. For example, the ozone column isopleth (concentration contour line) that cuts through the New York City area is 320 D.U., which means that if all the ozone were concentrated into a layer of pure gas at sea-level conditions it would be 0.126" (0.32 cm) in thickness. Ozone monitoring stations at Oxford, England and Arosa, Switzerland have been in operation since 1925. During the 47 year period ending in 1972 they measured an irregular total gain of about 6% in the ozone layer. However, the earlier measurements are subject to some questions of accuracy. A more reliable survey has come from a range of up to 39 Dobson station results between 1958 and 1975, showing a 4% gain in the Northern Hemisphere. The data in Figure 3 (Page 316) uses the results of several recent measuring sequences to suggest a 5% increase between 1954 and 1978. The significance of these increases is not known.

Fewer measurements have been made in the Southern Hemisphere, perhaps because less than 10% of the chlorofluorocarbon industry is located there. CFC emissions in the Southern Hemisphere are also probably less than 10% of those in the Northern Hemisphere. With this background it is interesting to note that the increase of ozone below the equator has occurred at only about 25% of the rate in the Northern Hemisphere. Again, the significance of this estimate is not known. Although the exchange rate between hemispheres is very slow, due to trade wind influences, nevertheless, there is speculation that some of the excess ozone in the north may have drifted south. This would suggest that long-term measurements of ozone over the

Northern Hemisphere have given increase figures that would have been larger, had it not been for the drain-off effect.

Until about 1980 all that could be suggested was that the sum total of natural and anthropogenic (man-made) injections of various chemicals into the stratosphere, plus other ozone-affecting factors, seemed to have caused a net increase in ozone averaging about 2% per decade and possibly increasing in rate. It was also recognized that about 4.7 billion pounds (2.13 million metric tons) of P-11 and 7.35 billion pounds (3.33 million metric tons) of P-12 had been produced by the Free World by the end of the 1960s, and that about 80 to 90% of this total amount had been released to the atmosphere. Given a ten year period for the slow vertical transport through the stratosphere and into the upper ozone layer area, one could point to an infusion of about 10 billion pounds (4.5 million metric tons) into the ozone layer by the end of the 1970s, and yet the only empirical result seemed to be a possible *increase* in ozone.

During the year 1980, satellite data was used to confirm that the results of the many ground-based ozone monitoring stations were globally representative, that no geographical bias was caused by the distribution of the stations throughout the world. But perhaps even more important, the complex technique of "ozone trend analysis" was developed. The technique involves the mathematical removal of all known natural varia-

tions in ozone concentrations using computers. After this, if the remaining ozone averages were changing from year to year, this would be due to man's activities, such as the production and emission of CFCs, or to hitherto unrecognized natural variations. The results of Reisel and Tiao at the University of Wisconsin, for instance, have shown that during the 1970s the most likely trend in ozone was an 0.8% increase globally. The calculated 95% confidence limit of this result is $\pm 1.3\%$ for the decade. In other words, it was very likely that the ozone inventory in the 1970s changed from the initial value to a range of from 2.1% upward to 0.5% downward.

When compared with the 1979 computer model results showing a range of from 0.6 to 3.6% downward (with a reduction of 2.1% being considered most probable), it is clear that the best empirical results obtainable are inconsistent with those obtained by the theoretical models in 1979. However, with the much-reduced 1981 calculations, one can only conclude that models and actual observations are not necessarily inconsistent and that further work to refine calculations and ozone trend analysis techniques is necessary.

In 1981 the technique of ozone trend analysis had developed to the point where a change of about $\pm 1.3\%$ in ozone averages could be detected. In subsequent years, with additional ozone measurements, the sensitivity and confidence of ozone trend analysis is expected to increase. During the 1970s the cumulative

