Excerpt from

Montreal Protocol on Substances That Deplete The Ozone Layer
United Nations Environmental Program (UNEP)
Technology and Economic Assessment Panel (TEAP)

REPORT OF THE TASK FORCE ON HCFC ISSUES AND EMISSIONS REDUCTION BENEFITS ARISING FROM EARLIER HCFC PHASE-OUT AND OTHER PRACTICAL MEASURES

July 2007

HCFC-225

While the military, aerospace, electronics, and medical sectors have eliminated CFC-113 in nearly all critical applications, in a few applications HCFC-225 cleaning solvent, and more specifically a special version of the solvent consisting almost entirely of the less toxic HCFC-225cb isomer, is the only currently available alternative that has proven acceptable as a safe and technically satisfactory replacement for these few applications.

Critical use considerations might apply to specialty military, aerospace, and medical use of HCFC-225, which is the closest chemical substitute for CFC-113. The use of HCFC-225 is generally self-limiting because it is so expensive to use that companies seek alternatives.

- *Cleaning of critical oxygen life support systems and components*

Oxygen is a strong oxidizer that contributes to the likelihood of ignition and vigorously supports combustion. As the concentration, pressure and temperature of oxygen increase, so does its reactivity. Common contaminants such as particulate and hydrocarbon oils and greases easily ignite in an oxygen-enriched atmosphere. This, combined with the fact that all plastics and rubber, and many metals, burn quite vigorously in oxygen-enriched atmospheres at high pressure, mandates rigorous cleaning of oxygen components and piping systems. In an oxygen fire, the fire cannot be extinguished until the oxygen source is isolated or depleted, and over 20 kilograms of stainless steel can vaporize in less than 1 second. The dangers involved with oxygen fires are real and both historic and recent. Between 1990 and 2002, the British Health and Safety Executive (HSE) reported 280 oxygen incidents in the commercial and medical sectors with 5 fatalities and 187 injuries. In 1967, the oxygen fire on the Apollo 1 launch pad killed three astronauts. In 1960, an oxygen fire on the *USS Sargo* killed one crewman, and it was only the flooding of the stern of the submarine at the pier to cool the affected area that prevented weapons from exploding and causing a far more devastating event.

CFC-113 was uniquely suited for the cleaning of oxygen components and piping systems. The solvent possessed excellent ability in removal of contaminants such as hydrocarbon, silicone and fluorinated oils and greases. Additionally, CFC-113 was non-flammable, had low toxicity, and was compatible with many metallic and non-metallic materials. Furthermore, the solvent was easily analyzed for residual contamination by infrared (IR) spectroscopy or evaporative non-volatile residue (NVR). This permitted quantitative verification of cleanliness, which provided a level of confidence commensurate with high value platforms such as nuclear submarines and nuclear aircraft carriers.

Most oxygen cleaning applications have switched from CFC-113 to other non-ozone depleting alternatives such as aqueous cleaners or HFE (hydrofluoroether) solvents. However, some applications with very complex geometries will not allow the mechanical agitation necessary to support these alternatives because these non-ODS alternatives generally have marginal performance without agitation. In similar complex geometries, HFE and HFC solvents are combined with other more aggressive solvents such as trans-1,2-dichloroethylene to enhance their performance. However, using a solvent blend like this in an oxygen-enriched environment 70 presents risk since any solvent remaining behind acts as a flammable contaminant in the system, potentially resulting in catastrophic fires. Additionally, in some cases, very small quantities of the blended solvents can be acutely toxic and rapidly disable a user, such as a high performance jet aircraft pilot, further increasing the risk of a catastrophic event.