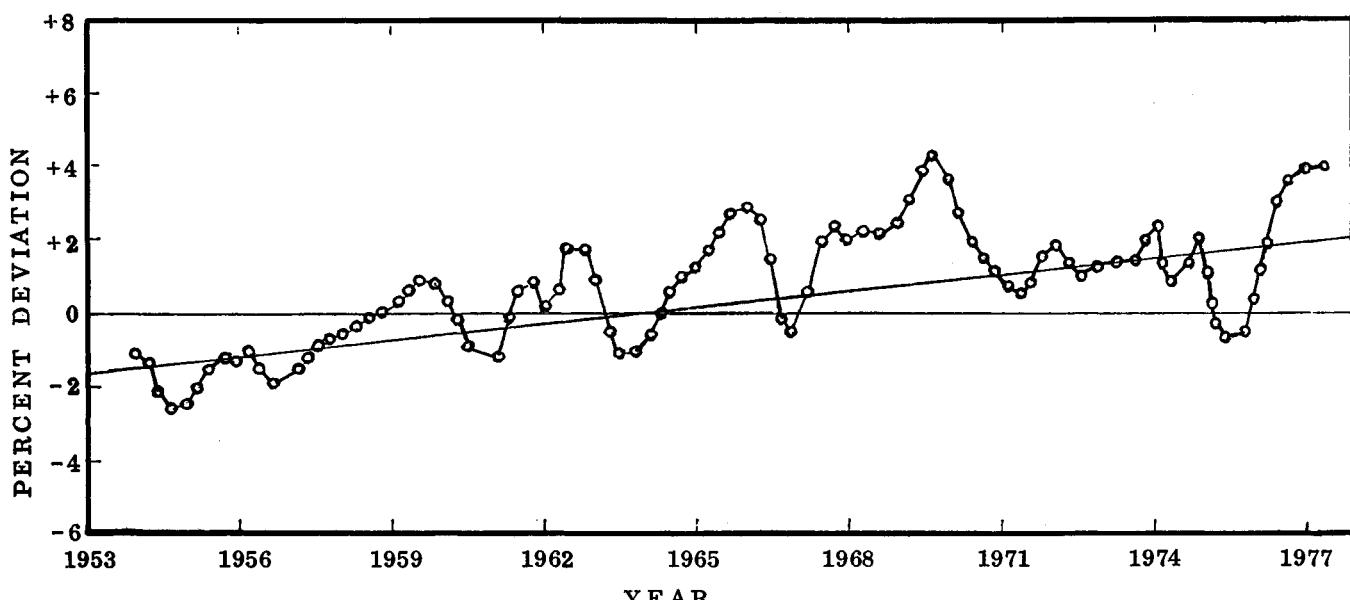


Figure 3. Total Ozone Over the Northern Hemisphere

Free World production of P-11 grew to 7.7 billion pounds (3.5 million metric tons) and P-12 increased to 11.2 billion pounds (5.0 million metric tons). These figures show an overall CFC inventory increase of 57%, discounting sinks.

Regulatory Activities

Almost immediately after the Rowland and Molina theory was promulgated in *Nature* and various other periodicals in 1974, the press and consumer groups applied pressure on Washington, D.C. to eliminate any further production of chlorofluorocarbons, especially for aerosol uses. Within several months a preliminary assessment was reported by the President's Council on Environmental Quality, which became known as the IMOS document. It cited the issue as a legitimate cause for concern, and that if the National Academy of Science confirmed the theory and predictions, then uses of P-11 and P-12 should probably be restricted to the recharging of existing refrigeration and air conditioning equipment. New fluids would have to be developed for essentially all other then current uses of CFCs.

The National Academy of Science first assessment was issued in September 1976 and acted to condemn the CFCs, based upon what was then known and conjectured. The report by their Panel on Atmospheric Chemistry suggested that ozone would be depleted slowly at about 0.07% per year, to a calculated 7% steady state reduced level in 100 to 200 years. However, the data was so uncertain that the probable range of final depletion could only be established within a range of from 2 to 20%. The second NAS report was provided by their Committee on Impacts of Stratospheric Change, sometimes called the Tukey Report. It suggested a moratorium of not more than two years be set up for the establishment of further test data, after which, in the absence of evidence to show that ozone levels would be reduced by no more than a few percent, various forms of restrictions on CFC uses should follow. While noting that such sanctions were a political matter, the report stated that aerosols were a major source of CFC release and that ozone depletion was a global concern requiring international attention. Other areas covered environmental concerns, such as skin cancers, climatological effects and so forth.

Under the Federal Clean Air Act Amendments, the Toxic Substances Control Act and other legislation it became apparent that three Executive federal agencies: EPA, CPSC and FDA had ultimate jurisdiction in

regulating the CFC problem. Of these, the EPA had very broad authority over not only aerosols but all other uses of CFCs. It therefore became the lead agency. During 1977 the CPSC indicated they would leave most future CFC decisions to the EPA and FDA. After assessing the NAS reports and hearing other testimony, the EPA and FDA proposed a phase-out schedule for CFCs in aerosols, except for a few special medical items and other justifiable products. Under the regulations no CFC aerosols could be shipped interstate after April 15, 1979, unless exempted. (See Table IV page 320.)

The EPA officials then attempted to export their policies to the rest of the Free World. In 1978, for instance, only 39% of the world production of CFCs was made in the U.S.A., with practically all of it going into non-aerosol applications, such as refrigeration, air-conditioning, solvents, flexible polyurethane foam, rigid foams, sterilization mixtures, fire extinguishers and fast-freezing. Canada rapidly passed regulations eliminating CFC propellents from certain toiletries, such as underarm products and hair spray aerosols. Since about 82% of CFC aerosol usage in both the U.S.A. and Canada had gone into cosmetic and toiletry products, the Canadian decision was very effective in limiting the further use of CFCs in aerosols. (Solvent-based applications of P-11 are still permitted in Canada, for all aerosol products.)

Meanwhile in Europe the nine-country bloc eventually reacted by asking for a voluntary 30% reduction in aerosol CFC uses (based on 1976 levels) by the end of 1981. This was accomplished with only moderate pain, and the Ministers are now recommending a voluntary "freeze" for the future at the end of 1981 level. But in the interim, a number of specific countries have become concerned over the highly publicized dire predictions of the EPA and consumer groups. They have now either enacted or are considering legislation which would restrict aerosol uses of CFCs on a unilateral basis. Norway and Sweden adopted virtual bans in 1980 and 1981, respectively. Denmark may ban propellant uses of CFCs during about 1983, or else slowly snuff them out by about 1986 to 1988. Switzerland is seeking regulatory authority to propose a propellant ban, if further reassuring data is not developed by about the beginning of 1983. In Portugal an investigation into the CFC/aerosol situation is in progress, with the industry hoping to avoid a ban. And in Austria, a CFC aerosol ban may be enacted if feasible alternatives become available locally. Japan and Latin American countries

have not taken positions, although Japan may well go the way of Europe if CFC aerosol bans on that continent become widespread. One of the current Japanese problems involves a long-standing law that forbids the use of any flammable propellents in cosmetic aerosol products. This law is now being challenged by firms wishing to sell dimethyl ether (DME) and other propellents in this important marketing area.

The effect of the U.S.A. regulations was to reduce the use of CFCs in aerosols from a peak of approximately 500 million pounds (230,000 metric tons) in 1973 to about 14 million pounds (6,300 metric tons) in 1981. Furthermore, the size of the aerosol industry itself was reduced by over 35% in the process. While this half billion pound (225,000 metric ton) reduction was significant, representing about a quarter of the world production figures for each of the years 1973 through 1976, the EPA noted that they would be unable to meet their goal of 5% maximum ozone reduction, based upon the National Academy of Science (NAS) figures. They also noted a slow domestic growth in the use of CFCs for non-aerosol applications: from about 370 million pounds (180,000 metric tons) in 1973 to some 550

million pounds (250,000 metric tons) in 1979. Faced with only slight success in Europe, and total frustration in Latin America, Africa and Asia, the EPA again turned their attack on American industry, this time to the non-aerosol CFC applications. See Table III.

On October 7, 1980, the EPA issued an Advance Notice of Proposed Rulemaking (ANPR) on CFCs. They started with the premise that the 1979 NAS figure of a 16.5% ozone depletion at sustained 1977 production levels was still valid. Also, that the world production of CFCs would grow at 9% (and the U.S.A. production by 7%) during the decade of the 1980s unless somehow stifled by regulations, thus, theoretically increasing ozone depletion into the 35 to 60% range. The agency then proposed placing a cap on domestic CFC productions, for instance at the 1979 level. Then, as one scenario, choke off even this much by instituting 25% reductions in both 1983 and 1988.

To handle the relationship to ozone depletion, instead of pounds of CFCs they introduced the concept of the "permit pound". The greatest potential ozone depleter on a weight basis was correctly identified as P-11, and a permit pound of any other CFC was

TABLE III
Production and Uses of P-11 and P-12

Year	World Production* (Kilotonnes**)		P-11 & P-12	Total	U.S.A. Production (Pounds × 10 ⁶)	Aerosol
	P-11	P-12				
1935	0	0	0	0	0	0
1940	0	1	2	2	0	0
1945	1	7	17	16	10	38
1950						
1960	52	98	331			
1965	123	190	690			
1970	235	324	1230	720	420	
1971	256	340	1314	755	398	
1972	303	385	1516	797	440	
1973	342	440	1724	822	446	
1974	377	452	1827	861	408	
1975	310	410	1587	782	326	
1976	330	428	1671	647	142	
1977	315	412	1602	615	68	
1978	296	359	1444***	560	18	
1979				551	15	
1980					14	

*Excludes the small increment from the Communist Bloc States, e.g. 11%.

**One kilotonne (metric ton) is 1000 kg or 2,204,000 pounds.

***About 50% of the 1978, 1979 and 1980 totals consisted of aerosols.

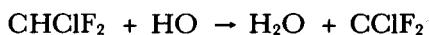
In 1979 U.S.A. CFC sales were valued at \$375 million; with world sales at \$1.00 billion.