One example of a complex geometry that requires HCFC-225cb usage is the flush cleaning of liquid oxygen producers installed on aircraft carriers and hospital ships. The equipment produces breathing oxygen for aircraft and medical usage, and also produces liquid nitrogen for aviation usage. The configuration of the liquid oxygen producer is inherently difficult to clean. They are composed of large distillation columns that are over 2 meters tall and 50 centimeters in diameter with multiple plates having small passages (1/3-cm holes) combined with spiral wound heat exchanges. Additionally, since the producers are installed within confined shipboard spaces and provide breathing oxygen, worker and user exposure to toxic chemicals is a major concern. While naval technical authorities have approved aqueous and HFE alternatives for other oxygen cleaning applications on a basis of cleaning performance, in this application the same level of safety could not be assured and the risk associated with a potential fire on ships with several thousand people aboard, powered by a nuclear reactor, and potentially carrying large amounts of conventional and nuclear weapons was considered unacceptable. So, while commercial industry has in similar applications moved to non-ozone depleting substance alternatives, the naval technical authorities have chosen not to adopt these practices because of the inherent risk of failure; regardless of how remote. Instead, the naval technical authorities have established extraordinarily high quality assurance criteria for acceptable alternatives to protect these high value tactical and strategic systems whose failure could risk national security, result in serious injury or death to military personnel, or have unintended consequences to civilian populations and the environment.

While precise amounts of HCFC-225 used in cleaning of oxygen systems is unknown, it is estimated that the total worldwide annual emissions from these types of cleaning processes is on the order of 5 ODP-weighted metric tons.

- Cleaning of precision inertial guidance systems

Inertial guidance systems used in many existing spacecraft and missiles consist of gyroscopes and accelerometers surrounded by electronics components and assemblies. Mechanical tolerances on these components can be as small as 0.15 millimeters resulting in a unique requirement for a near-perfect cleaning solvent to manufacture and maintain these systems. Necessary solvent properties include a volatile solvent with near-zero residues, sufficient solvent power to remove organic soils, low surface tension to penetrate small spaces, high density to assist the lift off of small particles, rapid drying, low toxicity and non-flammability. The solvent must also be compatible with the many materials and substrates of the system. Guidance systems include exotic metals such as beryllium, which is reactive or incompatible with many traditional solvents. In addition to the metallic components, there are numerous elastomers, epoxies, wire insulations, and organic coatings which could swell unacceptably or be damaged by a solvent that is too aggressive. The solvent of choice that met all of these properties was CFC-113. However, as early as the 1970s, military and space organizations began to look for an alternative to CFC-113 due to its environmental impacts. Over the next two decades many solvents including HFCs, HFEs, and others were evaluated as possible alternatives with no success. It was not until the introduction of HCFC-225cb that a solvent was found with properties that very closely replicated CFC-113.

As the failure of a guidance system on a missile or spacecraft could compromise scientific investigations or national security, risk loss of a high value spacecraft or satellite, or result in serious injury or death of personnel, extensive testing is required to qualify an alternative solvent in these applications. Testing usually begins with preliminary materials compatibility testing, followed by longer term mechanical, dimensional, and electrical properties testing on each component, and finally system testing. The final test on these systems often consists of manufacture and cleaning of the systems with the alternative followed by a multi-year operational test or system tear-down and inspection after it has been in storage for several years. As a result, it is not uncommon for the entire qualification cycle to take 6-8 years. Accordingly, even if an alternative to HCFC-225cb were identified today it would be 2015 before it could be fully qualified. Since many of these systems support a small number of spacecraft and missiles that have limited operational lives (although they may be very long inventory lives), it generally would not be economically feasible to invest in a multi-million dollar qualification program after such a program investment already occurred over the last decade to qualify HCFC-225cb as an alternative to CFC-113. In addition, chemical manufacturers are no longer investing in extensive research and development to find alternative solvents since these remaining critical uses do not provide a large enough market to receive a return on their investments.

While precise amount of HCFC-225 used in cleaning of precision guidance systems is unknown, it is estimated that the total worldwide annual emissions from all precision cleaning processes (military, aerospace, electronics, medical, etc) is less than 40 ODP-weighted metric tons. It is likely that only a small portion of these emissions result from cleaning of precision guidance systems.

- *Electronics manufacture*

There are a variety of miscellaneous uses in electronics manufacturing such as defluxing of flexible circuits made of polyimide, which may not be compatible with other cleaning processes or no-clean, and in the manufacture of high production rate electronics assemblies, particularly electronics assemblies and components with conformal coatings. HCFC-225 is used in these few specialized applications.

- *Medical applications*

HCFC-225 is used to clean some implantable or surgical medical devices and plastic medical equipment that are not compatible with other solvents or where soils residue must be very low.

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