In 1981 U.S.A. CFC sales were valued at \$505 million, due mostly to price increases.

In 1980 and 1981 the EPA forecasted a 9% worldwide annual increase in CFC production, also quoting a worldwide production figure of 1,927 million pounds in 1977, which undoubtedly included the contribution of the Communist Bloc States.

defined as the number of actual pounds of that substance calculated to be capable of equaling the depletion effect of one pound of P-11. The agency then proposed to stipulate the maximum permissible annual CFC production in terms of permit pounds and allocate permits by some method, for instance by holding auctions.

If CFCs should have to be further regulated, the permit pound is a logical concept. The EPA recognized that some CFCs would be less likely to survive in the troposphere, and thus would be less likely to harm the ozone layer. An important key to this is the relative rate of their reaction with tropospheric hydroxyl radical. For instance, in the case of P-22 the reaction:



acts to produce water and chlorodifluorocarbon radical much faster than the corresponding reaction of P-11 with hydroxyl, which is so slow as to be currently unmeasurable. In addition, P-22 has only one chlorine atom that can be stripped off by stratospheric photolysis, whereas P-11 has three. Using these and other considerations scientists at E.I. du Pont de Nemours & Co. have calculated that P-11 poses about 34 times the ozone depletion potential of P-22. Thus, the equivalent of one permit pound (a pound of P-11) would be 34 pounds of P-22.

Table IV provides the relationship of real pounds and permit pounds for the six most important CFCs. Similar information is presented for two chlorocarbons that the EPA will most likely also evaluate in this connection. The permit pound results published by the EPA are acknowledged now to be in error, since all the

relevant factors were not included during their development.

An alternative to auctioning permit pounds might be to tax permit pounds, with the EPA planning figures unofficially estimated as ranging from 25¢ initially to 65¢ by 1990. This would pose a disastrous burden for the small businessman, who could not afford to invest in costly recycling or other conservation equipment. The EPA proposal also ignores the beneficial aspects of CFCs, such as non-flammability, good performance and good economics. A Battelle Institute report, prepared for du Pont and submitted to the EPA, stated that the energy penalty associated with a ban on certain specified CFC uses would total the equivalent of as much as 50 billion gallons (190 billion liters) of fuel during the first decade the ban was effective, assuming alternatives such as ammonia were substituted. If P-22 were considered as the alternative, the difference would be about 28 billion gallons (106 billion liters) of fuel. For a benchmark, 9 billion gallons (34 billion liters) of fuel per year is equivalent to the energy output of 29 nuclear power plants for one year.

As one of their efforts to control the misdirected enthusiasm of the EPA, the business community has formed the Alliance for Responsible CFC Policy, which had over 500 members in 1981. With the alliance's support, Congress is now dealing directly with the CFC issue. Bills to amend the Clean Air Act and provide for more research on the ozone layer and stratosphere in general have been introduced by Sen. Lloyd Bentsen (D. Tex.) as S.517, and by Rep. Thomas A. Luken (D. Ohio) as H.R. 1853. These were incorporated more recently into H.R. 5252.

TABLE IV
Relative Ozone Depletion of CFCs and Certain Chlorocarbons

Formila	CFC Number	Chemical Name	Calculated HO Reaction Rate*	Calculated Number of Real Pounds per Permit Pound EPA Data**	Calculated Number of Real Pounds per Permit Pound Du Pont Data
CCl ₃ F	P-11	Trichloromonofluoromethane	< 4 × 10 ⁻¹⁶	1.00	1.00
CCl ₂ F ₂	P-12	Dichlorodifluoromethane	< 5 × 10 ⁻¹⁶	1.27	1.00
CCl ₂ F·CCl ₂ F	P-113	Trichlorotrifluoroethane	< 5 × 10 ⁻¹⁶	1.30	1.22
CCl ₂ F·CClF ₂	P-114	sym. Dichlorotetrafluoroethane	< 7 × 10 ⁻¹⁶	2.04	1.64
CCl ₂ F·CF ₃	P-115	Monochloropentafluoroethane	6 × 10 ⁻¹⁶	5.00	2.86
CHClF ₂	P-22	Monochlorodifluoromethane	24 × 10 ⁻¹⁶	5.56	34.00
CH ₂ Cl ₂	—	Methylene Chloride	870 × 10 ⁻¹⁶	—	(330.)***
CH ₃ ·CCl ₃	—	1,1,1-Trichloroethane	150 × 10 ⁻¹⁶	—	(50.)***

*Rate Constant K (at 265°K), as cm³·molecule⁻¹ sec⁻¹.

**Later shown to be incorrect; not all relevant factors considered.

***The reciprocal of relative ozone depletion against P-11. (Sanders, P.A. - 1979).

It is hoped that the results of this work, when added to research already done (du Pont alone has spent over \$30 million to date) will ensure that the EPA considers only the most recent scientific developments and seeks a rational international concensus. To its credit, the EPA in 1981 has repeatedly emphasized that the agency has made no decision on whether further regulation of

TABLE V
U.S.A. Exemptions From the Bans on Chlorofluorocarbon Propellents

1. Aerosol propellents, when not used to expel liquid or solid materials different from the propellant; e.g. CFC refrigeration or aid conditioning system refills, boat horns, fire extinguishers and so forth.
2. Mercaptan (thiol) stench warning devices for use in mines.
3. Release agents for molds used in the production of plastic and elastomeric materials.
4. Flying insect pesticides for use in non-residential food-handling areas and for space-spraying of aircraft.
5. Diamond-grit spray.
6. Non-consumer articles used as cleaner-solvents, lubricants or coatings for electrical or electronic equipment.
7. Articles necessary for the safe maintenance and operation of aircraft.
8. Uses essential to the military preparedness of the U.S.A. as determined by the EPA Administrator and the Secretary of Defense.
9. Metered-dose steroid human drugs for nasal or oral inhalation,
10. Metered-dose adrenergic bronchodilator human drugs for oral inhalation.
11. Contraceptive vaginal foams for human use.
12. Metered-dose ergotamine tartrate drug products administered by oral inhalation for human use.
13. Use of P-115 (chloropentafluoroethane) alone or with carbon dioxide, nitrous oxide, propane, and octafluorocyclobutane as an aerating agent for sprayed or foamed food products, with any propellant effect being incidental to and no more than is minimally necessary to achieve the aerating function, except that use is not permitted for those standardized foods that do not provide for such use.
14. Other temporary or permanent exemptions as may be approved from time to time, such as a blowing agent for polyurethane foams and a unique insect spray for tobacco barns.

Note: In a Final Rule (40 FR 55241, Nov. 27, 1978) aerosol propellents were clarified to positively include those substances such as P-11 and P-113, which have no gauge pressure at 75°F (23.9°C) or less.

CFCs is warranted, will submit future technical reports, for instance, from NAS, to careful peer review, will evaluate competent cost/benefit studies, and seek an international concensus on what further steps, if any, are needed.

During the opening months of 1982, as this is being written, the EPA has continued their 1981 stance. They are evaluating the huge industry response to their ANPR of October, 1980 and consulting with industry, scientific institutions and Congress in an effort to develop long-term and more rational strategies for the regulation of CFCs.

Only slight and often temporary relaxations have been made by either the EPA or FDA in permitting the utilization of saturated CFCs in aerosol products. As of 1982 the listing shown in Table V represents just about all the sanctioned aerosol uses for these propellents.

Costs of Conversion to Alternate Propellents

In 1975, almost 50% of the 2.7 billion aerosols produced in the U.S.A. contained a saturated CFC propellant or solvent, and the production of these fluids (for both aerosols and other uses) amounted to almost 800 million pounds (360,000 metric tons). Six domestic firms synthesized CFCs, and their shares of the aerosol propellant market in that year were about 39% du Pont (Freon), 39% Allied Chemical (Genetron), 11% Pennwalt (Isotron), 6% Union Carbide (Ucon), 4% Kaiser Chemical (Kaiser) and 1% Racon (Racon). About 326 million pounds (150,000 metric tons) of CFCs were used in aerosols, contrasted with about 180 million pounds (82,000 metric tons) of hydrocarbons and much smaller amounts of CO₂ and other propellents.

By 1981 this picture had changed radically. CFC production for aerosol uses had dwindled to almost nothing. Some firms, such as Union Carbide, dropped out. Hydrocarbon gases were now the major aerosol propellents, with about 300 million pounds (136,000 metric tons) of Aerosol Grade and Commercial Grade n-butane, isobutane and propane (and their blends) being used during the year. Over 90% of all U.S.A. aerosols now used hydrocarbon propellents.

During the late 1970s du Pont and other producers looked for CFCs that would be marginally less stable in the troposphere than P-11 and kindred compounds, yet not so unstable that they would contribute to smog formation, as does trichloroethylene. Many hydrogen-containing CFCs were found to have this desired intermediate stability. In addition, the true fluorocarbons

(which do not contain chlorine) were found to be acceptable from the standpoint that they do not contribute to any known ozone depletion mechanisms. Some fourteen initial compounds were singled out as candidates and all of them contained hydrogen in the molecule. They are included in a rather comprehensive listing provided in Table VI.

The most promising are P-22, P-142b and P-152a, although admittedly the last two are still somewhat flammable. Despite some very preliminary evidence

that P-22 and P-142b might be very weak mutagens, comprehensive studies covering the toxicological profile of these fluids should be completed in 1982 and the data thus far looks extremely encouraging. P-152a has now been fully cleared. A full profile of acute, sub-chronic and chronic toxicological tests now costs several million dollars and can take up to about four years to complete.

Because of its relatively low price and desirable properties, it looks like P-22 will become the workhorse of the U.S.A. CFC industry, particularly if the Rowland

TABLE VI
The Commercial Properties of Major Chlorofluorocarbons and Alternative Compounds

CFC Number	Formula	Boiling Point		Toxicology	Flammability	Comm. Mfg. Process	Worldwide Present or Potential Significant Commercial Applications			List Price (Dec-1981)	
		°F	°C				Aerosol	Refrig./A-c.	Blowing AG.	\$/Lb.	\$/Kg
11	CCl ₃ F	75	24	Low	None	Excellent	Excellent*	Excellent	Excellent	0.64	1.41
12	CCl ₂ F ₂	-22	-30	Low	None	Excellent	Excellent*	Excellent	Excellent	0.74	1.63
13	CClF ₃	-115	-82	Low	None	Good	None	Good	None	11.00 ^c	24.30 ^c
14	CF ₄	-198	-128	Low	None	Fair	None	Fair	None	18.62 ^c	41.06 ^c
21	CHCl ₂ F	48	9	Toxic	None	Fair	None	—	Good	—	—
22	CHClF ₂	-41	-40	Poss.v.wk.mutagen	None	Excellent	Good	Excellent	—	1.14	2.51
23	CHF ₃	-116	-83	Low	None	Fair	None	Fair	—	13.46 ^c	29.68 ^c
31	CH ₂ ClF	16	9	Toxic	Yes	None	Fair	None	None	—	—
32	CH ₂ F ₂	-61	-52	Low	Yes	None	None	None	None	—	—
113	CCl ₂ F-CClF ₂	118	48	Low	None	Excellent	Good*	Good	Good	0.79	1.74
114	CClF ₂ -CClF ₂	39	4	Low	None	Excellent	Excellent*	Excellent	Excellent	1.02	2.25
115	CClF ₂ -CF ₃	-38	-39	Low	None	Good	Good*	Good	Good	2.55 ^{tc}	5.62 ^{tc}
116	CF ₃ -CF ₃	-164	-109	Low	None	Fair	None	Fair	None	4.90 ^c	10.80 ^c
123	CHCl ₂ -CF ₃	82	28	Low	None	None	None	None	Fair	—	—
124	CHClF-CF ₃	12	-11	Low	None	None	None	Fair	Slight	—	—
125	CHF ₂ -CF ₃	-55	-48	Assumed low	None	None	None	Fair	None	—	—
132b	CH ₂ Cl-CClF ₂	116	47	Very incomplete	None	None	None	None	Poor	—	—
133a	CH ₂ Cl-CF ₃	45	7	Embryotoxic	None	None (USA)	None (USA)	None	Fair	—	—
134a	CH ₂ F-CF ₃	-16	-27	Very incomplete	None	None	None	None	Fair	—	—
141b	CH ₃ -CCl ₂ F	90	32	Weak mutagen	Slight	Developmental	None	None	Good	—	—
142b	CH ₃ -CClF ₂	14	-10	Very weak mutagen	Slight	Good	Good	Fair	Good	1.75 ^c	3.86 ^c
143a	CH ₃ -CHF ₃	-54	-48	Incomplete	Moderate	None	None	Fair	None	—	—
152a	CH ₃ -CHF ₂	-13	-25	Low	Moderate	Excellent	Very Good	Good	Good	1.55	3.42
3110	C ₄ F ₁₀	28	-2	Low	None	Discontinued	Fair	Good	None	—	—
C-318	C ₄ F ₈	22	-6	Low	None	Fair	Fair	—	None	11.00 ^{ec}	24.00 ^{ec}
—	(CHF ₂) ₂ O	28	-2	Very incomplete	None	Discontinued	Fair	—	—	12.00 ^{ec}	26.00 ^{ec}
—	(CF ₃) ₂ O	-67	-55	Very Incomplete	None	Discontinued	Fair	—	—	—	—
—	(CH ₃) ₂ O	-13	-25	Low	Yes	Very Good	Excellent	Poor	None	0.57	1.26
H-1301	CBrF ₃	-72	-58	Low	None	Very Good	Specialized	Specialized	None	3.50 ^c	7.72 ^c
H-1211	CBrClF ₂	28	-2	Low	None	Very Good	Specialized	Specialized	None	2.00 ^e	4.40 ^e
(LP Gases)	C ₃ H ₈ , etc.	—	—	Low	Yes!	Excellent	Excellent	None	None	0.22	0.48

*Banned in the U.S.A. for aerosols and partly banned or reduced in other countries. CFC-11 and 12 banned in Norway and Sweden.

Prices are for bulk (f.o.b.) unless noted by "c" = small cylinders (80 pound average net) or "tc" = ton cylinders. "e" represents an estimated price.

Some data may be slightly misleading due to brevity and those interested should pursue the available literature for more precise information.

and Molina theory continues to be sustained by the EPA for a number of additional years. Plant expansions have to be made to handle increased requirements. For instance, Allied Chemical added 25% capacity in 1980, and began a \$50 million HF expansion at Geismar, LA in that same year.

As of the beginning of 1982, P-22 had not been used in any aerosol productions. The use of P-142b (Pennwalt) was vanishingly small, due to the unresolved toxicological situation and other things, and the utilization of P-152a was significant but very small. It may have been included in up to 1% of U.S.A. aerosols. Outside the U.S.A. it probably was unobtainable.

A very major consideration in formulating aerosols is (of course) the cost of ingredients. Since the alternate fluorocarbon propellents cost between 5 to 8 times as much as the hydrocarbons, they must provide some special attribute to the product besides the simple propellant function in order to be used. The non-flammability factor, which applies only to P-22, is normally unimportant, since the other major ingredients of the formula, such as alcohols, petroleum distillates and the like, are flammable, thus making the total composition flammable. Borderline exceptions to this generalization can be made in the case of 1,1,1-trichloroethane, or for blends of methylene chloride and 1,1,1-trichloroethane, when they are used in large percentages. The alternate fluorocarbons do show far better solvency than the hydrocarbon propellents, which accounts for some of their uses. As dimethyl ether becomes more thoroughly tested, it may act to replace propellents such as P-152a, since it is a superb solvent and much less costly.

Aside from research and manufacturing costs to develop alternate propellents, the industry had to develop and test literally thousands of new "non-CFC" aerosol products. Of the approximately 65,000 aerosol formulas on the market in 1975, about 30,000 had to be reformulated due to the regulatory ban in the U.S.A. An additional 10,000 have been reformulated in Canada and Europe, and this process is continuing. Much of this work can be classed as duplicative, with one new formula generalization specifically being applied to a number of products. When it is considered that the costs are not merely those of reformulation, but include toxicological testing, efficacy testing, field testing and possible EPA re-registrations, the cost can be viewed as extremely high. The cost of the laboratory work alone has been estimated at about \$340 million.

The work occupied the full time resources of virtually every aerosol laboratory in the U.S.A. for almost three years. During this time research in all other directions was terminated, and the industry suffered many opportunities foregone, due to the EPA and FDA bans. It is impossible to measure the ultimate cost of this backslide.

Production costs increased, mainly due to the need to more safely handle hydrocarbons since these propellents were the principal heirs to the CFCs and were almost doubling in rate of use. There are an estimated 550 filling lines in the U.S.A., ranging in production speeds from about 10 to 380 cpm. In 1973 about 25% of these lines were "more or less" equipped to produce hydrocarbon-type aerosols. Depending upon the funds available to the filler and his commitment to safety, amounts of between \$10,000 to \$700,000 (in 1978 dollars) were spent for each line upgraded. The larger marketers and fillers, with larger production facilities, generally spent the higher amounts, from \$175,000 to \$700,000 per line. A rough calculation suggests that the purchase and installation of both improved and new safety equipment cost the aerosol industry about \$55 million (in 1978 dollars). The figure is about one-third of the "state of the art" cost and reflects the limited capital most fillers had after the aerosol business dwindled by about 35% in the U.S.A., in the aftermath of the Rowland and Molina theory and the bad press that came with it. The "missing" two-thirds of a full commitment to safety is possibly evidenced by the procession of fires and explosions that has occurred in filling plants during the last several years.

When the costs of reformulation, toxicological testing, consumer testing, new formula market introduction, safety engineering, new equipment, public relations programs, ozone studies, fires and so forth are fully considered, the penalty of the CFC ban in the U.S.A. amounts to an estimated \$1.0 to \$1.2 billion in 1982 dollars. The impact of industry shrinkage (plant closings, consolidations, etc.) has not been included, nor has the upstream effect upon suppliers of precursor chemicals and component parts. This huge cost has, as always, been passed along to the ultimate consumer. Considering the production during the period of 1975 through 1981, it would amount to an increment of about 7.5¢ per average can.

Outside the U.S.A. industry costs for conversion have been substantially less. In Canada, where CFCs are imported and many formulations now use alternate

propellant technology developed in the U.S.A. under the regulatory sword, the cost of their partial ban on CFCs has been estimated at about 1% of the U.S.A. total. In Europe, the EEC countries are typified by the U.K. which went from 95 million pounds (43,000 metric tons) of CFCs in 1977 to an estimated 66 million pounds (30,000 metric tons) in 1982. Production volumes in both years were about equal. The loss was compensated by an increase in hydrocarbon usage: from 28 million pounds (12,900 metric tons) to an estimated 38 million pounds (17,000 metric tons). Relatively little pain was caused by this voluntary transition, since the time frame was generous, there was little bad press, and the bulk of the change was handled by the top 20 or so of the 126 contract and marketer fillers. Nearly all of them already had hydrocarbon facilities, at least to some degree. In Norway and Sweden, which now have CFC bans, the process of change was very costly, forcing many smaller firms to go out of business and inviting a huge increase in imports from nearby Denmark and Germany. At this time, no large aerosol-producing country appears in danger of a ban, and there is hope that the CFC/ozone theories may be so strongly modified by new data during the next two or three years that no further political interdictions or bans will take place.

Properties of the CFC and FC Propellents

Because of the current ban on saturated CFC propellents in the U.S.A. only minor coverage will be accorded to P-11, P-12, P-113, P-114 and P-115. The first four are still very important outside the U.S.A., where they were estimated to account for about 480 million pounds (218,000 metric tons) of CFC production in 1980. The forerunner of the line is P-12, followed by P-11 and then (far behind) P-114. Only P-12 and P-114 can be considered as true propellents. P-11 and P-113 are incapable of forming a spray at room temperatures and are commonly thought of as volatile non-flammable solvents.

P-12 is used most commonly at levels between 20 to 50% of the total formula. At 20% the spray is fairly coarse, and light-bodied volatile concentrates are required to get a satisfactory spray down to the end of the can. Such solvents include 1,1,1-trichloroethane, ethanol and isopropanol. If a less volatile concentrate is required, then the minimum level of P-12 will have to be raised to about 25%. Where the concentration of P-12 is relatively small the distillation effect must be

considered. As the dispenser is sprayed, the outage space expands and P-12 vaporizes out of the liquid phase to maintain the equilibrium pressure. The result is a gradual reduction of the per cent P-12 in the liquid phase, becoming more serious near the end of the can since there is less of a reservoir to draw upon. The pressure and delivery rate can be expected to decrease at least slightly as any aerosol is used up, but the effect is more pronounced for products containing low percentages of propellant.

The properties of P-12 are shown in Table VII (Page 324) along with those of other common CFCs. Succinctly stated, it has a vapor pressure that can be tolerated at any concentration (although a "DOT Specification 2P" or "DOT Specification 2Q" can may be needed at levels of over about 70%), it is non-flammable, non-hydrolysable and a rather poor solvent.

On the basis of economics, and perhaps bans or other sanctions, products which used to have 20 to 25% P-12 as the propellant have now been reformulated to contain 3 to 5% CO₂. The spray may be a little coarser, particularly as the package is sprayed down, and perhaps somewhat more sensitive to propellant leakage rates, but otherwise there are very few problems with the transition. Products such as disinfectant/deodorants, wasp and hornet sprays, mothproofers, engine degreasers, carburetor and choke cleaners, bug killers and so forth may be sprayed with either propellant.

The early hair spray formulations typically contained 35% ethanol-based concentrate, plus 65% of a propellant blend consisting of about 20 parts P-12 and 45 parts P-11. The large percentage of CFCs were used to give elegant sprays (with the valves then available) and only a slight degree of flammability, such as an 8 inch (200 mm) flame in the Flame Projection Tester. However, in the U.S.A. at least, ethanol was only about half as costly as the CFCs, and this economic fact forced CFC levels inexorably downward, until by about 1968 hair spray formulas averaged about 50% concentrate, 26% P-12, 14% P-11 and 10% isobutane A31. The flame projection was now in the 16 to 18 inch (400 to 457 mm) range. During these transitions to less costly, more flammable products, the industry closely monitored the market to see if there were any hazardous consequences. Essentially none were reported. In 1975 through 1977, when the CFCs had to be removed from most U.S.A. aerosols, these data encouraged most marketers to go directly to ethanol/hydrocarbon formulations. A few more cautious ones tried to use CO₂,